

Thèse de Doctorat

Synthèse et conception de retardateurs de flamme intelligents

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Abstract

Polymeric materials have been increasingly used as replacement for other types of materials such as ceramics or metals. However, most polymers have a serious drawback: they need to be fire retarded. Nevertheless, thanks to advanced research in the field, high performance materials that resist high temperatures and fire scenarios have been developed. While these materials have extremely enviable properties, they are also very expensive. The aim of this PhD is to understand the fire behavior of high-performance polymers and design fire retardants that would mimic these high-performance materials under extreme heat or fire. To do so, the thermal and fire behavior of three high performance materials were studied: polyetheretherketone (PEEK), polyimide (PI), and polybenzoxazole (PBO). Their thermal decomposition pathways were evaluated thanks to high temperature analytical techniques like pyrolysis-GC/MS and TGA-FTIR. Model based kinetics of the thermal decomposition of these polymeric materials were also elucidated by using dynamic TGA under three different atmospheres (nitrogen, 2% oxygen, and air). These provided insight regarding the thermal behavior high performance polymers, which were used to conceptualize novel potential fire retardants. Therefore, a series of fire retardants that have demonstrated similar behaviors as high performance polymers in fire scenarios were synthesized. These fire retardants include a Schiff base: salen and its derivatives, as well as some of their metal complexes. The thermal behavior and fire performances of these fire retardants were evaluated in two polymeric materials using a relatively low loading (< 10 wt%): thermoplastic polyurethane, and polyamide 6. While some of the fire retardants had little effect, in terms of fire retardancy, some candidates showed a significant improvement in terms of peak of heat release rate. This reverse approach towards designing fire retardants has shown some promise and can be used as a complementary method for the design of highperformance materials at lower cost.

Résumé

Les matériaux polymères sont de plus en plus utilisés pour remplacer d'autres types de matériaux tels que la céramique ou le métal. Cependant, la majorité des polymères ont un désavantage : ils doivent être ignifugés. Néanmoins, grâce à la recherche dans le domaine des matériaux, des polymères haute performance qui résistent à la chaleur et aux scénarios feu ont été conçus. Malgré l'avantage technique qu'apportent ces matériaux, ils sont extrêmement chers. Le but de ce travail est de comprendre la réaction au feu des matériaux hautes performances afin de concevoir des retardateurs de flamme qui réagiraient comme ces polymères hautes performances quand ils sont soumis à des températures élevées ou dans un scénario feu. Dans cette optique, le comportement à haute température et la réaction au feu de trois matériaux hautes performances ont été étudiés : polyetheretherketone (PEEK), polyimide (PI), et polybenzoxazole (PBO). Les mécanismes de décomposition de ces matériaux ont été évalués à travers différentes méthodes analytique telles que le pyrolyseur GCMS et l'ATG-FTIR. La cinétique de décomposition de ces matériaux a aussi été évaluée en utilisant l'ATG dynamique sous différentes atmosphères (azote, 2% oxygène, et air). Cela nous a permis d'acquérir du recul par rapport aux comportements thermiques de ces matériaux hautes performances, que nous avons pu exploiter pour définir des nouveaux retardateurs de feu. Ainsi, une série de retardateurs de flamme ont été synthétisés. Ces retardateurs de flamme font partie de la famille de bases de Schiff et comprennent le salen et ses dérivées, ainsi que certains de leurs complexes métalliques. Le comportement thermique et réaction au feu de ses retardateurs de flamme ont été évalués dans deux polymères : le polyuréthane thermoplastique, et le polyamide 6. Bien qu'une partie de ces retardateurs de feu aient montré peu d'effet au feu, certains ont montré une amélioration importante en termes de chaleur dégagée. Cette nouvelle approche vers la conception de charges ignifugeantes est prometteuse et peut être utilisée comme une méthode complémentaire pour la conception de matériaux haute performance à bas cout.

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PA6 S27 BL Natural (Rhodia)	
PEEK Ketron 1000 (Quadrant Engineering Plastic Products)	
Polybenzoxazole (Zylon, Toyobo)	
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List of Abbreviations

ASTM	American Society for Testing Materials
ATH	Aluminium trihydroxide
DSC	Differential Scanning Calorimetry
DTG	Derivative of the thermogravimetric curve
Ea	Activation energy
EI	Electron Ionization
FAA	Federal Aviation Administration
FR	Fire retardants
FTT	Fire Testing Technology
FTIR	Fourier Transform Infrared
GCMS	Gas Chromatography-Mass Spectrometry
HRC	Heat release capacity
HRR	Heat release rate
MCC	Microscale Combustion Calorimetry
MLC	Mass loss calorimeter
MLR	Mass loss rate
NAFTA	North American Free Trade Agreement
OFW	Ozawa-Flynn-Wall
PAEK	polyaryletherketone
РВО	Polybenzoxazole
PBT	Polybenzothiazole
PCFC	Pyrolysis Combustion Flow Calorimetry
PEEK	Polyetheretherketone

pHRR	Peak of heat release rate
PI	Polyimide
PIPD	polyhydroquinone-diimidazopyridine
PMMA	Polymethyl methacrylate
STA	Simultaneous Thermal Analysis
TG	Thermogravimetry
TGA	Thermogravimetric analysis
THR	Total heat release
TIC	Total Ion Chromatogram
TPU	Thermoplastic Polyurethane
TTI	Time to ignition

General Introduction

Plastics have been part of the civilized world since early civilizations. However, it was not until the end of the 19th century, along with the development of the chemical industry, that the development of synthetic plastics began. Their versatility was adopted into various applications ranging from clothing to billiard balls (replacing ivory that was used in at that time). History had to wait until the end of the first war to see a significant rise in plastic production. Increased funding was injected into the chemical industry, which marked the beginning of mass production of plastics. Ever since, the plastic production around the world has kept on rising, except for the 1970s energy crisis and the credit crunch in 2008 (Figure 1). Europe's plastic production has reaches 64 million tons in 2015 as compared to the meagre half a million tons in the 1950s. Globally, the plastic production market is dominated by China, Europe, and the North American Free Trade Agreement (NAFTA) countries, which account for more than 65% of the plastic production in the world [1,2] (Figure 1).



Figure 1. Global plastic production since 1950 until 2015 (left), and distribution of plastic production in the world (right) [1,2]

For more than half a century, plastics have been increasingly used as alternatives to traditional materials such as wood or metals in various applications. They versatility and ease with which they can be processed make them valuable assets for their use in everyday life.

Despite their outstanding properties and their numerous applications, most of the polymeric materials (plastics) have one undeniable downside: they are highly flammable. In the event of a fire, most plastics, in their virgin form, would degrade and release fuel and toxic gases. This can cause severe material damage as well as human casualties and deaths. In Europe, 4000 fire-related deaths are reported every year. 90% of fires in the European Union happen

in buildings and because of the use of an increasing amount of flammable materials. Recent statistics have shown that it takes only 3 minutes for a fire to involve an entire room [3]. Therefore, most plastics need to be flame retarded in order to be used in most environments.

There are many ways to flame retard a polymeric material. These include

- physical methods, whereby a flame-retardants are incorporated into a polymer by melt blending,
- ii) chemical methods, whereby fire retardants are added into the structure of the polymeric material as a functionalized part of the polymer, or
- iii) surface treatment methods, whereby a coating of fire retardant is grafted/added to the surface of the material

Flame-retardants also come in many forms, they be in the form of inorganic fillers such as aluminium trihydroxide (ATH), boron-, phosphorus-, halogen-, or nitrogen-based additives. These flame retardants may enhance the fire properties of a particular polymeric material, but some of their properties (mechanical properties or processability) may be altered. An ideal flame retardant would be one which, when incorporated in a material, enhances its fire properties without altering the other properties of the material. This idealistic view on flame retardants have pushed the research on polymer systems such that inherently flame-retardant polymeric materials were synthesized. This led to high-performance polymers.

Indeed, advances in polymeric materials have allowed the development of high-performance plastics that resist high temperatures, release only little fuel, and are therefore virtually non-flammable. Some of these materials are used in industries whereby extreme conditions are met. Such industries include the aeronautics industry, microelectronics, or fireproof overalls. Examples of such materials are polyimide (Kapton®), polyetheretherketone (PEEK), or aromatic polyamides such as Nomex® or Kevlar®. These materials all exhibit extreme fire resistance and thermal stability.

While high-performance materials meet most of the fire and thermal requirements to be used as everyday materials, there are too expensive to replace the usual plastics that we use. As a result, the market share for high performance polymeric materials is less than 1% of the polymer market. Therefore, common and engineering plastics that require to be flame retarded are used. Having the knowledge of the existence of high-performance materials, a fundamental question regarding fire retardants came up: can there be a fire retardant that acts as a high-performance polymeric material when it is subjected to heat and fire?

Consequently, in the context of this work, we have attempted to follow the lead whereby a small molecule can act as an efficient fire retardant under low loadings. However, in order to achieve this, it was important to understand the thermal and fire behavior of the high-performance materials. This has the potential of providing valuable insight on the flame-retardant modes of action that are intrinsic to these materials.

In this context, a study performed at our laboratory has shown that a 10% loading of a fire retardant (salen-copper complex) could inculcate the traits of a high performance polymer to thermoplastic polyurethane [4]. This was achieved through the promotion of the formation of a protective fire barrier when the polymer/flame-retardant formulation was subjected to a fire test. From the gathered input on the thermal decomposition and fire behavior of high-performance polymeric materials and the pursuing of the previous work on salen based fire retardants, we intend to conceptualize a smart fire retardant that can promote a high-performance behavior in common/engineering plastics. With the abovementioned insight, this work aims at understanding the decomposition behavior of high-performance polymeric materials novel, smart fire retardants that would mimic high-performance polymers when subjected to thermally demanding solicitations and fire scenarios.

Moreover, this work is part of the Fire-Bar Concept project (2014–2020 ERC Advanced Grant Agreement no. 670747). One of the goals of the project is to design and assemble materials exhibiting low flammability, protecting substrates and limiting fire spread. In an attempt at answering this problematic hand in hand with the project, the contents of this work are divided into five chapters.

The first chapter deals with the state of the art regarding the thermal and fire behavior, as well as the fire retardancy of polymeric materials. A review concerning high performance polymeric materials and their reaction and resistance to heat and fire is also detailed. The last section of this chapter deals with the state of the art concerning the aforementioned flame retardant and its potential as mimicking a high-performance polymer under fire conditions.

The second chapter is focused on the materials and methods used in the context of this study. The polymeric materials used and the processing parameters are described. Syntheses of potential fire retardants are also described in this chapter. Finally, the different thermal characterization methods and fire behavior tests used throughout the study are described.

The third chapter concerns the study of three high-performance materials: polyetheretherketone, polyimide, and polybenzoxazole. The objective here was to extract insight on the characteristics that impropriate such high-performance characteristics to these particular polymers. To do so, the thermal stability of the polymers was evaluated under three types of atmospheres: nitrogen, low oxygen levels, and air. Their thermal decomposition products were analyzed so as to gain insight on their decomposition mechanisms. Their fire behavior was also evaluated and attempts were made to correlate them to their decomposition mechanisms.

The following chapter complements the previous one. It provides thermal decomposition models for the three atmospheres that were studied. This provides insight to further the comprehension of the thermal decomposition behaviors of the materials at different points in a fire scenario.

Chapter five concerns the study of the aforementioned potential fire retardant, salen, and its derivative when they are incorporated in two polymeric materials: thermoplastic polyurethane (TPU), and polyamide 6 (PA6). Their thermal stabilities were evaluated using thermogravimetric analysis. Their fire behavior was evaluated using the mass loss cone calorimetry.

Finally, a general conclusion pertaining to the work is provided and perspectives for further work concerning this study are proposed.

4

I. State of the Art

This chapter deals with existing knowledge concerning fire retardants and existing approaches that have been used to enhance the flame-retardant properties of some materials. In order to do so, it is essential to understand the need for flame retarding materials such as polymers. This is looked into in the first section of this chapter, which deals with the behavior of polymeric materials under thermally demanding environment. We will explore literature in order to explain why some materials have better resistance to fire than others. The second section deals with the world of fire retardation in general and the modes of action it involves. Finally, in the third subsection, the salen molecule, which can act as a high-performance polymeric material under thermal stress, is introduced in order to evaluate its potential as a thermally triggered fire retardant.

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I.1. Thermal and Fire Behavior of Polymeric Materials

Polymers consist of a range of materials that are used in a wide array of applications. They are versatile and they offer numerous possibilities in terms of processability and design. Indeed, polymers play an important role in cutting-edge technologies. For instance, nowadays, polymers make up about 50 % of the volume of a lightweight vehicle but only 10 % of its weight [5].

However, despite their widespread use, polymers still present some major drawbacks such as environmental degradation such as degradation due to UV light, hydrolysis due to water in air, or mechanical erosion, and flammability. In order to better understand the need for more resistant and better performing polymeric materials, it is essential to have an in-depth understanding of the physico-chemical aspects that impropriate their aforementioned properties to the polymers.

Firstly, understanding the thermal properties of a polymeric material would provide a deeper insight on its behavior in extreme thermal environments. In the case of this work, extreme thermal conditions would imply temperatures above which non-reversible thermal degradation and/or thermal decomposition take place.

It is therefore imperative to study the different physical and chemical processes involved when a polymeric material is heated and/or ignited to devise ways in which they can be made more resistant to heat. Moreover, it is also important to understand the subtle behavioral difference between a polymer subjected to heat and a burning one. Indeed, despite being closely related the fire behavior of a material is an even more complex process than is its thermal decomposition. The differences between the two phenomena will be explained in the coming sections. Therefore, in the following sub-sections, both the thermal reactions and the fire behavior of polymeric materials will be examined.

I.1.a. Thermal Behavior of Polymers

Polymeric materials undergo both physical and chemical changes when subjected to thermal stress. This brings about different, mostly unwanted, changes to the properties of the material. In order to further comment the thermal behaviors of polymers, a clear distinction needs to be made between thermal decomposition and thermal degradation. The American Society for Testing Materials (ASTM) provides clarifying definitions in this matter. Thermal decomposition is "a process of extensive chemical species change caused by heat" [6]. Thermal degradation is "a process whereby the action of heat or elevated temperature on a

material, product or assembly causes a loss of physical (mechanical or electrical) properties" [6] When subjected to a high thermal stress, thermal degradation and thermal decomposition both take place. However, in the context of fire scenarios, thermal decomposition is the more significant contributing factor. Indeed, thermal decomposition is the process whereby fuel is produced in a fire scenario (see I.2.a). Therefore, in order to have an in-depth understanding of the behavior of polymeric materials under thermal stress, the physical and chemical processes that occur when they are subjected to a thermally demanding environment need to be studied.

Indeed, as the thermal stress on a polymeric material is increased, there are different physical processes (such as phase changes) that may occur. These processes depend on the nature of the material itself. Thermosetting plastics, for example, are infusible and insoluble once they are synthetized; therefore, phase transitions are less likely to occur upon heating. Their structures are such that they cannot change states at temperatures below that at which thermal decomposition occurs. This is the case when the thermal stress applied on a polymer provides sufficient energy to overcome forces that hold the polymer chains together. This leads to the production of volatiles (decomposition products). These volatile molecules may accumulate within the decomposing polymer. If the polymer is molten at the decomposition temperature, bubbles of volatiles are formed and migrate upwards and eventually erupt from the surface.

Thermoplastic polymeric materials, on the other hand, can be softened when heated up without causing irreversible changes to the material, as long as the thermal stress does not exceed the minimum decomposition temperature of the material. Furthermore, when a thermoplastic polymeric material is heated, it can exhibit some well-known physical behaviors, which depend on its degree of crystallinity. Indeed, while crystalline materials (and semi-crystalline materials) have a well-defined melting temperature (melting point), amorphous materials, where there are both parts with ordered packing and parts with no ordered packing, do not exhibit a specific melting point. What they do have is a glass transition temperature. At this temperature, the polymer starts a transition to a soft and rubbery state. At this point, the material loses most of its mechanical properties. Further increase in temperature usually causes thermal degradation or melting.

However, some polymers such as polyetheretherketone or polyetherimide produce carbonaceous chars upon thermal decomposition [7]. The physical structure of the chars has

a significant impact on the way the polymer thermally decomposes. The physical characteristics of the char that play major roles in the rate of the thermal decomposition of the polymeric material are foaminess, coherence, adherence, oxidation-resistance, thermal insulation properties and permeability [8]. Low-density chars consisting of a high porosity are usually good thermal insulators. They can have a significant impact on lowering the heat flow from the heat source to the bulk of the material, thus slowing down the thermal decomposition process.

Nonetheless, this char can undergo glowing combustion (or smoldering) in the presence of oxygen. It is unlikely that both glowing combustion of the char and significant flaming can occur simultaneously in the same zone above the surface of the polymer, since the flame consumes all the oxygen in the surroundings (see section I.5). Moreover, the flow of volatiles from the decomposing polymer will tend to drive oxygen away from the char surface. Therefore, char oxidation will occur only after the flame has subsided.

Indeed, while thermal decomposition may occur solely by the presence of a thermal stress, it can also happen by the combined action of oxygen and heat. The presence of oxygen usually accelerates the decomposition of polymeric materials. It also lowers the minimum decomposition temperature of the material. Before ignition, the thermo-oxidative decomposition of the polymer leads to the pyrolysis of fuel and other species. After ignition (during flaming), the pyrolysis of the condensed phase remains mostly anaerobic, with the majority of the oxidation taking place in the gas phase [9]. It has been reported that for a vast majority of thermoplastic, even before ignition, volatile formation comes from the bulk of the polymer, and not its surface. The critical decomposition condition of a material remains anaerobic.

I.1.a.i. Thermal Decomposition Reactions in Polymers

The previous subsection has brought light upon the fact that sufficient heat may bring about the thermal decomposition of a polymeric material. However, different polymers decompose in different ways. There are different kinds of reactions that occur when a polymer is subjected to thermal stress. One of the first phenomena that can happen is the breaking of polymer chains, resulting in volatile molecules.

Four general chemical mechanisms may be used to describe possible pathways for the thermal decomposition of polymeric materials.

- Random chain scission, whereby chain scissions occur at random locations on the polymer.
- End chain scission, in which individual monomer units are stripped successively at chain ends.
- Chain-stripping, whereby individual atoms or groups which are not part of the backbone of the polymer are cleaved
- Cross-linking, in which covalent bonds are created between polymer chains.

These decomposition reactions depend on the chemical nature of the material. For instance, it has been reported that PEEK, which is a highly aromatic polymer, undergoes a high degree of crosslinking during its thermal decomposition [10].

I.1.a.ii. Characterizing Polymer Decomposition

A few indicators can be useful to understand the phenomenology of polymer decomposition:

- Degradation temperature (or temperature of initial decomposition, $T_{d,o}$). This corresponds to the temperature at which the weight loss is measurable during heating. It corresponds to the "degradation temperature" previously defined.
- Temperature at half decomposition $(T_{d,1/2})$. This corresponds to the temperature at which half of the final weight loss is attained during pyrolysis at a uniform heating rate.
- The temperature of maximum rate of decomposition $(T_{d,max})$. This can be measured from the rate of weight loss (maximum).
- Average activation energy (E_{act,d}), determined from the temperature dependence of the weight loss.
- The char-yield. The amount of residue remaining at the end of the pyrolysis (usually 800 °C)

These data can be obtained by performing thermogravimetric analysis on milligram scale samples of a material. It should be noted that these characteristics are highly dependent on the heating rate. As the heating rate increases, the characteristic temperatures shift to higher ones.

Table 1 summarizes the data regarding the thermal degradation of polymers. The decomposition onset of the polymers in shown vary from 473 K to above 900 K. It can also be observed that while some polymeric materials yield a high amount of their initial
monomer, most of the materials do not. This suggests that depolymerization is not the main reactions occurring during the thermal decomposition of a material.

Polymer	Td,o (K)	Td,1/2 (K)	Eact (kJ/mol)	Monomer yield (%)	Char Yield (%)
Poly(methylene)	660	687	300	0	0
Poly(ethylene) (branched)	653	677	264	0	0
Poly(propylene)	593	660	243	0	0
Poly(isobutylene)	_	621	205	20	0
Poly(styrene)	600	637	230	< 50	0
Poly(m-methyl styrene)	_	631	234	45	0
Poly(α-methyl styrene)	_	559	230	>95	0
Poly(vinyl fluoride)	623	663	—	_	_
Poly(vinyl chloride)	443	543	134	0	22
Poly(trifluoro ethylene)	673	685	222	<1	_
poly(chloro-trifluoro ethylene)-	653	—	239	27	-
Poly(tetrafluoro ethylene)	_	782	339	>95	0
Poly(vinyl cyclohexane)	_	642	205	0.1	0
Poly(vinyl alcohol)	493	547	_	0	7
Poly(vinyl acetate)	_	542	_	0	_
Poly(acrylonitril)	563	723	_	_	15
Poly(methyl acrylate)	_	601	_	0	0
Poly(methyl methacrylate)	553	610	218	95	0
Poly(butadiene)	553	680	260	2	0
Poly(isoprene)	543	596	250	_	0
Poly(p-phenylene)	> 900	>925	_	0	85
Poly(benzyl)	_	703	209	0	—
Poly(ethylene oxide)	_	618	193	0	0
Poly(2,6-dimethyl p-phenylene oxide)	723	753	_	0	25
Poly(propylene oxide)	_	586	147	1	0
Poly(ethylene terephthalate)	653	723		0	17
Poly(p-phenyleneterephthalamide)	~720	~800	-	-	40
Poly(pyromellitide)	723	~840	-	_	70
Poly(m-phenylene 2,5-oxadiazole)	683	~800	-	-	30

Table 1 Thermal degradation characteristics of polymers [11–13]

I.1.a.iii. Influence of Chemical Structure on Thermal Stability

The thermal stability of a polymer may be directly related to the temperature at which the material decomposes. Madorsky et. al have extensively studied the relationship between the chemical structure of a polymer and their thermal stability [12]. The experiments that were performed investigated the thermal stability of polymers by determining the temperature, T_h , at which 50 % of a polymer sample volatizes in 30 min in an inert atmosphere. Table 2 summarizes the structural factors that affect the thermal stability of a polymeric material.

Factor	Effect on thermal stability	Examples	T _h /K
Chain Branching	Weakens	Polymethylene	688
		Polyethylene	679
		Polypropylene	660
		Polyisobutylene	621
Double bonds in polymer	Weakens	Polypropylene	660
backbone		Polyisoprene	596
Aromatic ring in polymer	Strengthens	Poly-1,4-phenylene methylene	703
backbone		Polystyrene	637
High molecular weight	Strengthens	PMMA B (MW = 5.1×10^6)	600
		PMMA A (MW = 1.5×10^5)	556
Cross-linking	Strengthens	Polydivinyl benzene	672
		Polystyrene	637
Oxygen in polymer backbone	Weakens	Polymethylene	688
		Polyethylene oxide	618
		Polyoxymethylene	<473

Chain Branching

When comparing degradation temperatures with respect to chain branching, polyisobutylene (Figure 1) has the lowest thermal stability (Table 2). Its structure is such that there are two chain branches on alternating carbon atoms. Polypropylene (Figure 1, right) is the next least thermally stable polymer with one branching point at every alternate carbon. It should be noted that commercial polyethylene is not linear. It contains a number of branches on its linear chains, either in small CH₃ groups, or longer side chains. These branching occur randomly during the polymerization process. Indeed, low-density polyethylene contains about 60 branching points per 1000 carbon atoms. High-density polyethylene on the other hand has fewer branching points (7 branches per 1000 carbon atoms). During thermal

decomposition, the branching points are the first to break, starting the chain decomposition reactions [14].



Figure 1. Structure of polyisobutylene (left) and polypropylene (right)

Presence of Double Bonds

It was reported that double bonds present a reactive site to initiate chain decomposition reactions. Thus, the presence of double bonds tends to reduce the thermal stability of a polymer. This can be observed when comparing the thermal stability of polyisoprene ($T_h = 596 \text{ K}$) with that of polypropylene ($T_h = 660 \text{ K}$) [8,14].

Presence of Aromatic Rings in the Backbone

The presence of an aromatic backbone (as opposed to aromatic rings in sidechains) tends to increase the thermal stability of a polymer. The aromatic side chain increases the rigidity of the chain, decreasing the entropy of the liquid state thus causing an increase in the melting temperature. This high melting point reduces the rate at which the thermal degradation occurs. Indeed, the difference in decomposition temperature can be seen on Table 2 whereby polystyrene has a lower decomposition temperature than poly-1,4-phenylene methylene. Indeed, the latter contains the aromatic parts in its backbone, whereas polystyrene has its phenyl groups attached as side groups.

Molecular weight

When comparing two polymers with similar decomposition behavior (such as end chain scission in the case of PMMA) the decomposition starts at the end of the chain since the molecule is only held by one bond. PMMA A decomposes at a lower temperature (556 °C) as compared to PMMA B (600 °C) which has 50 000 repeat units. Indeed, the rate of decomposition of the polymer will depend on the number of end groups. In addition, the higher the molecular weight, the lower the number of end groups, therefore, the higher the degradation temperature [8,14].

Cross Linking

Cross-linked polymers usually either have very high melting points, or thermally degrade before reaching their melting point. The cross links inhibit the transport of degradation products to the surface of the polymers thus limiting gas phase fuels from being liberated. An everyday example of the result of a cross linking reaction is the vulcanization of rubber whereby natural rubber is reacted with sulfur (or other suitable agents) in order to increase the number of inter-chain covalent bonds, thus making a cross linked polymer [15].

The aforementioned factors play a major role in the thermal stability of a polymeric material. Polymers which have undergone some kind of degradation, thermal or other, have different physical and chemical properties than at the time they were processed. These can be mechanical, thermal, or fire properties. The next section sheds light on how the thermal properties of a polymer can affect its fire properties.

I.1.b. Fire Behavior of Polymers.

While knowledge of the thermal behaviors of a material is useful when high temperature applications are anticipated, it is also important to investigate their fire properties. Indeed, despite the common assumption that a thermally resistant material is also fire resistant, this is not entirely true. Fire properties depend on other factors such as the gases released during the thermal decomposition or the structural integrity of the resulting char formed upon burning. However, before delving into the actual behavior of organic polymeric materials, it is primordial to properly understand the mechanisms involved when a polymer burns.

I.1.b.i. The burning process

Gases and volatile liquids with weak intermolecular bonds such as methane or small organic molecules can form combustible mixtures in air. These mixtures can quite easily ignite and burn quickly. However, in the case of polymeric materials, the intermolecular bonds are much stronger since polymers are long chains of molecules which are neither volatile, nor gaseous. In order to evaporate a polymer, it is necessary to overcome the bond energy between these large molecules (macromolecules). Most polymeric materials degrade before evaporating. As a result, in order to make a proper combustible mixture, the chemical bonds within the polymeric materials need to be broken, releasing volatile gases, which, in turn, act as a fuel. This means that the burning material requires a constant supply of heat for it to ignite and keep burning.

The burning process of a polymeric material can be subdivided into different physical and chemical processes taking place in three distinct phases: gas phase, mesophase, and condensed phase [8]. The mesophase is the interface between the bulk material and the gases that are burning.

Figure 2 shows the different chemical and physical processes that take place during the burning of a polymer. The chemical processes are shown on the right-hand side while the physical processes on the left. The physical processes include radiative and convective heat transfer between the flame (burning gas phase) and the mesophase, heat loss in the mesophase due to mass transfer (evaporation of degradation products). While the mixing and burning of combustible gases is a fast process as compared to the diffusion of degradation gases from the intermediate phase, the rate-limiting step during polymer burning is the mass transport from the bulk material to the flame.



Figure 2. Physical and chemical processes during burning of a polymeric material [16].

On the other hand, the chemical processes occurring during the flaming combustion involve the thermal degradation of the polymeric material in the mesophase a result of heat transport, the air/volatile gases mixture forming due to the diffusion of the later, and the combustion of the air/fuel mixture in a combustion zone, which is bound by a fuel rich and fuel-thin region.

These physical and chemical processes occur in one or more of the three phases of the burning process of the polymeric material. In order to have a better understanding of the fire scenario on a burning material, the phenomena occurring at the three phases will be explained in the unfurling paragraphs.

I.1.b.ii. Gas phase

Condensed phase materials can only sustain an efficient burning process if they release combustible fuel that allow them to do so in air. It is, in fact, the gas phase that contributes to ignition and flame spread [8]. Because of the nature and the number of steps in the decomposition of polymeric materials, it is difficult to understand the exact underlying chemical reactions taking place during a fire scenario. However, through kinetic modeling and empirical data, it was shown that the rate of burning is due to the following reactions involving highly reactive radicals of fuel (R), hydroxyl (HO), hydrogen, oxygen (O), halogens or phosphorous (X).

 $Initiation: RH \to R^{\cdot} + H^{\cdot} \tag{1}$

Branching:
$$H^{\cdot} + O_2 \rightarrow HO^{\cdot} + O^{\cdot}$$
 (2)

$$Propagation: HO^{\cdot} + CO \to CO_2 + H^{\cdot}$$
(3)

$$Propagation: HO^{\cdot} + H_2 \to H_2O + H^{\cdot}$$
(4)

$$Termination: H^{\cdot} + O_2 \to H_2 O \tag{5}$$

$$Inhibition: HO^{\cdot} + HX \to H_2O + X^{\cdot}$$
(6)

$$Inhibition: H^{\cdot} + HX \to H_2 + X^{\cdot}$$
(7)

These reactions illustrate the main processes of initiation (equation 1), branching (equation 2), propagation (equations 3 and 4) and termination (equation 5) which are typical for the combustion of a hydrocarbon fuel. The highest heat bringing reactions are the propagation reaction (equations 3 and 4). The heat generated sustains the fire by causing the formation of more reactive radicals. On the other hand, the presence of halogen (or phosphorous) in some polymeric materials account for inhibition reactions because of their radical scavenging nature (equations 6 and 7). This can be a positive impact to flame retard a particular material.

Moreover, the combustion process occurring in the gas phase can be summarized by equation 8.

$$C_c H_h O_m N_n X_x + \left(c + \frac{h - x - 2m}{4}\right) O_2 \to c C O_2 + \frac{h - x}{2} H_2 O_2 + \frac{n}{2} N_2 + x H X$$
 (8)

In equation 8, it is assumed that there is complete combustion of the reactants. This is the case when there is sufficient oxygen provision for the reaction to occur. However, in real

life cases, flaming combustion efficiency ranges from 50 to 95%. This leads to the production of smoke, which is a mixture of the above-mentioned products as well as soot, carbon monoxide, or partially oxidized fuel gases. These products are even more present when the oxygen is low, the combustion time is too fast or if the temperature at the combustion zone is not high enough.

The gas phase reactions generate heat from flaming combustion. This heat can be absorbed at the pyrolysis zone, or at the mesophase.

I.1.b.iii. Intermediate phase

The intermediate phase corresponds to the liaison between the gas phase and the bulk of the polymeric material. This is where all the thermal degradation of the material occurs. Long polymer chains are degraded into small volatile fuel gases and the mesophase consists mainly of thermal degradation products. Moreover, the physical properties of the mesophase depends on the type of material that is burning. For instance, a charring material would have a higher density than a non-charring one.



Figure 3. Phenomenology in a burning polymeric material [17]

Figure 3 shows the link between the different phases of a polymeric material for a sustained flaming combustion. There are several inter-dependent factors that are required to have a sustained combustion. Firstly, there must be sufficient heat energy reaching the polymeric material for it to degrade and release volatile fuel (and non-combustible) gases. This phenomenon may also lead to the formation of a char structure, depending on the nature of the polymeric material. The volatile combustible degradation products then form a

fuel/oxygen mixture from the atmospheric air. Ignition of this mixture is what initiates the flaming combustion. This combustion produces further heat energy (proportional to the heat of combustion of the degradation products) than can be fed back to the bulk material (solid polymeric structure) by convection and radiation. In the case of a sustained flaming combustion, this energy must be sufficient to further degrade the bulk material and release more fuel.

The formation of a primary char may occur at the first stage of the decomposition of the polymeric material. This char can further degrade to release more combustible gases (mostly hydrogen) and a thermally stable carbonaceous residue. This can be evidenced when thermogravimetric analysis (TGA) of a charring material is performed.

As stated earlier, during the decomposition of the polymeric material, different forms of degradation products are formed. These are produced by various mechanism steps which are discussed in the previous section (thermal decomposition of polymers). Generally, the main decomposition reactions that are susceptible to occur are main-, end-, or side-chain scission of the polymer. After this step, the decomposition reactions that occur are largely dependent on the structure of the material.

Indeed, the reactions such as hydrogen transfer to neighboring carbons, side chain reactions, elimination reactions, rearrangements, and/or unzipping are all possible during the decomposition of a polymer matrix. For instance, polymeric materials with an aromatic backbone such as polybenzimidazole, polyaramids or polyarylsulfones have a tendency to form varying levels of carbonaceous residue due to complex rearrangement reactions or inter- and intramolecular rearrangements. This char formation can act as a heat and mass transfer barrier that can have an effect on the feedback heat transferred to the polymer during burning. Charring usually decreases the heat release rate during flaming combustion. This is an enviable property for a polymeric material as it means that it has an enhanced fire behavior. However, virgin polymers do not usually intrinsically possess such a property. There are nonetheless some high-performance materials that have the ability to withstand high temperature and form dense and thermally robust chars during their decomposition.

I.1.b.iv. High Performance Polymeric Materials

While most engineering polymers have some similarities in their thermal degradation behavior (such thermal degradation temperature and char yield), there exist highperformance organic polymers such as polyetheretherketone (PEEK) or polyimide (PI), that have proved to have much higher performances under thermal stress. They also present outstanding fire resistance that make them particularly good candidates as materials for use in highly demanding applications such as the aerospace industry. In order to better understand why some polymeric materials offer a better resistance to extreme temperatures and fire, a comprehensive review has been carried out and is annexed at the end of this section (page 21).

The review deals with a series of organic, non-halogenated, high performance polymeric materials. One of the main criteria for being a part of this review was to have a sufficiently high thermal stability. This high thermal stability was defined as Hergenrother et al. did in 2003 - a high performance polymer is one that retains usable properties at temperatures above 177 °C [18].

It was seen that there are various intrinsic properties of a material that may impropriate thermal stability and desirable fire properties in a material. It was clear that the fire behavior and thermal stability of polymeric materials were somewhat correlated. Highly ordered polymeric materials such as polyetheretherketone (PEEK), polybenzoxazole (PBO), polyimide (PI), and polyhydroquinone-diimidazopyridine (PIPD) showed both high thermal stability and promising fire behavior [10,19]. However, it was not the case for para-aramids whereby the fire performance was not comparable to its high thermal stability. A high degree of aromaticity also seemed to be common to all high-performance polymers with good fire properties. These properties are even more prominent in the case of heterocyclic aromatic polymers which depicted strong interchain interactions [20].

Moreover, the fire behavior of the polymeric materials is strongly influenced by the thermal decomposition behavior and the decomposition products that are released when the material is heated. Indeed, materials that release a large amount of combustibles show poor fire performance. On the other hand, highly charring polymeric materials show promising fire behaviors. However, this cannot be a generalized rule as the physical integrity (structure and density) of the char formed during burning also plays a significant role in the fire properties. A typical example of such a material would be Kevlar (*p*-aramid) whereby a fragile char is formed during burning and little or no protection of the bulk of the material is observed.

I.1.c. Conclusion

Polymeric materials exhibit highly desirable properties when it comes to fields such as construction or aerospace industry. Indeed, their strength to weight ratio as well as their versatility in terms of processing and molding make them great candidates to replace steel and concrete. However, the major drawback of such materials lies in their flammability and resistance to high temperatures. Nonetheless, there are some polymers that have shown excellent resistance to heat and fire (see annexed review , page 20). However, these polymeric materials are often very costly. It is therefore judicious to find a compromise with usual engineering polymeric materials and fire retardants in order to achieve similar, or better fire behavior at a lower cost.

Thermal Degradation and Fire Performances of High-Performance Polymers

- Polymer Reviews -

REVIEW



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Thermal Degradation and Fire Behavior of High Performance Polymers

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ABSTRACT

High performance and high temperature polymers are a class of polymeric materials exhibiting high thermal stability and their resistance to fire makes them valuable assets for many applications. Those applications include as typical examples high temperature gas separation membranes, automotive and aerospace industry as well as the construction industry. The high performance polymers have been synthesized since the early 1960s, and have developed rapidly over the past few decades. Most high performance polymers comprise a highly aromatic backbone, linear chains, and strong interchain interactions. This review deals mostly with commercial polymeric materials. Studies regarding their thermal behavior, degradation mechanism and their reaction to fire have been synthetically combined in order to bring out potential insight concerning the effect of the thermal decomposition and thermal behavior on the fire properties of those polymers.

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1. Introduction

Over the past few decades there has been significant effort put into the elaboration and design of stronger, more resistant, and capable polymers. Numerous new families of polymers with novel properties have been reported with potential applications in challenging areas such as aerospace, defense, energy, electronics, or automotive. Such polymers exhibit enhanced service-temperatures and outstanding resistance to environmental stress.¹ With the coming into market of polymers that have such significantly enhanced properties as compared to common ones, the terms "high performance" or "advanced engineering" have been employed to describe them.²

High performance polymers have existed for more than half a century. Considerable effort was attributed to high performance polymers in the 1960s where most thermally stable heterocyclic rings were incorporated within polymers. At the time, the goal was to achieve as high a thermal stability as possible. DuPont's well-known Kapton[®], a poly-imide film, emerged during this decade. Other high performance polymers as Vespel[®] and polysulfones also appeared in the market during this period.

However, the proper definition for a high performance polymer is yet to be established. Indeed, numerous attempts at defining high performance polymers have been

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made. This high number is mostly because the term "high performance" is a constantly evolving one. Indeed, high performance polymers may be defined in many ways, depending on the end-use and the organization developing or using the material. A general definition for high performance polymers would be polymers that meet even higher requirements than standard engineering plastics.³ This leads to "high performance" polymers being a broad term that can be used to describe many polymeric materials. However, in the context of this investigation, the definition of "high performance" polymer will be closely related to what was reported by Hergenrother et al.—a high performance polymer is one, which retains usable properties at temperatures >177 °C.⁴

In the 1970s, routes to developing polyetheretherketones (PEEK, ICI), polyetherketones (PEK, ICI) and Polyetherimide (UltemTM, General Electric, GE) were found. These products were launched in the 1980s. High performance polymeric fibers were also made during this period. A high modulus, rigid rod polymer, Polybenzoxazole (PBO), first made by the Air Force Wright Patterson Laboratories, and subsequently developed by Dow Chemical and commercialized in the 1990s by Toyobo joins the family of high performance fibers. Another high performance rigid rod polymer that shows excellent thermal and mechanical properties is polypyridobisimidazole (PIPD) first developed by Sikkema in 1997.⁵

Polymers may be classified into two major classes: thermoplastic and thermosetting. These two categories may be subdivided further depending on their crystallinity. Indeed, amorphous polymers are those which have a near-zero degree of crystallinity (such as polyetherimide). This implies that they have high levels of irregularities in their structure. This may come from different reasons ranging from high levels of branching or the presence of bulky side groups in the polymer. On the other hand, polymers that possess highly ordered structures dispersed in an amorphous phase are called semi-crystalline (for example, polyether ether ketone). Another type of polymer that will be discussed in this work is rigid rod polymers. These types of polymers exhibit outstanding thermal and mechanical properties and considerable interest has been paid to them. Some examples of rigid rod polymers are polybenzoxazole or polybenzimidazole.

The thermal stability of a polymer may be studied by different methods. One of the most extensively used method is thermogravimetric analysis (TGA). This method provides data on the evolution of the mass of a material with respect to the temperature in different atmospheres. Isothermal or varying temperatures may be used for such analyses. Indeed, by studying the evolution of the weight of a material with respect to a heating rate, the degradation temperature and the behavior at specific temperatures may be deduced. However, this method does not give any information about the thermal decomposition products that are released. For this reason, TGA is often coupled with other analytical techniques such as mass spectrometry (MS) or Fourier-transform infrared spectrometry (FTIR).

However, with MS and FTIR coupled with TGA, it is not possible to separate decomposition products. Very often, spectra with all the different degradation products are obtained. Therefore, another instrument that is often chosen to identify degradation products is the pyrolysis-gas-chromatography/mass spectrometry (Py-GC/MS). Py-GC/ MS at different pyrolysis temperatures can be used to separate and identify the different decomposition products at those temperatures.

The kinetic parameters of the thermal decomposition of a polymer are also an important factor in elucidating the degradation mechanism of a polymeric material. There are various methods for such thermal analysis and two of them are the most popular. The first method is based on the isoconversion procedure developed by Ozawa Flynn and Wall (OFW).^{6,7} The second method was developed by Friedman.⁸ It uses the derivatives of mass loss and it can be applied for *n*-order reactions. This may be done using various methods based of TGA results of a given material.

The evaluation of fire performances of high performance polymers was also reviewed. The most common tests for the evaluation of the fire performance of a material are the limiting oxygen index test and the Underwriters Laboratories 94 (UL-94) test. Other tests such as the pyrolysis combustion flow calorimetry (PCFC) or microscale combustion calorimetry (MCC) and cone calorimeter are also used to measure the heat release rates during the combustion or degradation of a material. This provides insight on the susceptibility of a material to feed or extinguish a fire.

PCFC (or MCC) provides heat release rates on small samples (usually milligrams) by measuring oxygen consumption. It is a non flaming, 1 dimensional test that does not take into account surface properties of the material. It provides insight on the heat of combustion and specific heat release rate (in W/g).

Cone calorimeter compares to PCFC in the sense that the heat release rate may also be measured by oxygen consumption. However, in the case of cone calorimetry, the heat release rate is actually heat flux (in kW/m²). Indeed, for cone calorimetry, test samples are larger (about $10 \times 10 \times 0.3$) mm³. The test comprises of irradiating a sample with an incident heat flux. The material reacts and may (or may not) flame up. The oxygen consumption due to the burning sample is measured and this leads to the heat release rate of the burning sample.

When it comes to reviewing the thermal properties of high performance and high temperature polymers, a number of works already exist. Indeed, in 1979, Arnold et al regrouped a large number of high performance polymers that were available at the time in order to study their thermal behavior. Since then, quite a number of reviews that have been written regarding the thermal properties of high performance polymers.^{4,9-11} However, few works encompass the thermal stability and the fire behavior of high performance polymers in 2011.¹² However, thermal decomposition data are scarce in the review. Polymer specific reviews have also been made, regrouping the thermal properties of a specific type of high performance polymer.¹² Among the few papers that have both an in-depth review on the thermal stability and the fire performances of polymeric materials, Bourbigot et al. have regrouped high performance fibers. Their work also consisted in furthering the fire behavior with fire tests for materials that were not yet tested in flame tests.¹³

In this work, a different approach will be adopted. A series of halogen-free polymeric materials exhibiting high performance and thermal stability will be reviewed (Table 1). The focus of this work lies on the study of their thermal stabilities and their behavior at elevated temperatures. Possible decomposition mechanisms will be elucidated where

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Chemical name or designation	Generic name	Chemical structure	Trade name
Polyetherimide	PEI	$\left[\begin{array}{c} 0\\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$	Ultem®
Polyether ether ketone	PEEK		PEEK®
Poly(phenylene sulfone)	PPSU		Radel [®] R
Polyimide	PI		Kapton®
Polyamide-imide	PAI	$\begin{bmatrix} H \\ H \\ N \\ O \end{bmatrix}_{n}$	Torlon®
Poly- <i>p</i> -phenylene-2-6- benzobis-oxazole	PBO		Zylon®
Poly(2,2'-(m-phenylene)- 5,5'-bisbenzimi-dazole)	PBI		PBI
Poly(2,6-diimidazo(4,5-b:4',5' e)pyridi-nylene-1,4 (2,5- dihydroxy)-phenylene)	'- PIPD	HO H H H H H H H H H H H H H H H H H H	M5 [®]
Poly(p-phenylene terephtal-amide)	ΡΡΤΑ		Kevlar [®]

 Table 1. High performance polymers, their generic name, repeat unit, and trade names.

possible and a relationship with the thermal stability of the polymers will be attempted. A relationship between the fire behavior and the thermal decomposition will also be attempted. This work is limited to polymers that are widely available on the market these days. New high performance polymers are still being researched but so far, there has been little or no success in developing new classes of them.

2. Polyetherimides

Polyetherimides (PEI, Figure 1) are amorphous, high performance thermoplastics; its color is from amber to transparent. They have outstanding mechanical, thermal and chemical properties. Because of these properties, they are often chosen for highly demanding applications whereby high temperature and harsh environments are encountered. Some applications include lighting reflectors,¹⁴ electrical industry,¹⁵ automotive,¹⁵ and wire coating.¹⁵

Polyetherimides are polyimides, which consist of ether linkages in the aromatic polymer backbone. The presence of these ether linkages provides flexibility to the polymer, allowing for a good melt processability while the aromatic-rich backbone keeps the thermal and mechanical properties of the polymer excellent.

The most widespread polyetherimide is commercialized under the trademark ULTEM resin (Figure 2). It was made available commercially in 1982 by the General Electric's Plastics Business group. Presently, it is commercialized by Sabic.

2.1. Synthesis

There are two main synthetic routes of PEI (Ultem). Both comprise of the melt polymerization of bisphenol A dianhydride with a diamine, most often, m-phenylenediamine as shown in Scheme 1. The dianhydride is synthesized by the reaction of two moles of a phtalic anhydride derivative with one mole of bisphenol A. The condensation of the dianhydride and the diamine forms a polyamic acid. A heat or catalytic treatment of this acid leads to the polyetherimde, Ultem. Another pathway comprises of making the imide in the first step, followed by a nucleophilic substitution process to yield the polymer. The first route is the most widely used pathway in industry, since it gives better yields due to the stability of tetracarboxylic dianhydrides.

2.2. Thermal properties

Polyetherimides have a glass transition temperature of 217 °C.¹⁴ They can be subjected to conventional melt-processing techniques at temperatures of 350–425 °C.¹⁵ It is







Figure 2. Structure of Ultem (General Electric).



Scheme 1. Synthetic route for the production of Ultem.

thermally stable up to 500 °C. Commercial grades of PEI include additives (such as glass fiber reinforced PEI) because they tend to increase further the temperature resistance of the material.

Thermogravimetric analyses at different heating rates have been performed on polyetherimides in order to study their thermal stability.^{16,17} Foreman et al. studied the service lives of PEI under different criteria. The 60-min half-life temperature (temperature at which half the material degrades within 60 min under pyrolytic conditions) of PEI was found to be 477 °C in nitrogen. The service life curves correspond to the time required for 5% of the material to degrade at a specific temperature in nitrogen. In the case of PEI, the TGA service life temperature for 1 year was found to be 318 °C and that for 10 years was 292 °C. This corresponds to the temperature at which a 5 w% mass loss is observed for this period. This temperature was higher than for regular engineering polymers (for example, polyphenylene sulfide has a TGA service lifetime for 1-year lifetime at 230 °C).

Thermogravimetric analyses (TGA) of PEI at different heating rates, in air and in inert atmospheres were also reported. $^{\rm 18-22}$

Figure 3 shows the TGA plot of Ultem with a heating rate of 10° C/min. It was reported that the onset of the degradation occurs at around 450 °C under nitrogen.^{22,23} The maximum rate of decomposition temperature is about 510 °C (DTG curve). The DTG curve shows a second, less significant decomposition stage that occurs in the range 600–650 °C under nitrogen. The weight loss at 800 °C under nitrogen is around 40%.

In this case, the degradation temperature is given as the temperature at which the polymer starts to degrade (weight <100 wt%). However, a more generally accepted definition for this criterion is the temperature at which 5 wt% of a material is degraded (T_{onset}). With this definition, the degradation temperature (in nitrogen) of PEI is in fact closer to 500 °C than 450 °C.

When it comes to TGA, it is suggested that the degradation temperature of a material can be different depending on the atmosphere. The TGA plot of PEI in air with a heating rate of 10° C/min was reported by Halawani et al. in 2017 (Figure 3).²⁰ It can be observed from the TG plots under the air and nitrogen that the nature of the atmosphere does not have a significant impact on the onset of the thermal degradation of PEI. However, when subjected to high heat in an oxidative environment, PEI degrades in two fast steps. Contrarily to its behavior in nitrogen, the second decomposition step observed in the TGA plot of PEI in air leads to the near-complete decomposition of the polymer. The residual mass in air at 800 °C is 0 wt% as compared to 50 wt% in nitrogen.

The TG plot shows two apparent weight loss stages, which are clearly observed on the DTG curve (Figure 3), of the TGA of PEI in nitrogen. The two temperatures at which the weight loss rates are maximum are 540 °C (first stage) and 585 °C (stage two). It can also be observed, from the TGA plot that the residual weight above 700 °C does not show significant decrease. This suggests that carbonization plays a vital role in the solid-phase mechanism.

In addition to making the determination of the different decomposition temperatures possible, TGA also provides a way to determine the kinetic parameters for the thermal decomposition of a material. The kinetic parameters of the thermal degradation of PEI



Figure 3. Thermogravimetric analysis of and DTG curve of PEI under nitrogen (left)²⁴ and TGA plot under air²⁰ (right) at a heating rate of $10 \degree C/min$.²⁵

has been thoroughly studied in the past.^{19,23,26} One of the first works concerning the kinetics of the thermal decomposition of PEI consisted in using thermogravimetry at different heating rates under nitrogen.¹⁹ However, the kinetics studied was limited to the first stage of the degradation when it is in fact a two-stage decomposition. The bivariate fitting method was used and a comparison to other model-free kinetics (MFK) fitting methods was reported. A summary of these results are shown in Table 2. These methods assume an Arrhenius dependence of the reaction rate on the temperature and have been applied in a wide range of kinetic studies.

In a more recent study, the kinetic parameters of the two stages of the thermal decomposition of PEI was performed using the ThermaKin²⁰ model. It was possible to separate the two decomposition stages of PEI. The results are summarized in the Table 3.

In this study, the two steps of the decomposition are taken into account and the kinetic parameters of each degradation steps are calculated. The first activation energy, which corresponds to the first decomposition step was determined to be 465 kJ/mol and had a corresponding pre-exponential factor of $1.06 \times 10^{27} \text{ min}^{-1}$. As for the second step, the activation energy was determined to be 36 kJ/mol with a corresponding pre-exponential factor of $6.5 \times 10^2 \text{ s}^{-1}$. These results are not consistent with the initial kinetic parameters determined in the previous paper. This might be because the two-step decomposition of PEI not taken into account in earlier papers. Therefore, this work seems to provide a more accurate simulation of the kinetic parameters of the thermal degradation of PEI.

Even if TG plots gives valuable information regarding the temperature and the energy required for thermal degradation to within the material, they do not cater for the identification.

Moreover, the decomposition products of a material may play a crucial role in the context of fire behavior. Therefore, it is of interest to investigate the mechanism adopted when a polymeric material thermally decomposes. Works at elucidating the thermal decomposition mechanism of PEI has been carried out using various methods such as pyrolysis/gas chromatography/mass spectrometry (Py-GC/MS),²⁵ stepwise Py-GC/MS,²⁸ thermogravimetry/mass spectrometry/Fourier Transform Infrared spectrometer (TG/MS/ FTIR),²² direct pyrolysis/mass spectrometry (DPMS)²⁹ as well as thermogravimetry/mass spectrometry (TG/MS).²²

Method	Apparent activation energy (kJ/mol)	Apparent order	Pre-exponential factor (min $^{-1}$)
Bivariate fitting ¹⁹	192	5.33	1.45×10^{12}
Ozawa's ²⁵	184		
Friedman's ²³	192	6.09	$1.45 imes 10^{12}$
Kissinger's ²³	178		

 Table 2. The kinetic parameters of the thermal decomposition of PEI using different methods.

Table 3. Kinetic parameters of the thermal decomposition of PEIusing generalized functions.27

Property	Value
First Apparent activation energy (kJ/mol)	465
First Pre-exponential factor (min ⁻¹)	$1.06 imes 10^{27}$
Second apparent activation energy	36
Second pre-exponential factor (s ⁻¹)	$6.5 imes 10^2$

These methods allows for the identification of decomposition products that are released when a material is subjected to thermal stress. Py-GC/MS allows the identification of decomposition products when a material is subjected to a specific temperature for a given duration. Evolved decomposition products are separated using gas chromatography and identified using mass-spectrometry. However, using this method, the different phases of decomposition cannot be discerned from each other. This is why some researchers have adopted stepwise Py-GC/MS, whereby the material is subjected to different pyrolysis temperatures. These temperatures may be determined prior to the analyses by using TGA. TG/MS/FTIR provides real time data on the remaining weight of a material simultaneously with the mass spectra of all the decomposition products along with the FTIR of the gases that are evolved. This method combines three analytical techniques, each providing information of different nature on the degradation products. Indeed, by coupling FTIR and MS, the nature of the bonds involved in the decomposition gases is identified by FTIR. This makes the identification of the possible decomposition using MS easier. Finally, direct pyrolysis mass spectrometry (also known as evolved gas analysis - mass spectrometry) provides the possibility of identifying different pyrolysis products at specific temperatures.

Py-GC/MS has the advantage of collecting all the decomposition products in a trap before separating the degradation products with respect to their boiling points and polarity. This provides the possibility of identifying individual species. However, by allowing the degradation products to stagnate all in the same place before separating them, there is the risk that individual decomposition products recombine in the trap.

However, unlike Py-GC/MS, the other methods mentioned do not separate the different degradation products. This makes the identification of specific products using mass spectrometry more challenging as the mass spectrum data of all the degradation products at a specific temperature are observed on the same spectrum.

Table 4 shows the volatile decomposition products of PEI, determined by flash pyrolysis at different temperatures up to $850 \,^{\circ}$ C.²⁸ Most of the high temperature decomposition products are identified and can be used to devise a tentative decomposition mechanism for PEI.

The main products of PEI decomposition have been identified as CO, CO₂, phenol, benzonitrile, and aniline.²⁹ It was first suggested that PEI decomposes following two main mechanisms: ether bond breaking mechanism and carboxyl induced chain breaking mechanism.¹⁹ Further works allowed to conclude that the decomposition was a two stage mechanism. The first-stage reaction is assigned to the main-chain random scission of hydrolyzed imide groups induced by water existing in the sample as the primary mechanism. The second stage of the pyrolysis involves the scission of ether and isopropylene groups with the evolution of water that was consumed during hydrolysis of other imide groups.²⁸

In another study, the analysis of the thermal decomposition of PEI was performed by direct pyrolysis mass spectrometry (DPMS).²⁹

By using DPMS, the mass spectra acquired allowed the identification of low temperature degradation products that are evolved during the decomposition of PEI. At 400 $^{\circ}$ C, the mass spectrum was assigned to an open chain compound containing part of the repeat unit of PEI (Figure 4).

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Compound	Name	Compound	Name
C0 + C02		он	4-Ethylphenol
\bigcirc	Benzene	но	<i>p</i> -Vinylphenol
	Methyl-benzene		Naphthalene
	Ethylbenzene	>ОН	4-(<i>p</i> -lsopropenyl)phenol
\rightarrow	<i>p</i> -Xylene		2-Vinylnaphthalene
	Styrene		Diphenylether
	Isocyanatobenzene		Diphenylmethane
NH ₂	Aniline		1-Methyl-4-phenoxybenzene
-он -см	Phenol + benzonitrile		Dibenzofuran
ОН	2-Methylphenol		Fluorene
он	4-Methylphenol	HO	4-(1-Methyl-1-phenylethyl)phenol
См	4-Methylbenzonitrile	CH ₃ CH ₂	4-(1-Methylvinyl)-1-phenoxybenzene
	H ₃ C CH ₃		
			$\langle \rangle$

Table 4. Identification of the products in Flash Py-GC/MS of PEI up to 850°C in heliui



HO'

Figure 4. Structure corresponding to m/z of 594 for the mass spectrum recorded at 400 $^\circ\text{C}.^{29}$

However, 400 °C corresponds to merely the onset of the degradation of PEI. Therefore, in order to get better insight on the degradation products, it is important to look at the products evolved at higher temperatures. The mass spectra of the pyrolysis products evolved at 520 and 620 °C have been reported.²⁹

0=



Scheme 2. Postulated hydrolysis of imide groups followed by random chain scission.²⁸



Scheme 3. Postulated disproportionation and C-H transfer mechanism occurring at lower temperature.²⁹

The mass spectrum at 520 °C evidenced that the main products evolved are phenol, isopropylidenephenols, isopropylidenediphenyl ether. phtalimide ring substituted with other groups, such as aromatic ethers and OH. These phtalimide rings may have been generated by the disproportionation of the isopropylidene bridge of the bisphenol A units of PEI, followed by hydrogen transfer reactions (Scheme 3).

The formation of phtalimide based structures containing phenyl rings substituted with hydroxyl group or bisphenol A or both can be explained by the scission of ether bridges (Scheme 4a and 4b). The presence of nitrogen containing end groups may be explained by the scission of phenyl-phtalmide bonds (Scheme 4c). Extensive associated hydrogen transfer reactions may explain the high char residue in the pyrolysis of PEI.



Scheme 4. Postulated hydrogen transfer mechanism leading to different phtalimide derivatives.²⁹



Scheme 5. Hydrogen transfer and decomposition in NH phtalimide end-groups.²⁹



Scheme 6. Poly(amic acid) formation and tautomerization equilibrium of phtalimide rings.²⁹

At 620 °C, the mass spectrum recorded shows the presence of lower molecular weight molecules. The peaks are assigned to CO_2 , benzene, toluene, aniline, benzonitrile, and amine-substituted benzene derivatives. Some phtalamide derivatives are also observed, albeit with lower intensity. This may be due high temperature pyrolysis of N-H phtalimide end-groups, involving the formation of thermally unstable isocyanate intermediate that decomposes to form nitriles and carbon dioxide²⁹ (Scheme 5).

The high char residue coming from the pyrolysis of PEI may be explained by the formation of polyamic acid that undergo decarboxylation at T > 600 °C. This leads to the formation of aromatic imides. The tautomeric equilibrim of imides is shifted towards iminolization when the temperature is high. The iminols undergo dehydration and form cross-linked structure, contributing to the char residue and nitrile formation^{30,31} (Scheme 6).

DPMS analysis allowed the deduction that the main preliminary degradation products of PEI are phtalimide derivatives. These derivatives offer a plethora of decomposition pathways that lead to the formation of nitrile derivatives, carbon dioxide and water (Schemes 5 and 6)

2.3. Fire behavior

One of the notable properties of PEI is its inherent flame retardancy. Indeed, PEI has a limiting oxygen index of 45.2,³² which is an extremely high value considering that it is neither a halogen containing polymer, nor is it flame retarded chemically. It can achieve V0 rating in the UL-94 test.³³

Cone calorimetry at 50 kW/m^2 have been performed on samples of PEI in evaluate its reaction to fire. The results of these tests are summarized in Table 5. PEI has a relatively low ignition time when subjected to 50 kW/m^2 (67 s). It has two peaks of heat release rate, which are relatively low (74 and 65 kW/m^2) as compared to a regular polyester (131 kW/m²) when tested in similar conditions. The total heat released during a 5min cone calorimeter test at 50 kW/m^2 sums up to 58 kJ, which is among the lowest values for an amorphous thermoplastic. The effective heat of combustion of PEI is reported as 18 MJ/kg. Moreover, PEI has an average smoke specific extinction area of $270 \text{ m}^2/\text{kg}$ and a carbon monoxide yield of 0.13 kg/kg.³⁴

2.4. Concluding remarks

PEI is the only amorphous thermoplastic polymer that is stable at such a high temperature. Its high glass transition temperature allows it to retain a high percentage of its mechanical strength at high temperatures.

The relatively high degradation temperature of PEI may be attributed to the highly aromatic imide backbone. This also accounts for the high char residue that is yielded when the polymer is subjected to high temperatures.

The decomposition products suggest that when under thermal stress, the first degradation corresponds to a depolymerization reaction. During this reaction, it is reported that amidoiminol tautomerization occurs, favoring crosslinking and the formation of nitriles. This causes an increased char formation. These two characteristic decomposition behaviors may explain the inherent flame retardancy of PEI. Indeed, the high char residue may create a protective layer upon exposure to outside heat flux. This can limit the liberation of combustibles during the combustion of the polymer, thus decreasing the total heat released.

3. Polyetheretherkeetone (PEEK)

Polyether ether ketone (PEEK) is a subfamily of polyarylketones (PAEK). PAEKs are semi-crystalline engineering thermoplastic polymers that show high thermal, mechanical, chemical, and electrical properties. They have a plethora of applications in various industries including automotive, aerospace, chemical, and oil industries. It has a continuous use of 260 °C and a melting point of 343 °C.

Table 5.	Summary	of	cone	calorimeter	results	at	50kW/m^2	of PEI.	34
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PEI	Value
Time to sustained ignition (s)	67
Peak heat release rate (kW/m ²)	74
Time to peak heat release rate (s)	167
Total heat released (MJ)	58
Effective heat of combustion (18 MJ/kg)	18
Mass loss (%)	13

PEEK was the first PAEK to be fully commercialized.³⁵ This was possible thanks to Rose et al.,³⁶ from Imperial Chemical Industries (ICI),² who identified diphenyl sulfone as a suitable solvent for making PEEK with similar toughness and crystallinity.

3.1. Synthesis

The first syntheses of polyaryletherketones (PAEK) were reported in the early 1960s.³⁷ They were based on electrophilic substitution reactions, more precisely, Friedel-Crafts Acylation. However, because of the low solubility of the crystalline polymers, strongly acidic media were required. Polyphosphoric acid³⁸ and HF/BF₃³⁹ were later used to dissolve the polymers by protonating their carbonyl groups.

PEEK is one of the most commercially prepared PAEK on the market.³⁵ It is prepared by reacting 1,4-benzenediol (hydroquinone) with 4,4'-difluoobenzophenone in diphenyl sulfone in the presence of alkali-metal carbonates under an inert atmosphere at temperatures close to the melting point of the polymer³⁹ (Scheme 7).

However, since PEEK was first synthesized, many routes have been developed for its production. An in-depth review on the synthesis and modification of PEEK in 2012 reported five main routes, as follows⁴⁰:

- Electrophilic substitution route or Friedel-Crafts acylation⁴¹
- Nucleophilic substitution route or displacement reaction⁴²
- Nickel-catalyzed coupling polymerization⁴³
- Synthesis by removing bulky substituent from soluble amorphous pre-polymer^{44,45}
- Ring opening polymerization of cyclic PEEK oligomers⁴⁶

The synthetic routes of PEEK production may have different effects on the physicochemical properties of the polymer. Indeed, the retrosynthetic history of a polymer may allow it to have higher molecular weight or inherent viscosity as well branching.⁴⁰ Purity of the polymers may also depend on the synthetic route. Depending on the volatility of the reactants used and by-products formed, the end product may be more or less pure at the end of the reaction.⁴⁰

It was also reported that it is possible to bring post-polymerization modifications to PEEK. However, because PEEK is insoluble in most organic solvents, usual application of many organic methods is impossible to functionalize PEEK.

3.2. Thermal properties

PEEK has a relatively high temperature resistance, with a reported continuous use at $260 \degree C$ and a melting point of $343 \degree C$.⁴⁷ Thermal degradation starts between 575 and



Scheme 7. Synthetic pathway for PEEK.

580 °C. PEEK being an organic polymer, this decomposition temperature is relatively high.⁴⁸ In order to better understand the thermal behavior of PEEK, it was subjected to thermogravimetric analyses.

Figure 5 shows how the residual weight of PEEK evolves with temperature under inert (nitrogen) and thermo-oxidative (air) atmospheres under different heating rates.

Under nitrogen, the TG plot of PEEK shows two distinct mass loss steps. A sharp weight loss occurs at around 580 °C, causing a decrease of around 45% of the initial mass. This first mass loss is assigned to the random chain scission of ether and ketone bonds.⁴⁹ The remaining mass was assigned to carbonaceous char,⁵⁰ which has a slower rate of decomposition. This first mass loss was previously reported and was assigned to the loss of phenol derivatives as degradation products.⁵⁰ Moreover, CO and CO₂ were also identified over this temperature range.^{50,51} CO and CO₂ may be attributed to being by-products of the decomposition of PEEK to phenols derivatives.

From the TG plot in air, it can be clearly observed that the decomposition occurs in two-steps, similarly to the thermal decomposition under nitrogen. The first step occurs at slightly lower temperatures than when the analysis is performed under nitrogen (data summarized in Table 6). It may be attributed to random chain scission and of ether and ketone bonds.⁴⁹ The second step is attributed to the oxidation of the carbonaceous char formed as a result of the first decomposition step.⁵¹ The onset of the thermal decomposition occurs at 507 °C. PEEK decomposes at a lower temperature in air than



Figure 5. Thermal decomposition of PEEK nitrogen (left) and in air (right) @ heating rates: $5 \degree$ C/min, $10 \degree$ C/min, $15 \degree$ C/min, and $20 \degree$ C/min.⁵²

Table 6. Thermal characteristics of PEEK at different heating rates under pyrolytic and thermo-oxidative conditions.

	Nitrogen				Air			
Heating rate (°C/min)	5	10	15	20	5	10	15	20
Tonset (°C)	526	537	562	572	507	531	542	546
T _{max} (°C)	567	588	599	605	600	587	602	630
Residue (wt%)	48	46	46	44	0.4	0.1	0	0

under nitrogen (-19 °C). The amount of residue generated is also significantly higher when the thermal analysis is performed under nitrogen (about 45 wt%) than in air (< 1 wt%).

Table 6 shows the decomposition onset temperature (T_{onset}) , the maximum mass loss rate (T_{max}) , and the percentage residue after the TGA of PEEK under nitrogen and in air. At low heating rates, the degradation temperature is lower than at higher heating rates. A sharp mass loss is observed just below 600 °C both in air and under nitrogen. This causes a decrease in mass of around 45%.

Vasconcelos et al. made TGA of PEEK at different heating rates both in air and under nitrogen in order to determine the kinetic parameters of its decomposition.⁵³

Under nitrogen, the activation energy for a conversion rate of 5% was found to be 238 kJ/mol.^{53} The lifetime of the material at $350 \,^{\circ}\text{C}$ was found to be 216 years for this decomposition under nitrogen.

Patel et al. found and activation energy of around 220 kJ/mol with an Arrhenius preexponential factor corresponding to 1×10^{23} s⁻¹ using the Kissinger method.⁴⁹ The parameters were also extracted using the iso-conversion method. It was concluded that the up to 70% conversion, the average activation energy for the thermal decomposition of PEEK was constant at around 250 kJ/mol.

In synthetic air atmosphere, the activation energy for a conversion rate of 5% was about 135 kJ/mol. The time required for the material to decompose by 5% in air at $350 \degree \text{C}$ is reduced to 1.05 years.⁵³

3.2.1. Mechanism of the thermal decomposition of PEEK

Pyrolysis products of PEEK were determined by stepwise pyrolysis/gas-chromatography/ mass-spectrometry (Py-GC/MS), flash pyrolysis and stepwise pyrolysis.⁵⁴ Table 7 shows the degradation products of PEEK under flash pyrolysis conditions at different temperatures.⁴⁹

Hull et al. have performed an in depth review on the decomposition studies of PEEK in 2010.⁴⁹ From the degradation products that were detected by Py-GC/MS, an attempt to elucidate the degradation pathway of PEEK was made. The results are summarized in Table 7.

In the initial stage of the decomposition (at $450 \,^{\circ}$ C), the identified decomposition products are reported to be 4-phenoxyphenol and 1,4-diphenoxybenzene. This suggests that the decomposition of PEEK is initiated in two possible mechanism: cleavage of the main chain followed by cleavage at chain ends/branches or solely by the cleavage of chain ends and branches.⁴⁹

At higher temperatures, lower molecular weight compounds are identified. This may be because the main chain scission is less targeted to solely the low energy bonds. This leads to other volatile products such as CO, CO_2 or diphenyl ether, which are identified at 650 °C. At 750 °C and higher, dibenzofuran, biphenyl, and naphthalene are identified.

Phenol has been identified as the main decomposition product at temperatures above $650 \,^{\circ}\text{C}^{.54}$ Another major decomposition product is reported to be dibenzofuran. This can be associated to a ring closure reaction occurring between diradicals at the ether

groups of PEEK monomer units. Dibenzofuran is also found at 750 °C. This high temperature environment favors the recombination of adjacent radicals⁵⁴ (Scheme 8).

At temperatures higher than 900 °C, significant amount of phenylphenol has been identified.⁵⁰ This may be attributed to the pyrolysis of ether containing species in the partially carbonized solid residue.

Temperature (°C)	Structure	Decomposition Product
450	OL OH	4-phenoxyphenol
		1,4-diphenoxybenzene
650	$CO + CO_2$	$CO + CO_2$
		Diphenyl Ether
750	OH	Phenol
		Benzene
		Dibenzofurane
	НОСН	Hydroquinone
	OH OH	4-Dibenzofuranol
	HOLD	4-Hydroxybenzophenone
		p-Benzoquinone
		Biphenyl
	Č	Naphthalene
		Fluorene
1100	HO	4-Hydroxybenzophenone
		1,4-Diphenoxybenzene
	OH	4-Phenylphenol

Table 7. Decomposition of PEEK by temperature analyzed by flash Py-GC/MS.^{49,54}

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Scheme 8. Decomposition mechanism leading to phenoxyphenol at 450 °C.⁵⁴



Scheme 9. Preparation of PPSU using nickel based catalyst.⁶⁰

Tentative pathways to the decomposition products at different temperatures have been proposed in order to explain the thermal decomposition mechanism of PEEK.

The low temperature degradation (at around 450 °C) is associated with the random scission of the lowest energy bond. This corresponds to the carbonyl-aromatic bond. This scission would form two resonance-stabilized groups.

At 650 °C, phenol and diphenyl ether are identified. Their formation requires higher energy because the radical intermediates formed are not stabilized by resonance with the presence of an aryl ketone or phenol ring. The formation of CO at this temperature may be explained by the decarbonylation of aldehydes and CO_2 may be formed by the decarboxylation of carboxylic acids formed during the initial decomposition.⁴⁹

At 750 °C, phenol is still formed and the formation of benzene is detected. In addition, the formation of hydroquinone and benzoquinone are observed. This high temperature allows for the formation of less energetically favored radicals. A diradical pathway may lead to the formation of benzoquinone. However, to explain the formation of hydroquinone, a stepwise process is suggested. Ring closure reactions followed by random chain scission could lead to further formation of benzofuran and dibenzofuranol.⁴⁹

The high char yield suggests that aforementioned random chain scission reactions are coupled with carbonization processes. The pyrolysis gas chromatography-mass spectrometry data suggest that the dominant pyrolysis route at temperatures above 800 °C correspond to carbonization.⁵⁴

These tentative mechanistic pathways give a good idea of the possible modes of decomposition that may be adopted when PEEK is subjected to high temperatures. However, they are not conclusive and further work is required to ascertain the actual thermal decomposition mechanism of PEEK. However, the nature of the decomposition products account for its apparently low flammability (see Fire behavior below). Indeed, despite the release of small molecules that could eventually act as a fuel in a fire scenario, it is noteworthy that a large fraction of the material is carbonized during its thermal decomposition. This means that in the event of a fire, only a small fraction of the material would actually decompose into possible fuel to feeding a flame.

3.3. Fire behavior

There are several types of fire tests that may be performed on a material, each giving different properties of the material. An in-depth study of the different fire properties of PEEK has been previously carried out.⁵² It has a Limiting Oxygen Index of 35% v/v and an UL 94 rating V0.⁵⁵

A non-flaming test, PCFC, was used to examine PEEK sampled with different molecular weight. The results are summarized in the Table 8. The samples 90G, 150G, and 450G correspond to three different viscosities of the polymers with 90G being the least viscous and 450G the most viscous. The onset temperature is slightly lower in low viscosity PEEK. The same may be observed regarding the peak temperature. However, the peak of heat release rate is higher in 450G as compared to 150G (+24 W/g) and 90G (+69 W/g). In addition, the char yield and the total heat released are similar for the three samples.⁵²

	Onset Temperature (°C)	Peak Temperature (°C)	PHRR (W/g)	Char (%)	THR (kJ/g)
90G ⁵³	571	615	287	52	11
150G ⁵³	575	616	332	48	11
450G ⁵³	580	617	356	50	11

Table 8. PCFC experiments for different types of PEEK⁵² (heating rate: 1 °C/s)

Another study dealing with the pyrolysis combustion flow calorimetry of PEEK has been previously reported.⁵² The average heat release capacities of PEEK were determined via PCFC at a heating rate of $258 \degree$ C/min. The heat release capacity was 180 J/g-K,⁵⁶ the total heat released was 12.4 kJ/g and the char yield was 47%.

A flaming test was also used to determine the fire properties of PEEK.⁵⁷ The Cone Calorimeter test, from Fire Testing Technology (FTT) was used to study the burning behavior of PEEK. An irradiance of 50 kW/m^2 was used. The results are shown in Figure 6 and average values summarized in Table 9.

The time to ignition was 110 s. The heat release rate increased to a shoulder around 200 kW/m^2 in about 140 s, and then continued to burn reaching a peak of heat release rate of 415 kW/m^2 . The total heat released was reported to be around 36 MJ/m^2 . The char yielded was around 51%.

Moreover, after flaming out, it was reported that the heat release rate does not return to zero. This phenomenon was attributed to a non-flaming oxidation of the char (Figure 6).

3.4. Concluding remarks

The high aromatic proportion in PEEK, like in PEI accounts for its high thermal stability. The semi-crystalline nature of PEEK allows it to keep its dimensional stability until its glass transition temperature.

A thorough review was carried out concerning the decomposition mechanism of PEEK but the actual decomposition pathway was not conclusively reached. However, decomposition mechanism proposed has shown that there is a major fraction of the polymer that crosslinks when it is subjected to thermal stress. This means that the



Figure 6. Cone colorimeter data for HRR of PEEK 450G and the average.⁵²

Table 9. PEEK at 50 kW/m². Summary: time to ignition, Peak Heat Release Rate (PHRR); Time to Peak Heat Release Rate (tPHRR), Char Yield, Total Heat Released.⁵²

_	Time to ignition (s)	PHRR (kW/m ²)	tPHRR (s)	Char yield (%)	THR (MJ/m ²)
PEEK	110	415	182	51	36

decomposition releases a lower amount of combustibles when is decomposes as opposed to if it were to completely decompose. Since it is the release of combustibles that fuels a fire, the enhanced thermal stability of PEEK evidences its low flammability.

Moreover, the cross-linking nature of PEEK also protects the polymer when it is exposed to a heat flux. This is observed in the cone calorimeter test results. Firstly, the incident heat flux required for the material to ignite is itself relatively high (50 kW/m^2) . This may be explained by its enhanced thermal stability. However, when is it ignited, the peak of heat release rate is relatively low. Indeed, when compared to polystyrene under similar conditions, the heat release rate of PEEK is about three times lower $(1294 \text{ kW/m}^2 \text{ for polystyrene}^{52} \text{ as compared to } 400 \text{ kW/m}^2 \text{ for PEEK}).$

4. Poly(phenylene sulfone)

Poly(phenylene sulfone) (PPSU or PPSF) is a high performance polymer which exhibits outstanding mechanical and thermal stability. It is an amorphous thermoplastic polymer with sulfone and ether linkages in the backbone (Figure 7). These properties make it a potential candidate for materials in electronic circuit boards or in the aeronautics industry.⁵⁸ One of the highest performing polyphenylene sulfone on the market is known under the trademark Radel[®] R and is commercialized by Solvay. The structure of Radel[®] consists of a highly aromatic backbone with sulfone bonds contributing to it resonant structure.

4.1. Synthesis

There are many different ways that may be adopted to prepare PPSU. One of the first methods was the condensation reaction between the sodium salt of bisphenol A with 4,4'-dichlorodiphenyl sulfone in dimethylsulfoxide.⁹

Another method of preparing PPSU involves the nickel-catalyzed coupling of an aromatic dihalides. It is a two-step process whereby the first reaction consists of forming aromatic dichloride intermediates possessing the desired structure in the polymer to be synthesized.⁵⁹ This aromatic dichloride then self-reacts in the presence of Ni⁰, triphenylphosphine and zinc to form the polymer.⁶⁰

4.2. Thermal properties

PPSU is one of the highest performing sulfone polymers. It has a glass transition temperature of around 220 °C and a continuous use temperature of 180 °C. An unannealed sample of Radel[®] 5000 has a deflection temperature of 207 °C when it is subjected to a 1.8 MPa stress.⁶¹

The thermal stability of PPSU has been studied by TGA in pyrolytic and thermooxidative atmospheres at different heating rates.^{62–64} When subjected to an identical



Figure 7. Structure of Radel[®] R.

heating rate, PPSU starts to decompose at a higher temperature in an inert atmosphere as compared to an oxidative one.

The thermal stability of PPSU under nitrogen is illustrated by the TGA plot on Figure 8 (left). It suggests that at this heating rate, the decomposition of PPSU occurs in one step. The onset of the degradation is around 600 °C. This high thermal stability may be due to the high aromatic backbone on the polymer. Moreover, the residual mass at 800 °C is significant (> 40 wt%).

However, the thermal stability of PPSU is different in air. The TGA plots performed in air of three sulfur containing polymers polysulfone (PSU), polyethersulfone (PES), and PPSU are shown on Figure 9. It can be observed that the onset of thermal degradation occurs at similar temperatures for all three polymers. However, PPSU appears to degrade at a lower temperature (around 500 °C) in air than under nitrogen (600 °C). The first step of the thermal decomposition may be dependent on oxygen. Moreover, the decomposition of PPSU appears to consist of two steps when it is heated in air.

A study concerning the kinetics of the thermal degradation of PPSU has been reported by Youjie et al.⁶² It consisted of applying the Ozawa-Flynn-Wall method on a commercial unfilled PPSU from BASF. TGA analysis at different heating rates were performed under nitrogen and in air.



Figure 8. TGA plots of PPSU under nitrogen (left) and TGA plots of polysulfone (\square), polyethersulfone (\blacksquare) and PPSU (\diamondsuit) (right) at a heating rate of 10 °C/min.^{58,64}



Figure 9. TGA plots of PPSU under nitrogen (left) and in air (right) at 10, 15, 20 (only for measurement under nitrogen), and 25 °C/min.⁶²

			Peak intensity (%)	
Structure	Mw (g/mol)	Name of compound	850 °C	950 °C
SO ₂	64	Sulfur dioxide	85	80
\bigcirc	78	Benzene	26	39
СН3	92	Toluene	4	5
	104	Styrene	<1	2
SH	110	Benzenethiol	1	1
ОН	94	Phenol	100	100
	128	Naphtalene	<1	5
	154	Biphenyl	21	27
	170	Diphenyl ether	42	36
	168	Dibenzofuran	17	21
C S C	186	Diphenyl sulfide	3	3
ОН	170	p-hydroxyl diphenyl	3	3
	184	Dibenzothiophene	1	3
S-s-S	218	Diphenyl disulfide	2	1
	246	<i>p</i> -diphenyl phenylether	8	4

Table 10. Structural assignments for pyrolysis products obtained via Py-GCMS analyses at 850 and 950 $^{\circ}$ C.⁶⁵

The average activation energy for the degradation of PPSU in nitrogen was calculated to be 299 kJ/mol (average value) under nitrogen. Under thermo-oxidative atmosphere, two decomposition steps were observed. Therefore, two activation energies were extracted. For the first decomposition, the activation energy was calculated to be 211 kJ/mol mol and the second decomposition step was reported to be 111 kJ/mol.

To further understand its thermal decomposition pattern, Py-GC/MS analyses were performed on PPSU.⁶⁵ The analyses were performed at 850 and 950 °C in order to properly pyrolyze the sample. Table 10 shows the different pyrolyzates that were analyzed when PPSU was subjected to aforementioned temperatures under helium.



Scheme 10. First step for the thermal decomposition of PPSU.⁶⁵

On top of Py-GCMS, MALDI-TOF experiments were also carried out. This allowed the identification of low energy fragmentations of the polymer. The study of the decomposition products coupled with MALDI-TOF analysis has made it possible to attempt at elucidating the thermal decomposition pathway for PPSU.⁶⁵

The first step of the thermal decomposition involves the cleavage of phenyl-sulfone $(Ph-SO_2)$ linkages. Depending on the amount of energy single or multiple $Ph-SO_2$ bonds releasing sulfur dioxide (Scheme 10).

The second thermal decomposition step may involve the cleavage of Phenyl-Oxygen or Phenyl-Phenyl bonds. The cleavage of phenyl-oxygen bonds would lead to the formation of phenol, p-diphenyl phenylether, or biphenyl radicals. On the other hand, the cleavage of phenyl-phenyl linkage would lead to the formation of diphenyl ether radicals. The third step of the decomposition would involve the cleavage of the same bonds as in the second step, albeit from smaller molecules.⁶⁵

Ellison et al. have performed an in-depth analysis of the Py-GCMS of PPSU in an attempt to elucidate its thermal degradation mechanism. The first step of the suggested mechanism is reported in this review but readers are invited to consult the original art-icle for a more integral version of the decomposition mechanism.⁶⁵

4.3. Fire behavior

The high char yield in the TGA plot of PPSU suggests that it exhibits some sort of fire retardancy. However, in order to confirm this assumption, fire tests need to be carried out. Indeed, the fire properties of PPSU have been studied by different methods. Cone calorimetry has been used to investigate time to ignition and heat released by burning PPSU upon exposure to an external heat flux.⁶⁶ Milligram scale combustion calorimetry tests was also performed on PPSU.⁶⁶

Standard tests such as UL-94, LOI, and smoke density tests are reported for PPSU. Table 11 summarizes the results of these tests.
Table 11.
 Summary of some fire properties of PPSU.

Property	Test Method	Result
Flammability rating	UL-94	V-0 at 0.8 mm
Limiting oxygen index (LOI)	ASTM D-286	38.0
Smoke density (Specific optical density at flaming condition)	ASTM E662	30 at 6.2 mm (thickness)

Table 12. Ignition parameters for PPSU from cone calorimeter and microscale combustion calorimeter.⁶¹

PPSU		Value
MCC Based Measurements	Onset temperature (°C)	544
	Critical heat flux for sustained pyrolysis (kW/m ²)	27
Cone Calorimeter based measurements	Temperature at ignition (s)	503
	Critical heat flux for piloted ignition (kW/m ²)	23

The V-0 rating from the UL-94 and the high LOI (38%) show that the PPSU possesses great flame resistance.

Microscale combustion calorimeter (MCC) and cone calorimetry were performed on PPSU. MCC provided another method for the onset of the decomposition based on heat release parameters.⁶⁶ Moreover, the critical heat flux for ignition was also extracted from the same measurements. The parameters calculated from MCC measurements (which is a milligram-sample based instrument) were compared to those of the cone calorimeter. The ignition parameters for PPSU are summarized in Table 12.

The onset of the degradation is coherent with TGA. Indeed, the MCC has a heating rate of 60 °C/min. This is lower than in usual TGA. Therefore, the degradation onset is expected to be higher. Moreover, the temperature at ignition is lower than the degradation onset. This may be due to the experimental conditions which had to sacrifice some precision on the measurement of surface temperature. The critical heat flux for sustained pyrolysis (27 kW/m^2) was slightly higher than the critical heat flux for piloted ignition (23 kW/m^2) .

The study of the heat release rate of PPSU was performed on PPSU which had sustained hygroscopic conditioning prior to the measurements. Only dry PPSU is of interest.

At 50 kW/m^2 incident heat flux, PPSU has a time to ignition at around 200 s. The average peak of heat release rate was around $250-350 \text{ kW/m}^2$. This is lower than other engineering polymers, such as PA66 (pHRR at around 500 kW/m^2) (Figure 10).⁶⁶

Moreover, at 70 kW/m^2 , the peak of heat release rate is almost lower than at 50 kW/m^2 . The time to ignition is lower, as expected. There seems to be a residual heat flux that is maintained in the last 100 s of the measurement (Figure 10).

The authors also made some visual observation when performing the cone calorimeter test and it was reported that there was not foam or bubbling.

4.4. Concluding remarks

The study of the thermal stability of PPSU using TGA provided some interesting insight on the decomposition behavior of the material. The high char residue at high temperatures may imply that there is some form of cross-linking that occurs during the pyrolysis process. This cross-linked structure is thermo-oxidized when the TGA is performed in air. However, the formation of a carbonaceous char is promising in



Figure 10. Cone calorimetry results for tests on PPSU at 50 kW/m² (left) and 70 kW/m² (right).⁶⁶

the field of fire retardancy as it can act as a heat and mass transfer barrier in a fire scenario.

Moreover, the degradation temperature of PPSU is quite high for a non-loaded polymeric material. This high thermal stability may be attributed to the high aromatic content in the polymer backbone. Moreover, thanks to its high glass transition temperature, it can keep its dimensional stability at relatively high temperatures, making it suitable for some high temperature use.

An in-depth study concerning the mechanism of thermal decomposition of PPSU has been performed. The first step of the thermal decomposition was quite properly described as the breaking of sulfone–carbon bonds. However, despite some highly interesting insights on possible degradation pathways of PPSU, there lacks supporting evidence other than the Py-GCMS and MALDI-TOF to properly understand the pathway of the degradation. Indeed, there are possible recombination reactions that may occur within a Py-GCMS. This may lead to the identification of products that may not occur other than in the instrument conditions.

The peak of heat release rate of PPSU is relatively low and is consistent with that of high-performance polymers (about 300 kW/m^2 at an incident heat flux of 50 kW/m^2). This is around 3 times lower than that of polystyrene (1294 kW/m^2 at the same heat flux).⁵² However, it still lies within the range of engineering polymers. Moreover, the cone calorimeter results show that there is a relatively high residual heat flux during the last 150 s of the experiments. This is assigned to smoldering leading to further thermo-oxidative decomposition of the material.

5. Polyimide

Polyimides are among the most popular high temperature/high performance polymers on the market (Figure 11). They are a generation of polymers with inherently rigid chains and possess high thermal and electrical properties. They are used in many fields, such as microelectronics, high temperature matrices, as well as adhesives for gas separation membranes. Polyimides are used in various forms such as high temperature



Figure 11. Typical structure of a polyimide (Kapton[®]).⁴



Scheme 11. Typical synthetic pathway to polyimide.⁶⁹

structural adhesives, coatings, films, or laminating resins. Their excellent thermal stability is attributed to the inert imide ring and high interchain interactions.⁵⁶

In fact, aromatic polyimides make up most of the polyimide market today. They have been considered, more than once, as a replacement for metals and glass in many high performance applications such as electronics, aerospace and automotive industries.⁶⁷

5.1. Synthesis

The first synthesis of a polyimide was carried out by Bogert and Renshaw in 1908.⁶⁷ However, it was not until 1959 that a patented high-molecular weight polyimide was synthesized by Dupont. The result of this synthesis gave rise to the widely known Kapton, which was commercialized in the early 1960s.⁶⁸

Depending on monomers used, a very large variety of polyimides can be made. They can be roughly classified as aromatic, semi-aromatic, and aliphatic polyimides. Since this review concerns high temperature polymers, this chapter will be limited to aromatic polyimides, which possess the highest thermal properties.

Many reaction pathways to form polyimides have been devised by different specialists in the field. Typically, aromatic polyimides are prepared via a two-step procedure: a ring opening polyadition of aromatic diamines to aromatic tetracarboxylic diangydrides in N-methyl pyrrolyidone (NMP) solution to give polyamic acid. The latter thus formed is imidized into polyimides by thermal cyclodehydration. This is illustrated in Scheme 11.

5.2. Thermal properties

Polyimides are known to have high thermal stability. This is mostly due to their rigid heterocyclic imide and aromatic rings on the polymer backbone. It is reported that



Figure 12. (Left): TGA curves of Kapton in air at different heating rates and (right) and the corresponding DTG curves.⁷⁰



Figure 13. TGA curve of polyimide at heating rate of 5°C/min under nitrogen (black).⁷¹

polyimides have a continuous service temperature in air that is as high as $260 \degree C$ and short-term use temperature of up to $482 \degree C$.⁶⁸

Thermogravimetric analysis has been performed on PI at different heating rates in air in order to investigate their thermal stability (Figure 12). The temperature of the onset of the degradation increases with increasing heating rate. By using increased heating rates, the authors observed that the degradation of PI occurs in more than one step. This was further observed on the DTG curves (Figure 12) whereby the maxima can be easily distinguished.⁷⁰

Other TGA performed on similar kinds of polyimides have shown that aromatic PI remain stable up to over 500 °C in inert atmospheres (heating rate 3 °C/min, helium atmosphere). After this temperature, there is significant weight lost until about 65 wt% of the original sample. This weight is maintained until 1000 °C.⁷¹

The TGA of PI under nitrogen shows that the temperature of the onset of the degradation is higher than in air (approximately $550 \degree$ C) (Figure 13).

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	Activation energy (kJ mol^{-1})	Log (Al/s ⁻¹)	Reaction order	Log (K _{cat})
Step I	189.62	8.40	0.77	0.94
Step 2	189.48	8.38	0.75	0.93
Step 3	168.73	7.73	0.89	0.09
Step 4	0.10	-3.43	3.17	1.65
Step 5	9.79	-3.17	0.40	1.38

Table 13. Parameters used in the kinetic modeling of PI.⁷⁰

Isothermal thermogravimetry performed on PI suggest that at low temperatures (below 520 $^{\circ}$ C), the thermal decomposition of PI occurs in a single step. At higher temperatures, the degradation is a two-step process.⁷²

The thermo-oxidative degradation of PI was carried out in order to explore the kinetics of the decomposition.⁷⁰ Isoconversional kinetic methods were used in order to determine the activation energy as a function of conversion. The method made use of thermogravimetric techniques at different heating rates and calculations using Friedman analysis.

A multi-step (five steps) decomposition mechanism was chosen for the study. The parameters used for the kinetic model is given in Table 13.

These parameters were used to develop an isothermal model, which had a maximum error or 16% with experimental results.^{70,72} Isothermal kinetic parameters were calculated using various methods.⁷³ The activation energy calculated was in the range 346-370 kJ/mol and lnA ranging from 43.4 to 50.1 min⁻¹.

The thermal decomposition products under pyrolytic and thermo-oxidative atmospheres have been studied using different methods.^{70,73,74}

The early stage of the thermal decomposition of was studied using thermogravimetry coupled with GC/MS and solid-state nuclear magnetic resonance.⁷⁵ Pyrolysis GC/MS at 600 and 700 °C, Evolved gas analysis were also performed on PI.⁷⁴ Another study using NMR suggested a mechanism for its decomposition.⁷⁵

The results of the pyrolysis gas chromatography mass spectrometry at 600 and 700 °C of PI are presented in Table 14. The peak areas of the different identified products were also reported. This provides and insight on how temperature may affect the amount of a certain decomposition product that evolved when a material is subjected to thermal stress.

The main decomposition products at 600 °C include aniline, phenol. At 700 °C, the major pyrolysis product identified was carbon dioxide. Benzene and benzonitrile were also identified. These products were not identified at 600 °C. This suggests that the main pyrolysis product under 700 °C is carbon dioxide. From these decomposition products, two probable pathways have been reported by Zhang et al. for the thermal decomposition of PI^{76} (Scheme 12).

The first suggested pathway involves the cleavage of the imide ring. This cleavage would generate intermediates that can further react to form aniline and N-phenylphtalamide by hydrolysis and the evolution of carbon monoxide (Scheme 12a).

From the relative intensities of the products evolved (Table 14) it can be observed that there is a greater proportion of phenol as compared to aniline when the pyrolysis is performed at 600 °C. This suggests that the C–N bond is easier to break than the imide ring. A decomposition pathway starting with the cleavage of C–N bonds is also suggested (Scheme 12b).

The presence of flammable products such as phenol, aniline and benzonitrile among the decomposition products and indicate that PI may potentially release combustibles

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			Peak a	rea (%)
Structure	Mw (g/mol)	Name of compound	600 °C	700 °C
CO ₂	44	Carbon dioxide	4.93	37.5
\bigcirc	78	Benzene	/	2.2
	103	Benzonitrile	/	7.1
NH ₂	93	Aniline	13.7	7.8
ОН	94	Phenol	44.6	16.1
	128	1,4-Benzenedicarbonitrile $+$ 1,3-benzenedicarbonitrile	8.2	7.4
\bigcirc \bigcirc	170	Diphenyl ether	0.95	1.6
	168	Dibenzofuran	8.4	6.7
H ₂ N	185	4-aminophenylether	10.1	1.6
	223	N-phenylphtalamide	2.4	2.2
H ₂ N OH	109	4-aminophenol	5.9	

Table 14. Decomposition products of PI when subjected to pyrolysis at 600 and 700 °C, and identified by GC/MS.⁷⁷

during its thermal degradation. This implies that if sufficient heat is given to the material, it could feed a flame. However, TG plots have evidenced the high char residue that PI leaved when it is heated. This may also play a role in the fire behavior of PI.

5.3. Fire behavior

Pyrolysis combustion flow calorimetry performed on different PI revealed that they have a heat release capacities of ranging from 13 to 38 J/g-K.^{77} The peak of heat release rate is reported to be 84 W/g, occurring at $602 \,^{\circ}\text{C}$ (heating rate: $1 \,^{\circ}\text{C/s}$).⁵⁵ The heat of combustion of degradation of PI is reported to be $6.6 \,\text{kJ/g}$. It leaves around 51% char after combustion.

Cone calorimeter was performed using an incident heat flux of 35, 50, and 75 kW/m^2 for 300 s on knitted PI fibers (Figure 14). Ignition was only observed at an incident heat flux of 75 kW/m^2 . The time to ignition recorded was 33 s. The peak of heat release rate was 53 kW/m^2 and the total heat released summed up to 72 MJ/m^2 .⁷⁷

Low-density PI (LDPI) foam was also studied under similar conditions. By varying the incident heat flux on the material, it was found that the minimum heat flux to

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Scheme 12. Possible thermal decomposition process for PI.75



Figure 14. Heat Release Rate vs time for PI fibers under different heat flux.⁷⁷

ignite LDPI was 54 kW/m^2 . Such a high heat flux may be attributed to the fact that PI is highly thermally stable. This means that it does not decompose until enough heat is supplied for it to release combustibles, leading to ignition.⁷⁸

PI (Kapton[®]) has a documented LOI of 37%⁷⁸ Vertical burning test performed on both woven and knitted PI showed the absence of ignition when approached with a flame.

5.4. Bismaleimide resins (BMI)

Bismaleimide resins are a subclass of thermosetting polyimides. They are a relatively recent class of addition curable polyimides which have become prominent in the field of high performance thermosetting polymers due to their unique qualities. They depict excellent mechanical and electrical properties in hot-wet environment, are relatively



Figure 15. General structure of a bismaleimide monomer. R = alkyl or aryl.⁸¹

cheap, exhibit high thermal stability and processability, and are relatively cheap.⁷⁹ BMI resin is commercialized under the trade name Kerimid[®] by Huntsman.

One of the most widely used BMI building block is 4,4'-bismaleimidodiphenylmethane (MDA-BMA) combined with diallylbisphenol A.⁸⁰ This is partly due to its high availability and low cost. However, most aromatic diamines can be converted to their corresponding bismaleimide. This suggests that there is a plethora of possible polymeric materials that can arise from BMI building blocks (Figure 15).

The high thermal stability of BMI based materials comes from their highly crosslinked structures.⁸¹ BMIs also present a few drawbacks such as brittleness due to its high crosslink density after curing, poor processability due to poor solubility in common solvents, high melting point, and a narrow temperature window for processing.⁷⁹ However, owing to the development of new monomers, new types of BMIs with improved properties have been synthesized.⁸² An in-depth review discussing the different properties of a large variety of BMI based polymers has been carried out by Iredale et al. recently.⁸²

5.5. Concluding remarks

Polyimides comprise of a rather wide range of thermally stable polymers. Their enhanced thermal stability is mostly due to their rigid and well-ordered heterocyclic aromatic backbones.

In terms of fire performances, PI only ignites when the incident heat flux is at 75 kW/m^2 . This implies that the surface temperature of the polymer is as high as $890 \,^{\circ}\text{C}$. This is extremely high and enough to overcome the bond energy within the polymer backbone and release sufficient combustibles to ignite. Despite this high a heat flux, the peak of heat release rate is relatively low ($53 \,\text{kW/m}^2$).

Indeed, when looking at the reported decomposition behavior of PI, there is evidence of the formation of combustibles. However, the highly charring nature of PI means that relatively large portion of the polymer does not release combustibles. This could explain the relatively low burning rate of PI and its flame retardancy.

6. Polyamide-imide

Polyamide-imides (PAI) are a class of amorphous high performance polymer, which can be either thermosetting or thermoplastic. The most widespread PAI is known under the tradename Torlon[®], commercialized by Solvay Specialty Polymers. PAI exhibits exceptional thermal resistance and mechanical properties. It has the highest strength and stiffness of any thermoplastics up to 275 °C.⁸³ The general structure of a polyamideimide is shown on Figure 16.



Figure 16. Repeat unit of a typical PAI.



Scheme 13. Reaction scheme synthesis of PAI via diisocyanate pathway.⁸⁶



Scheme 14. Synthesis of PBO.

6.1. Synthesis

There are two major routes reported for the synthesis of PAI: amide-imide forming reactions and reactions involving amide or imide-containing monomers.

Amide-imide forming reactions were the original pathways towards PAIs. This route makes use of trimellitic anhydride (TMA) or trimellitic anhydride chloride (TMAc) with a diamine⁸³ or with diisocyanate.^{84,85} A reaction scheme using the diisocyanate and TMA is illustrated in Scheme 13.



Figure 17. TGA plot of Torlon[®] PAI and polyetherimide under nitrogen at a heating rate of 10 °C/min.⁸⁷



Figure 18. TGA of PAI and silica-based PAI nanocomposite films in air at a heating rate of 10 °C/min.⁸⁸

6.2. Thermal properties

Polyamide imides possess great thermal stability. The decomposition onset is at $450 \,^{\circ}$ C. It has a weight loss of 10 wt% at 540 $^{\circ}$ C (10 $^{\circ}$ C/min heating rate) in air. Long term aging tests on the polymer performed at 250 $^{\circ}$ C showed that only 10–20% drop in tensile strength over 10,000 h.

Thermogravimetric analysis on a commercial version of PAI (Torlon[®]) was performed by Abbasi et al. (Figure 17).⁸⁷ The thermal behavior of PAI was compared to PEI (polyetherimide). The TGA curve of neat PAI shows that the onset of the degradation occurs around 450 °C. Under these conditions, the onset of the degradation of PAI occurs at a lower temperature than that of PEI. However, the rate of degradation is also slower.

The TGA of PAI in air (Figure 18) shows that there is a first degradation at around 200 °C and another major degradation step at 550 °C. It is noteworthy that first degradation is not visible under nitrogen.

Pyrolysis gas-chromatography/mass-spectrometry performed on PAI at 800 and 1000 °C revealed that the major peaks were those of carbon dioxide, benzene and aniline, phenol, methylaniline, 1H-isoindole-1,3(2H)-dione, 4-phenoxyaniline, 2-phenyl-1Hisoindole-1,3(2H)-dione and 3,5-diphenyl-1,3,4-oxadiazol-2(3H)-one. This suggests that the degradation of PAI begins with the release of small molecules followed by condensation reactions that produce larger compounds.

Evolved gas analysis was also performed on PAI with a heating rate of 20 °C/min under helium. It revealed that most of the decomposition products are evolved between 450 and 700 °C.

Py-GC/MS at 600 $^{\circ}$ C revealed that there are some other pyrolyzates that are released at lower temperatures. These mostly correspond to isocyanates, cyanobenzene, and phtalamide derivatives. The repeat unit of PAI was also identified among the decomposition products of PAI.⁸⁸

PAI is reported to thermally decompose via intramolecular scission. The activation energy for the pyrolysis is approximately 275 kJ/mol.⁵⁶

6.3. Fire behavior

The heat of combustion of PAI is reported to be 19.3 kJ/g. The heat release rate of PAI when is ignites is $48 \text{ kW/m}^{2.56}$ The ignition temperature of PAI is $526 \degree \text{C.+}$

PAI has an LOI of 45%v/v and a V-0 UL 94 rating. This implies that PAI does not readily burn in air nor does it sustain combustion when there it is approached by a flame. These two tests bring forward the inherent fire retardant nature of PAI. Moreover, the smoke extinction area of PAI is $120 \text{ m}^2/\text{kg}$, which is relatively low, as compared to polyethylene ($325 \text{ m}^2/\text{kg}$).⁵⁶ This means that in a fire scenario, PAI would release less than half the amount of smoke per unit mass of the polymer than would PE.

The critical heat flux for PAI is reported to lie between 40 and 50 kw/m². This means that the polymer would not sustain ignition if it were exposed to a lower heat flux. This confirms the high fire resistance of PAI. Indeed, when compared to PA6, the critical heat flux is much lower ($15-17 \text{ kW/m}^2$). This suggests that PA6 will readily sustain a flame if it is exposed to a heat flux above 17 kW/m^2).⁷⁴

6.4. Concluding remarks

PAIs encompass a relatively wide variety of polymers. In this review, we have seen that PAI is thermally stable in nitrogen at temperatures above 450 °C. However, the decomposition behavior in air differs greatly as compared to the decomposition under nitrogen. It occurs in more than two steps, contrarily to the decomposition in nitrogen, which occurs one fast degradation step closely followed by another slow step. The early degradation of PAI in air may be attributed to the loss of water, which was absorbed in the polymer.

The Py-GC/MS of PAI has allowed the identification of its decomposition products at different temperatures. However, work still has to be done in order to elucidate a thermal decomposition mechanism in air or under inert atmosphere.

Evolved gas analysis confirms that under inert atmosphere, most of the volatile decomposition products evolve at temperatures superior to 450 °C. More work has to

be done in order to investigate the nature of the residual char that is left after the burning process of the material.

Few works study the fire performances of PAI. Using a micro scale calorimeter, nonflaming fire tests were performed on PAI and some combustion parameters were retrieved. Furthermore, the LOI test and the UL-94 rating suggest that PAI has great potential as a fire resistant polymer.

7. Polybenzoxazole fibers

Poly(p-phenylene-2,6-benzobisoxazole) (PBO), known by its trademark Zylon[®], is a rigid rod isotropic liquid crystal polymer. It consists of a polybenzoxazole backbone containing an aromatic heterocyclic ring (Figure 19). It exhibits excellent flame resistance and thermal stability,⁸⁹ solvent resistance, and remarkable tensile strength⁹⁰ and modulus.⁹¹

7.1. Synthesis

PBO is a rigid rod polymer made from lyotropic liquid crystal polymer solutions.⁹¹ It is prepared using 2,6-diamino-1,3-benzenediol (DABDO) and terephtalic acid in polyphosphoric acid (PPA) as shown in the reaction scheme below.

This original reaction pathway was reported as being expensive in terms of preparation and purification.⁹² Other reaction pathways for the synthesis of PBO have been devised since its first synthesis.^{90,94–95} Due to the high viscosity and low solubility of PBO, a dry-jet, wet spinning technique is adopted for its production.⁹⁶ It was commercialized by Dow Chemical Company, using the patent license from Stanford Research institute (William, 1989 and 1990) and by Toyobo Co. Ltd.

7.2. Thermal properties

The thermal stability of PBO has been extensively studied in different atmospheres.^{97–99} The glass transition temperature or melting temperature for PBO are unknown because PBO degrades before that. Therefore, these values are predicted to be above their degradation temperature (above $680 \degree C$).⁹⁰

A recent study on the thermal stability of PBO emphasized the difference of its thermal stability in air as compared to inert atmospheres. Indeed the onset of the degradation of PBO in air (610° C) is lower than in nitrogen (634° C). This is evidenced by the thermogravimetric analyses performed under the aforementioned atmospheres (Figure 20). In air, the peak rate of decomposition occurs at 646° C whereas in nitrogen it is at 704°C. The residue at 900°C is 3 wt% and 16 wt% in air and nitrogen,



Figure 19. Structure of PBO.⁹⁷



Figure 20. Thermogravimetric analysis of PBO under (left) nitrogen and (right) air with a heating rate at 10 °C/min.¹⁰⁰

Table 15. Thermal decomposition data for the degradation of PBO in air and nitrogen.

Decomposition data	Air	Nitrogen
Temperature at Peak decomposition rate (°C)	646, ¹⁰⁰ 610 ¹⁰¹	704, ¹⁰⁰ 648 ¹⁰¹
Residue at 900 °C (wt%)	3 ¹⁰⁰	16 ¹⁰⁰
Temperature at onset of degradation (°C)	610, ¹⁰⁰ 515 ¹⁰⁰	634, ¹⁰⁰ 557 ¹⁰⁰
Temperature of half decomposition (°C)	683, ¹⁰⁰ 615 ¹⁰⁰	670 ¹⁰⁰



Figure 21. Simultaneous TG/DSC curves of PBO fibers under (left) nitrogen and (right) air with a heating rate at 10° C/min.⁸⁹

respectively. This indicates that oxygen has a significant impact upon the decomposition behavior of PBO.¹⁰⁰ The data for the TGA of PBO are summarized in Table 15.

Another paper aiming at understanding the thermal degradation of PBO utilized TGA simultaneously with differential scanning calorimetry. The DSC analysis showed that the decomposition of PBO in air is exothermic while that in nitrogen is endothermic (Figure 21). This brought even more light upon the influence of oxygen on the thermal degradation of PBO.⁸⁹ Oxidative degradation is suggested to be the weight loss process of PBO in air.¹⁰²

Isothermal aging study in air was also performed on PBO fibers.⁹⁸ At 343 °C, 10% weight reduction was observed after 200 hours at this temperature. At 371 °C, PBO retained 78% of its weight and at 316 °C, no weight reduction was observed, displaying its excellent thermal stability.

Moreover, the DSC curve of PBO under nitrogen shows a weak exothermal effect just before its degradation. This has been assigned to an increase in crystallinity of the fiber.¹⁰²

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TGA data also allowed for the determination of the kinetic parameters of the thermal decomposition of PBO.^{98,103}

One of the former attempts at evaluating the Arrhenius parameters for PBO was carried out by Nielsen et al. in 1993.⁹⁸ Isothermal weight loss curves at different temperatures were plotted for PBO. It was observed that the mass loss rate was close to zero at 500 °C but increased rapidly at 600 °C. Arrhenius plots allowed for the comparisons of the weight loss rates of PBO with other polymers (Figure 22). The activation energy and pre-exponential factor for the thermal degradation of PBO, obtained by least squares analysis of data are reported in Table 16.⁹⁸

From the kinetic analysis, it was reported that PBO has a thermal degradation in air that seems to correspond to a Prout-Tompkins autocatalytic model process. However, further information regarding this assumption was not provided. This study allowed, to some extent, predictions of remaining PBO weight percent when subjected to an iso-thermal stress.⁹⁸

In a more recent study, Bourbigot et al. thoroughly investigated the thermal behavior of PBO where TG analyses were performed at different heating rates in air and nitrogen. The invariant kinetic parameters (IKP) method was used to compute the invariant kinetic parameters of the thermal degradation of PBO (Table 17).⁸⁹ As opposed to the



Figure 22. (left) Isothermal weight loss curve of PBO at different temperatures and (right) Arrhenius plots of maximum weight loss rate plotted against 1/T (K⁻¹).⁹⁸

Table 16. Kinetic parameters calculated using Arrhenius plot at maximum weight loss rates at different temperatures.⁹⁸

Polymer	Atmosphere	Activation energy (kJ/mol)	Pre-exponential factor (s^{-1})
РВО	Nitrogen	289	$1.0 imes 10^{-16}$
РВО	Air	163	$6.5 imes 10^{10}$

1	Table	e 1	7.	Invariant	kinetic	parameters	of	PBO.°	'

Atmosphere	Invariant Activation energy (kJ/mol)	Invariant Pre-exponential factor (s^{-1})	Temperature range (°C)
Nitrogen	327	$2.6 imes10^{14}$	500-800
Air	85	1.7	400-900



Figure 23. FTIR spectra of the degradation of PBO in air at different temperature.¹⁰⁴

kinetic analysis carried out by Nielsen et al., this method used a dynamic system whereby the temperature was not constant.

In the IKP method, a constantly changing temperature is used to derive the kinetic parameters. This is not the case for the first method, whereby the isothermal mass loss is observed. Both methods agree on the fact that more energy is required for the decomposition of PBO in nitrogen rather than in air. Moreover, the values obtained by both methods are in the same order of magnitude.

In attempts at elucidating a decomposition mechanism of PBO, the thermal decomposition products PBO needed to be analyzed. This has been studied via TG/FTIR,¹³ pyrolysis gas-chromatography/mass-spectrometry (Py-GC/MS),¹⁰⁴ TG/MS,¹⁰⁵ and Raman spectroscopy.¹⁰⁰

TG-FTIR, in air, was performed on PBO (Figure 23). The TG plot of PBO in air evidenced that the main mass loss occurs in the temperature range 550-750 °C. Infrared spectra of evolved gases were recorded at different temperatures. From these, the main decomposition gases observed were HCN, NO₂, CO, CO₂, and water. The peaks of water and CO₂ start to appear at 550 °C whereas those of HCN, NO₂, and CO became more apparent as from 650 °C. It is suggested that complex chemical reactions occur at temperatures above 650 °C. The infrared spectrum at 800 °C shows that there is a decrease in the peak intensity corresponding to water, NO₂, and an increase in CO₂ peak intensity. This increase of CO₂ is attributed to the oxidation of heterocycles present in the polymer.¹⁰⁴

FTIR is limited by its measurement nature. For instance, large degradation products, such as monomer units of PBO cannot be accurately identified. Therefore, Py-GC/MS can be used to further analyze the degradation products of PBO. PBO was pyrolyzed at 750 °C under inert atmosphere and the pyrolyzates were analyzed by GC/MS. A short pyrolysis time of 12 s was carried out. GC/MS only gives partial pyrolysates and do not take into consideration the possibility of the recombination of fragmented bonds during pyrolysis.

From the identified pyrolysis products of PBO, it can be observed that carbon dioxide accounts for a major proportion of the thermal decomposition of PBO. However, PBO molecular chain was also recorded. In fact, it accounts for the highest peak area among the pyrolysates analyzed¹⁰⁶ (Table 18). This suggests that the main process occurring

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Compound	Assigned Molecular Mass	Peak area (%)
CO ₂	44	23.8
\bigcirc	78	9.92
\frown	92	3.97
	160	1.32
	103	14.72
	128	8.07
H ₂ N-NH ₂	108	1.26
	236	34.7
НО ОН	110	2.28

Table 18. Identified products from the pyrolysis and GC/MS of PBO at 750 °C.

during its thermal decomposition is depolymerization reaction.¹⁰⁴ Another study regarding the pyrolysis products analyzed by Py-GC/MS was also reported in 2008.¹⁰⁷ The proportion of the monomer unit was higher (46%). This is coherent with the possibility that the degradation is ruled by depolymerization.

The thermal decomposition pathway has been further investigated by using model compounds. Fragments of thermal decomposition products of PBO were identified and the effect of end-chain functional groups was studied.¹⁰⁷ These analyses, coupled with the use of ¹³C-enriched precursor for the synthesis of PBO to study its decomposition, a better understanding of the decomposition mechanism was achieved.

From the decomposition products identified using TG/MS and GC/MS, it was possible to suggest a tentative thermal degradation mechanism. Two modes of degradation were assumed.

The first mode consists of the homolytic scission of single bonds, which generate benzoxazole and phenyl radical (Scheme 15). The unstable benzoxazole radical is further fragmented. This produces aromatic nitrile and possibly HCN, CO_2 , and H_2O along with other hydrocarbons. The phenyl radical may graft onto another PBO molecule or abstract hydrogen to generate phenylbenzoxazole, producing benzonitrile and benzene.

The second mode of decomposition starts with the decomposition of the heterocyclic ring. This leads to the formation of a nitrile, which could generate benzonitrile, dicya-nobenzene, and a diradical. The latter, further fragments to form an aromatic nitrile and possibly, HCN, CO₂, water, and other small carbon compounds (Scheme 16).

Work on the study of the thermo-oxidative degradation of PBO was also reported. The first steps of the degradation reported were similar to the Scheme 15, consisting of the homolytic scission of single bonds. The study involved using Py-GC/MS to determine



Scheme 15. Possible mode of thermal decomposition for PBO, initiated by the homolytic scission of C–C bond.



Scheme 16. Possible thermal degradation pathway for PBO with the decomposition of the heterocyclic ring.¹⁰⁵

the decomposition products and coupling the results with TGA-DTA/MS to reach a plausible mechanism. The presence of oxygen caters for the oxidation of aromatics that are formed during the pyrolytic degradation of PBO, leading to CO_2 , H_2O , and NO_2 .

7.4. Fire behavior

PBO has proved to have outstanding thermal stability as well as excellent oxidation tolerance.



Figure 24. Rate of heat release curves of knitted PPTA and PBO fibers.¹⁰⁹



Figure 25. Reaction to fire of PBO fibers in cone calorimeter conditions with an external heat flux of $75 \text{ kW/m}^{2.109}$

Different studies have been carried out in order to evaluate the fire properties of PBO.^{89,108} Cone calorimetry of knitted PBO fibers was compared with poly(p-phenylenediamine-terephtalamide) fibers (PPTA). The experiment was carried out at two different heat flux (50 and 75 kW/m^2) (Figure 24 and 25). The cone calorimetry results showed that the peak of heat release rate of PBO under either heat flux is relatively low. In fact, it is one of the lowest heat release rates for a purely organic polymer.

The time to ignition of PBO with an external heat flux of 50 kW/m^2 is 56 s and the peak heat release rate is 60 and 150 kW/m^2 .¹³ This is extremely low for a polymer. For instance, the peak heat release rate of Kevlar, another high performance polymer reaches 400 kW/m^2 .¹⁰⁹ PBO burns with a small flame until the peak heat release rate is reached. After that, the fibers glow, leading to their degradation. The aspect of PBO



Figure 26. VSP curves (external heat flux = 75 kW/m^2) of some knitted fibers, including PBO.¹⁰⁹

before and after being subjected to an external heat flux is mostly unchanged. However, due to the degradation of the material, the mechanical properties are inexistent.⁸⁹

However, when comparing the total heat released by PBO and p-aramid, it was reported that very close values were recorded. This may be due to the post-glowing phenomenon, which endured for the remaining duration of the test.¹⁰⁹

The fire growth rate (FIGRA) is a good indicator of the flame spread potential of a material. That of PBO is close to zero at 50 kW/m^2 . With an external heat flux of 75 kW/m², the FIGRA of PBO peaks at 25 W/s. After this, the FIGRA decreases and remains close to zero.¹⁰⁹

Smoke density was also measured during the cone calorimetry test. The results showed that the smoke evolved during the combustion of PBO is low. This is evidenced in the volume of smoke production (VSP) curve, whereby the smoke obscuration of different polymers were tested during cone calorimetry tests with an incident heat flux of $75 \text{ kW/m}^{2.109}$ It can be observed that the VSP curve corresponding to PBO remains close to zero (Figure 26).

7.5. Concluding remarks

Polybenzoxazole fibers are rigid rod polymeric materials with very well-ordered structure. As with most rigid rod polymeric materials, this accounts for their excellent thermal properties.

The study of the decomposition mechanism of PBO has led to the conclusion that the major mechanism corresponds to depolymerization of the neat polymer. This implies that there are few volatile combustibles released when the polymer decomposes. This could explain why peak of heat release rate is relatively low when the material is tested with a cone calorimeter. Moreover, PBO has shown that it has a tendency to char when it degrades. This means that the depolymerization decomposition reaction is also accompanied with some crosslinking. This, coupled with a low release of combustibles might explain the excellent results from the cone calorimeter tests. Indeed, the formation of a char between the radiation source and the inner part of the material may protect the later from further decomposing.



Figure 27. Structure of poly(2,2'-(m-phenylene)-5,5'bibenzimidazole) (PBI).

However, the highly exothermic peak in the differential scanning calorimetry means that the presence of oxygen has a strong influence on the degradation of PBO. This implies that in air, the high temperature resistance of PBO is greatly diminished.

The low heat release rate and almost inexistent smoke obscuration make PBO an excellent candidate for high performance fibers.

8. Polybenzimidazole (PBI)

Polybenzimidazoles are a class of high performance heterocyclic polymers. Aliphatic polybenzimidazoles were first synthesized by Robinson and Brinker in the late 1950s.¹¹⁰ However, it was not until 1961 that the first aromatic PBI was synthesized by Vogel and Marvel.¹¹¹ Hoechst Celanese commercialized a polybenzimidazole fiber for thermal protective clothing and fire blocking applications in 1983. The most commercially available polybenzimidazole on the market is poly(2,2'-(m-phenylene)-5,5'bibenzimidazole) (Figure 27, referred to as PBI) under the trade name Celazole. PBI is reported to have the highest compressive strength among all high performance, commercially available thermoplastics. Nowadays, PBI Performance Products Inc. is the major producer of high performance PBI materials.

PBI is typically synthesized via a condensation reaction of aromatic bis-o-diamines and dicarboxylates. The benzimidazole moiety is the repeating unit of the molecular backbone of the polymer.

8.1. Synthesis

Poly[2,2'-(*m*-phenylene)-5,5'-bibenzimidazole] (PBI) is the most studied commercially available polybenzimidazole. It is prepared from tetraminobiphenyl, TAB, with diphenylenephtalate, DPIP.

The commercial production of PBI is a two-stage process; both required a controlled, inert atmosphere. The first stage involves the melting of DPIP which solubilizes TAB. Increase in temperature initiates the polymerization, generating phenol and water. This causes the formation of a foam brittle foam. The second stage consists of crushing the foam to obtain the powdered polymer.

8.2. Thermal properties

PBI has excellent thermal properties and flame resistance. It has a glass transition temperature of 425 °C. It is reported that the polymer decomposes before melting. PBI has the highest mechanical property retention over 205 °C among all unfilled resins.



Figure 28. Thermogravimetric analyses on PBI at a heating rate of 10°C/min in air (___) and under nitrogen (- - -).¹¹²

When it comes to short-term use, PBI can be exposed to $450 \,^{\circ}\text{C}$ (approximately 10 min exposure time). For long-term exposures in air (>200 h) the maximum temperature capability is reported to be $320 \,^{\circ}\text{C}$.¹²

TG analyses in air at a heating rate of 10° C/min has shown that the polymer does not decompose until 500 °C. Under inert atmosphere, the thermal stability is increased to 600 °C (Figure 28).

The TGA plots suggest that loosely bound water is not readily released from the polymer. The polymer keeps its initial weight until around 375 °C, whereby a small mass loss is observed. In air, a slow decomposition starts at around that temperature, followed by a rapid degradation above 500 °C. The sample was completely degraded at 700 °C. However, under nitrogen, it kept its initial weight until 550 °C. A slow weight loss is observed at this temperature onwards.

This is further evidenced when the DTG curves are analyzed (Figure 29). Indeed, two peaks are observed on the DTG curve of PBI under nitrogen. The first peak is relatively narrow and has a maximum at 570 °C and the other is a broad peak, which starts at around 575 °C and continues until 825 °C.

At 570 °C, the mass loss recorded on the TG curve is only 3%. Papers suggest that this could be due to terminal or end group losses of light compounds such as hydrogen followed by further condensation of the polymer.¹¹³

The second weight loss accounted for 23% of the total weight of the polymer. It is suggested that this degradation step corresponded to further condensation process resulting from extensive chemical rearrangement.⁶⁷

From the differential thermal analyses (Figure 30) and the derivative thermogravimetric (Figure 29) analysis of PBI in air and under nitrogen, it can be deduced that oxygen plays a significant role in the thermal degradation of PBI. Indeed, under nitrogen, the thermal decomposition of PBI is slightly endothermic. However, non-flaming oxidative degradation of PBI was exothermic, with a peak at 570 °C. In addition, the DTG of PBI in air shows a mass loss rate at 570 °C, which is approximately six times higher in air than under nitrogen with the same heating rate.¹¹²



Figure 29. DTG plot of PBI in air (___) and under nitrogen (- - -).¹¹²

Isothermal thermogravimetric analyses in air and under nitrogen were also performed on PBI at temperatures from 200 to 350 °C (Figure 31). The rate of weight loss at these temperatures are relatively low both in oxidative and inert atmospheres.¹¹⁵

A detailed study of the thermal degradation of PBI has been carried out by Chatfield et al.¹¹⁴ Stepwise pyrolysis of PBI was carried out at 570, 700, and 1000 °C. The mass loss (of the original weight) during each step is summarized in Table 19. The total mass lost was 30.6%. The additional 3.6% corresponds to the elimination of water occurring at $100 \,^{\circ}C.^{114}$

There are other papers concerning the thermal behavior of PBI.¹¹⁴ The study of the kinetics of the thermal decomposition of PBI was attempted by Wrasidlo et al. in 1964¹¹⁶ and by Schulman and Lochte in 1967.¹¹⁷ They used of isothermal kinetics, thermogravimetry, and mass-spectrometric thermal analysis (MTA) to determine the kinetic parameters of the thermal degradation of PBI. It was concluded that the decomposition of PBI occurred in two steps and a tentative degradation pathway was suggested (see mechanism of decomposition, Scheme 18).

Schulman and Lochte reported the difficulty in reaching accurate results of kinetic parameters due to the complex decomposition pattern of PBI. Firstly, being a highly temperature resistant polymer, PBI still exhibits significant residual weight at 1000 °C. In addition, PBI has a hygroscopic and resistant to drying nature, making it complicated to be certain of its initial weight. Indeed, depending on the amount of water that is absorbed in the polymer, the weight loss due to water may greatly vary. This makes



Figure 30. Differential thermal analysis (DTA) response of PBI in air (___) and under nitrogen (- - -).¹¹⁴



Figure 31. Isothermal TGA of PBI in air (left) and under nitrogen (right).¹¹⁵

the identification of the different decomposition steps tricky. This is observable on the TG curve-PBI decomposes via many steps; therefore, the activation energy depends on the temperature.

The energy for the formation of individual degradation products were determined form Arrhenius plot and were used to find an average activation energy for the thermal decomposition of PBI. The average activation energy was somewhat temperature dependent (Figure 32).

It was concluded that below $720 \,^{\circ}$ C, the activation energy of the thermal degradation of PBI is $75 \,$ kJ/mol. The rate constant of the degradation decreases above this temperature and was observed to be $142 \,$ kJ/mol. This is coherent with a two-stage reaction,

Temperature range (°C)	Mass lost (%
300–570	2.3
570–700	13.3
700–1000	11.4

Table 19. Summary of weigh lost during stepwise degradation of PBI.



Figure 32. Temperature dependence of the activation energy for the thermal decomposition of PBI.¹¹⁷

whereby the second step corresponds to final dehydration step of the polymerization being the main low temperature reaction. This is accompanied by slow degradation, which is the principal reaction when polymerization is completed.¹¹⁷

The degradation products were separated via a gas chromatography and were identified using mass spectrometry. A possible degradation pathway based on hydrolytic ring opening was suggested.¹¹⁷ However, a more recent literature review simplified the originally proposed mechanism for the formation of HCN¹¹⁸ (Scheme 18).

The mechanism suggests that the lower energy carbon-nitrogen bond undergoes homolytic scission, leading to a diradical. This highly unstable configuration would abstract hydrogen on an adjacent phenyl group. Subsequently, a new ring unit can be formed, eliminating HCN in the process.¹¹⁷ Further thermal decomposition of this relatively stable and would decompose at high temperatures, fracturing the phenyl group, yielding small fragments such as methane and amines.

8.3. Fire properties

PBI fiber does not sustain burning in air. This is evidenced by its limiting oxygen index of 41%.¹¹⁷ Later studies on "newer" versions of the polymer have found a limiting oxygen index of 58% by D2863 ASTM test.¹²⁰ PBI was tested in a Flame Tunnel Test (ASTEM-84), there was no smoke developed, not any fuel contribution to the flame. The char length from the Vertical Burn Test (FSTM 191-5903) was 0.3 inches (76.2 mm).

Tests performed in a fire calorimeter have brought about some properties regarding the fire performances of PBI. The mass loss rate at the ignition is reported to be $1.5 \text{ g/m}^2\text{s}$ with and a heat release rate of 24 kW/m^2 at ignition. This value is relatively high,

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Scheme 17. Synthesis of PBI.



Scheme 18. Suggested decomposition mechanism of PBI.¹¹⁹

considering that it is a high performance polymer (HRR at ignition for PEEK = 15 kW/m^2). However, the effective heat of combustion of PBI is 16.2 kJ/g which is less than half of that of neat polyethylene (40 kJ/mol). PBI also has a UL-94 V0 rating.¹²¹ The smoke extinction area of PBI is 100 m²/kg, a relatively low value when compared to polyethylene (325 m²/kg) or polystyrene (1150 m²/kg).⁵⁶

8.4. Concluding remarks

PBI has one of the highest glass transition temperatures among organic polymers. It has a rigid aromatic structure and neither burns nor sustains burning when removed from a flame. It has a high LOI and is classified as V0 under the UL-94 test.

Thanks to the char forming nature of the polymer, PBI maintains its integrity when exposed to an external heat flux. This char formation protects the polymer from further incident heat flux, making it highly flame resistant.

DSC analysis leads to believe that oxygen has a strong influence on the degradation of PBI. Indeed, the degradation of PBI under air releases much more energy than the amount of energy it absorbs when pyrolysis is performed on it. 50 👄 A. RAMGOBIN ET AL.

The significant remaining mass after thermal tests shows that PBI has strong thermal stability. This also makes the study of the degradation more complex because there are more than one degradation pathways that are competing with each other.

Therefore, a thorough mechanistic study is needed in order to clarify the degradation mechanism of PBI as well as extract the kinetic parameters of its thermal degradation.

9. Polypyridobisimidazole (PIPD or M5)

Polypyridobisimidazole (PIPD or M5), formally poly(2,6-diimidazo[4,5 b:4',5' e]pyridinylene-1,4-(2,5dihydroxy)phenylene) is a relatively recent polymer in the rigid rod polymer family.¹²² It was first developed by Akzo Nobel Central Research and is now developed by Magellan Systems. PIPD has a structure that is close to PBO with the exception of –OH functional groups present in PIPD (Figure 33). This allows for interchain hydrogen bonding, giving it extremely high compression strength. PIPD has a promising array of potential applications such as personnel protection, fire resistance, advanced composite materials and advanced fabrics.

9.1. Synthesis

The first synthesis of PIPD was carried out by researchers at Akzo Nobel and Co. in 1998. A schematic representation of the formation of PIPD is shown in the scheme below.

The polymerization reaction involves 2,3,5,6-tetraaminopyridine (TAP) and 2,5dihydroxyterephtalic acid (DHTA) to form 2,3,5,6-tetraaminopyridine 2,5-dihydroxyterephtalate (TD salt) as a reaction intermediate (Scheme 19). The obtained dopes are spun into fibers, usually via dry jet wet-spinning process.⁵

9.2. Thermal properties

PIPD is reported to have high thermal stability. This is due to its rigid chain molecular structures. The thermal decomposition of PIPD in air is reported to be around $530 \,^{\circ}\text{C}^{123}$ Bourbigot et al. have studied the degradation of PIPD via thermogravimetric analysis in air and under inert atmosphere.¹²⁴

From thermogravimetric analysis, it was observed that PIPD was highly sensitive to oxygen. In thermos-oxidative conditions, PIPD decomposes between 450 and 650 °C, leaving a residue of about 4 wt%.

Under nitrogen, the thermal decomposition of PIPD starts at approximately the same temperature as it does in air. However, the rate of degradation is much slower. This can



Figure 33. Repeat unit of Polypyridobisimidazole PIPD (M5).¹²⁴



Scheme 19. Preparation of PIPD from TAP and DHTA.⁵



Figure 34. TG curves of PIPD (M5) and PPTA under air flow and nitrogen flow at a heating rate of $10 \,^{\circ}C/min$.¹²⁴



Figure 35. Simultaneous TG/DSC curves of PIPD fiber at a heating rate of 10°C/min in air.¹²⁴

be observed on the TG curve (Figure 34). The residue formed at 1200 °C corresponds to 55 wt% of the original mass of PIPD.

Thermogravimetry coupled with differential scanning calorimetry (in air) was also performed on PIPD (Figure 35). The results showed that the degradation of PIPD fibers is highly exothermic and is due to thermo-oxidative degradation. The enthalpy of decomposition of PIPD is reported to be around -17 kJ/g.

9.3. Fire behavior

PIPD exhibits excellent fire performances due to its rigid rod structure, not unlike PBO. This is partly due to its non-existent melting point, its rigid chain, and the strength of its chain-to-chain interaction.

PIPD does not burn in air and is self-extinguishing. It has a documented LOI superior than 50 vol%. Cone calorimeter test give outstanding results. With an external heat flux of 75 kW/m², the peak of heat release rate (pHRR) of PIPD is 50 kW/m² and the time to ignition (TTI) is 77 s. For comparison purposes, it is interesting to note that the pHRR and TTI of PBO is 48 kW/m^2 and 56 s, and in the case of p-aramid pHRR = 300 kW/m^2 and TTI = 20 s. Upon burning, PIPD fibers form a char, which remains at the surface of the fiber.⁵ This means that the fiber is partly protected from incident heat flux. One explanation of such excellent heat properties may be the fact that the crystal structure of PIPD contains around 21% water.¹²²

A thorough fire performance investigation comparing PIPD and PPTA has been carried out by Bourbigot et al.¹²⁵ The HRR curve is given in Figure 36. The heat release rate when PIPD is subjected to 75 kw/m^2 increases rapidly upon ignition (around 80 s) and plateaus at around 50 kW/m^2 . The heat release rate remains relatively constant for the remaining experiment time. This suggests that the char layer formed on top of the polymer protects its inner layer from further degradation, and thus prevents the release of combustibles, which could cause the ignition.

Pictures of the polymers were taken during the test to evidence the low flammability of PIPD (Figure 37). It can be observed that under 75 kW/m^2 , there is hardly any visible flame on the PIPD sample.

The fire growth index (FIGRA) curve of PIPD shows a only one peak at 80 s (near the ignition time) and corresponds to FIGRA =50W/s. This confirms the low contribution to fire of PIPD.¹²⁴



Figure 36. HRR curve of knitted PPTA and PIPD (M5) fibers with an external heat flux of 75 kW/m².¹²⁴



Figure 37. Fire behavior of M5 when subjected to 75 kW/m².¹²⁴

The VSP curve of PIPD under the cone calorimeter conditions shows that there is a negligible amount of smoke produced when PIPD is subjected to $75 \text{ kW/m}^{2.124}$

9.4. Concluding remarks

The structure of PIPD gives it the ability to form hydrogen bonds between adjacent chains. This gives it extremely high fire resistance, not unlike other rigid rod polymeric fibers.

PIPD has extremely high thermal stability in nitrogen. Indeed, there is more than 50% of the weight is retained at 1200 °C. This is exceptional for a wholly polymeric unfilled fiber. However, it is very sensitive to oxygen. This is evidenced by the TGA where we can see that the decomposition is abrupt and almost complete.

The DSC curve confirms the strong influence of oxygen in the decomposition process of PIPD. Indeed, a wide and high exothermic peak is observed, suggesting that the thermo-oxidative degradation of PIPD is favored under such conditions.

However, under external heat flux of 75 kW/m^2 , a relatively low peak of heat release rate is observed (44 kW/m^2 as compared to around 400 kW/m^2 for Kevlar[®]). This may be because PIPD forms a protective char layer at the surface of the fiber during the cone calorimeter test. This could account for the low pHRR reported.

Moreover, the fire behavior of PIPD is reminiscent of that of PBO. Indeed, PIPD exhibits a pHRR at 75 kW/m^2 of around 50 kW/m^2 and PBO has a pHRR of about 150 kW/m^2 at when exposed to the same heat flux. Despite the latter being higher than that of PIPD, it is a very low value as compared to other supposedly inherently fire retardant polymers such as p-aramid (pHRR =400 kW/m² when exposed to 75 kW/m^2). We observe that rigid rod heterocyclic polymeric structures with strong interchain interactions may have a positive impact on the fire behavior of the material.

This interesting fire property is further evidenced with the low fire growth index of PIPD also contributes to making it an excellent fire retardant with outstanding mechanical properties.

10. Aramids

Aromatic polyamides (aramids) form part of one of the first classes of high performance polymers. They present outstanding potential in terms of mechanical properties, thermal and electrical insulation. The first commercially introduced aramid was a meta-aramid fiber produced Dupont under the trade name Nomex[®] in the 1960s. A para-aramid, with much higher tenacity and modulus fiber was developed and commercialized by the same company under the trade name Kevlar[®] in 1971 (Figure 38). Twaron is another para-aramid that appeared on the market in the early 1980s. It is similar to Kevlar[®] and shares some properties.

Since this article deals with high performance polymers, Kevlar and Twaron will be those primarily discussed in this section.

10.1. Synthesis

Para-aramid, formally poly(*p*-phenylenediamine-terephtalamide) (PPTA) was first developed by Stephanie Kwolek from DuPont.

The specific conditions for this synthesis have been reported by Kwolek¹²⁶ and Blades.¹²⁷ There are two major routes towards the preparation of aromatic polyamides:

Polycondensation using an aromatic dichloride and a corresponding diamine;

Direct polycondensation via a dicarboxylic acid and a diamine.

The first route is performed by the condensation 1,4-phenylenediamine (PPD) and terephtaloyl chloride (TCl) (Scheme 20) using N-methyl-2-pyrrolidone as solvent. The process is carried out at low temperatures.

The direct polycondensation uses lower costs monomers. Indeed, TCl is costly and highly sensitive to air. However, the reaction between the diacid and the diamine does not proceed readily. A catalyst such as triphenyl phosphate is required for the reaction to occur readily. The reaction needs to be carried out at high temperatures in order to achieve high molecular weight yields.



Figure 38. Structure of Kevlar[®].



Scheme 20. PPTA synthesized via low condensation polymerization of PPD and TCI.



Figure 39. Thermogravimetric analysis of dry p-aramid at a heating rate of 2°C/min under nitrogen.¹²⁸



Figure 40. TGA plot of p-aramid at a heating rate of 10 °C/min under nitrogen (left)¹²⁸ and in air (right).¹³⁰

10.2. Thermal stability

p-aramid is one of the first polymers to display the combination of high temperature resistance and high mechanical properties in the same material. This is partly due to its highly ordered structure. Different classes of Kevlar[®] exist on the market, mostly commercialized by Dupont. However, the thermal properties of the different classes are relatively similar.¹⁰²

p-aramid has a relatively high structural chain rigidity and a second order transition temperature of about 340 °C and a melting point of about 560 °C.¹²⁷ It is reported that p-aramid resist temperatures of up to 450 °C for a few minutes and 250 °C for at least 1 month.

Thermogravimetric analysis performed on p-aramid at a heating rate of 2° C/min under nitrogen led to the conclusion that there is a significant weight loss as from 460 °C (Figure 39). About 40 wt% of the material is lost from 480 to 560 °C. There seems to be further slower degradation from 560 °C onwards.

TGA of p-aramid was also performed at 10 °C/min under nitrogen and in air (Figure 40).¹²⁹ As expected, the onset of the thermal degradation is higher when the heating rate is higher.

The onset of the degradation under nitrogen was 562 °C and the maximum derivative weight loss occurred at 577 °C. 43% of residue remained at 700 °C. According to the heat flow, which was measured simultaneously with the mass loss, the decomposition temperature of p-aramid at the aforementioned conditions was 579 °C.

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In air, at a heating rate of 10° C/min, the onset of the decomposition occurred at 526 °C and the maximum derivative weight loss occurred at 569 °C. At 600 °C, 56% of the initial weight of p-aramid was still present.^{128,122–133}

The thermal degradation of p-aramid has also been studied by high-resolution thermal gravimetric techniques, 134 Py-GC/MS. 74

The single-step, rapid thermal degradation of *p*-aramid was confirmed by high resolution TG. A slow weight loss was observed at around 300 $^{\circ}$ C under nitrogen but not in air. This was assigned to concurrent oxidation.¹³²

This technique was also used to determine the kinetic parameters of the thermal degradation of p-aramid.¹³² Different other methods were also used to calculate the different kinetic parameters. Using these results, the average activation energy for the degradation of p-aramid in nitrogen atmosphere was reported to be 133 kJ/mol and a pre-exponential factor of (4.8 10^8) min⁻¹. In air, the activation energy was determined to be 154 kJ/mol and the pre-exponential factor (8.6 10^6) min⁻¹. The order of the degradation reaction was found to be 0.7 in air and 1.1 in nitrogen. The degradation process in this reported study was for a temperature range (470–540 °C).¹³⁰

The invariant kinetic parameter (IKP) method has also been applied on p-aramid.¹⁰⁹ The invariant method found an invariant activation energy of 378 kJ/mol and an invariant pre-exponential factor of $(8.2 \ 10^{19}) \ s^{-1}$ in nitrogen and $103 \ kJ/mol$ and $3232 \ s^{-1}$ in air. The degradation process in this study ranged from 500–650 °C.¹⁰⁹

Pyrolysis-gas-chromatography-mass-spectrometry was performed on p-aramid at 600 °C in order to identify its different decomposition products. Evolved gas analysis at a heating rate of 20 °C/min was also reported. The pyrogram (at 20 °C/min heating rate) of p-aramid shows that most of the degradation products are released from 550 to 650 °C.⁷⁴

The identified products of the pyrolytic decomposition of p-aramid are reported in Table 20.

Electron paramagnetic resonance (EPR) analysis on p-aramid 49¹³⁶ coupled with Py-GC/MS¹³⁷ led to a tentative degradation pathway accounting for the formation of radicals in the polymer. The initial process is suggested to be homolytic scission of aromatic

Product	Name	Product	Name
NH2 + N	aniline + cyanobenzene	N NH2	p-cyanoaniline
N	p-tolunitrile		benzanilide
+ H ₂ N	p-dicyanobenzene + p-phenylenediamin	H ₂ N NHa	4'-aminobenzanilide
	phenylbenzene	N H H	4-cyano-4'-aminobenzanilide
-			

Table 20. Major products identified by Py-GC/MS on p-aramid at 600 °C in inert atmosphere.^{74,135}

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Scheme 21. Tentative thermal degradation pathway for the thermal decomposition of p-aramid 49.¹³¹

NH and amide NH-CO linkages. This could be followed by a cyclization reaction initiated by the previous scission. Phenoxyl radical produced may lead to extensively delocalized and polycyclic free radical systems^{132,138} (Scheme 21).

Moreover, studies on the thermal degradation mechanism of p-aramid led to some pioneering conclusions. It was reported that the scission of NH in the thermal degradation of p-aramid is both thermodynamically and kinetically favorable.¹³⁸ An early report on the thermal degradation of different kinds of aromatic polyamides led to the conclusion that it occurred via the hydrolysis of amide bonds whereby water was generated with acid end groups and generated during the dehydration of other groups.¹³⁹ Another study suggested the possibility of bond cleavages and free radical intermediates as being the major degradation reaction. It was concluded that the main route was that of the cleavage of aromatic C–CO of the amide linkages, which led to the formation of carbodiimide bonds.¹⁴⁰ Temperature dependent mechanisms involving iminol tautomerization, condensation of iminols, hydrolysis and decarboxylation was also reported.¹⁴¹

A paper concerning the formation of nitrogen oxides during the thermal decomposition of p-aramid was also reported.^{109,136}

Moreover, the study on the degradation of a model monomer unit led to useful insights regarding the decomposition pathway of p-aramid. It is suggested that the degradation occurs via two competing mechanism: Homolysis and hydrolysis. Indeed, there is always some water remaining in the polymer during its formation and this could initiate a hydrolysis reaction in the polymer.

10.3. Fire behavior

The fire performances of p-aramid were studied using different testing methods. One of the most widespread methods concerning the flammability rating of a polymer is the limiting oxygen index (LOI). The LOI of p-aramid is between 28 and 30 vol%,¹⁴² which may seem to be low for an inherently fire retardant polymeric system. However, p-aramid also has a high char yield when it degrades under inert atmosphere, as it is revealed by the TGA plots under nitrogen. It also has a high degradation temperature, which makes gives it an enhanced resistance to high heat.^{128,143}

Pyrolysis combustion flow calorimetry (PCFC) was also performed on p-aramid. This was performed at a heating rate of 4.3 °C/s up to a temperature of 930 °C. The heat release capacity of p-aramid was found to be 292 J/g-K and the total heat released was

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Figure 41. Burning behavior of p-aramid when subjected to 75 kW/m² heat incident heat flux.⁸⁹

reported to be 15 kJ/g. It is generally accepted that in order to be considered flame resistant, a material should have a heat release capacity less than 100 kJ/g-K.¹¹ These results suggest that *p*-aramid is not inherently flame retardant.

P-aramid was also subjected to cone calorimeter tests under different incident heat flux (50 and 75 kW/m^2).⁸⁹

At 75 kW/m^2 , the time to ignition (TTI) of p-aramid is 26 s and peak heat release rate of around 400 kW/m^2 , occurring at 55 s. It burns with a relatively high flame (Figure 41) and leaves little char residue.¹⁴⁴

P-aramid has a similar total heat release curve to PBO when submitted to 50 kW/m^2 . It has a maximum fire index of growth rate of around 60 W/s under 50 kW/m^2 and 110 W/s under 75 kW/m^2 .⁸⁹

In terms of smoke obscuration, *p*-aramid evolves smoke with a peak at $0.012 \text{ m}^3/\text{s.}^{89}$ This is much higher than PBO, which has a peak smoke obscuration at less than $0.001 \text{ m}^{3/\text{s.}}$.

10.4. Concluding remarks

p-aramid is one of the first high performance polymers that was commercially available. It has a relatively high thermal stability both in air and under inert atmosphere. This high thermal stability may be attributed to its rigid like structure, as it is the case for PBO and PIPD. Interchain hydrogen bonds, made possible thanks to the para orientation of the monomers, enhance the stiffness of the polymer.

p-aramid is stable until 400 °C but at temperatures over 450 °C, there is a drastic weight loss, meaning that the polymer completely degrades. Indeed, the thermo-oxidative degradation of p-aramid is similar to that of PIPD.

However, when subjected to external heat flux, p-aramid does not melt under the flame. However, a glowing phenomenon is observed. This means that it can more or

less retain some of its properties. Its relatively high LOI (28%) makes it a good candidate as a flame retardant material. When compared to PIPD (LOI =50%), p-aramid does not seem to be as good a fire retardant. However, additives can be used to increase the flame retardant capabilities of p-aramid.^{145,146}

11. Discussion

The high performance polymeric materials have all proved to stand up to their criteria as defined in the introduction. They exhibit a very high thermal stability (decomposition temperature >450 °C) and a good flame retardancy (high LOI, low HRR, and relatively low smoke obscuration) as compared with usual engineering polymers (such as nylon or polyesters).

It was observed that a high aromatic content in the backbone of a polymeric material has a positive impact on its thermal stability and fire behavior. Moreover, a highly ordered polymeric backbone can also contribute to having these properties.

Among fully amorphous polymeric materials, PEI has great thermal stability and fire resistance. This may be partly explained by its highly aromatic backbone. Moreover, when looking at its decomposition behavior under nitrogen, it is observed that it leaves a high weight residue. This suggests that the polymer is somewhat heat resistant and does not readily degrade. This behavior is characteristic of fire retardant materials. The highly charring nature of PEI also plays a role in its fire retardant property. Charring creates a carbonaceous layer that may protect the bulk of the material when it is exposed to a heat. This is evidenced by a relatively low HRR measured by cone calorimetry. However, despite a low HRR, the presence of a flame is also recorded. This means that some combustibles are released when the polymer decomposes and there is sufficient heat released to sustain a fire. This can be explained by the decomposition mechanism of PEI. It suggests that the random scission of the polymer backbone may lead to volatile, combustible products. These products, which were identified by Py-GC/MS undergo thermo-oxidation in the presence of oxygen. Therefore, in a fire scenario, these decomposition products of PEI will feed an eventual flame.

Among amorphous polymers, PAI has also proved to have high thermal stability. Despite decomposing at a temperature slightly lower than PEI (temperature at onset of decomposition for $PAI = 450 \,^{\circ}C$ and for $PEI = 500 \,^{\circ}C$), the rate of decomposition of PAI is lower than PEI when tested by TGA under inert atmosphere. Moreover, one of the major products of the thermal decomposition of PAI at 600 $^{\circ}C$ under inert atmosphere arises from a depolymerization reaction. This may explain the high yield of char residue. This high char residue may also explain its low flammability (LOI of 45 vol%). However, there is still work to be done in order to obtain more information concerning the thermal decomposition and fire behavior of PAI. Indeed, in order to understand fully the fire behavior, a more complete thermal decomposition behavior is required. Therefore, a mechanism of the decomposition needs to be established. This would provide a better insight on the combustibles that are susceptible to form during a fire scenario. A proper understanding of the thermal decomposition behavior may also explain the high charring, thus the high fire properties of PAI.

PEEK, being a semi crystalline polymer, behaves somewhat differently as compared to wholly amorphous polymers. When it comes to thermal behavior under nitrogen, PEEK has shown outstanding stability, with an onset of degradation at around 575 °C. This is exceptional even for a wholly aromatic polymer. Indeed, other aromatic polymers, such as aromatic polyamides usually decompose at temperatures around 450 °C (as is it the case for Kevlar). Moreover, the residue yield at high temperatures is above 45% at 900 °C. This high a residue suggests that during the thermal degradation of the material, only a small fraction of the material releases combustibles. In addition, the studies of the thermal degradation mechanism of PEEK, the high char residue seems to be due to crosslinking reactions that take place at high temperature. This crosslinking may also explain the high flame retardancy of PEEK. Indeed, as with PEI, a highly charred material implies a lower release of fuel for a fire. This may occur due to the carbonization of a fraction of the polymer when it is subjected to thermal stress. Moreover, if charring occurs at the surface of the polymer, it can act as a barrier, preventing heat from reaching the bulk of the polymer, but also prevents fuel from reaching the flame. All these factors play some role to the inherent fire retardancy of PEEK. However, further decomposition and flame behavior studies need to be performed in order to understand fully the role of each individual factor that contribute to the fire retardant behavior of PEEK.

Another type of polymeric structure that has stood out among the high performance polymers is those with a heterocyclic backbone. It is explained by the inherent high stability of these polymers. Indeed, heterocyclic polymers such as PI, PBO, and PIPD have highly ordered structures with strong interactions between polymer chains making them thermally stable.

Polymers with a heterocyclic polymer backbone have shown the best thermal stabilities and fire behavior. PI, PBI, PBO, and PIPD are among the best candidates in terms of flame retardancy. Indeed, when subjected to a cone calorimeter test, all these materials had an HRR that was below 60 kW/m^2 when irradiated with a heat flux of 50 kW/m^2 . These are significantly low values considering the high incident heat flux on the material.

These high performances can be explained by their decomposition behavior. Indeed, when it comes to fire, it is the release of combustibles from the bulk of a material that contributes to a sustained fire.

For instance, PI analyses of the decomposition products have shown that a large fraction of the polymer contributes to char formation. However, the decomposition mechanism has revealed that there some small molecules are evolved when the material is under thermal stress. These small molecules are combustibles (such as phenol and aminophenol) that can contribute to the propagation of a fire. This explains that PI presents a flame when it is exposed to a high heat flux (75 kW/m^2). However, considering the high heat flux that was used, the heat release rate remains relatively low (53 kW/m^2).

PBI on the other hand is somewhat different from PI. The thermal behavior of PBI seems to be dependent on its thermal history. Indeed, PBI possesses a hygroscopic nature, meaning that it will take up water if left in a humid environment. This affects the thermal properties of PBI because depending on the amount of water present in the material, the first decomposition process that is observed is usually that of the elimination of water. This usually occurs over a range of temperatures, making it difficult to predict the decomposition behavior. However, a tentative decomposition mechanism has been reported. A ring
opening reaction within the polymer backbone is suggested to occur. This means that the first reaction is a bond scission that does not directly lead to the breaking of the polymer chain, implying that there the release of combustibles does not occur readily when the material stars to degrade. It suggests that the bond scission occurring leads to the formation of a protective char. Nevertheless, methane and amines are also reported as decomposition products, which can fuel a flame upon burning. This means that in a fire scenario, its decomposition behavior may cause an increase in flame spread, thus endangering lives.

In the case of PBO, the decomposition mechanism suggests that a large fraction of the material is converted to char. Moreover, the mechanism also suggests that the main reaction occurring during the thermal decomposition is a depolymerization. This means that the decomposition products may remain as somewhat large molecules. These molecules contribute less to a fire as compared to small combustibles. Another possibility is that the result of depolymerization contributes to charring of the polymer. The decreased released of combustibles and the high char residue in PBO may explain its low heat release rate when subjected to fire tests. Indeed, when PBO is subjected to fire calorimetry, there was no visible flame. The polymer degraded due to the high heat flux and a brittle charred structure remained. However, the thermal decomposition of PBO under thermo-oxidative conditions is not great. Indeed, despite still having a high temperature for the onset of the degradation, the decomposition is abrupt and complete. This means that under thermo-oxidative conditions, the totality of the polymer is oxidized.

Similarly, PIPD has a highly charring nature. TGA of PIPD also shows a high char residue when tested under nitrogen. Under thermo-oxidative atmospheres, the residual mass of PIPD at high temperature is significantly lower than under nitrogen. However, this does not seem to affect its high fire performance. Indeed, when exposed to a high heat flux of 75 kW/m^2 , only a small peak of heat release rate is observed (44 kW/m^2). This could be explained by the formation of a protective carbonaceous layer that forms on the surface of the polymer. This protective layer prevents the bulk of the polymer from being exposed to the high temperature of the incident heat flux. It also limits the release of combustibles from the bulk to the flame by creating a physical barrier for mass transport from bulk to surface (where the flame lies). However, few studies deal with the thermal decomposition and decomposition mechanism of PIPD. Therefore, a proper understanding of how the thermal degradation products of PIPD may contribute or not to a flame is not achieved. It may be of interest to emphasize some effort on the comprehension of the decomposition behavior of PIPD both in thermo-oxidative and inert atmospheres in order to extract the structural and physico-chemical factors that contribute to the highly interesting thermal and fire properties of PIPD.

PIPD, PBO, and PBI fall in the category of rigid rod polymers. It evidences that such a structural property would imply excellent thermal stability. However, this is only partially true. P-aramid, also possesses a rigid rod structure. However, despite having relatively good thermal and fire behavior, the performances are not as good as the heterocyclic polymers mentioned before. This could be explained by the fact that the thermal decomposition of p-aramid yields a smaller char fraction. Indeed, when examining the thermal decomposition products that are released during its thermal decomposition, many small aromatic compounds are identified. These may fuel an eventual flame in a fire scenario. This is further evidenced in the cone calorimeter test that was performed on p-aramid. High flames were

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observed (pHRR of around $400 \, \text{kW/m}^2$), suggesting that despite the apparently high char yield observed on TGA, the nature of the degradation products also play a significant role in fueling a flame. Another explanation might be that the char that forms with p-aramid is not dense enough to protect the underlying bulk of the material. This could be due to a lower amount of crosslinking occurring at high temperature, causing the heat to reach the bulk of the material and the degradation of the polymer. It might be of interest to study the density and the structure of the char to see if the amount of crosslinking. Finally, another possible explanation for the high heat release rate could be that the scission of the amide bonds occurs throughout the material, breaking the chains cleanly, thus leading to a higher proportion of small combustible molecules to feed the flame.

12. Conclusion

In this work, we have seen that there are many aspects of a polymeric material that may have a more or less significant role in the thermal stability and fire behavior of a polymeric material. However, it is clear that the two properties are somewhat correlated. Highly ordered structures in the polymeric structure of a material often leads to a high thermal stability and a high fire performance. This was observed in PEEK, PIPD, PI as well as PBO. However, it is important to note that this does not always suffice. This was observed with p-aramid which, despite being highly ordered (to the point of behaving like a rigid rod polymer), the fire performances do not match what the thermal stability promises. Moreover, a high degree of aromaticity may cause and enhancement in the fire and thermal properties of a material. This was observed in most polymers that were reviewed in this paper. In terms of structural properties, it was observed that highly aromatic, heterocyclic polymers with high inter-chain interactions have highly desirable thermal and fire performances. We have also observed that the reaction to fire of a material can have a strong dependence on its thermal decomposition pattern. Indeed, polymers that release a high amount of combustibles often behave poorly in fire scenarios. On the other hand, polymers that favor a cross-linking reaction seems to behave positively in a fire scenario. However, this does not suffice, the structure and density of the char is important when it comes to a fire scenario. A fragile char would not bring much fire protection, as it can be seen with Kevlar.

Glossary

D) (7	D. 1 1
BMI	Bismaleimide
DPMS	Direct Pyrolysis Mass spectrometry
DSC	Differential Scanning Calorimetry
DTG	Derivative Thermogravimetric Analysis
EPR	Electron Paramagnetic Resonance
FIGRA	Fire Growth Rate
FTIR	Fourier Transform Infrared
HRR	Heat Release Rate
IKP	Invariant Kinetic Parameter
LOI	Limiting Oxygen Index
MCC	Microscale Combustion Calorimetry
MS	Mass Spectrometry
OFW	Ozawa Flynn Wall

- PAEK Polyaryletherketone
- PAI Polyamide imide
- PBI Polybenzimidazole
- PBO Polybenzoxazole
- PCFC Pyrolysis Combustion Flow Calorimetery
- PEEK Poly(ether etherketone)
- PEI Polyether imide
- PEK Polyetherketone
- pHRR Peak of Heat Release Rate
- PIPD Polypyridobisimidazole
- PPSU Poly (phenymene sulfone)
- PPTA Poly(*p*-phenylene terephthalate)
- Py-GC/MS
 - Pyrolysis-Gas Chromatography/Mass Spectrometry
- TGA Thermogravimetric Analysis
- THR Total Heat Released
- TONSET Temperature at degradation onset
- TTI Time to Ignition
- VSP Volume of Smoke Produced

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I.2. Flame Retardancy of Polymeric Materials

While the previous section explores the principles adopted during the decomposition and burning of a polymeric material it also brings light upon some exceptionally enviable resistance to heat and fire of some high-performance polymers. However, most of the polymers commonly used do not possess such extreme thermal properties. Therefore, in order to meet the legislation, they need to be flame retarded. There exist various ways to flame retard a material.

Before delving deeper into the fire retardancy of a material, it is essential to understand the different modes of action that they undertake to achieve their fire retarding goal. Indeed, there are many types of fire retardants that have different behaviors with respect to a fire scenario.

I.2.a. Mode of action of Flame Retardancy

A flame-retardant is a coating or additive that delays or suppresses the combustion process of a material. The way they react to achieve such an end depends on the nature of the flame-retardant. Indeed, flame suppression may occur at different stages of a fire scenario – upon the initial heating, at ignition, during the decomposition, or during burning. Most of the time, the flame retardants act at different stages simultaneously.

Two possible ways in which flame retardants may interrupt a combustion process are via physical actions or chemical actions.

I.2.a.i. Physical Action

Physical actions that lead to flame retardancy are many. First of all, some flame retardants may form a protective layer on the surface of the polymer. This prevents heat from reaching the inner parts of the materials, attenuating the decomposition process, therefore decreasing the availability of fuel for the fire. This protective layer may also act as a barrier preventing mass transfer from the bulk of the polymer to the surface (or the flame), bringing about a lack of combustibles. This is the case for intumescent systems [21].

Another way in which a flame retardant may act is by decreasing the heat in its immediate environment, or, more simply, by cooling effect. Indeed, some fire-retardant additives decompose endothermically, taking a high amount of energy from its surroundings. This cools the material, slowing down its decomposition, possibly interrupting the combustion process. This is the principle used in one of the most widely used fire-retardant – aluminium

trihydroxide (ATH)– whereby three water molecules are released per molecule of ATH in an endothermic reaction.

A third physical action that may retard a fire is the dilution of combustibles in the surrounding atmosphere. This can be achieved by incorporating flame retardants that release inert gases when it decomposes. This decreases the concentration of combustibles, causing a lack of fuel to feed an eventual flame.

I.2.a.ii. Chemical Action

Chemical reactions occurring during the thermal decomposition may lead to fire retardancy. This fire retarding process may occur in condensed phase or in gas phase.

Condensed phase fire retardancy corresponds to two types of chemical reactions. First, the flame retardant promotes the formation of a protective carbonaceous layer on the surface of the material, decreasing the heat flux on the material. This also decreases the mass transfer to an eventual flame. This type of reaction occurs mostly in polymers with cyclizing and cross-linking potential. Another condensed phase reaction corresponds to the instance whereby the flame retardant increases the rate of degradation of the polymer. This acts on its viscosity, bringing about a higher flow velocity, hence taking the polymer away from the flame. This cuts the supply of combustibles in the burning process attenuates the fire.

Gas phase flame retardancy often occurs through the interruption of the radical mechanism of the combustion process, in which highly reactive free radicals react to sustain a flame. This can be achieved either via the formation of radical scavengers, that react preferentially to free radicals, poisoning the flame and taking away its heat source and cooling down the system. These radical scavengers correspond to the flame retardant itself or its decomposition products.

While it is possible to find flame retardants that act solely in terms of physical action, it is rare to find fire retardants which act only in chemical form. Indeed, the chemical reaction brought about by a chemical would eventually have some physical action brought to it (formation of a protective layer or dilution of the flame).

I.2.b. Flame Retardant Additives

The use of additives is the major option to flame retarding polymeric materials. Their use dates from early civilizations and date back to as far as ancient Chinese, and later adopted by Romans, making use of vinegar and alum to flame wooden structures to prevent the spread of fire. One of the first documented attempt understanding flame retardancy came from Gay-Lussac in 1821. He made use of ammonium phosphates and borax to flame retard a cellulosic material [22]. Since then, the industry of flame retardancy has grown significantly. Indeed, the consumption of flame retardants has drastically increased, and the trends show that their production is ever rising. Nowadays, with the demand for polymeric materials being at a record high, so is the fire-retardant requirement. Consequently, the fire retardant market is divided into 6 major types of additives (Figure 4): aluminium trihydroxide (ATH), brominated flame retardants, antimony oxides, chlorinated flame retardants, organophosphorous flame retardants, and some other types of flame retardants, such as nitrogen based flame retardants.



Figure 4 Global distribution of fire retardants by chemistry (source: IHS Consulting 2017)

I.2.c. Current Situation of Flame-Retardant Additives

Flame retardant chemicals (brominated, chlorinated and organophosphorous) form a whopping 40% of the market share of the global flame retardants. However, with evolving markets and the constricting strictness of current norms, some of these fire retardants are bound to disappear in the next few decades. Indeed, market share of halogenated flame retardants is on the decline.

Aluminium trihydroxide (ATH) is the most abundantly used flame retardant in industry nowadays. However, it has some drawbacks in the sense that a high loading (approximately 60 %) is required for it to be effective [23]. Such high a loading is bound to have an impact on the physical properties of the polymeric material.

Moreover, nitrogen-based additives are also used as flame retardants in polymeric materials. One of the major nitrogen-based additives used as flame retardants is melamine, which acts as a fire retardant in the condensed phase: its thermal decomposition enhances crosslinking reactions in a polymeric material, favoring char formations. Furthermore, there are other ways to flame retard a material other than using flame retardant additives. Indeed, surface modifications such as intumescent coatings, or simply the use of intumescence-based fire-retardant additives show promise in the development of novel fire-retardant systems.

I.2.d. Conclusion

The direction that the fire-retardant market has adopted has caused the research for different and more efficient flame retardants to rise. The demand on halogen-free fire retardants is becoming a must as the toxicological strictness of some current flame retardants are being reviewed. Therefore, novel flame retardants are a requirement. One such flame retardant that has emerged in the past decade are halogen-free Schiff-base based ones[24]. These are simple molecules that can show positive effects at relatively low loadings. The next chapter introduces such a Schiff base acting as an efficient flame retardant under relatively low loadings.

I.3. Salen

Salens are a class of ligands corresponding to bisimines with a structure derived from N'N'bis(salicylaldehyde)ethylenediamine. The first salen-metal complex was reported by Pfeiffer et al. in 1933 [25].

Salen and its derivatives are highly versatile ligands that have been frequently reported. This is mostly due to its facile production, and their wide range of metal with which complex. Indeed, salen derivatives can be easily made chiral or sterically hindered, the properties of the molecules are highly modulable, making it an enviable target for synthetic chemists.





The formation of the salen ligand is a simple condensation reaction. Two equivalents of salicylaldehyde precursor reacts with one equivalent of a diamine (Scheme 1). The reaction is spontaneous. This reaction is often made in protic solvents such as ethanol or methanol. The product is also easily purified by crystallization.

I.3.a. Salen-Metal Complexes

Salen ligands may form metal complexes with different coordination numbers. Salen-metal complexes with most transition metals, post-transition metals, actinides and lanthanides have been reported [26–33]. Most salen metal complexes (or metallosalens) may be synthesized from the base salen and a metallic salt as shown in Scheme 2.



Scheme 2. Synthesis of salen metal complex

Thanks to the versatility of the salen-metal complexes, they have been used in a wide array of applications: catalysis [26,34,35], depollution, magnetism [36–38], medicine, biomimetics, liquid crystals, nanotechnologies [39–43] and fire retardancy [4,44,45].

I.3.b. Salen Derivatives as a Flame Retardant

As mentioned previously, salen derivatives have shown they can act as a fire retardant when incorporated in thermoplastic polyurethane [46]. The first report in for such an application was published by Fontaine et. al. whereby salen copper complexes showed a promising decrease in the peak heat release rate (evaluated by mass loss cone calorimetry) of polymer/fire retardant formulations as compared to the neat polymeric material (thermoplastic polyurethane). The copper complex studied showed that the presence of a metal-chelate had a positive effect (improved fire performance) on the flame retardancy effectiveness of the salen molecule.

Another work that furthered the study of salen-copper complexes as a flame retardant in TPU was reported in 2018 [4]. In this work, the mode of action of salen-copper complexes in TPU was elucidated. A synergistic effect was found between the thermal degradation of TPU and that of the salen complex. This led to the formation of highly cross-linked phenolic resins, which are also thermally resistant. This means that when salen-copper complex is present in TPU, the char residue formed during the decomposition of the material is higher. It was shown that complexes increase both thermal stability and provides a platform for

structural transformation by promoting the formation of a charred structure, possibly due to a different decomposition mechanism.

Moreover, the flame retarding efficiency of salen molecules when incorporated in polyamide-6 (PA6) was also reported by Naik et. al. [44]. It was reported that salen molecules, when under thermal stress, would react to form a hyperbranched cross-linked phenolic resin. These resins, when subjected to thermal stress, form a carbonaceous layer called "char", which can be an indicator of fire retardancy. Indeed, when tested in PA6, a decrease in the peak of heat released (-14 %) was observed when PA6/salen was compared to its unfilled counterpart. It was reported that the salen molecules were crosslinked during the processing of the polymer, which, in turn, increased the thermal stability of the polymeric material. This crosslinking phenomenon is often seen in high performance polymers when they are subjected to extreme temperatures (see previous section).

I.3.c. Conclusion

Salen and its derivatives are indeed highly versatile molecules. The fire properties that have been studied are promising, owing to its ability to mimic high performance materials when subjected to high temperature. Indeed, this phenomenon of crosslinking under thermal stress is often observed in high performance polymers with enviable resistance and reaction to fire. This trait makes salen based molecules a viable asset as a thermal trigger against fire scenarios. By formulating salen based complexes to common polymeric materials, high performance traits may be achieved, making salen based molecules an asset in the fire retardation world.

I.4. General Conclusion and Strategy

The review on high performance polymers provided insight as to how their main fireretardant characteristics lies in their ability to form a much more significant char as compared to common engineering polymers. In order to better understand this aspect of high-performance polymers, it was deemed interesting to study their decomposition behavior under different kinds of thermal stress and fire scenarios. Indeed, understanding the fire behavior of such materials would bring us insight on the key elements that make those materials fireproof.

The role of oxygen in the thermal decomposition of these high-performance materials will also be studied. Indeed, in a fire scenario, due to the combustion of the degradation products in the gas phase, the underlying polymeric material finds itself in an oxygen poor, or oxygenfree environment. Understanding the thermal decomposition behavior of polymeric materials under low oxygen concentration levels may provide crucial information concerning the actual decomposition pattern that a material adopts in a flaming combustion scenario. Moreover, by studying the thermal decomposition of high-performance polymers under low oxygen concentrations, insight on some possible fire retarding behavior of the materials should be acquired. The approach adopted is to use the understanding of the decomposition of highly stable and fireproof polymeric materials to devise and conceptualize a flame retardant that would make a common material act as a high performing one under fire constraints. This has already been shown to happen when a salen derived complex was used in thermoplastic polyurethane. Indeed, this fire-retardant increased char formation in a polymeric material and improved its fire performance.

Therefore, in order to complement the previously initiated study concerning salen and its derivatives, analogues of salen complexes will be used to investigate their fire retarding potential in TPU and PA6. Different metal complexes will be investigated in order to study the effect of the coordination metal on the thermal stability of the molecule itself and the fire performance that they lead to when they are formulated with common polymeric materials.

Finally, an attempt to extrapolate the thermal trigger behavior of salen in polymeric materials will be further discussed and possible pathways to find new thermal triggers as fire retardant additives will be investigate.

II. Materials and Methods

This chapter is dedicated to the different techniques and materials that contributed to the completion of the project. A subsection pertaining to the high-performance materials and the polymeric materials studied is detailed This part is dedicated to the introduction of the said polymeric materials and the reasons why they were studied. Furthermore, a subsection is dedicated to the description of the different experimental procedures for the synthesis of fire retardants. Subsequently, different physico-chemical characterizations methods employed during this work are described. These involve structural and thermal characterizations. Gas phase analyses were also performed in order to identify decomposition gases of the studied polymeric materials. A description of the extraction of the kinetic parameters for the thermal decomposition of high-performance materials is included. These were important in order to have a deep insight on the comparison between well-performing polymeric materials and our own flame-retarded ones. Finally, the fire tests that were used to evaluate the fire performance of the polymeric materials are described in the following subsection. These syntheses, characterizations and evaluations were indispensable in the elaboration of potential smart flame-retardant additives because they were used to conceptualize potential flame retardants

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II.1. Materials

II.1.a. High Performance polymers

High performance polymeric materials were studied in order to gain insight on their decomposition behavior under different types of thermal stress. Indeed, in the previous it was mentioned that the decomposition pathway of such materials has led them to possess enviable thermal and fire properties. The main aim of this project was to be able to obtain such properties using additives.

The thermal and fire properties were evaluated using different tests that are described in this chapter. Thermal tests involved heating the material under inert, oxidative (air) as well as under low oxygen atmospheres (2 % oxygen). Pyrolysis-GCMS and TGA-FTIR were used for the identification of the different evolving gases during the decomposition processes. Flaming combustion tests (mass loss cone calorimetry) were also carried out where possible.

Three high performance polymers were used in this study polyetheretherketone (PEEK), polybenzoxazole, and polyimide. These materials show extremely high resistance to fire and heat, therefore, by studying their decomposition and fire behaviors, we hope to gain insight on the structural properties of the materials that impropriate such high thermal and fire resistance to these materials.

Polyetheretherketone was supplied by Quadrant Engineering Plastics (Tielt, Belgium). Polybenzoxazole was supplied by Teijin Frontier Ltd (Tokyo, Japan). Polyimide was purchased from Goodfellow Cambridge Limited (Huntington, England).

II.1.b. Other Polymers

In order to test the efficiency of developed flame retardants, they are incorporated into polymers. Previous studies have been done with thermoplastic polyurethane (TPU, see below), thus, TPU was chosen to compare the flame-retardant efficiency of the new flame-retardant additives. Moreover, in order to study the versatility of the flame retardant, they were also tested in polyamide 6. This is a highly versatile engineering grade polymeric material that are used in various applications ranging from the textile industry to the automobile industry. However, in order to be used for these applications, they need to be flame retarded. This functionality is achieved via the incorporation of flame retardants in the bulk or through coatings.

Thermoplastic polyurethane was kindly supplied by BASF (brand name Elastollan C85A). Polyamide 6 used was supplied by Rhodia (now Solvay) and referenced by the manufacturer as S27-BL natural S. The technical data sheets of the two materials are annexed at the end of this chapter.

II.2. Synthesis of salens and salens metal complexes

II.2.a. Synthesis of Salen

For this project, a particular class of additives was chosen: salen. These small organic molecules have proved to exhibit interesting fire properties both in their non-complexed and complexed forms. Therefore, both metal complexes of salen and some salen derivatives were studied. Scheme 3 summarizes the different potential fire retardants were synthesized for the project.



Scheme 3. synthesis of salen, hydroxysalen and their metallic complexes

N,N'-bis(salicylidene)ethylenediamine (s1) and N,N'-bis (4-hydroxysalicylidene) ethylenediamine (s2) were obtained using a conventional procedure for salen synthesis based on the condensation of salicylaldehyde or its hydroxy-derivatives with diamine [44]. Most salen complexes were synthesized according to procedure described in [46]. Zincsalen complexes were prepared according to the procedure described in [47]. Hereafter are the experimental protocols that were adopted to synthesize the different aforementioned fireretardants.

Reagents were purchased from Aldrich or Lancaster and were used without further purification. Diethyl ether, methanol and absolute ethanol were reagent grade commercial solvents and were used without further purification.

NMR spectra were recorded on a Bruker AVANCE 300 spectrometer. Chemical shifts (δ) are referenced to internal solvent and given in ppm. Coupling constants (J) are given in Hz. The following abbreviations apply to spin multiplicity: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and bs (broad singlet).

II.2.a.i. N,N'-bis(salicylidene)ethylenediamine (s1)



Figure 6. Chemical structure of N,N'-bis(salycylidene)ethylenediamine (s1)

To a solution of ethylenediamine (5.34 mL; 4.8 g; 0.08 mol) in 60 mL of absolute ethanol, salicylaldehyde (16.7 mL; 19.5 g; 0.16 mol) in 80 mL of ethanol was added dropwise with vigorous stirring. The product immediately precipitates and the mixture was refluxed for two hours. After cooling to room temperature, the yellow solid was filtered and washed with ethanol 3 times. The product recrystallized from ethanol (EtOH), was filtered, washed with cold ethanol and ethyl ether, then dried at 80 °C to give the desired Schiff base **s1** as yellow crystals, 20.2 g (0.075 mol, 94 %).

¹H NMR (DMSO-d₆): δ 3.92 (s, 4H), 6.81-6.95 (m, 4H), 7.35 (m, 4H), 8.57 (s, 2H); ¹³C NMR (DMSO-d₆): δ 58.8 (CH₂), 116.4 (C_{Ar}), 118.5 (C_{Ar}), 118.6 (C_{Ar}), 131.6 (C_{Ar}), 132.3 (C_{Ar}), 160.4 (C_{Ar}), 166.8 (CN).

MS (NanoESI): *m*/*z* 269.1 (M+H)⁺.

 $Mp = 130 \ ^{\circ}C$

II.2.a.ii. N,N'-bis(4-hydroxysalicylidene)ethylenediamine (s2)



Figure 7. Chemical structure of N,N'-bis(4-hydroxysalicylidene)ethylenediamine (s2)

According to the method described for s1, 21.9 g (0.16 mol) of 2,4-dihydroxybenzaldehyde and 5.34 mL (4.8 g, 0.08 mol) of ethylenediamine yielded compound s2 (22.5 g; 0.075 mol 94 %) as an orange solid;

¹**H NMR** (**DMSO-d**₆): δ 3.77 (s, 4H), 6.15 (d, J = 2.4 Hz, 2H), 6.26 (dd, J = 2.4, 8.6 Hz, 2H), 7.16 (d, J = 8.6 Hz, 2H), 8.35 (s, 2H); ¹³**C NMR** (**DMSO-d**₆): δ 57.8 (CH₂), 102.5 (C_{Ar}), 106.9 (C_{Ar}), 111.2 (C_{Ar}), 133.4 (C_{Ar}), 161.7 (C_{Ar}), 164.3 (C_{Ar}), 165.7 (CN).

MS (NanoESI): *m*/*z* 301.2 (M+H)⁺. Mp > 260 °C

II.2.b. Synthesis of Salen metal complexes

II.2.b.i. N,N'-bis(salicylidene)ethylenediamine copper (II) complex, **s1-Cu**



Figure 8. Chemical structure of N,N'-bis(salicylidene)ethylenediamine copper (II) complex (s1-Cu)

N,*N*'-bis(salicylidene)ethylenediamine **s1** (8.1 g, 0.03 mol) was dissolved in 70 mL absolute ethanol then a solution of copper (II) acetate (6.0 g, 0.03 mol) in 40 mL of water was added dropwise and the green suspension was refluxed under vigorous stirring for 2.5 h. The green precipitate was collected by filtration, washed thoroughly with ethanol then dried at 80 °C to give *N*,*N*'-bis(salicylidene)ethylenediamine copper (II) complex **s1-Cu** (6.96 g, 0.02 mol, 70%) as a fine green powder. NMR spectra of the complex was not recorded due to paramagnetism of Cu(II) (this well-known phenomenon leads to poor resolution of the spectra).

II.2.b.ii. N,N'-bis(salicylidene)ethylenediamine nickel (II) complex, **s1-Ni**



Figure 9. Chemical structure of N,N'-bis(salicylidene)ethylenediamine nickel (II) complex (s1-Ni)

According to the experimental protocol for the synthesis of **s1-Cu**, N,N'bis(salicylidene)ethylenediamine **s1** (6.01 g, 0.022 mol) made to react with nickel (II) acetate (5.51 g, 0.022 mol). The orange precipitate was collected by filtration, washed thoroughly with ethanol 3 times then dried at 80 °C to afford N,N'bis(salicylidene)ethylenediamine Nickel (II) complex **s1-Ni** (5.87 g, 0.02 mol, 80.6 %) as an orange powder. ¹**H NMR (300 MHz, DMSO-***d*₆): δ ppm 3.29 - 3.35 (m, 1 H) 3.42 (s, 4 H) 6.51 (t, *J*=7.25 Hz, 2 H) 6.70 (d, *J*=8.67 Hz, 2 H) 7.17 (ddd, *J*=8.43, 6.92, 1.79 Hz, 2 H) 7.25 (dd, *J*=7.82, 1.60 Hz, 2 H) 7.89 (s, 2 H). ¹³**C NMR (75 MHz, DMSO-***d*₆): δ ppm 58.45 (s, 1 CH₂) 114.75 (s, 1 C_{Ar}) 120.22 (s, 1 C_{Ar}) 120.79 (s, 1 C_{Ar}) 133.22 (s, 1 C_{Ar}) 133.98 (s, 1 C_{Ar}) 163.07 (s, 1 C_{Ar}) 164.40 (s, 1 CN).

MS (NanoESI): *m/z* 324.0 M⁺.

II.2.b.iii. N,N'-bis(salicylidene)ethylenediamine zinc (II) complex, s1-Zn



Figure 10. Chemical structure of N,N'-bis(salicylidene)ethylenediamine zinc (II) complex (s1-Zn)

The procedure used for the synthesis of the two previous complexes did not have an acceptable yield when the synthesis **s1-Zn** was attempted. Therefore, the synthesis of **s1-Zn** was based on another experimental protocol from literature which reported a higher yield [47].

The complex **s1-Zn** was prepared by first treating salicylaldehyde (2.15 mL, 0.02 mol) with zinc (II) acetate (2.26 g, 0.01 mol) in methanol (100 mL) for 30 min at room temperature. Then, ethylenediamine (0.68 mL, 0.01 mol) was added to the solution, and stirring was maintained at room temperature overnight. During that time, a light-yellow precipitate formed. The precipitate was collected by filtration, washed with cold methanol and ether, and dried at 80 °C, affording 3.00 g, 0.009, 90 %.

¹**H NMR (300 MHz, DMSO-***d*₆): δ ppm 3.72 (s, 4 H) 3.92 (s, 1 H) 6.34 - 6.50 (m, 2 H) 6.55 - 6.68 (m, 1 H) 6.61 (d, *J*=8.29 Hz, 1 H) 7.09 - 7.44 (m, 4 H) 8.43 (s, 2 H) 13.34 - 13.45 (m, 1 H). ¹³**C NMR (75 MHz, DMSO-***d*₆): δ ppm 55.75 (s, 1 CH₂) 112.15 (s, 1 C_{Ar}) 119.31 (s, 1 C_{Ar}) 122.68 (s, 1 C_{Ar}) 132.77 (s, 1 C_{Ar}) 134.73 (s, 1 C_{Ar}) 167.97 (s, 1 C_{Ar}) 171.01 (s, 1 CN).

MS (NanoESI): *m*/*z* 331.0 (M+H)⁺

II.2.b.iv. N,*N'-bis*(4-hydroxysalicylidene)ethylenediamine copper (*II*) complex, **s2-Cu**



Figure 11. Chemical structure of N,N'-bis(4-hydroxysalicylidene)ethylenediamine copper (II) complex (s2-Cu)

According to the method described for s1-Cu, N,N'-bis(4-hydroxysalicylidene)ethylenediamine s2 (9.0 g, 0.03 mol) was made to react with copper (II) acetate (6.0 g, 0.03 mol). A purple powder was (9.7 g, 0.026 mol, 89%). NMR spectra of the complex was not recorded due to paramagnetism of Cu(II) (this well-known phenomenon leads to poor resolution of the spectra).

MS (NanoESI): *m/z* 362.0 (M+H)⁺ mp > 260 °C

II.2.b.v. N,*N'-bis*(4-hydroxysalicylidene)ethylenediamine manganese (*II*) complex, **s2-Mn**



Figure 12. Chemical structure of N,N'-bis(4-hydroxysalicylidene)ethylenediamine manganese (II) complex (s2-Mn)

According to the method described for s1-Cu, N,N'-bis(4-hydroxysalicylidene)ethylenediamine s2 (3.60 g, 0.012 mol) was made to react with manganese (II) acetate (2.94 g, 0.012 mol). A brown solid of manganese (II) complex s2-Mn (3.1 g, 0.0088 mol, 73%) was obtained. NMR spectra of the complex was not recorded due to paramagnetism of Mn(II) (this well-known phenomenon leads to poor resolution of the spectra).

MS (NanoESI): m/z 353.0 (M)⁺. Mp > 260 °C

II.2.b.vi. N,*N'-bis*(4-hydroxysalicylidene)ethylenediamine nickel (*II*) complex, **s2-Ni**



Figure 13. Chemical structure of N,N'-bis(4-hydroxysalicylidene)ethylenediamine nickel (II) complex (s2-Ni)

According to the method described for s1-Cu. N,N'-bis(4hydroxysalicylidene)ethylenediamine s2 (7.00 g, 0.022 mol) made to react with nickel (II) (5.51)0.022 acetate g, mol) А red powder of *N*,*N*'-bis(4hydroxysalicylidene)ethylenediamine cobalt (II) complex s2-Ni (5.36 g, 0.015 mol, 68 %) was obtained.

¹H NMR (300 MHz, DMSO-*d*₆): δ ppm 3.25 - 3.31 (m, 2 H) 6.04 (d, *J*=8.69 Hz, 2 H) 6.05 (s, 1 H) 7.05 (d, *J*=8.10 Hz, 1 H) 7.62 (s, 1 H) 9.73 (br s, 1 H). ¹³C NMR (75 MHz, DMSO-*d*₆): δ ppm 58 (s, 1 CH₂) 104 (s, 1 C_{Ar}) 106 (s, 1 C_{Ar}) 115 (s, 1 C_{Ar}) 135 (s, 1 C_{Ar}) 161 (s, 1 C_{Ar}) 163 (s, 1 C_{Ar}) 166 (s, 1 CN). MS (NanoESI): *m*/*z* 356.0 (M)⁺.

II.2.b.vii. N,*N'-bis*(4-hydroxysalicylidene)ethylenediamine zinc complex, **s2-Zn**



Figure 14. Chemical structure of N,N'-bis(4-hydroxysalicylidene)ethylenediamine zinc complex (s2-Zn)

The complex s2-Zn was prepared using the same protocol as the one used for the preparation of s1-Zn. 4-hydroxysalicylaldehyde (2.82 g, 0.020 mol) was made to react with $Zn(OAc)_2 \cdot 2H_2O$ (2.26 g, 0.010 mol) in methanol followed by the addition of ethylenediamine (0.68 mL, 0.01 mol). A yellow precipitate was obtained (3.23 g, 0.0089 mol, 87 %.).

¹H NMR (300 MHz, DMSO-*d*₆): δ ppm 3.59 (s, 2 H) 5.89 - 5.96 (m, 1 H) 5.90 - 5.95 (m, 1 H) 5.95 (s, 1 H) 5.98 (s, 1 H) 6.92 (d, *J*=8.48 Hz, 1 H) 8.21 (s, 1 H) 9.39 (br s, 1 H). ¹³C NMR (75 MHz, DMSO-*d*₆): δ ppm 56 (s, 2 CH₂) 103 (1 C_{Ar}) 107 (1 C_{Ar}) 113 (1 C_{Ar}) 136 (1 C_{Ar}) 162 (1 C_{Ar}) 167 (1 C_{Ar}) 173 (1 CN).

MS (NanoESI): *m*/*z* 363.1 (M+H)⁺. Mp > 260 °C.

II.2.c. Formulation and Processing of salen and salen metallic complexes in TPU and PA6

In order to test the synthesized additives, they were incorporated in different polymers. This was performed by physically mixing the polymeric material with the additive at predefined temperatures.

Processing of the polymeric materials were carried out using a DSM Xplore Micro15 twinscrew microextruder. Extrusions were carried out under a continuous flow of nitrogen in order to limit the degradation of the polymer at high temperatures.

II.2.c.i. TPU formulations

TPU is dried for 12 hours at 70 °C prior to use. Compounding of formulations with a ratio of 10:1 wt% (TPU: additive) of salen and their complexes was performed using the microextruder under nitrogen atmosphere at 190 °C (50 rpm for a total 5 minutes of mixing). This was performed in a two-step process: Approximately 10 g of the neat polymer was added to the microextruder and was allowed to mix for 1 min. after this minute of mixing, the remaining 5 g of the polymer was physically pre-mixed with the additive (1.5 g) was added and allowed to mix for 4 more minutes. This was repeated as many times as needed in order to obtain the required mass of formulated polymeric materials.

II.2.c.ii. PA6 formulations

The processing protocol of PA6 was the same as that for TPU except for the temperature of the microextrusion, which was performed at 250 °C instead of 180 °C.

II.3. Characterization

To evaluate the physico-chemical properties of the different flame-retarded polymers and the flame retardants themselves, a series of characterization techniques were adopted. These allowed the obtention of important parameters such as the degradation temperature of the material or of the flame-retardant additive. Gas phase analysis of the evolved gases during thermal decomposition of the formulated samples were essential in evaluating the eventual differences in the decomposition behavior of the polymeric materials with respect to the different flame retardants that were used.

II.3.a. Physico-chemical and Thermal analysis

II.3.a.i. Cryogrinding of the polymeric materials and formulations

In order to perform microscale tests of the high-performance polymeric materials as well as the formulated polymers, they were required to be cryoground. This was performed in liquid nitrogen using an ultracentrifuge. After the grinding, the polymeric materials were dried at 80 °C under reduced pressure before use.

II.3.a.ii. Thermogravimetric analysis (TGA)

Thermogravimetric analyses (TGA) were conducted on a Netzsch Libra instrument. Powdered samples (or in the case of fibers ,cut into small filings) of 9 - 10 mg (according to the good practice of TGA, it can be assumed the samples are thermally thin) were placed in open alumina pans and heated up to 900 °C under different percentages of oxygen and nitrogen at different heating rates (1, 2, 5, 10, 20 and 60 °C/min) up to 900 °C.

TG curves allow for the determination of characteristic points such as the temperature at the onset of the decomposition and the residual mass of a material at the end of the measurement. The derivative of the TG curve (DTG) allows the identification of the mass loss rate at a given temperature. This gives insight on the different steps of the thermal decomposition of the sample.

II.3.a.iii. TGA-Fourier Transform InfraRed Spectroscopy

Gas phase analysis were carried out in TGA Discovery (TA instruments) coupled with FTIR Nicolet spectrometer (ThermoFischer). Samples (~10mg) were heated in a 250 μ L alumina crucible from 50 °C to 800 °C with a heating rate of 20°C/min under nitrogen atmosphere. A balance purge flow of 15mL/min and a sample purge flow of 50 mL/min was maintained. A transfer line with an inner diameter of 1mm was used to connect TGA to the infrared cell. The temperature of the transfer line and the gas cell was kept at 225 °C. Prior to this, samples were kept for 2h under nitrogen stream. IR spectra were collected in 400- 4000 cm⁻¹ spectral range (resolution: 4, laser frequency: 15798.7 cm⁻¹).

II.3.a.iv. TGA at different oxygen levels

In order to study the influence of oxygen in the thermal decomposition of some highperformance polymeric materials (they are known to be sensitive to a small amount of O₂), thermogravimetric analyses under different oxygen concentrations were carried out. This was performed in a Netzsch Libra TGA instrument. The concentration of oxygen was controlled by means of a dual gas entrance (oxygen and nitrogen). A total flow of 100 mL/min was used. The oxygen levels were variable, with the lowest concentration being 2% (corresponding to a nitrogen flow of 98 mL/min and oxygen flow of 2 mL/min). Before increasing the temperature, three vacuum/fill cycles were performed. To ensure repeatability of the experiments, they were performed in duplicates.

II.3.a.v. Simultaneous Thermal Analysis (STA)

A simultaneous measurement of thermogravimetry (TGA) and Differential Scanning Calorimetry (DSC) were conducted using a Netzsch 449 F1 Jupiter simultaneous thermal analysis device (STA). Samples were put in alumina pans with platinum lids. The lids had a small orifice (0.25 mm in diameter) for gas escape. This container configuration was used to maximize the thermal contact between a degrading sample and heat flow sensing thermocouples located underneath the pan. Before each experiment, a blank with empty crucibles was performed and subtracted to the experiments so both mass and heat flow signal were independent of the crucibles. Samples were tested at a heating rate of 10 K/min from - 30 to 900 °C.

II.3.a.vi. Pyrolysis Gas Chromatrography Mass Spectrometry (Py-GC/MS)

Samples (approx. 200 µg) were analyzed by pyrolysis GC/MS (Frontier Lab inc. Double Shot Pyrolyzer Py 2020iD and Shimadzu, GCMS-QP2010 SE). GC preparation was carried out with a fused silica capillary column (SLB 5 ms) of 30m length and 0.25 mm thickness. Analyses were carried out both in direct pyrolysis mode and desorption method. The temperature selection for desorption is based on TGA pattern of concerned sample with a heating rate of 10 °C/min. The initial column temperature was held at 35 °C for a period that corresponds to desorption time followed by a temperature ramp at 10 °C/min to a final temperature of 300 °C and isotherm for 5 min. For direct pyrolysis the furnace is set for the degradation temperature (700 °C which corresponds to completion of second major degradation step) and sample is pyrolyzed for 0.5 min. Column oven temperature is programmed in the following way: the initial column temperature was held at 35 °C for 1 min followed by a temperature ramp at 10 °C.min⁻¹ to a final temperature of 300 °C and an isotherm for 20 min. Helium was used as a carrier gas at pressure of 94.1 kPa with a split ratio of 100. The transfer line was maintained at 280 °C. The MS was operated under Electron Ionization (EI) mode. An online computer using GC/MS real time analysis and PY-2020iD software-controlled GC/MS system. The eluted components were identified by library search and only significant peaks observed in the total ion chromatograms were studied and compared to a mass spectral database (GC/MS postrun analysis, and NIST mass spectral database).



Figure 15. Schematic representation of the Py-GCMS

II.3.a.vii. Pyrolysis Combustion Flow Calorimetry (PCFC) or Microscale Combustion Calorimetry (MCC)

The combustibility of the gas phase was evaluated using a PCFC supplied by Fire Testing Technology Ltd. PCFC was developed by Lyon [48] from Federal Aviation Administration (FAA), it can be used to evaluate the flammability and the combustion parameters of small samples. Figure 16 shows the basic principles of the PCFC device. Powdered samples were placed in open alumina pans and were degraded in a nitrogen atmosphere ("pyrolyzer") at a heating rate of 1 °C/s and with a nitrogen flow of 80 mL/min. The decomposition gases were then combusted in a nitrogen/oxygen mixture ("combustor") with 80 mL/min and 20 mL/min flows respectively. The heat released is measured as a function of the temperature using an oxygen analyzer, according to the Huggett relation [49]. Using a heating ramp of 1 °C/s, pHRR value in W/g equals heat release capacity (HRC) in J/(g.K) [48].



Figure 16. Schematic representation of the PCFC

In order to get the most repeatable measurements, the maximum oxygen consumption has to reach around 50% of the total O₂ in the mixture. This means that from a mixture containing 20% of O₂, the peak of consumption needs to reach 10 ± 3 % O₂. Determination of the optimal sample mass was performed in accordance to this condition. When the decomposition gases are released from the pan, a certain amount of time is needed for them to reach the combustor (residence time), and for the oxygen analyzer to measure the oxygen depletion. Therefore, a slight shift of temperature is often observed between TGA and PCFC analysis (+ 20°C approximately in PCFC). By comparing the peak mass loss rate in TGA performed at 60 °C/min and the peak heat release rate using the PCFC, the residence time can be calculated. Also, by taking into consideration the real time mass of the sample, the real time heat release rate can be calculated by correcting the measured value with the real time mass percentage of the sample. The real time mass of the sample was obtained by performing TGA at the same heating rate as in the PCFC.

II.3.b. Kinetic Analysis

Kinetic analysis and modeling of the degradation of the samples were made using a Kinetics Neo software package developed by Netzsch Company. The principle has been discussed by Opfermann in [50] and here we only briefly remind the reader of the basic concepts of the method. For kinetic analysis, it is assumed that the material decomposes according to Eq. (1):

$$A_{\text{solid}} \rightarrow B_{\text{solid or liquid}} + C_{\text{gas}}$$
(9)

The rate expression de/dt, where *e* is the concentration of educt (reactant), is assumed to be defined by Eq. (10):

$$\frac{de}{dt} = k(T) \times f(e, p)$$
(10)

Where k is the kinetic constant, p is the concentration of the product, $k = A\exp(-E/RT)$ according to the Arrhenius law, A is the frequency factor, E is the activation energy and f(e,p) is the so-called "reaction equation" or in the case of TGA, the "reaction model".

All reactions are assumed to be irreversible. In the case of degradation and since the evolved gases are continuously removed by the fluid flow in the TGA chamber, this is a reasonable assumption. It is also assumed that the overall reaction (Eq. (9)) is the sum of individual reaction steps (formal or true step) with constant activation energy, as generally accepted in chemistry. The model can then include competitive, independent and successive reactions. The equations are solved with multivariate kinetic analysis (determination of the parameter via a hybrid normalized Gauss-Newton method or Marquardt method) [51].

By optimizing the models used for the kinetic analysis, the kinetic parameters of each step in the thermal decomposition model of the material can be extracted, allowing for a better understanding of the thermal decomposition behavior of the material.

II.3.c. Mass Loss Cone Calorimetry

Thermal characterizations provided insight concerning the thermal degradation of the polymeric materials. The fire behavior of materials cannot be evaluated using thermal characterization techniques. It was therefore necessary to perform additional fire tests in order to evaluate the burning behavior of the flame retarded materials. To do so the mass loss cone calorimeter (MLC) was used.

MLC is a bench-scale reaction to fire test which provides a combustion scenario that is typical of developing or developed fires. The measurements were carried out on a Fire Testing Technology (FTT) mass loss calorimeter device (ISO 13927 [52], ASTM E906 [53]). The schematic representation of the device is shown in Figure 17. The procedure involved exposing plates (100 x 100 x 3 mm³, or 100x100x3.7 mm³ for PEEK, and 100x100x1.5 mm³ for PI) in horizontal orientation with heating elements. Samples were

wrapped in aluminum foil leaving the upper surface exposed to the heater (external heat flux of 35 kW/m² corresponding to a mild fire scenario, (or 50 kW/m² corresponding to an established fire scenario) and placed on a ceramic backing board at 25 or 35 mm from the cone base. For some measurements, a thermocouple was placed at the bottom of the sample in order to plot the evolution of the temperature as a function of time



Figure 17. Schematic representation of the Mass Loss Cone Calorimeter

The MLC measures the temperature of the evolved gases using a thermopile located at the top of the chimney while the mass loss is recorded with a balance. The calibration of the heat release rate (HRR) is performed with methane. A methane flow of 0 to 6.7 mL/min is burnt above the sample holder to obtain a calibration curve of the heat release as a function of methane flow [54].

The values measured by MLC are the heat release rate (HRR), the peak of heat release rate (pHRR), the total heat release (THR), the time to ignition (TTI) and the mass loss of the sample during combustion (ML). All measurements were performed at least thrice. The presented curves are the worst case of repeatable results. The acceptable error of measurement is estimated at 10 % for all values.

To identify the gases released during the burning of the polymeric materials tested, the MLC was coupled with a Fourier Transform Infra-Red using a heated transfer line (to avoid condensation of combustion products).
Gas picking pistol and transfer line are provided by M&C Tech Group. FTIR, AntarisTM Industrial Gas System, is provided by ThermoFisher. The transfer line between MLC and FTIR is 2 m long and is heated up to 180 °C. Before analyzing the gases by FTIR, soot particles are filtered by two filters (2 and 0.1 μ m) made of glass fibers and ceramic respectively. The FTIR gas cell is set to 185 °C and 652 Torr. The optical pathway is 2 m long and the chamber of the spectrometer is filled with dry air. FTIR spectra obtained using MLC-FTIR are treated using OMNIC software (laser frequency: 15798.0 cm⁻¹, resolution: 0.500). To quantify gases, spectra need to be recorded at different concentrations for targeted gases and a quantification method needs to be created using TQ Analyst. Creating a method, representative regions in the spectra of the selected gas need to be chosen and interactions with other gases have to be taken into account. Using MLC-FTIR the following gases can be quantified: water, carbon monoxide, carbon dioxide, nitrogen dioxide and hydrogen cyanide. Quantification is reproducible within 10 %.

II.4. Conclusion

The different high-performance polymeric materials studied as well as the materials that were flame retarded have been described in the first section. The different characterization methods, both in terms of structural analyses and their thermal properties have been described.

These analyses are essential to affirm assumptions concerning the physicochemical properties of the polymeric materials that will be investigated. They will also provide insight regarding the decomposition pathways that are adopted during the thermal decomposition of some materials.

Furthermore, the details concerning the fire tests that were carried out have also been described.

The results of the study concerning the thermal decomposition and fire behavior of the highperformance polymeric materials studied will be described in more detail in the following chapters.

The aim of this chapter is to deepen the comprehension concerning the thermal and fire behavior of high-performance polymeric materials. These polymeric materials have proved to exhibit extremely enviable properties in those aspects. In order to extrapolate these properties and attempt to emulate them in fire retardants as thermal triggers for other engineering polymers, an in-depth knowledge on the modes of action of the thermal and fire behavior of these materials is primordial. To achieve these aforementioned goals, three different high-performance polymeric materials have been selected and investigated: polyetheretherketone (PEEK), polyimide (PI), and polybenzoxazole (PBO). These materials are known to be possess high stability and are inherently fire retardant. Despite being all highly aromatic polymeric materials, they do not share the same backbone. Therefore, in our quest to finding novel fire retardants, studying these materials can provide different leads towards finding the key structural properties that impropriate such high performances to them. Their structures are shown in Figure 18.



Figure 18. Chemical structures of polyetheretherketone, polyimide and polybenzoxazole

The thermal stability and thermal decomposition behaviors have been studied using different methods. As mentioned before, the polymeric materials that were studied only share their end properties (fire retardancy and high thermal stability), and not their fundamental structures (Figure 18). Therefore, it was deemed appropriate to investigate their behaviors individually so as to extract the most information on the driving factors that give them such impressive properties.

One of the most popular method adopted to investigate the thermal stability of the materials was TGA at different oxygen levels. This provided insight to the effect that the nature of the surrounding atmosphere has on the modes of decomposition of the materials. Moreover, we

attempted to elucidate the thermal decomposition pathway of the materials when they are subjected to an elevated temperature. To achieve this, the gases evolved during the thermal decomposition of the materials were identified via two different methods: <u>pyrolysis-Gas-Chromatography/Mass-Spectrometry</u> (py-GC/MS) and TGA coupled with a <u>Fourier Transform InfraRed spectrometer</u> (TGA-FTIR). However, before going into the elaboration of a thermal decomposition pathway, the fire behavior of these materials was also studied. This provided further insight regarding the thermal decomposition of the materials. Finally, attempts at elucidating the thermal decomposition mechanism were made for each polymeric material. This furthered the comprehension of the enhanced fire behavior and thermal stability that they possess as compared to common polymeric materials.

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III.1. Thermal Stability and Fire Behavior of Polyetheretherketone (PEEK)

Polyether ether ketone (PEEK) is a subfamily of polyarylketones (PAEK). PAEKs are semicrystalline engineering thermoplastic polymers that show high thermal, mechanical, chemical, and electrical properties. They have a plethora of applications in various industries including automotive, aerospace, chemical, and oil industries. PEEK has a continuous use temperature of 260 °C and a melting point of 343 °C.

III.1.a. Thermal Stability

TGA is an efficient method to study the thermal decomposition temperatures of a material using milligram scale samples. By applying a thermal stress on a material in a controlled atmosphere, the decomposition temperature of the sample can be deduced simply by analyzing the temperature at which the onset of mass loss is observed on the plot for the thermal stress applied. Under pyrolytic conditions, temperature is the only factor that affects the decomposition of the material. As mentioned previously, in a fire scenario, the bulk of a burning material undergoes pyrolysis in absence of oxygen. Therefore, the first thermal stability tests to which PEEK was subjected was TGA under an inert atmosphere (nitrogen).

III.1.a.i. Thermal stability of PEEK under Nitrogen

Subjecting PEEK to a heating rate of 10 K/min under nitrogen provided insight regarding the temperature at the onset of the decomposition as well as the minimum number of steps involved in the thermal decomposition of the material in the temperature range studied.

The TGA plots and the corresponding derivative of the thermogravimetric curve (DTG plots) of PEEK when heated at 10 °C/min under nitrogen are shown in Figure 19. The data are summarized on Table 3.



Figure 19. TGA and DTG plots of PEEK when heated at 10 °C/min under pyrolytic conditions

From the TGA curve of PEEK, the temperature at the onset of its thermal decomposition ($T_{95\%}$) was read at 574 °C. Moreover, the maximum mass loss rate (11.0 wt%/min), occurs at 592 °C. This is also visible as a sudden mass loss on the TGA plot. A non-zero DTG value is also observed at temperatures ranging from 700 °C to 800 °C corresponding to a mass loss ranging from around 60 wt% at 615 °C to around 50 wt% at 800 °C. At higher temperatures, there is very little mass loss recorded. Indeed, the final residual mass of PEEK at 900 °C °C is 48 %. This suggests that the product formed during the pyrolysis of PEEK is quite stable under pyrolytic conditions and at this temperature. This also suggests that the pyrolysis of PEEK is at least a two-step process, one occurring at the onset of the decomposition, and another that overlaps with the first degradation process. Furthermore, it was reported that the PEEK is a highly charring polymer. This suggests that during the first step of the decomposition, the reaction occurring leads to a thermodynamically stable char structure [55,56]. Following this char-formation, a second decomposition step corresponding to the slow degradation of the char which explains the low, albeit non-zero, values on the DTG curve.

Table 3. Summary of the data from the TGA of PEEK under nitrogen

PEEK/	T _{95%} (°C)	T@ MLR _{MAX} (°C)	MLR _{MAX} (%/min)	Residue (wt%)
	574	592	11.0	48

While the key temperatures relating to the thermal stability and decomposition behavior of PEEK under inert atmosphere were extracted using TGA. To obtain enthalpic data concerning the thermal behavior STA was performed (Figure 20).



Figure 20. TGA and DSC plot for PEEK with a heating rate of 10 °C/min under nitrogen atmosphere

From the STA performed on PEEK, both a DSC and a TGA curve were obtained. Since the TGA curve has already been described previously, we will mainly focus on the DSC curve. A small exothermic peak can be observed at around 170 °C. This corresponds to the glass transition temperature of the material. At around 343 °C, a larger, endothermic, peak is observed, corresponding to the melting temperature of the polymer. Two exothermic peaks are observed at temperatures corresponding to the decomposition of the material (580 °C), thus confirming that the decomposition of PEEK is at least a two-step process when it is heated at 10 °C/min under nitrogen.

The enthalpy of decomposition was measured using STA and was found to be - 417 J/g. The exothermic nature of these peaks is unusual in the sense that common polymers show an endothermic peak during their decomposition. This could be explained by the fact that PEEK is a highly charring polymer. This means that during its thermal decomposition, it forms a highly stable carbonaceous structure. This implies that there are many strong bonds that are formed (exothermic) as compared to the bonds that are broken during the decomposition.

We have seen that for a completely organic polymeric material, PEEK has depicted highly interesting thermal properties under inert atmospheres. However, the exothermic nature of its thermal decomposition means that it releases heat when it degrades. While this property

is not highly enviable in a fire scenario, it also means suggests that the char structure that is formed during its initial decomposition is highly stable. This means that it can possibly act as a fire barrier, protecting the underlying material while the exposed surface decomposes.

III.1.a.ii. Influence of Oxygen on the Thermal Stability of PEEK

Understanding behavior of a material under pyrolytic conditions is a significant step in the comprehension of its fire behavior as it provides insight on temperatures at which it may release combustibles when it is subjected to heat in a fire scenario. However, while many reports suggest that in a fire scenario, a burning polymeric material is only subjected to pyrolytic thermal stress, the presence of even a small amount of oxygen may influence the decomposition behavior of the material [57], and as such, on its burning behavior. Therefore, the impact of low oxygen concentrations on the decomposition of a polymer can provide us with a deeper insight on its behavior in a fire scenario.

To do so, TGA was performed on samples of PEEK under a low concentration of oxygen (2 % oxygen and 98 % nitrogen). The resulting TGA curve is plotted with that of PEEK under nitrogen in Figure 21



Figure 21. TGA and DTG plots of PEEK under nitrogen (red) and under 2% O2 (black) at a heating rate of 10 °C/min

Two major steps can be observed on the TGA plot of PEEK under 2% O₂. The first mass loss step of the decomposition of PEEK under low oxygen concentration is similar to that under nitrogen. For instance, the temperature onset of the degradation starts at around 573

°C under 2% oxygen as compared to 570 °C under nitrogen. Moreover, this decomposition step corresponds to a mass loss of around 35 wt%. The similarity in the decomposition is further confirmed when comparing the DTG curves. It can be observed that the first peak on the DTG curves have the same shape whether the analysis is performed under nitrogen or low oxygen concentration. This suggests that the initial decomposition step is not greatly affected by the presence of a thermo-oxidative atmosphere at the decomposition temperature. Similarly to the first step of thermal decomposition under nitrogen, that under 2% oxygen is also assigned to the formation of a char.

Unlike the first decomposition step, the second step of the decomposition shows some major differences when comparing the TGA plot of PEEK under nitrogen and that in low oxygen concentrations. Indeed, while the mass loss rate (MLR) for the second decomposition step is low (< 5 wt%/min) under inert atmosphere, that under 2% O₂ remains relatively high after the first step of the decomposition (around 10 wt%/min). Moreover, at 900 °C, the sample is still decomposing (MLR = approx. 2 wt%/min). This suggests that the char formed during the first step of the decomposition starts to undergo oxidation at high temperatures (> 650 °C). We have seen that despite a low concentration of oxygen, the second step of the thermal decomposition is apparently influenced. Therefore, to further the study of the influence of low levels of oxygen on the thermal and thermo-oxidative decomposition of PEEK, TGA was performed on samples of PEEK at the same heating rate, but at different oxygen levels until 12% of oxygen. These TGA and DTG plots corresponding to TGA of PEEK at a heating rate of 10 °C/min under different oxygen concentrations is shown on Figure 22.



Figure 22. TGA and DTG plots of PEEK at 10 °C/min under different oxygen levels

From the TGA plots, it can be observed that the onset of the degradation is mostly independent on the atmosphere until around 12 % oxygen, whereby a slight decrease in the onset of the decomposition temperature is noted. This is probably be due to oxygen attacking the bonds in the polymer. However, whatever the oxygen concentration, the onset of the degradation still occurs at around 570 - 580 $^{\circ}$ C.

O ₂ %	T95% (°C)	T@ MLR _{MAX} ($^{\circ}$ C)	MLR _{MAX} (%/min)	Residue (wt%)
2%	573	593	10.0	22
4%	565	589	11.4	0
8%	575	589	9.2	0
12%	572	590	10.5	0

Table 4. Summary of the TGA of PEEK under different oxygen levels.

On the other hand, the presence of oxygen has a major impact on the second degradation step. We suggested that the first step of thermal decomposition of PEEK correspond to the formation of a char. This char can be thermo-oxidized if oxygen is present in atmosphere. In low oxygen atmosphere, only part of the char can be oxidized because the oxygen in the atmosphere is being entirely consumed. Therefore, the higher the concentration of oxygen, the faster the thermo-oxidation process. This is evidenced by the DTG curve, which shows that there is an increase in the mass loss rate for the second step of the thermal decomposition with increasing oxygen levels.

III.1.a.iii. Thermal Stability of PEEK in Air

In order to further the investigation of the thermal decomposition behavior of PEEK, TGA was also performed in air. Even though the oxygen concentration is often considered as limited in the fire scenario in a closed room, this is not the case in a well ventilated one, where oxygen can be brought by convection. Additionally, when a material is far from a flame, it can still be subjected to an incident heat flux. In this case, the material is subjected to thermo-oxidative degradation. It is therefore equally important to evaluate the thermal stability of the material in air. The TGA and DTG plots corresponding to the thermo-oxidative degradation of PEEK in synthetic air and the ones corresponding to the thermal decomposition in nitrogen are shown in Figure 23 for comparison.



Figure 23. TGA plot and DTG plot of PEEK @ 10 °C/min in synthetic air(black) and under nitrogen (red)

The onset of the degradation, ($T_{95\%}$) is observed at 559 °C, which is slightly lower than the onset of the degradation observed on the TGA plot corresponding to the analysis performed under nitrogen. However, before reaching this mass loss, an initial mass loss (about 4 wt%) that begins at a slightly lower temperature is also visible on the TGA plot. After this initial degradation step, two sharp mass-loss steps can be distinguished both in the TGA and the DTG curve. The initial degradation step is clearly visible on the DTG plot. Indeed, three peaks can be observed in the DTG of PEEK in synthetic air. A first, small peak is visible at around 520 °C. Another two peaks are also clearly distinguishable, having a maximum point

at 585 °C and 645 °C. Finally, there is no residual mass at 700 °C meaning that the polymer has been completely degraded.

Table 5. Summary of the TGA of PEEK in air

PEEK/Air —	T95% (°C)	T@ MLR _{MAX} (°C)	MLR _{MAX} (%/min)	Residue (wt%)
	568	592	11.0	0

The first step of the degradation is assigned to the oxidation of some organic substances that are present in the polymer due to its processing (plasticizing agents and such) (CO₂ observed in TGA-FTIR, see next section). When analyzing the second peak in the DTG plot, some similarity can be clearly observed with the DTG plot of PEEK under nitrogen. However, the third peak in the DTG plot (at 645 °C) suggests that the products formed during the second step are being thermo-oxidized. Indeed, one explanation of the three peaks would be the first two steps corresponding to the formation a char. That char remains stable when the atmosphere is inert. However, in the presence of oxygen, the char is oxidized at high temperatures.

Of the two main peaks in the DTG of PEEK in air, the first peak at 585 °C occurs at a temperature that is relatively close to the peak mass loss rate of PEEK under nitrogen. This suggests that the first step of the thermal decomposition corresponds to the formation of a char, whatever the atmosphere.

Studying the thermal stability of PEEK under different oxygen concentration has provided insight on the dependence of the oxygen concentration on the different steps of the thermal decomposition of PEEK. Indeed, we have seen that whether a thermal stress is applied in the absence of oxygen or under air, the temperature at which the first step of decomposition occurs is only slightly affected. This implies that the reigning reaction that occurs as the polymer first starts to degrade and decompose thermally is the action of heat only. It is therefore of interest to study the nature of the decomposition gases that are evolved during the thermal decomposition of this material.

III.1.a.iv. Conclusion

From the thermal stability measurements recorded on PEEK, it was observed that there was an unusual independence of the onset of the decomposition on the nature of the atmosphere. Indeed, the temperature at the onset of the decomposition of PEEK was within 10 °C, whether the measurement was performed in air or under nitrogen This suggests that the first step of the thermal decomposition shares the same mechanism whether it is in air or under nitrogen.

However, as the oxidative nature of the atmosphere was increased, the residual mass at high temperature was impacted. While the residual mass at 800 °C of PEEK under nitrogen is incredibly high (> 40 wt%), there is no residual mass when the material was heated in air. A trend of decreasing residual mass with increasing oxygen concentration is also observed. This suggests that the first step of the decomposition leads to a char that is thermo-oxidized when it is in the presence of oxygen at high temperature.

Moreover, it was also noticed that the rate of the first decomposition was quite high (>10 wt%/min, in air, under 2% oxygen, and nitrogen). One explanation to this could be the exothermicity of the first thermal decomposition step. Indeed, STA analyses have shown that the first decomposition step is highly exothermic. This means that, unlike most polymeric materials, heat is released when the material is decomposing [57]. This can be explained by the fact that the char formation reactions involved the coupling of many radicals. These reactions are highly exothermic, and the heat released may energetically aid the thermal decomposition process to proceed [7,58].

III.1.b. Identification of Decomposition Products of PEEK

While insight on the critical temperatures concerning the thermal decomposition of PEEK have been extracted using TGA, we are still sitting on square one concerning the nature of the decomposition reactions that leads to the said high thermal performance of the material. it is therefore of utmost importance to scrutinize the decomposition products that are released when the polymeric material is subjected to intense thermal stress.

III.1.b.i. Pyrolysis Products of PEEK

In order to identify the products released during its pyrolysis, PEEK was subjected to TGA coupled with a Fourier Transform Infrared (FTIR) spectroscopy under nitrogen and at a heating rate of 20 °C/min. The measurements under nitrogen provided information regarding the decomposition products evolved during the pyrolysis of the material.

TGA-FTIR of PEEK under nitrogen yielded many different pyrolysis products. The main decomposition products identified correspond to carbon dioxide and carbon monoxide. In order to qualitatively compare the gases evolved, intensity profiles corresponding to characteristic peaks of some degradation products were plotted (Figure 24). This provided insight on the nature of the evolving gases at the different stages of the degradation.

The peak intensity of CO_2 (2356 cm⁻¹) remains stable until around 30 minutes (approx. 530 °C). At this temperature, there is a negligible mass loss recorded on the TGA plot. After this, the peak intensity of CO_2 increases gradually until it reaches a maximum at around 35 minutes (600 °C). It then decreases to a local minimum at 40 min (737 °C) before increasing again. These maxima/minima suggest that there may be more than two steps involved in the thermal decomposition mechanism of PEEK. The presence of maxima at different temperatures suggest that there are different scission reactions occurring at different temperatures, therefore a different step in the mechanism reaction.

The release of carbon monoxide could also be followed thanks to its characteristic peak at 2184 cm^{-1} . The intensity profile corresponding to CO in the FTIR shares a similar shape to that of CO₂ at the beginning. However, as opposed to the CO₂ intensity plot, the CO plot shows a maximum at 42 min. This suggests that there might be different reactions producing CO at different temperatures.

It was also possible to follow the intensity of a characteristic methane peak height of methane at 3018 cm⁻¹. From the peak profile, it can be seen that methane is released at a higher temperature than CO and CO₂. Indeed, the intensity of the methane peak (3018 cm⁻¹) starts to increase at 32 minutes (570 °C), peaks and somewhat plateaus at 36 minutes until 42 minutes, where the intensity starts to decrease again. This means that the peak release of methane occurs after the main pyrolysis step (first decomposition) of PEEK. This can be explained by the secondary pyrolysis of volatile aromatics and the decomposition of the charred structure during the graphitization process(see mechanism, Scheme 4, page 148) whereby hydrogen may be released. This hydrogen can react with the carbonized structure to form methane[59].



Figure 24. TGA curve of PEEK under nitrogen at a heating rate of 20 °C/min (top) and intensity profiles of characteristic peaks of CO, CO₂, and CH₄ (bottom)

In addition to the previously mentioned decomposition gases, other evolved gases were also identified. However, due to overlapping of some peaks, characteristic peak profiles of the identified gases were not singled out. By comparing with reference FTIR spectra, other decomposition products were identified (Table 6). Of the decomposition gases, aromatic ethers, phenols, and furans were the main groups of products identified. These suggest a decomposition whereby the polymer chains are cut randomly.

The FTIR spectra corresponding to two different temperatures in the TGA were selected such that the two visible steps of decomposition were isolated. The temperatures selected were 600 °C, which corresponds to the maximum MLR (Figure 24), and at 720 °C corresponding to the second, slower, decomposition mentioned previously (Figure 24). These FTIR spectra are represented in Figure 25 and Figure 26. The different decomposition gases that were identified and are reported in Table 6

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Figure 25. IR spectrum of evolved gases from PEEK decomposition at 600 °C when heated at 20 °C/min under nitrogen

Figure 26 IR spectrum of evolved gases from PEEK decomposition at 720 °C when heated at 20 °C/min under nitrogen

The main decomposition products identified at 720 °C were methane, phenol, carbon dioxide and carbon monoxide. The products identified were previously reported in a study concerning the mechanism of the thermal decomposition of PEEK [60]. However, the release of methane was not reported.

Temperature	Product	Structure
600 °C	Carbon dioxide	*o≡c-+
	and carbon monoxide	0=0=0
	Phenol	ОН
	Benzoquinone	0
	Benzophenone	
	Diphenylether	
	1,4- diphenoxybenzene	
	Dibenzofuran	
	2- hydroxydibenzofuran	СССОН
720 °C	Carbon monoxide +	*o≡c-
	Carbon dioxide	0=c=0
	Methane	CH ₄
	Phenol	ОН

Table 6. Decomposition gases identified with TGA-FTIR at two decomposition steps of PEEK (600 °C and 720 °C).

In order to have better accuracy in the identification of evolved gases during the pyrolysis of PEEK, Pyrolysis-Gas-Chromatography/Mass-Spectrometry (Py-GC/MS) was used. By subjecting a PEEK sample to the same heating rate, the evolved gases during its thermal decomposition are collected and separated via a gas chromatography column, which are then analyzed using a mass spectrometer. However, due to the nature of the instrument, the

pyrolysis program can only be used in helium, therefore, this analysis "only" provides information regarding the pyrolysis products of the thermal decomposition of the material.

This allowed for the separation of the decomposition products that are evolved when PEEK is heated at 20 K/min. The decomposition gases analyzed using Py-GC/MS were coherent with those identified with TGA-FTIR. However, this did not provide a real time analysis of the evolved gases. Indeed, using this technique, all the evolved gases during thermal decomposition are kept at 35 °C the beginning of the chromatography column. It is only after the heating process that the separation of the gases is initiated. The advantage of this method is that it provides the possibility of identifying individual mass spectra per decomposition product.

In order to have a real time analysis of the evolved gases during thermal decomposition, EGA-MS was performed on samples of the material. The sample was left for 1 minute @ 50 °C, then heated up at a heating rate of 20 °C/min up to a temperature of 750 °C. The GC column was kept at 300 °C for 42 minutes. This allowed the real time analysis of the evolved gases during thermal decomposition as they travel straight to the MS analyzer as soon as they are evolved. This allowed for the plotting of the intensity profiles of specific m/z values, which correspond to decomposition products that were identified by TGA-FTIR and Py-GC/MS. It also provides insight regarding different steps of the thermal decomposition of PEEK under pyrolytic conditions.

Figure 27 shows the intensity profiles of carbon dioxide and phenol, measured using EGA-MS method. Phenol has the highest intensity, followed by carbon dioxide. This suggests that there is a significant amount of decarboxylation reactions occurring during the thermal decomposition of PEEK. The CO₂ profile also evidences that there are two major steps occurring when PEEK is decomposing. Two peaks are observed, one at 620 °C and the other at around 680 °C.



Figure 27. Intensity profiles of carbon dioxide (gold) and Phenol (violet) using EGA-MS at a heating rate of 20°C/min

EGA-MS of PEEK at 20 °C/min shows that phenol has the intensity profile with the highest intensity (> 150 000, Figure 27) as compared to the other decomposition products (< 15 000, Figure 28).



Figure 28. Intensity profiles of biphenyl (blue), 2-phenoxydibenzo[b,d]furan (olive), hydroquinone(black), 4diphenoxybenzene (pale blue), 4-hydroxybenzophenone (purple), benzoquinone (red), diphenylether (pale brown), dibenzo[b,d]furan-2-ol (green), 4-phenoxyphenol (Prussian blue), and dibenzofuran (magenta), analyzed using EGA-MS at a heating rate of 20 °C/min.

The intensity profiles of the different decomposition gases evolved from PEEK and analyzed by EGA-MS are shown in Figure 27 and Figure 28. The dashed lines indicate the moment where the corresponding product is detected. The filled lines correspond to the temperature (or time) whereby the maximum intensity of a product is analyzed.

From the intensity profiles, it can be observed that the onset of dibenzofuran release occurs at the lowest temperature (575 °C). CO_2 is the next gas to be observed at around 600 °C. Most of the other decomposition gases start to be released within the temperature range 620 – 650 °C. The maximum intensities observed are within the range 640 – 670 °C.

III.1.b.ii. Thermal Decomposition Products of PEEK under Low Oxygen Concentration

In order to better understand the effect of oxygen on the thermal decomposition products released by PEEK, TGA FTIR was performed with low (<2%) oxygen concentration. Figure 29 shows the intensity profiles of the different products that were identified during the TGA-FTIR analysis with 2% oxygen. From the TGA plot, it can be observed that the onset of the decomposition temperature is close to that of the onset of the thermal decomposition of PEEK in nitrogen (570 °C).



Figure 29. TGA plot (top) of PEEK at 2% O₂ at heating rate 20 °C/min and peak intensity profiles (bottom) corresponding to gases evolved during the TGA measurement

It can be observed on the peak intensity profiles that the highest intensity corresponds to that of CO_2 peak. However, at the beginning of the decomposition (33 min), other evolved gases

are identified. These are phenol, carbon monoxide, methane and 4-phenoxyphenol. Similar to the thermal decomposition of PEEK in nitrogen, the release of methane occurs at a slightly higher temperature as compared to the release of phenol and carbon monoxide. This suggests that not all the methane produced during the pyrolysis is oxidized under low oxygen concentrations.

From the thermal decompositions studied in TGA, it can be deduced that the first step of the decomposition is not greatly influenced by the presence of oxygen. However, the second step, which corresponds to the degradation of the char formed, undergoes thermal oxidation when the atmosphere contains 2% oxygen. This is even clearer when comparing the CO₂ intensities.

As mentioned previously, the onset of the thermal decomposition of PEEK does not seem to depend on the atmosphere it is in (oxidative or inert). Therefore, TGA-FTIR was also performed in a synthetic air atmosphere so as to get further information concerning its first step of degradation. The peak profiles of the main degradation products as well as the corresponding TGA curve are shown in Figure 30.



Figure 30. TGA plot (top) of PEEK in synthetic air at a heating rate of 20 °C/min and peak intensity profiles (bottom) corresponding to gases evolved during the TGA measurement

Only a few decomposition products were identified. Indeed, all the pyrolysis products evolved are suspected to thermo-oxidize before reaching the FTIR spectrometer. However, the presence of methane and phenol were recorded via TGA-FTIR. The TGA plot as well as

the series profiles of carbon dioxide, carbon monoxide, methane, and phenol are illustrated in Figure 30. This means that at low temperature (600 °C), despite the abundance of oxygen, these decomposition gases are not oxidized. This is coherent with our previous hypothesis: the first decomposition step has little or no dependence on the oxidative or inert nature of the atmosphere it is in and at the heating rate that was used.

Despite seeing a lesser amount of decomposition products, those identified when the TGA was performed under 2% O₂ were also observed under nitrogen. This implies that the thermal decomposition pathway is very close whether oxygen is present or not.

The decomposition products that have been identified are potential flammable volatiles that can contribute to feeding a flame during a fire scenario. However, seeing as a large proportion of the decomposition gases correspond to carbon dioxide (and possibly carbon monoxide), it is possible that some dilution may occur in the gas phase when the material is subjected to heat. Indeed, this was evidenced by comparing the net the heat of combustion of PEEK to that of the gas phase decomposition products using a combustion flow calorimeter. The total heat of combustion of PEEK, measured using an oxygen bomb calorimeter [61] was found to be around 31 kJ/g, whereas the heat of combustion of its decomposition products, measured using a microscale combustion calorimeter summed up to around 12 kJ/g. This means that during a fire scenario, more than 50 % of the heat released during the burning of PEEK comes from the thermal oxidation of the char structure, and not from the decomposition gases themselves.

We have seen that the thermal decomposition of PEEK leads to a plethora of decomposition products, whatever the atmosphere in which it is heated in. However, we hypothesize that in an oxidative environment, the gases released during the initial decomposition step are, for the most part, thermo-oxidized to form mostly carbon dioxide. This means whatever the atmosphere, the first reactions occurring would correspond to the formation of a char and the release of the decomposition gases. However, the fire behavior of the material will depend on the concentration of these decomposition gases as a material will only ignite if there is a sufficient amount of combustibles. Therefore, it is important to verify that the fire behavior of PEEK is coherent with its thermal stability.

III.1.c. Fire Behavior of PEEK

Understanding the thermal decomposition products of the material provided insight on the nature of the gases evolved when the material is subjected to elevated temperatures.

However, in order to have a deeper understanding on the behavior of the material in a fire scenario, it is also important to study its fire behavior.

To do so, the fire behavior of PEEK was studied using an MLC. A thermocouple was also placed at the back of the sample to record the temperature profile at that point. Two different heat fluxes were used: 50 kW/m² and 60 kW/m². The results of the experiment are summarized by the heat release rate and the temperature at the back of the sample on the graphs in Figure 31.



Figure 31. HRR (top) and temperature profile (bottom) of PEEK samples subjected to an incident heat flux of 50 kW/m² using the MLC. Sample dimensions: (100x100x3.7) mm³. Distance from the heating cone: 35 mm.

When subjected to an incident heat flux of 50 kW/m², the HRR of the material remains zero until it ignites (843 s). After ignition, there is a sudden increase in HRR, which peaks at 125 kW/m² (990 s). As for the temperature at the back of the sample, a rapid increase is recorded from room temperature to around 500 °C. This temperature is maintained until ignition occurs at 843 s. After having lit up, the temperature at the back of the samples increases rapidly to a peak temperature of 780 °C. This temperature is close to the decomposition temperature observed when TGA was performed on PEEK (570 °C @ 10°C/min). The increase in temperature can be explained by the flaming combustion of the burning decomposition products such as methane, that are released during the thermal decomposition of PEEK; The lower decomposition temperature can be explained by the fact that when the TGA was carried out, a constant heating rate of 10 °C/min was used whereas in the case of

the MLC, the thermal constraint corresponds to the incident heat flux. It should also be noted that the temperature at the back of the sample is likely to be lower than that on the surface of the material because it is protected by the charred layer formed.

While the graph provides numbers to support the barrier effect that the material may exhibit when it is subjected to 50 kW/m^2 heat flux, the visual aspect of the sample also has a story to tell. Indeed, right before ignition, the material had swollen by more than 1000 % (visual observations). This means that the gases released during the thermal decomposition of PEEK at this incident heat flux do not readily ignite, however, upon their release, they pull up the char formed. This protects the underlying polymeric material by preventing the incident heat flux from reaching it. It is also possible that non-flammable gases that are released (such as CO and CO₂) dilute the concentration of flammables during this time.

The swelling phenomenon can be observed on Figure 32, which corresponds to pictures taken at different times during the test. Indeed, well before ignition occurs, at 307 s, significant swelling is already observed. As the swelling increases, the material gets increasingly close to the heating resistance. This means that the actual incident heat flux reaching the material is higher than the one measured at the initial sample position. Moreover, it should be noted that the igniter (encircled in red) does not contribute to the ignition. In fact, the region below the igniter is less swollen, possibly because of the lower heat flux incident on that part of the material due a shielding effect brought about by the presence of the igniter. Once the polymer ignited, the exposed surface smoldered (Figure 32, middle) before properly flaming up (Figure 32, right). It is interesting to note that the ignition occurs on the inside of the material.



Figure 32. Pictures of PEEK taken at 307 s (left), 852 s (middle) and 889 s (right) when it is subjected to an incident heat flux of 50 kW/m² using the MLC

Thanks to the nature of the thermal decomposition of PEEK, the back of the material was maintained at less than 500 °C for more than 13 minutes. However, the structural integrity of the material is probably compromised at this point as the formation of the char usually renders the material brittle.

In order to dig deeper in the reactions that may be occurring during the thermal decomposition of PEEK under the incident heat flux, an FTIR was connected to the exhaust to analyze the gases evolved during the whole test.

The method allowed for the quantitative analysis of water, carbon monoxide and carbon monoxide evolved during the test. Figure 33 shows the HRR curve as well as the profiles of the aforementioned gases with respect to time during the MLC test.



Figure 33. HRR curve (red) and intensity profiles of CO (black), carbon dioxide (blue) (CO_2] vol% = [CO_2] ppm/1000) and water (magenta).

From the intensity profile of water, it can be observed that there is no water released before ignition. During the burning process, the intensity curve of water has a similar shape as the HRR curve. However, after the attenuation of the flame, the intensity profile of water is negative. This means that there is less water being detected than there was at the beginning of the experiment.

Furthermore, the intensity profile of CO and CO_2 reveal that before ignition, there is a nonnegligible amount of these gases that is produced. This means that the swelling that is observed during the charring phenomenon is partly led by the release of CO and CO_2 (see mechanism in section III.1.d, page 150).

Under 60 kW/m², PEEK exhibits a very different behavior than at 50 kW/m². The HRR curve concerning the burning behavior of PEEK can be split into two parts, the first one corresponds to the rapid increase of HRR from its ignition to the first peak of HRR. The second, whereby the heat release rate starts to increase again and plateaus before slowly decreasing to zero. Moreover, under these conditions, the temperature at the back of the sample increases rapidly from room temperature to around 288 °C, just before ignition. At this point, the temperature stagnates for around 40 s. After that, the polymer ignites, and the temperature continues to rise rapidly until 900 °C.

As the material swells, the thermocouple that was attached at the back of it rose with it. However, at 1250 s, it detached from the polymer and is no more recording the temperature of the material but is in fact only measuring the temperature of the surrounding air. This explains the sudden decrease and erratic readings of the temperature profile as from this time. At 1750 s, the thermocouple was removed in order to protect it from the incident heat flux that was directly on it.

Similarly to the test carried out under 50 kW/m², the heat release rate of PEEK when it is subjected to 60 kW/m² remains close to zero until ignition at 113 s. After ignition, the heat release rate increases rapidly until around 105 kW/m² before decreasing again. This decrease in the HRR may be explained by the limited supply of fuel by the polymer, due to the char structure that is formed during this first phase of burning which may have temporarily protected the inner layer of the material. However, this protective layer is quickly smoldered into ashes, and the fire on the polymer rises again. This is visible on the HRR curve whereby the HRR starts to increase again at 309 s. The peak HRR reached after this is 107 kW/m². It remains relatively constant around this value until 480 s, where it starts to gradually decrease again until the material flames out.

In order to visualize the first peak HRR, photographs of the tested sample just before and after the ignition are shown on Figure 34.



Figure 34. Photographs of PEEK when subjected to 60 kW/m² under the MLC at different times. Left: 79 s; middle: 150 s; right: 252 s.

From the pictures of PEEK taken just before ignition, some swelling can be observed (Figure 34, left). Fumes are escaping the bulk material on the left-hand side of the material just before ignition. It is, in fact, these fumes that are ignited, leading to the subsequent burning of the material. This ignition causes the whole polymer to start burning, causing a rapid increase in the HRR, which peaks at 105 kW/m^2 (Figure 34, middle). However, at this stage, as PEEK burns, significant swelling is still observed (Figure 34, right). This swelling corresponds to significant char formation reactions and is coupled with a slight decrease in the heat release rate.



Figure 35. Photographs of PEEK under 60 kW/m² at 382 s (left), 756 s (middle), and at the end of the test (right)

The second part of the burning process of PEEK under 60 kW/m² is also curious. Indeed, after a slight decrease in HRR at 150 s, the HRR starts to rise again. This HRR increase is this is not clearly visible when watching the polymer burn. A relatively small flame is present for around 3 minutes and subsides. During this time, the HRR stagnates at around 107 kW/m². After the attenuation of the flame, the heat release rate does not instantaneously reach a lower value. It decreases gradually. During this time, the material is in a smoldering state, whereby it slowly degrades. This corresponds to the incandescence observed at t > 400 s. It means that the material is being thermo-oxidized due to the high incident heat flux. The

degradation effect is clearly visible on the material (Figure 35, right) as there is hardly any of it left at the end of the test.

From the investigation of its fire behavior, PEEK has proved to exhibit excellent resistance to fire. This is in accordance with the high thermal stability that was observed in the previous section. Indeed, the first step that was observed when PEEK was subjected to an incident heat flux corresponded with the formation of a char. However, the swelling behavior was not predictable from the TGA analyses. There seems to a synergy between the thermal decomposition products and the charring behavior of the polymeric material that enhances the fire behavior of PEEK, especially at 50 kW/m². The next section will attempt to elucidate this by analyzing the thermal decomposition pathway that may be adopted when the material is subjected to a thermal stress.

III.1.d. Thermal Decomposition Reactions of PEEK

From the STA of PEEK, a highly exothermic decomposition peak was observed (-417 J/g). This was attributed to the fact that a large energetic contribution goes to the formation of a stable char. In order to better understand this char formation, the decomposition mechanism of PEEK will be investigated hereafter.

From the TGA analyses, it was deduced that the thermal decomposition process was at least a two-step one. This was confirmed by the TGA-FTIR and pyrolysis GC/MS whereby different sets of decomposition products were detected at different temperatures. Moreover, the thermal decomposition products evolved during the MLC test have also provided insight as to the different stages of thermal decomposition occurring in PEEK when it is subjected to an incident heat flux.

In order to properly understand the decomposition mechanism, it is essential to first understand the formation of these products from possible thermal decomposition reactions that may occur when PEEK is subjected to thermal stress. A thorough review concerning the thermal decomposition of PEEK was reported by Patel *et al.* [62]. The review deals with the decomposition pathways that lead to the products that were identified using different gas phase and solid phase analyses in the literature.

From the MLC-FTIR and TGA-FTIR results that we have obtained, it was observed that the first degradation products correspond to the formation of carbon monoxide and carbon dioxide. The formation of carbon monoxide is directly related to the graphitization mechanism (Scheme 4). This corroborates perfectly with the MLC test as both swelling and

charring were observed during the test (Figure 32, page 143). Previous reports have suggested that the charring process occurs at temperatures above 750 °C. However, in the case of the MLC test at 50 kW/m², charring was observed while the temperature at the back of the sample was at around 500 °C. This means that the temperature on the surface is higher than 500 °C. Indeed, at this temperature, random scission of the polymer chain may release aromatic radicals. These radicals, when reacted with adjacent benzene rings on a benzophenone moiety leads to the formation of a fullerene-like structure. Succeeding this reaction, the release of CO leads an aromatic diradical, two of which can react together to form a crosslinked aromatic structure. Scheme 4 is a summary of this charring process[62].



Scheme 4. Proposed mechanism for the graphitization process of PEEK at high temperature [62]

Another possible pathway explaining the formation of carbon monoxide is illustrated in the first step of the decomposition mechanism in Scheme 5. Homolytic scission of a carbonyl-phenyl bond would lead to the formation of a carbonyl radical. This radical species is stabilized by the highly conjugated aromaticity in the structure. This radical can abstract a hydrogen from an adjacent structure to form an aromatic radical and an aldehyde. At high temperatures, this aldehyde can undergo decarbonylation by abstracting its alpha hydrogen

[63]. However, since the reaction takes place at a relatively high temperature, it is possible that the pathway undertaken correspond to a radical one, producing two aromatic radicals (similarly to the graphitization reaction on Scheme 4). Seeing the amount of char formed, we can hypothesize that the carbonyl groups play a major role in the carbonization/graphitization process, with the production of CO (and possibly carbon dioxide).

Moreover, from the EGA-MS measurements, it was observed that dibenzofuran was one of the first components to be detected. This suggests that it is released relatively early during its degradation. However, a direct mechanism for its formation seems improbable. Indeed, these two molecules involve a furan ring, which is unlikely to form at high temperatures because decomposition products such as phenol or phenoxyphenol are much more likely to occur [60]. One suggested pathway which could explain the formation of dibenzofuran and dibenzofuranol involves a two-step process. One, which occurs at low temperature, leading to the formation of the furan moiety on the polymer backbone, and another whereby random scission of the backbone leads to the release of dibenzofuran and dibenzofuranol. From the relative intensity profiles on the EGA-MS of PEEK, it can be deduced that the major product of such a decomposition it the dibenzofuran rather than dibenzofuranol. Indeed, dibenzofuranol is detected at a higher temperature with a lower relative intensity than dibenzofuran (Figure 28). As for the formation of phenoxydibenzofuran, a similar mechanism is probable, whereby the carbonyl-phenyl bond is cleaved rather than an ether-phenyl one (Scheme 5).

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Scheme 5. Decomposition mechanism explaining the formation of carbon monoxide as well as furan derivatives.

Moreover, another bond that is susceptible to be cleaved at high temperatures is the etheraromatic one. Indeed, it would lead to the formation of a phenoxy radical that is stabilized by an aromatic ring. Therefore, following the release of CO, it is likely that the cleavage of the ether-aromatic linkage leads to the formation of phenol (Scheme 6).



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R= decomposed parts of polymer chain

Scheme 6. Decomposition mechanism explaining the formation of aromatic decomposition gases and benzoquinone (adapted from [62])

However, when the cleavage occurs over two adjacent ether-phenyl bonds, it leads to the formation of a benzoquinone (diphenoxy radical mesomere shown in Scheme 6). This diradical can abstract two hydrogens to from a hydroquinone. During the pyrolysis GC/MS, both hydroquinone and benzoquinone were observed, suggesting that both reactions are occurring during the thermal decomposition.

Furthermore, at around 620 °C, phenol and diphenylether were detected both by TGA FTIR and by Py-GC/MS. The same two bonds as for the explanation for the formation of 4-phenoxyphenol are involved. However, the placement of the scission and the subsequent reactions occurring are not the same.

Moreover, a cleavage of two adjacent carbonyl-phenyl bonds would lead to the formation of 1,4-diphenoxybenzene diradical. It can abstract a hydrogen on its either side leading to the formation of 1,4-diphenoxybenzene [62].

Despite the extensive graphitization assumed during the thermal decomposition of PEEK, hydroxybenzophenone was also detected during EGA-MS. Its formation can be explained by the fact that at high temperature, two ether-phenyl bonds are cleaved in such a way that they form the hydroxybenzophenone diradical. By abstracting two hydrogens, the volatile hydroxybenzophenone is formed.

III.1.e. Conclusion

The thermal stability investigation on PEEK under different oxygen concentrations have brought to light that the onset of the thermal decomposition of PEEK is mostly independent of the oxidative or inert nature of the atmosphere. This suggests that the onset of the decomposition may involve the same reactions. However, when looking at the decomposition products at the beginning of the decomposition under low oxygen concentrations, a higher relative amount of carbon dioxide is observed as compared to inert atmosphere, suggesting that thermo-oxidation of the decomposition products occurs in the presence of oxygen. This step probably corresponds to the formation of a charred structure. However, when the char formed is in the presence of oxygen at high temperature, it starts to degrade thermally.

As a result, the fire behavior of PEEK may be explained by its thermal decomposition. Indeed, while the decomposition of PEEK first leads to the formation of a char, it also releases a large amount of CO and CO₂. Before flaming up, PEEK swells by a very large amount. The polymer first starts to melt, before quickly forming a growing char. This char

swells as non-flammable gases such as CO and CO_2 as well as some other flammable gases such as phenol and dibenzofuran are released. The rising gases take with some of the polymer surface structure with them. This protects the underlying material for a while. The presence of the large amount of non-flammable gases also dilutes the fuel concentration found just above the surface, causing a delay in the ignition.

The charring of the polymeric material was possible thanks to the presence of a high amount of aromatic structures in the backbone of the polymer. From the mechanism of char formation, it was seen that having adjacent phenoxy radicals (stabilized thanks to the oxygen connected to the aromatic ring) is a valuable property to look for if char formation is to be promoted.

However, this phenomenon is not observed to the same extent when the incident heat flux is increased. Indeed, under a higher heat flux, the release of combustibles occurs at a higher rate (higher temperature). There is less time for the polymer to start melting, form a char and for the released gases to rise and drive with them the surface of the polymer. This also means that the decomposition occurs faster and that the concentration of decomposition products is higher. Py-GC/MS and EGA-MS have allowed us to identify the decomposition products that are released at high temperatures, some of which are highly inflammable. It is probable that the concentration of these products becomes high enough to cause ignition. As ignition occurs, the decomposition mechanism of the material continues at a higher rate as there is little protection of the bulk material by the charred surface.

Despite catching fire when subjected to high incident heat flux, the heat release rate of PEEK remains relatively low (< 125 kW/m^2 both with an incident heat flux of 50 and 60 kW/m²) which is an impressively low value for a wholly organic polymeric material.

III.2. Thermal Stability and Fire Behavior of Polyimide (PI)

Polyimides are among the most popular high temperature/high performance polymers on the market. They are a generation of polymers with inherently rigid chains and possess high thermal and electrical properties. They are used in many fields such as microelectronics, high temperature matrices, as well as adhesives for gas separation membranes[64]. Polyimides are used in various forms such as high temperature structural adhesives, coatings, films, or laminating resins. Their high temperature resistance makes them enviable polymeric materials for aeronautics and transport industry. It is therefore of interest to study its thermal and fire behavior to extract invaluable information about the mode of action of its decomposition.

III.2.a. Thermal Stability

In order to study its thermal stability, TGA was performed on samples of PI. This yielded TG and DTG curves that provide valuable insight on the critical temperatures concerning the thermal decomposition of polyimide.

III.2.a.i. Thermal Stability of PI under Nitrogen

As a first approach, the thermal decomposition of PI was studied under inert atmosphere using TGA. The TGA and DTG plots of PI is shown in Figure 36.



Figure 36. TGA and DTG plot of PI when heated at 10 °C/min under nitrogen
The onset of the thermal decomposition of PI (T_{95%}) occurs at 573 °C when it is heated at 10 °C/min under an inert atmosphere. The decomposition occurs in at least two steps. The first step corresponds to the onset of the decomposition (at $T_{95\%}$). The maximum mass loss rate (4.8 wt%/min) occurs at 608 °C (T_{MLR}) and corresponds to a mass loss of around 18 wt%. Indeed, a relatively sharp mass loss is observed on the TGA curve in the temperature range of 500 - 700 °C, whereby the mass loss is at around 35 wt%. At higher temperatures, the mass loss rate is much lower, but is still present. This means that there are still decomposition reactions occurring in the material. This is assumed to be the second step of the decomposition. This step partly overlaps the first one and has a much lower mass loss rate. This second mass loss rate can be viewed as a pseudo shouldering of the DTG curve at 700 - 850 °C. This means that there is a slow mass loss that occurs with increasing temperature and suggests that the virgin polymeric material has undergone a first, sharp decomposition step, forming a carbonaceous char, which is more robust thermally than the initial structure of the polymer. Moreover, with increasing temperature, some of the char formed, keeps on degrading at a slower rate. At 900 °C, there is still some mass loss that is recorded. This is confirmed by the non-zero mass loss rate at the same temperature. The residual mass at 900 °C is around 56 wt%. This is a very high residual mass considering that this is a neat polymeric material.

Table 7.	Summary	of the	TGA	of PI	under	nitrogen
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DI/NI -	T _{95%} (°C)	T@ MLR _{MAX} (°C)	MLR _{MAX} (%/min)	Residue (wt%)
F1 /1 N 2 -	573	608	4.8	56

To further the study, STA was also performed on PI. The sensitivity of the apparatus used was not high enough to discern the glass transition temperature of the material. However, it was reported that PI exhibits a second order glass transition temperature at around 360 - 400 ° C [65]. Moreover, the decomposition enthalpy was calculated to be around 181 J/g.



Figure 37. TGA (black) and DSC (blue) curves of PI using STA under nitrogen

III.2.a.ii. Influence of Oxygen Concentration on the Thermal Stability of PI

Similarly to the study of the influence of oxygen on the thermal decomposition of PEEK, PI was studied using TGA under an oxygen-poor atmosphere (2% oxygen and 98% nitrogen). The resulting TGA and DTG curves are compared with those obtained under pure nitrogen and are shown in Figure 38.



Figure 38. TGA and DTG of PI, under nitrogen (blue) and under 2% O2 (black) at a heating rate of 10 °C/min

One major step can be observed from the TGA plot of PI when it is heated at 10 °C/min under 2% oxygen concentration. The temperature at the onset of the decomposition ($T_{95\%}$) is observed at 575 °C. This temperature is relatively close to the onset of the decomposition of the one under nitrogen, suggesting that the first decomposition may be independent on the atmosphere. Moreover, when comparing the maximum mass loss rates of PI under nitrogen *vs* under 2% oxygen, it can be observed that the MLR_{MAX} is slightly lower when TGA is performed under a slightly oxidative atmosphere.

However, it seems that the onset of the decomposition is closely followed by the other decomposition steps. This is evidenced by the DTG curve of PI under 2% O_2 , which shows that it has a much higher mass loss rate at high temperatures (> 700 °C) under low oxygen concentrations than when the analysis is performed under inert atmosphere (approx. 0 wt%/min under nitrogen and -2 wt%/min under 2% O_2). The explanation to this is the same as for PEEK, whereby the mass loss at high temperatures is due to the oxidation of the char that is formed at lower temperatures (at the onset of the decomposition). Another observation that can be made is that the oxidation of the char seems to occur almost as soon as it is formed. The two apparent steps that were observable on the DTG curves from the TGA of PI, are therefore somewhat overlapping and undiscernible.

In order to further study the influence of oxygen on the thermal decomposition behavior of PI, TGA was performed at other oxygen concentrations. The corresponding TGA curves are shown on Figure 39



Figure 39. TGA and corresponding DTG curves of PI under different oxygen levels at a heating rate of 10 °C/min

From the TGA plots of PI under different oxygen concentrations, it can be confirmed that an increase in oxygen concentration increases the extent of the apparent second step of the decomposition. It can also be observed on the DTG curves that there is a shift of the MLR_{max} towards higher temperatures as the oxygen concentration is increased. Indeed, under nitrogen, the MLR_{MAX} corresponds to a temperature of 610 °C whereas under 12% oxygen, the MLR_{MAX} corresponds to a temperature of 637 °C. This suggests that there may be a slight stabilization on the structure formed during the onset of the thermal decomposition. While it may be inferred that the presence of oxygen brings about some form of stability, it should be noted that the temperature ranges within which the stabilization occurs is very narrow. Indeed, from the DTG curve the MLR_{MAX} is slightly shifted to higher temperature, representing a slight stabilization. However, the MLR is much higher. This means that despite the slight stabilization, the polymer decomposes more quickly in the presence of oxygen than under nitrogen, possibly via another mechanism.

O ₂	T95% (°C)	T@ MLR _{MAX} ($^{\circ}$ C)	MLR _{MAX} (%/min)	Residue (wt%)
2%	575	612	4.0	9
4%	578	647	5.0	0
8%	577	642	8.2	0
12%	572	635	10.4	0

 Table 8. Summary of the TGA of PI under different oxygen levels

III.2.a.iii. Thermal Stability of PI in Air

To complete the study concerning the thermal stability of PI, TGA was performed under synthetic air containing 21% oxygen and 79% nitrogen (Figure 40).



Figure 40. TGA and DTG plot of PI measured in 21% oxygen and 79% nitrogen at a heating rate of 10 °C/min

The onset of the degradation corresponds to a temperature of 565 °C. This temperature is slightly lower than when the analysis is performed under nitrogen ($T_{95\%} = 573$ °C), suggesting that the thermal stability is slightly lower under oxidative atmospheres. When looking at the TGA curve, the thermo-oxidative degradation seems to occur in a single step within the temperature range 550 – 700 °C, whereby there is an abrupt mass loss from 100 wt% to 0 wt%. However, the DTG curve shows two peaks at 622 °C and at 638 °C. This means that there are at least two different steps during the thermo-oxidative decomposition of PI (it can be related to the DTG curves recorded as a function of O₂ content showing a two-step decomposing steps). Moreover, the two DTG peaks are relatively close to each other. This means that the reaction steps are probably overlapped.

Table 9. Summary of the TGA of PI in air

DI/Ain —	T _{95%} (°C)	T@ MLR _{MAX} (°C)	MLR _{MAX} (%/min)	Residue (wt%)
FI/AIr —	565	622	13.7	0

Since the temperatures at the onset of the degradation are relatively close to each other whether the analysis is performed in air or under nitrogen, it means that there is a strong probability that the first step of the thermal decomposition still possesses a pyrolysis step which is closely followed by thermo oxidation.

III.2.a.iv. Conclusion

TGA of PI have revealed that PI has an enhanced thermal stability in air and under inert conditions. Indeed, it has a relatively high decomposition temperature (>500 °C) in both thermo-oxidative and inert atmospheres.

The temperature at the onset of the decomposition is less than 15 °C lower in air than under nitrogen. This suggests that, like PEEK, the first step in the thermal decomposition of PI is initiated by a similar mechanism. However, when looking at the mass loss rates at different oxygen levels, it was observed that the mass loss rate for the first step of the decomposition of PI is higher as the oxygen level is increased. Therefore, we can conclude that despite the initial reactions occurring at almost the same temperature, the presence of oxygen influences rate of decomposition of PI.

When performed under nitrogen, the residual weight at 800 °C is very high (>50 wt%). However, this is not the case when the oxygen level is increased. Indeed, a decrease in the residual mass was observed as the oxygen level was increased. This suggests that under nitrogen, the main decomposition reaction occurring leads to the formation of a charred structure. However, as the concentration of oxygen is increased, the first peak in the DTG curves becomes increasingly high. This means that there is a higher mass loss rate for the first degradation step, suggesting that the char formation process is coupled with its thermo-oxidation. This is even more perceptible on the DTG curve of PI under air, whereby the first and second maxima are almost completely overlapped.

III.2.b. Identification of Decomposition Products of Polyimide (PI)

In an attempt at identifying the decomposition products of PI, Py-GC/MS was used on PI. This enabled the separation of the evolved gases and it was possible to single out other individual decomposition gases. After their identification, pyrolysis MS provided intensity/temperature curves of the identified gases. The intensity profiles of these decomposition products are shown in Figure 41.



Figure 41. Intensity profiles of phenol (black), aniline (red), cyanobenzene (blue), dicyanobenzene (green), 4-aminophenol (magenta), benzene (dark blue), 2-(4-hydroxyphenyl)isoindoline-1,3-dione (pale blue), phthalimide (purple), dibenzofuran (wine), and diphenylether (green), obtained using EGA MS at a heating rate of 20 °C/min.

The temperature at which the different gases are evolved, provides information about the stages of the thermal decomposition. From the intensity profiles obtained by EGA-analysis, it can be observed that the first decomposition gases to be obtained are benzene, cyanobenzene and dicyanobenzene, detected at 540 and 560 °C respectively. There are some other early decomposition gases such as phenol, 4-aminophenol and aniline which are

detected. These are the first evolved gases that are released during the thermal decomposition of PI.

Other identified decomposition products are: phthalimide, dibenzofuran, diphenylether and phthalanil. These structures are more reminiscent of depolymerized polyimide or the result of recombination reactions that may have occurred at high temperatures (see mechanism, Scheme 7, page 171).

The peak release intensities of the evolved gases all occur between 640 and 660 °C. It should be noted that the evolution of water was also observed during the analysis of the evolved gases.

Moreover, TGA-FTIR was performed on PI in order to identify the pyrolysis gases that are evolved during its thermal decomposition. However, unlike the thermal decomposition of PEEK, very few decomposition products were identified. Figure 42 shows the TGA of PI and the corresponding chemigram recorded during the experiment by the FTIR instrument. The chemigram intensity is closely related to the total amount of evolved gases that has gone through the FTIR and therefore provides a judicious choice for the time and temperature at which the instantaneous FTIR spectra should be analyzed.



Figure 42. TGA and corresponding chemigram from the TGA FTIR analysis of PI, with a heating rate of 20 °C/min under nitrogen

Indeed, by extracting the FTIR-spectra corresponding to the highest intensities of released products, primordial insight regarding the nature of the evolved gases at different temperatures can be obtained. The two spectra corresponding to different temperatures, therefore different stages of the degradation, are shown in Figure 43 and Figure 44.



Figure 43. FTIR spectrum corresponding to decomposition gases of PI released at 600 °C

Figure 44. FTIR spectrum corresponding to the decomposition gases released from PI at 733 $^{\circ}C$

At the onset of the decomposition, only carbon dioxide and carbon monoxide are observed on the corresponding FTIR spectra. This means that oxygen-involving bonds are the first to be broken during the thermal decomposition mechanism of PI. A detailed mechanism pathway has been attempted in the following section (Scheme 7, page 171)

Absorption peaks corresponding to CO_2 and CO are clearly visible on the FTIR spectrum that corresponds to the evolved gases released at 600 °C. At higher temperatures (733 °C), other characteristic elongations such as those of hydrogen cyanide (approx. 3300 cm⁻¹) and methane (3018 cm⁻¹) and ammonia (two narrow peak elongations at 933 and 970 cm⁻¹) can be distinguished among the other peaks. The intensity profiles of these gases as well as the TGA curve of PI recorded during the TGA-FTIR are shown in Figure 45.

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Figure 45. TGA curve (middle), intensity profiles of CO₂ and CO (top), and intensity profiles of HCN, CH₄, and NH₃ (bottom) when the analysis is performed at a heating rate of 20 °C/min.

From the two intensity profile graphs corresponding to the TGA-FTIR analysis of PI, it can be observed that carbon dioxide and carbon monoxide are evolved in the highest proportions. A small amount of CO_2 is recorded at low temperatures (500 °C) and corresponds to less than 2 wt% mass loss. Carbon monoxide starts to evolve at 550 °C, corresponding to a mass loss of about 3 wt%. The peak intensities corresponding to the maximum release of carbon dioxide and carbon monoxide are both recorded at 611 °C.

At higher temperatures, the release of carbon dioxide and carbon monoxide decrease, as does the mass loss rate (Figure 36). However, as the amount of CO_2 and CO are decreased, other decomposition gases are released. Indeed, as from 611 °C, the intensity profiles of hydrogen cyanide, methane and ammonia start to increase. It should be noted that the intensity of these gases is inexistent at lower temperatures, but only starts to increase when the peak release of CO_2 and CO has been reached. This suggests that first part of the decomposition, whereby CO and CO_2 are released, corresponds to the formation of a char and that at higher temperatures, this char starts to decompose, causing the release other decomposition products.

In the case of PI, a more exhaustive detection of the decomposition products was possible through py-GC/MS as compared to TGA-FTIR. However, small molecules such as methane and ammonia, which were not identified via py-GC/MS were identified and the intensity

profiles were plotted. We have also seen that with respect to carbon dioxide and carbon monoxide, the amount of volatiles released is relatively low. This suggests that in a fire scenario, there might be a low amount of fuel generation during the thermal decomposition of the material. To confirm this, the fire behavior of PI needs to be evaluated.

III.2.c. Fire Behavior of PI

As a high-performance polymeric material, PI is expected to have good fire properties. To evaluate these properties, MLC experiments were carried out at three different heat fluxes: 35, 50, and 60 kW/m². The graphs on Figure 46 shows the heat release rate and the temperature profile at the back of the sample during the MLC test with an incident heat flux of 35, 50, and 60 kW/m².



Figure 46. Heat release rate curve (top) and temperature profile at the back of a $(100 \times 100 \times 1.5) \text{ mm}^3$ plate of PI subjected to 35 kW/m² (black), 50 kW/m² (red) and 60 kW/m² (blue) under a mass loss cone calorimeter. Sample dimensions: $(100 \times 100 \times 1.5) \text{ mm}^3$. Distance from the heating cone: 35 mm

At 35 kW/m²; there is no HRR recorded on the MLC experiment. The temperature at the back of the sample increases rapidly to around 400 $^{\circ}$ C and stagnated for the whole experiment. Visually, some deformation is observed on the material, but neither melting nor fumes are seen.

From the HRR curve obtained when PI is subjected to an incident heat flux of 50 kW/m^2 , it can be observed that the heat release rate is almost null throughout the experiment. There was no ignition of the material. Some values of HRR are recorded but it can be considered

they are not significant even though we should recognize thermo-oxidation could occur at the surface of the material.

Moreover, when looking at the temperature profile at the back of the sample, a rapid increase from room temperature to around 300 °C is observed in the first seconds of the test. After this, there is a steady increase in temperature until around 700 seconds, whereby a more rapid temperature increase until around 600 °C is observed, extensive thermal and thermo-oxidative decomposition occurs at this temperature.

The visual aspect of the material also changes throughout the test. At first, a slight swelling of the material is observed (Figure 47, left). After around 564 s, the material is clearly degraded (Figure 47, middle) and fumes can be seen leaving the surface of the material. When left under the same incident heat flux, the decomposition of the material continues. This can be seen by the presence of the white residues on the top of the polymer on the picture on the right in Figure 47. The absence of ignition is assigned to the high amount of carbon dioxide and carbon monoxide released during the thermal decomposition, as seen on the TGA-FTIR. These gases dilute the flammable gases which are also released during the decomposition process. The resulting concentration of flammable gases is therefore lower than the critical concentration required for ignition to occur.



Figure 47. Pictures taken of PI when subjected to 50 kW/m² at different times during the experiment: 120 s (left), 564 s (middle), 1300 s (right).

The thermal decomposition and thermo-oxidation of the sample pursued without the presence of a flame for several minutes. However, the visual aspect of the decomposing material did not evolve greatly during this time (Figure 48, right and center).



Figure 48. Pictures taken of PI when subjected to 50 kW/m² at 1300 s (left), 1541s (middle) and after the removal of the sample from the heat source (right).

When the sample was removed, it could be noticed that there was significant degradation that had occurred on the sample. The polymer had almost completely degraded, leaving only bits and pieces of a charred solid on the sample holder (Figure 48, right). Since flaming combustion was not observed during the MLC at 50 kW/m², the sample was subjected to a higher heat flux (60 kW/m^2). The distance between the heat source and the sample was kept at 35 mm (same as before) for comparison purposes. The resulting HRR curve and the temperature profile at the back of the sample are shown in Figure 46.

The HRR curve of PI under 60 kW/m² shows a heat release rate is detected as from 394 s. This also marks the point where ignition occurs. The HRR increases sharply until around 29 kW/m², peaking at 446 s, and decreases as sharply to a very low HRR. This low value is maintained for the remainder of the experiment.

Upon ignition, a small flame is visible on the surface of the material (Figure 49, right). This flame seems to be the major contributing factor towards a positive HRR during the burning of PI. However, despite the high incident heat flux on the material, one may notice that the visual aspect of the flame corresponds to a small one (Figure 49, right).



Figure 49. Pictures taken of PI when subjected to 60 kW/m² at different times during the experiment: 60 s (left), 360 s (middle), 401 s (right).

The temperature profile, on the other hand, increases sharply upon exposure to the heat source. This is accompanied by a slight swelling of the material and the formation of some fissures (Figure 49, left). This increase peaks at 357 °C and a slight decrease in temperature

is recorded. However, this decrease in temperature does not last for long, as it is closely followed by a steady rise in temperature until around 600 °C whereby further deformation of the material is observed (Figure 49, middle). Ignition is also observed at around this point. After ignition, the temperature at the back of the sample keeps increasing, albeit at a relatively low rate, from 613 °C to 760 °C. This can be explained by the flaming of the material (Figure 49, right) which feeds heat back to the sample.



Figure 50. Pictures taken of PI when subjected to 60 kW/m² at different times during the experiment: 511 s (left), 25 min (middle), 40 min (right).

The flame was almost subsided shortly after ignition. Indeed, quickly after the peak HRR was observed (around 460 s, Figure 46) both the HRR and the size of the flame had greatly diminished (Figure 50, left). As the experiment carried on, the HRR stayed relatively close to zero. There was a constant, barely visible flame throughout the process (Figure 50, middle, encircled in blue). This flame also explains the non-zero value of the HRR throughout at times of the experiment after the peak HRR was reached. Despite the absence of the flame, combustion (oxidation) of the material is occurring. Indeed, at the end of the experiment, the presence of some white ash on the surface of the material strongly suggests that the polymer has endured combustion. This can be complemented by the fact that the polymeric material degrades at 573 °C. The temperature at the back of the sample being at values higher than the decomposition temperature, we can assume that there are degradation products that are being released at these temperatures (meaning that the polymer is decomposing).

III.2.d. Thermal Decomposition Reactions of PI

From the fire behavior of PI, it was observed that despite being subjected to a high heat flux, the heat release rate of PI remained relatively low (HRR $< 30 \text{ kW/m^2}$ under 60 kWm²). In an attempt to explain this low heat release rate on a molecular level, the thermal decomposition pathway of PI has been studied.

Pyrolysis GC/MS and TGA-FTIR experiments have allowed us to identify different decomposition products that are evolved when PI is subjected to high temperatures.

The initiation decomposition reactions that may occur correspond to either the imide ring cleavage or the cleavage of the carbon nitrogen bond between the phenyl and the imide. The suggested decomposition pathway in the early stage of the thermal degradation of PI is described in [66]. From this, a deeper reasoning towards the formation of the products from the thermal decomposition of PI was attempted. A schematic representation of the pathways that can be adopted during the thermal breakdown of PI is shown on Scheme 7.

According to the decomposition products that were identified during the thermal decomposition of PI, random scission was identified as a probable pathway that is undertaken during the decomposition of PI. The easiest bond to break being the C-N bond between the phenyl and the nitrogen, a bisimide diradical is formed. This diradical can rearrange to form a carbonyl isocyanate. An attack of the double bond on the carbonyl CO leads to the formation of carbon dioxide and isophthalonitrile (red route, Scheme 7).

Moreover, random scission of the ether bonds may lead to some small aromatics such as phenol (blue route, Scheme 7) or benzene (magenta, Scheme 7). However, if the cleavage is between two C-N bonds from the phenyl-imide linkage, it leads to the formation of diphenylether (pink route, Scheme 7) which was identified via Py-GC/MS.

Opening of the imide ring can also lead to different decomposition products. Indeed, if the ring opening occurs between the C-C bond between the phenyl and the carbonyl, it leads to the formation of two carbon monoxide and an amine end. Further decomposition of this part of the chain would lead to the formation of aniline and aminophenol with the cleavage of the next ether linkage (violet, Scheme 7).

The formation of dibenzofuran can be explained in with the same arguments as for its formation during the thermal decomposition of PEEK (Scheme 5, and turquoise route on Scheme 7). Abstraction of 2 hydrogens from adjacent phenyl from the diphenylether moiety at low temperatures would lead to the formation of a dibenzofuran structure that can be liberated at high temperatures upon cleavage of two opposite imide/phenyl linkages. Abstraction of two hydrogens generates dibenzofuran.

In order to explain the formation of 2-(4-hydroxyphenyl)isoindoline-1,3-dione (brown route, Scheme 7) the imide ring must first be cleaved on the aromatic side. This leaves a phenyl

diradical linked to another imide group on the other side. Cleavage of the ether bond that is opposite to this imide ring leads to the formation of the 2-(4-hydroxyphenyl)isoindoline-1,3-dione tri-radical. This radical can easily abstract three hydrogens, giving rise to 2-(4-hydroxyphenyl)isoindoline-1,3-dione.

Similarly, the formation of phthalimide comes from the same initial reaction, whereby one of the two imide rings on the same phenyl is decomposed. However, the subsequent cleavage comes from that of the imide-phenyl bond (green route, Scheme 7), leading to phthalimide.

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Scheme 7. Possible decomposition pathway of PI

It should be noted that unlike PEEK, the fire behavior of PI did not lead to a high amount of char. Moreover, the absence of a significant flame during the mass loss cone test implies that there is a high probability that thermo-oxidation is occurring at the polymer/air interface. This means that most of the volatile products that are released during the thermal decomposition of the material in a mass loss cone, is being oxidized on the surface of the material.

Despite the release of flammable substances upon its thermal decomposition, PI also releases non-flammable derivatives such as carbon dioxide and carbon monoxide. This means that only part of the gases evolved during the thermal decomposition of PI have the potential of feeding an eventual flame. Moreover, among the volatile products, the presence of these non-flammable gases dilutes the concentration of combustibles, causing a lower concentration of fuel for ignition and/or the sustaining of an eventual flame.

III.2.e. Conclusion

From TGA measurements, we have seen that PI has exceptional thermal stability both in inert and thermo-oxidative conditions. PI can form a char when it is heated under inert conditions. We have seen that under oxidative atmosphere, this char already starts to degrade at the onset of the decomposition. However, despite a higher rate of degradation in air, the temperature at which the onset of the thermal decomposition of PI occurs is relatively close to that under nitrogen.

Moreover, the mass loss cone calorimetry tests performed on PI have shown the enviable fire properties of PI. Indeed, the material does not catch fire at all when it is subjected to a high incident heat flux of 50 kW/m². It does, nonetheless, ignite at a higher heat flux of 60 kW/m², but only to achieve a peak heat release rate of around 30 kW/m². It should also be noted that despite the low heat release rate recorded, the material does undergo thermal decomposition when it is subjected to such high heat fluxes. It is highly likely that the underlying phenomenon that is undergone during the experiment corresponds to the thermo-oxidation of PI. This can be inferred because hardly any flame is visible during the experiment, suggesting that oxygen is effectively present near the surface of the material.

The degradation of the char in the presence of oxygen is evidenced by TGA under different oxygen levels. Indeed, some it could be argued that the presence of a small flame would mean that the immediate surrounding environment of the material can be considered poor in oxygen (intermediate region between the flame and the bulk of the material). However,

despite being in oxygen poor environment, thermo-oxidation of PI does occur, as it can be seen on Figure 38, whereby a non-zero mass loss rate is observed despite being at a relatively low oxygen concentration (2%)

Furthermore, the decomposition pathway of PI was also investigated. The main decomposition reactions occurring in polyimide involve the scission of the imide ring and that carbon-carbon bond between the imide ring and the phenyl. Subsequently, phenyl derivatives containing CN, OH, and NH₂ are generated. Moreover, it is also possible that the imide ring remains intact, generating phthalimide and 2-(4-hydroxyphenyl)isoindoline-1,3-dione. These are non-inflammable and may contribute to the dilution of an eventual flame.

III.3. Thermal Stability, of and Fire Behavior of Polybenzoxazole (PBO)

Poly(p-phenylene-2,6-benzobisoxazole) (PBO), known by its trademark Zylon®, is a rigid rod isotropic liquid crystal polymer. It consists of a polybenzoxazole backbone containing an aromatic heterocyclic ring. It exhibits excellent flame resistance and thermal stability [67], solvent resistance, and remarkable tensile strength [68] and modulus [69].

III.3.a. Thermal Stability

Similarly to the study of the thermal stability of the two previous polymeric material, that of the thermal stability of PBO is also studied using TGA.

III.3.a.i. Thermal Stability of PBO under Nitrogen

TGA was performed in milligram samples of PBO in order to identify the characteristic decomposition temperatures of PBO under inert atmosphere. Figure 51, shows the TGA plot and the corresponding DTG curve of PBO at a heating rate of 10 °C/min under nitrogen.



Figure 51. TGA and DTG curves of PBO at with a heating rate of 10 °C/min under nitrogen.

From the TGA curve of PBO at 10 °C/min, it can be observed that the onset of the decomposition ($T_{95\%}$) corresponds to a temperature of 710 °C. The maximum mass loss rate (5.1 wt%/min) occurs at 741 °C and corresponds to a mass loss of around 18 wt%. This occurs during the first step of the decomposition of PBO, corresponding to a total mass loss of around 30 wt%. After this step, there is a slow mass loss of around 2 wt% from 800 °C

to 900 °C. This final mass loss stage leads to a residual mass of 68 wt%, suggesting a that PBO is also a highly charring polymeric material.

Table 10.	Summary	of the	TGA	of PBO	under	nitrogen
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	T _{95%} (°C)	T@ MLR _{MAX} (°C)	MLR _{MAX} (%/min)	Residue (wt%)
$\mathbf{F}\mathbf{B}\mathbf{O}/\mathbf{N}_2$ –	710	741	5.1	68

Moreover, the enthalpy of degradation of PBO was measured using STA. The resulting TGA and DSC curves are shown in Figure 52. No visible Tg was observed on the DSC curve of PBO. However, an endothermic thermal decomposition enthalpy was observed at 720 °C (489 J/g). This can be assigned to the energy required for the cleavage reactions taking place during the thermal decomposition (see mechanism in section III.3.d.)



Figure 52 TGA (black) and DSC (blue) curves of PBO when subjected to STA at 10 °C/min under nitrogen

III.3.a.ii. Influence of Oxygen on the Thermal Stability of PBO

As with the two previous polymeric materials, PBO was subjected to TGA under low oxygen concentration (2% oxygen). The resulting TGA and DTG curves corresponding to the TGA of PBO under low oxygen concentration are shown in Figure 53. Two major steps can be observed on the TGA curve of PBO under 2% oxygen.



Figure 53. TGA and corresponding DTG curves of PBO when heated under nitrogen (black) and under 2% oxygen atmosphere at 10 °C/min

The first step corresponds to the onset of the decomposition ($T_{95\%}$) and occurs at 675 °C. This temperature is lower than that from the analysis under nitrogen, suggesting that the influence of oxygen in this material is more significant. Moreover, from the DTG curve, it can be observed that the MLR_{MAX} is higher when the analysis is performed under 2% oxygen (approx. 6 %/min) as compared to the one performed under nitrogen (approx. 5 %/min). This suggests that there is indeed a large influence of oxygen on the thermal decomposition of PBO. The MLR_{MAX} occurs at 740 °C under 2% O₂, which is relatively close to the temperature at the MLR_{MAX} for the measurement under nitrogen. The residual mass at 900 °C, on the other hand, is much lower under 2% oxygen (19 wt%) than under nitrogen (65 wt%)

Moreover, as the temperature of the material is increased further, the TGA plot shows that there is another decomposition step that follows the onset of the degradation. This is confirmed by the DTG curve where a relatively constant mass loss rate is recorded at temperatures above 800 °C. The residual mass at this temperature is 21 wt%.

From the TGA curve of PBO under nitrogen and under low oxygen concentration (2%) it can be deduced that the first step of the reaction corresponds to the formation of a char. However, due to the already high temperature of the decomposition, oxidation of the char takes place almost simultaneously. This is confirmed by the higher mass loss rate for the first step of the decomposition of PBO when the analysis is made under low O₂ levels as compared to the one made under inert atmosphere.

Since a low oxygen concentration seems to have a large impact on the thermal stability, the study was furthered at different concentrations in order to evaluate an eventual trend concerning the dependence of oxygen concentration on the thermal decomposition of PBO.

As with the other two high performance polymeric materials, TGA was performed on milligram samples of PBO under different oxygen concentrations. However, since this case exhibits a higher sensitivity to oxygen, we have also performed TGA at 0.7% O₂ in order to observe the extent of this oxygen sensitivity. The TGA and DTG curves corresponding to the different analysis performed under various oxygen concentrations are shown in Figure 54.



Figure 54. TGA (top) and corresponding DTG (bottom) curves of PBO when heated at a heating rate of 10 °C/min under different oxygen levels

The influence of oxygen on the thermal stability is even more apparent on the TGA curves with increasing oxygen concentrations. The temperature at the onset of the decomposition decreases with increasing oxygen levels. Indeed, when the oxygen concentration is as low as 0.7%, the temperature at the onset of the decomposition is almost the same as for the measurement under 2% oxygen (678 °C). However, when the concentration of oxygen is increased above 2%, the temperature at the onset of the decomposition decreases further.

O ₂	T _{95%} (°C)	T@ MLR _{MAX} (°C)	MLR _{MAX} (%/min)	Residue (wt%)
0.7%	677	729	5.1	47
2%	674	735	6.3	20
4%	661	722	7.5	6
8%	651	690	9.1	0
12%	643	676	11	0

Table 11. Summary of the TGA of PBO under different oxygen levels

This decrease in the thermal stability is also observable on the DTG curves of PBO. Indeed, the maximum mass loss rates occur at a lower temperature under 12% oxygen (approx. 650 °C) as compared to the curve corresponding to the measurement made under nitrogen (approx. 740 °C).

Moreover, increasing the concentration of oxygen decreases the residual mass at 900 °C. This can be explained by the fact that the rate of oxidation of the char is limited by the concentration of oxygen in the atmosphere. Indeed, from the DTG curve, the mass loss rate is generally higher as the oxygen level is increased.

III.3.a.iii. Thermal Stability of PBO in Air

To further the study of the thermal stability of PBO, TGA was performed in synthetic air. The resulting TGA and DTG curves are shown in Figure 55 and the data are summarized in Table 12.

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Figure 55. TGA and DTG curves of PBO under nitrogen (black) and in air (green) at a heating rate of 10 °C/min

From the TGA curve of PBO under air, a sharp decomposition step is observed, with an onset temperature ($T_{95\%}$) at 620 °C. This onset of decomposition corresponds to a sharp mass loss (77 wt%). This is followed by another slower step until there is no residual mass. The MLR_{MAX} corresponds to a temperature of 658 °C.

Table 12. Summary of the TGA of PBO in air

DRO/Air	T _{95%} (°C)	T@ MLR_{MAX} (°C)	MLR _{MAX} (%/min)	Residue (wt%)
rb0/All -	620	658	16.0	0

The DTG curve of the analysis in air shows that there is a small shouldering occurring evidenced by the mass loss rate at around 750 °C. This suggests that there has been the formation of a charred structure that is oxidized at a lower rate than the initial material.

III.3.a.iv. Conclusion

The thermal stability of PBO is highly dependent on the atmosphere in which the thermal stress is applied to it. Indeed, when the material is heated under nitrogen, a very high thermal stability is observed (decomposition temperature > 700 °C). However, when the same thermal stress is applied to the material under very low oxygen concentrations (0.7% O_2), the thermal decomposition occurs at a temperature that is 30 °C lower. In air, the thermal decomposition occurs at 100 °C lower than under nitrogen.

Moreover, the residual mass at 800 °C is also largely affected by the presence of oxygen. Indeed, while the residual mass of PBO under nitrogen at 800 °C corresponds 60 wt% of the initial mass of the material, 2% oxygen in the atmosphere changes this weight to around 20 wt%. This suggests that the char that is formed during the first decomposition step is quickly thermo-oxidized in the presence of even a low amount of oxygen. However, it should be noted that the temperature at which the char degrades is still a very high temperature for a completely organic polymer. Another possible explanation is that oxygen influences the very mode of decomposition of PBO, meaning that the pathway adopted for the thermal decomposition is different and more rapid.

It is also of interest to point out that the mass loss rate of both the first step and the second step of the thermal decomposition increases as the concentration of oxygen increases (for the same heating rate). This hints towards a conclusion whereby there is some form of catalytic behavior brought about by the presence of oxygen [58]. In order to investigate this possibility, it was deemed appropriate to attempt to identify the different decomposition gases that are evolved during the thermal decomposition in air and under nitrogen. This can provide insight to explain the high dependence of the thermal stability of PBO on oxygen.

III.3.b. Identification of the Decomposition Products of PBO

As with the other two high performance polymeric materials studied, an attempt at identifying the thermal decomposition products of PBO was made.

TGA FTIR was performed on PBO under nitrogen atmosphere at a heating rate of 10 °C/min. The chemigram recorded on the FTIR as well as the corresponding TGA curve are plotted on the same graph in Figure 56.



Figure 56. TGA plot (red), temperature profile (dashed), and FTIR chemigram (blue) of PBO when subjected to a heating rate of 20 °C/min under nitrogen

The FTIR spectrum corresponding to the onset of the decomposition showed that the first decomposition products that are released when PBO is subjected to thermal stress were carbon dioxide and carbon monoxide. As the temperature increased, so did the extent of the thermal decomposition and its corresponding products. It was therefore possible to identify the different evolved gases by analyzing the FTIR spectrum corresponding to the one recorded at the maximum mass loss rate on the TGA. This spectrum is shown on Figure 57.





Figure 57. FTIR spectrum corresponding to the FTIR of the decomposition gases released at 770 °C

Figure 58. Intensity profiles of the maxima of the FTIR spectra of evolved gases during the thermal decomposition of PBO when heated at 20 °C/min under nitrogen

The intensity profiles of the most abundant peak (except for HCN, where the maximum peak coincides with another product) of the different evolved gases are plotted on Figure 58.

From the intensity profiles of the FTIR spectra, it can be observed that the carbon dioxide is one of the earliest decomposition products evolved, first detected at around 12.5 minutes (668 °C). CO is the next decomposition product that is identified under FTIR. Ammonia is also released during the thermal decomposition of PBO. However, its release occurs at a slightly higher temperature (714 °C) as compared to the release of CO and CO₂. Hydrogen cyanide and methane are released at even higher temperatures (730 °C) suggesting that they are released only in a later step of the decomposition.

Moreover, seeing as the thermal decomposition of PBO seems to be highly dependent on the oxygen concentration, TGA FTIR was performed at low oxygen levels in an attempt to identify eventual decomposition gases under such conditions. However, only carbon dioxide, carbon monoxide, and HCN were identifiable through this technique

While TGA FTIR enabled the identification of some of the lighter decomposition products such as HCN and ammonia, it also evidences that there are other unidentified decomposition products. This can be seen on the FTIR spectrum at 770 °C, whereby many peaks are observed in the region 1000 - 2000 cm⁻¹. To identify these thermal decomposition products, another analytical tool was used: Py-GC/MS.

By using double shot analysis on the pyrolysis GC/MS, several decomposition products were identified. The main decomposition products that were identified were phenol, cyanobenzene and dicyanobenzene. Moreover, many small portions of linear alkenes, alkanes, aldehydes, and ketones were also identified. However, since the mass spectra of these linear structures share a great resemblance, we were unable to identify their individual structures.

The decomposition gases that were identified during the pyrolysis of PBO were not of a great aid towards explaining the oxygen dependence of the thermal stability of PBO. However, it provided insight on which bonds are likely to be broken when the material is under an elevated temperature scenario. This will be discussed in section III.3.d.

III.3.c. Fire Behavior of PBO

Seeing the promise that PBO hold in terms of thermal stability, one may be eager to find out its fire behavior. However, since the mass loss cone calorimeter is not adapted for the

evaluation of the fire properties of fibers. However, the laboratory has previously investigated the fire properties of PBO (knitted and woven as double woven rib) under the cone calorimeter, and the results were compared to *p*-Aramid. It was observed that the peak HRR when PBO was subjected to an incident heat flux of 75 kW/m² is as low as 160 kW/m² [67].

III.3.d. Thermal Decomposition Pathway of PBO

We have seen that the decomposition of PBO is greatly affected by the presence of oxygen in the atmosphere. The thermal decomposition of PBO identified during pyrolysis GC/MS have shown a plethora of aromatic products that are evolved during the thermal decomposition of PBO. In order to explain the formation of these products, an attempt at elucidating the decomposition pathway is shown in Scheme 8. This mechanism is similar to decomposition mechanism of polybenzothiazole (PBT, Figure 59) which is reported to have a similar thermal decomposition behavior as PBO [70].



Figure 59. Chemical structure of polybenzothiazole

One of the most abundant decomposition products that was identified corresponds to cyanobenzene. Its generation is probably initiated by the scission of the heterocyclic part of the benzimidazole moiety, leading to the formation of benzonitrile species.

Chen *et al.* studied the thermal degradation mechanism of PBT [71] and it was also reported that the decomposition of PBO and PBT followed the same mechanism [72]. By combining these assumptions and our study on the thermal decomposition of PBO, a decomposition pathway for the degradation of PBO can be deduced.

The study of the thermal decomposition of model compounds of PBO led to the conclusion that the most important reactions occurring when PBO is subjected to elevated temperature is the homolytic scission of the single C-C bond, followed by the decomposition of the heterocyclic ring. This leads to formation of cyanobenzene, dicyanobenzene, and benzene which were observed by Py-GC/MS. In order to explain the formation of cyanobenzene, a possible decomposition pathway involving the scission of the CC bond between the benzoxazole and the phenyl groups is shown in Scheme 8. After this scission, further decomposition of the heterocyclic part of the benzoxazole group would generate a

cyanobenzene group. On the other hand, scission between the phenyl and the bisbenzoxazole would lead to the formation of benzene.



Scheme 8. Decomposition pathway of PBO involving the scission of C-C bond between the benzoxazole and the phenyl groups as initial reaction

On the other hand, if the initial cleavage occurs on the heterocyclic ring, cyanobenzene, dicyanobenzene and an unstable diradical is generated [73]. The latter decomposes further and generates a nitrile ended polymer end chain (Scheme 8, route a). Taking this reaction further may also produce smaller molecules such as HCN, CO, and water. This scheme is evidenced by the detection of these decomposition gases during the TGA-FTIR of PBO [74].

Chapter III- Thermal Behavior and Fire Properties of High-Performance Polymeric Materials



Scheme 9. Decomposition pathway of PBO involving the decomposition of the heterocyclic ring.

While the previous reaction pathways provide insight concerning the volatile products evolved during the thermal decomposition of PBO, it should be noted that a large part of the polymer is transformed into char during its thermal decomposition. This is evidenced by the TGA of PBO under nitrogen, whereby more than 65 wt% of residual weight is recorded at 800 °C.

The carbonization step possibly intervenes after the opening of the heterocyclic ring, leaving a phenoxy radical to react with another, forming a peroxide bridge. At this point, the elimination of CO_2 and subsequent coupling may lead to the graphitization of the polymeric material [75].

Chapter III- Thermal Behavior and Fire Properties of High-Performance Polymeric Materials



Scheme 10. Proposed thermal decomposition pathway of PBO leading to the crosslinked carbonaceous structure [75]

The thermal crosslinking mechanism of PBO postulated by Ehler *et al.* involved the opening of the heterocyclic part of the benzoxazole, which leads to the formation of a peroxide. Elimination of carbon dioxide generates a Schiff base which can then crosslink with other parts of the remaining polymer chains [75].

III.3.e. Conclusion

The thermal stability of PBO was successfully evaluated thanks to a plethora of thermal analyses. PBO has depicted an impressively high thermal decomposition temperature, which rivals several high-performance polymeric materials. However, this temperature is highly dependent on the inertness of the atmosphere. Indeed, when the thermal stability was evaluated under atmospheric conditions, the thermal stability of PBO was greatly diminished. It was concluded that oxygen plays a role on the initial mechanism of the thermal decomposition of PBO.

However, evidence of this was only achieved through TGA. Indeed, TGA-FTIR could not provide enough information on the immediate decomposition products of PBO under low oxygen information. This is probably because the presence of oxygen in the surrounding atmosphere caused the total oxidation of all the evolving decomposition products. From this, we can infer that oxygen plays some form of catalytic role in the thermal decomposition of PBO. Indeed, it was already reported that the presence of oxygen has a major impact on the thermal decomposition of PBO [74]. Indeed, it was also reported that the presence of oxygen accelerates the degradation of its tensile strength, which results from an oxygen-carried free-

radical mechanism. By extrapolating these results to a chemical perspective, it can be deduced that there is structural degradation occurs during this process, leading to the decrease in the thermal stability.

Moreover, the thermal decomposition mechanism provided insight on how the material behaves when it is subjected to elevated temperature. The cross-linking of the polymer goes through a Schiff base type intermediate which promotes crosslinking in the decomposing material. This crosslinking can have a positive effect on the fire behavior of the material by creating a protective layer on the surface of the material during a fire scenario. This layer limits the transfer of fuel from the bulk of the material to the surface (flame) [76].

III.4. Conclusion

The thermal stability of three different high-performance polymeric materials were investigated. Despite being very different materials, all three materials have shown that under nitrogen, they start to decompose at temperatures above 550 °C. It was also observed that initial step of thermal decomposition may or may not be dependent on the oxidative/inert nature of the atmosphere it is in. Indeed, the thermal stability of PEEK under different oxygen levels has revealed that the first step is almost completely independent on the atmosphere. On the other hand, the same cannot be postulated about PBO, for which the onset of the decomposition occurs at a temperature which is less than 15 % in air as compared to that under nitrogen. This high difference may be reason to investigate further the effect of oxygen on the thermal decomposition of PBO.

Moreover, all three polymeric materials form a char when they are subjected to elevated temperatures. The char formed in all cases are relatively stable at high temperatures under inert atmospheres. However, when under a slightly oxidative atmosphere, the char formed from all three of the materials studied start to thermo-oxidize. This was expected, as carbon, in the presence of oxygen, is also oxidized to carbon dioxide and carbon monoxide. Moreover, the rate of thermo-oxidation is similar for the three polymers. Indeed, when looking at the mass loss rate of the polymers at 750 °C under 2% oxygen are all around 2.5 wt%/min.

Furthermore, the degradation pathways of the three polymeric materials have provided invaluable insight on their fire behaviors. When subjected to heat, PEEK swells thanks to the combined facts that it starts to melt, char and release non-combustible gases. This phenomenon is often sought for when fire retarding polymeric materials. Indeed, a large

portion of intumescent flame retardants are intended to release inert gases and cause char formation at the same time.

PI, on the other hand, simply does not ignite at 50 kW/m². This can be due to the thickness of the PI used was relatively small (1.5 mm). It is therefore possible that there is a lower concentration of decomposition gases that are released during the thermal decomposition. This means that the critical concentration of flammable gases to ignite is not reached sufficiently fast. Another explanation can be that the decomposition of the material does not release sufficiently flammable products.

The fire performances of PBO, was not evaluated in the context of this work. However, its extremely enviable fire properties have been reported previously [19]. In an attempt to explain this fire properties, the thermal decomposition pathway was suggested. The presence of a Schiff base intermediate that aids to promote cross-linking and graphitization has brought out attention that its char formation mechanism can be regarded as a fire-retardant behavior.

This chapter has brought light on the thermal decomposition behavior of these highperformance material. However, kinetic parameters of the materials were not evaluated. A model based kinetic simulation of a material can aid in better understanding its decomposition behavior as well as provide further insight on the influence of oxygen on the thermal decomposition behavior of these polymers. Indeed, now that the thermal decomposition pathways of the three polymeric materials have been elucidated, they can be used to devise model based kinetic mechanism for their thermal decomposition.

IV. Thermal Decomposition Kinetics of High-Performance Polymeric Materials

The previous chapter has provided insight on the thermal stability and the nature of the decomposition products of the three high performance polymers that were studied. In order to further this study, it was deemed worthwhile to understand the key kinetic parameters that govern the thermal decomposition of these materials. Indeed, it was observed that the presence of oxygen may have very different effects on the onset of the thermal decomposition of a material. Therefore, investigating the effect that different oxygen concentrations may have on the kinetic parameters of the thermal decomposition of these materials can also allow the prediction of their behavior in a flaming or non-flaming combustion, whereby the conditions at the polymer surface are either completely pyrolytic, oxygen poor, or atmospheric.

Therefore, this chapter deals with the investigation of the kinetic parameters for the thermal decomposition of the three high performance polymeric materials discussed in chapter 3. Three different oxygen levels will be studied: 0%, 2%, and 20%. Kinetic models will be devised in order to match the decomposition behaviors of the materials under the previously mentioned atmospheres.

In order to expound the results of the kinetic analyses, this chapter is divided into three main sections each pertaining to a single polymeric material. The first section, corresponding to the kinetic analysis of PEEK, is subdivided into three parts, one for each oxygen levels. This structure is adopted for PI (second section) and PBO (third section) as well. At the end of the chapter, a general conclusion is provided.

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The approach used to do so was similar to that adopted by Moukhina et al, whereby a model free analysis was used to determine the initial kinetic decomposition parameters and gain insight regarding the number of steps involved and the types of kinetic models that govern the decomposition [77]. To this approach, we added our own understanding of the thermal decomposition based on the previous chapter, whereby the thermal decomposition mechanism was attempted.

The reflection behind the methodology that we have adopted is briefly summarized hereunder.

In order to model the kinetic degradation of a polymeric material, two separate functions can be assumed. One being temperature dependent (K(T)), and the other governed by the conversion, α , f(α). The latter can be of any value from 0 (no degradation) to 1 (complete degradation). Therefore, the differential equation that defines the kinetics of thermal degradation can be written as equation 1 [78].

$$\frac{d\alpha}{dt} = K(T)f(\alpha) \tag{1}$$

 $\frac{d\alpha}{dt}$ is the rate of degradation, K(T) is the temperature dependent rate constant, and $f(\alpha)$ corresponds to the reaction model. K(T) can be described by the Arrhenius equation (equation 2):

$$K(T) = Ae^{-\left(\frac{E}{RT}\right)}$$
(2)

Where R is the universal gas constant, *E*, the activation energy, and *A*, the pre-exponential factor [79].

The time dependence of equation (2) can be eliminated by using a constant heating rate $\beta = \frac{d\alpha}{dt}$, by dividing by it (equation 3).

$$\frac{d\alpha}{dT} = \frac{A}{\beta} f(\alpha) e^{-\frac{E}{RT}}$$
(3)

Linearizing equation 3 leads to obtainable kinetic parameters (A and E) by using the equation 4.

$$\ln\left(\frac{\frac{d\alpha}{dt}}{f(\alpha)}\right)\ln\left(\frac{A}{\beta}\right) - \left(\frac{E}{RT}\right) \tag{4}$$

One approach for kinetic modelling involved the assumption that the activation energy and the preexponential factor is constant. A well-known technique that uses this method is the Friedman method, whereby the activation energy and pre-exponential factor are obtained by plotting the logarithmic form of the rate equation of each heating rate (equation 1). α represents the value at a certain degree of conversion, and *i* the data from the corresponding heating rate experiment [80].

$$\ln\left[\beta_{i}\left(\frac{d\alpha}{dT}\right)_{\alpha,i}\right] = \ln\left(A_{\alpha}f(\alpha)\right) - \frac{E_{\alpha}}{RT_{\alpha,i}}\right)$$
(5)

The activation energy at particular conversion degrees can be calculated with linear regression from a plot of $\ln \left[\beta_i \left(\frac{d\alpha}{dT}\right)_{\alpha,i}\right]$ against $\frac{1}{T_{\alpha,i}}$ for the heating rates that were used. The plot can provide confirmation as to whether there is more than one step involved in the degradation process. Moreover, the nature of the decomposition step can also be intuitively guessed by comparing the slope of a constant heating rate data [81]. By comparing the magnitudes at the peak slope (the one that is on the right side of the peak) and that of isoconversion lines, three types of reactions are defined: normal, accelerated, and retarded (Figure 60).



Figure 60. Friedman plots corresponding to a normal type of reaction (left), an accelerated reaction (middle), and a retarded reaction (right).

A normal reaction corresponds to the curve whereby the magnitude of the peak slope (slope to the right of the peak) and that of the isoconversion lines are of the same magnitude. An accelerated reaction is one whereby the peak slope is steeper than that of the isoconversion lines. Contrarily, a retarded reaction has a peak slope which is gentler than that of the isoconversion lines. However, one of the major limitations of this method is that it does not cater for the possibility of competitive parallel reactions that may occur during the thermal decomposition process.

It should be noted that for the reaction model to make physical sense, reaction orders above three are not taken into account. However, because of the complexity of the reactions occurring during the thermal decomposition of a polymeric materials, optimizations based on experimental data can lead to non-integer values of reaction orders. This often happens when a step involves more than one pathway towards the same decomposition product.

Another similar method that is used for model free analyses of kinetic degradation is the Ozawa-Flynn-Wall integral isoconversional method [82,83].

The Ozawa-Flynn-Wall analysis involves an integral method for the calculation of the kinetic parameters, therefore, there is no separation of variables involved. As a result, competitive reactions show variations in activation energies between the Ozawa-Flynn-Wall and the Friedman analyses [81]. This will be helpful in determining the nature of the steps involved in the thermal decomposition of the materials investigated.

Moreover, the insight regarding the thermal decomposition behavior of the polymeric materials will be used in order to devise an experiment-based model, aided by the model free analysis detailed above.

There are several reaction types that can be attributed to a decomposition step. The typical homogenous reactions and classic solid reactions are listed in Table 13.

The models were optimized using the KineticsNeo software (Netzsch). We have attempted to make kinetic models with the lowest number of steps that gave an acceptable fit and that were consistent with the thermal decomposition mechanism of the material studied.

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Code	Function	Type of reaction
F1	$f = (1 - \alpha)$	Reaction of 1st order
F2	$f = (1 - \alpha)^2$	Reaction of 2nd order
Fn	$f = (1 - \alpha)^n$	Reaction of nth order
R2	$f = 2(1-\alpha)^{\frac{1}{2}}$	Two-dimensional phase boundary
R3	$f = 3(1-\alpha)^{\frac{2}{3}}$	Three-dimensional phase boundary
D1	$f = \frac{1}{2} \cdot \frac{1}{\alpha}$	One-dimensional diffusion
D2	$f = -\frac{1}{ln((1-\alpha))}$	Two-dimensional diffusion
D3	$f = \frac{3}{2} \cdot \frac{(1-\alpha)^2}{1-(1-\alpha)^{\frac{1}{3}}}$	Three-dimensional diffusion Jander's type
D4	$f = \frac{3}{2} \cdot \frac{1}{((1-\alpha)^{-\frac{1}{3}} - 1)}$	Three-dimensional diffusion Ginstling- Brounstein type
B1	$f = (1 - \alpha) \cdot \alpha$	Prout-Tompkins equation
Bna	$f = (1 - \alpha)^n \cdot \alpha^{K_{cat}}$	Expanded Prout-Tompkins equation
C1	$f = (1 - \alpha) \cdot (1 + K_{cat} \cdot \alpha)$	Reaction of 1st order with autocatalysis by product
Cn	$f = (1 - \alpha)^n \cdot (1 + K_{cat} \cdot \alpha)$	Reaction of nth order with autocatalysis by product
Cnm	$f = (1 - \alpha)^{n} \cdot (1 + K_{cat} \cdot \alpha^{m})$	Reaction of nth order with m-Power autocatalysis by product
A2	$f = 2(1 - \alpha) \cdot [-ln(1 - \alpha)]^{\frac{1}{2}}$	Two-dimensional nucleation according to Avrami
A3	$f = 3(1 - \alpha) \cdot [-ln(e)]^{\frac{2}{3}}$	Three-dimensional nucleation according to Avrami
An	$f = n \cdot (1 - \alpha) \cdot \left[-ln((1 - \alpha)) \right]^{\frac{n-1}{n}}$	n-dimensional nucleation according to Avrami- Erofeev

Table 13.	Reaction	types and	corresponding	reaction	equations $\frac{d}{d}$	$\frac{d\alpha}{dt} = -1$	$A e^{\frac{E}{RT}} f(\alpha)$
					- (dt	

IV.1. Thermal Decomposition Kinetics of PEEK

The thermal decomposition kinetics of PEEK has been previously studied using dynamic TGA in air or under nitrogen and using an integral model free analyses such as the Ozawa-Flynn-Wall method [83,84] or using the Coats-Redfern models [85,86]. While these types of analyses provide valuable information concerning kinetic parameters of the material, they assume that the thermal decomposition is a single step reaction, with one activation energy. In order to integrally simulate the thermal decomposition of a material, it is imperative that a model taking into account the different steps of the thermal decomposition be used.

In the context of this work, model-based analysis for the thermal decomposition kinetics of PEEK was carried out, using dynamic TGA at 4 different heating rates (1 K/min, 2 K/min, 5 K/min, and 10 K/min) under the three aforementioned atmospheres. This allows for the simulation of the thermal behavior of PEEK under different heating rates. It also provides the kinetic parameters and contribution of each thermal decomposition steps that is occurring during the thermal breakdown of the material.

IV.1.a. PEEK decomposition under nitrogen

TG curves and corresponding DTG curves of PEEK for the four different heating rates of PEEK under nitrogen are shown in Figure 61.



Figure 61. TGA (left) and the corresponding DTG (right) curve of PEEK at 1 (black), 2 (red), 5 (blue), and 10 K/min (magenta), under nitrogen

As a high-performance polymeric material, PEEK is highly stable at intermediate temperatures (up to around 450 °C). The temperature at the onset of the decomposition increases with increasing heating rate and involves a sharp mass loss step, which is followed by another smaller mass loss of moderate slope (slow mass loss rate). The two steps can be seen on the DTG curve (Figure 61), whereby a sharp peak is observed, corresponding to the first mass loss. The second mass loss process is deduced by the non-zero derivative value

on the DTG curve. This suggests that there are at least two steps involved in the thermal decomposition of PEEK.

From the DTG curves there seems to be a trend whereby the peak mass loss rate decreases with increasing heating rate from 1 K/min to 5 K/min. However, this is not the case for the heating rate at 10 K/min, suggesting that there might be a different mechanism at higher heating rates. Therefore, in order to have a better insight concerning the activation energies regarding the thermal decomposition under nitrogen, a model free (Friedman) analysis of the TG curves was performed, and the Friedman plot is shown on Figure 62.



Figure 62. Friedman analysis of PEEK using 4 different heating rates under nitrogen

From the Friedman analysis under nitrogen (Figure 62), it can be observed that the reaction is multi-stepped. Two peaks are clearly discernible from the heating rates corresponding to 1, 2, and 5 K/min. However, at 10 K/min, there is a less obvious discernibility of the second peak, suggesting that the thermal decomposition mechanism may be different at higher heating rates. From the isoconversion lines (shades of red to blue lines corresponding to a particular conversion degree), it is clear that the peak slope is much steeper than the isoconversion lines, suggesting an accelerated reaction. An autocatalytic decomposition model may explain this first step of decomposition.

Moreover, from the Friedman analysis, the activation energy and the pre-exponential factor with respect to the conversion can be calculated (Figure 63).



Figure 63. Activation energy (black) and pre-exponential factor (red) plot for PEEK under nitrogen, obtained by Friedman analysis.

From the activation energy plot (Figure 63), it can be seen that the activation energy is not constant throughout decomposition process. This, coupled with the DTG curves, suggests that there are at least three steps in the thermal decomposition of PEEK under nitrogen. While two peaks were seen on the DTG curves, the activation energy plot shows that there are at least three steps – the first at the beginning of the conversion, the second whereby the activation remains relatively constant until around 60% conversion, and a third, corresponding to the peak seen at around 80% of conversion.

It should be noted that a 100% conversion means that the whole decomposition has been achieved. This hypothesis is not always verified in the case of our investigation. However, seeing how the DTG is almost constant at 800 °C, it can be assumed that the conversion is nearly 100 % at that temperature for the corresponding step of the decomposition.

While the DTG plots provide insight on the major steps involved in the thermal decomposition of PEEK, and the Friedman plot allow the identification of the initial kinetic parameters, they do not take into consideration the possibility of competitive reactions that may occur during the thermal decomposition. To do so, the activation energies calculated using the Friedman method was compared to that obtained using the Ozawa-Flynn-Wall method. The Figure 64 shows the activation energy plots from the two methods on the same graph.



Figure 64. Activation energies calculated using Friedman analysis (black) and the Ozawa-Flynn-Wall method (magenta) under nitrogen

From the two activation energy plots, it can be seen that the first step corresponds to an activation energy around 200 kJ/mol for both plots from a conversion of 0 to around 50 %. However, as from a conversion of around 50 %, a difference in activation energy is observed. This suggests that there are possibly competitive reactions occurring.

From the insight gathered by the model free analyses, it was possible to define a model for the decomposition of PEEK under nitrogen. The decomposition used for model the thermal decomposition kinetics of PEEK under nitrogen is shown on Scheme 11. The model chosen was such that it remains coherent with the thermal decomposition pathway that was elaborated in chapter 3. The explanations of each step are detailed in the subsequent paragraphs.



Scheme 11. Kinetic model used to model the thermal decomposition kinetics of PEEK under nitrogen

From the mechanism of the thermal decomposition of PEEK under nitrogen, it was seen that the first reactions are the random scission of the polymeric chain. Therefore, for our kinetic model, random scission, leading to char formation, should correspond to the first step of the reaction (A-B on Scheme 11). Moreover, from the Friedman plot, this step was assigned to an accelerated reaction. Therefore, an autocatalyzed reaction model was be adopted for this step. This can be explained by the fact that random scission of polymeric materials at high temperature leads to the production of highly reactive radical species. These species can in turn react with the remaining polymer to further the decomposition process. In some ways, the product of the reaction is aiding in the first step of the reaction. Therefore, the first decomposition step was assigned to an nth order reaction (whereby n needs to be optimized) involving an autocatalysis by the product (reaction order to be optimized).

Furthermore, from the Ozawa-Flynn-Wall (OFW) and Friedman plots, it was seen that the second degradation step potentially involves competitive reactions. These reactions involve the rearrangement of the char and further scission reactions. However, from the TGA-FTIR, it was observed that after the first step of the decomposition, the amount of decomposition gases released were much diminished. Therefore, it is less likely that the decomposition reactions occurring during this step lead to the generation of any reactive species that would increase the rate of the reaction. Thus, the competitive reactions involved in the second step of the thermal decomposition were both modelled by a simpler nth order reaction.

The last step modelled is assigned to the decomposition of the char. It corresponds to very little mass loss and has a very high activation energy (Figure 64) as it involves the decomposition of a very stable structure.

A summary of the optimized parameters based on the kinetic model above are shown on Table 14.

Step (reaction type)	1 (Cna)	2.1 (Fn)	2.2 (Fn)	3 (Fn)
Ea (kJ/mol)	208	226	163	383
Log(A) (log(1/s)	9.7	11.9	7.4	23.4
Reaction order	1.5	1.2	0.8	2.3
Kcat	1.5	/	/	/
Contribution	0.136	0.556	0.085	0.223

	Table 14.	Kinetic	parameters	used in	the model	for the thermal	decomposition	of PEEK	under nitroger
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The first step of the thermal decomposition of PEEK under nitrogen was assigned to an autocatalytic reaction, with an activation energy of around 208 kJ/mol, a reaction order of 1.5 and an autocatalytic order of 1.5. This activation energy for the first step is in accordance with the Friedman analysis whereby the initial activation energy was calculated to be around 220 kJ/mol. Subsequently, two competitive decomposition reactions have been modelled, the first, with an activation energy of around 226 kJ/mol and a reaction order of 1.2. The other competitive reaction is of the same nature, but a lower order (0.8). It also has a lower contribution (0.085 as compared to 0.556). The final reaction is also an nth order reaction with a reaction order of 2.3. The high activation energy is coherent with the Friedman activation energy plot (Figure 63, page 197).

In order to visualize our model, a simulated TG curve based on the kinetic parameters in Table 15 was plotted on the same axes as the experimental TG curve. The resulting graph is shown on Figure 65.



Figure 65. Best fit of the TG data for the three-step reaction models in Scheme 11, with the parameters given on Table 14. The curves represent the experimental data and the symbols represent the model.

From a statistical point of view, the experimental curve and the simulated curve had a correlation coefficient of 0.99990.

From Figure 65, we see that the simulated curves are consistent with the experimental ones. Each of the 4 reactions in the kinetic decomposition model have a contribution above 8 %, meaning that they all play a significant role in the thermal decomposition of PEEK under nitrogen. Having modeled the kinetics of the thermal decomposition of PEEK under nitrogen, the method will now be applied to the thermal decomposition of PEEK under 2% oxygen.

IV.1.b. PEEK decomposition under 2% oxygen

In the previous chapter, it was inferred that the first decomposition step was only slightly dependent on the onset of the thermal decomposition temperature of PEEK. However, from the temperature at the onset of the decomposition at a heating rate of 10 °C/min, there was no further evidence to support this hypothesis. Therefore, extracting the kinetic parameters concerning the thermal decomposition of PEEK under a slightly more oxidative atmosphere (2% oxygen) would challenge the hypothesis and can either support or contradict it. To do so, the same method as before was used.

The TGA of PEEK at the same heating rates as before was performed under 2% oxygen. The resulting TG curves and their corresponding DTG curves are shown on Figure 66.



Figure 66. TGA (left) and the corresponding DTG (right) curve of PEEK at 1 (black), 2 (red), 5 (blue), and 10 K/min (magenta), under 2% oxygen

Similarly to the measurements under nitrogen, and not unexpectedly from the previous study on the thermal stability of PEEK, its TG curves under a low level (2%) of oxygen also depict the high stability of PEEK. As expected, the onset of the thermal decomposition temperature increases as the heating rate increases. The onset of decomposition temperatures under low heating rates is lower under 2% oxygen than under nitrogen. In addition, mass loss rate for the first decomposition step is much lower at 1 K/min (0.5 %/°C) as compared to the other heating rates (> 0.8%/°C). On the other hand, the second decomposition step is much higher at low heating rates than at high ones. This suggests that the first step of the decomposition might involve a competitive reaction that occurs faster at high temperatures than lower ones.

The first decomposition step is followed by a second one, whereby the mass loss rate is higher at lower heating rates (except at 1 K/min). This reaction can be assigned at least two

competitive reactions whereby the oxidation of the char coupled with the subsequent pyrolytic decomposition of the initial char that was formed during the first stage of the decomposition. The higher mass loss rate at lower heating rates can be explained by the limited oxygen availability, suggesting that thermal oxidation is a limiting factor at high heating rates.

Similarly, when looking at the DTG curve, it can be confirmed that there are at least 2 steps during the thermal decomposition of PEEK under low oxygen concentration.

The DTG curves of PEEK under 2% oxygen (Figure 66) evidence that there is a definite difference in the mass loss rate when the heating rate is low as compared to higher ones. This suggests that there is a difference in thermal decomposition mechanism at low heating rates. Moreover, the peak mass loss rate for the second decomposition of PEEK decreases with increasing heating rate.

To dig deeper in the kinetics of the thermal decomposition of PEEK under 2% of oxygen, the Friedman analysis corresponding to the aforementioned heating rates was plotted (Figure 67).



Figure 67. Friedman analysis of PEEK using 4 different heating rates under 2% oxygen

From the Friedman analysis (Figure 67) deeper insight concerning the multi-stepped thermal decomposition of PEEK under 2% oxygen was perceived. Indeed, at high heating rates, it

can be observed that the first decomposition reaction corresponds to an accelerated one. This is observed on the slope of the isoconversion lines which is gentler than the first peak slope on the Friedman analyses curves. Two peaks are visible on the Friedman plots at heating rates corresponding to 1 K/min and 2 K/min. The absence of a clear second peak for 5 K/min and 10 K/min on the Friedman plot can be explained by the incompletion of the decomposition at 800 °C.

To further our insight concerning the thermal decomposition of PEEK under 2% oxygen, the activation energy and corresponding pre-exponential factor were plotted, based on the Friedman analysis calculations. The resulting plots are shown on Figure 68.



Figure 68. Activation energy (black) and pre-exponential factor (red) plot for PEEK under 2% oxygen, obtained by Friedman analysis

The activation energy increases in the first part of the conversion and a small shouldering is observed before the subsequent peak at around 800 kJ/mol. This suggests that there are two steps occurring right at the beginning of the decomposition. Moreover, the activation energy for the subsequent decomposition decreases sharply and is even negative. This means that the mass loss rate decreases as the temperature is increased. Indeed, on Figure 66, we can observe that the second decomposition has a higher mass loss rate at lower temperatures at low heating rates as compared to higher heating rates. This suggests that the second decomposition step has a negative dependence on the temperature. From a phenomenological point of view, this can be interpreted as a barrierless reaction step, or as a decomposition reaction that occurs spontaneously. A possible explanation for this barrierless decomposition step can come from the initial decomposition of PEEK. It was observed that the first decomposition step of PEEK is highly exothermic. The heat released during the initial decomposition of the polymer is not taken into account in the equations used to calculate the activation energies. This heat released is enough to start the second step of the decomposition, which is assigned to a thermo-oxidative decomposition step of PEEK. Furthermore, at conversions above 50%, there seems to be a relatively constant activation energy for the decomposition, suggesting that a final step is involved.

Valuable insight concerning the minimum number of steps involved in the thermal decomposition of PEEK under 2% oxygen was brought thanks to the model-free analyses. In order to have a better understanding on the possibility of competitive reactions that can be involved during the thermal decomposition of PEEK, the activation energy plot from the Friedman method was compared with that from the OFW method (Figure 69).



Figure 69. Activation energies calculated using Friedman analysis (black) and the Ozawa-Flynn-Wall method (magenta) under 2% oxygen

By comparing the activation energies from the two model free methods (Figure 69), it is evident that the from 0% conversion to around 50% conversion, the activation energy with respect to the conversion are not the same. This implies that there are competitive reactions occurring during the thermal decomposition of PEEK under 2% oxygen. moreover, the activation energy for is conversion dependent throughout the decomposition.

From the model free analyses, we have seen that the decomposition of PEEK adopts a complex pathway involving both competitive and consecutive reactions. In order to model this, a kinetic pathway was required. Moreover, the thermal decomposition pathway that was elucidated in the previous chapter was required so that a deep understanding of the kinetics of the thermal decomposition of PEEK could be achieved.

A model for the kinetics of the decomposition of PEEK under 2% oxygen is suggested and illustrated in Scheme 12. The details of the model are explained hereafter.



Scheme 12. Kinetic model used to model the thermal decomposition kinetics of PEEK under 2% oxygen

From the thermal decomposition reactions arising during the onset of the decomposition, the first step of the thermal decomposition was one leading to the formation of a carbon monoxide, radical-ended polymer chains as well as a charred graphite-like structure. This reaction was assigned as the first step in the thermal decomposition of PEEK under 2% oxygen. Indeed, it was reported that an increase in oxygen partial pressure (therefore concentration) amplifies the cross-linking phenomenon in PEEK at temperatures between 380 - 440 °C [87]. Moreover, the radical ended polymeric chains can react with the undecomposed polymer to further the decomposition reaction. Therefore, from a reaction kinetics perspective, this step was assigned to an autocatalytic decomposition reaction (step 1.1).

Once the charred structure formed, the presence of oxygen means that it can be thermooxidized. However, since the availability of oxygen is relatively low, the governing mechanism that limits the rate of the reaction is the diffusion of oxygen towards the char. Therefore, the kinetic step following the char formation is assigned to a three-dimensional Jander's type diffusion type (equation 7) [88]. Additionally, further decomposition of the char occurs at higher temperatures, along with thermo-oxidation of the remaining polymeric materials. This decomposition step is assigned as an nth order Arrhenius decomposition model.

Moreover, along with the formation of the charred structure, random scission all over the material was also suggested. These scissions lead to reactive radicals as well as small molecules. The reactive radicals can further react with the remaining polymer chain to further the thermal decomposition of polymeric materials. This behavior is reminiscent of an autocatalytic reaction as the products are taking part in initial reaction. Therefore, an autocatalytic reaction was assigned as a competitive reaction to the above-mentioned decomposition (step 1.2). during this step, the small molecules are thermo-oxidized by the oxygen present in the atmosphere. However, it has little impact on the kinetics of the decomposition of PEEK.

Based on the model decomposition pathway in Scheme 12, the kinetic parameters for the thermal decomposition of PEEK under 2% oxygen were optimized. A summary of the kinetic parameters for each step is given in Table 15.

Step (reaction type)	1.1 (Cn)	1.2 (Cn)	2 (3D-Diff)	3 (Fn)
Ea (kJ/mol)	160	75	122	68
Log(A) (log(1/s)	6.0	0.147	5.2	0.1
Reaction order	2.4	0.4	-	0.11
Kcat	2.7	0.7	-	-
Contribution	0.443	0.184	0.154	0.219

Table 15. Kinetic parameters used in the model for the thermal decomposition of PEEK under 2% oxygen.

In order to visualize our model, a simulated TG curve based on the kinetic parameters in Table 15 was plotted on the same axes as the experimental TG curve. The resulting graph is shown on Figure 70.



Figure 70. Best fit of the TG data for the three-step reaction models in Scheme 12, with the parameters given on. The curves represent the experimental data and the symbols represent the model

From a statistical point of view, the correlation coefficient between the experimental and the simulated curve is 0.99940.

The multi stepped decomposition kinetic pathway is consistent with the thermal decomposition mechanism of PEEK. However, while the presence of oxygen appeared to have only little influence on the thermal stability of PEEK during the previous investigation (chapter III.1.a.ii, page 127), the kinetic analysis has shown that the decomposition pathway is highly affected. The main evidence to this is the competitive reaction in the first step of the thermal decomposition of PEEK under 2% oxygen. This step is assigned to a single decomposition step in the kinetic model for the decomposition pathway of PEEK under nitrogen.

Moreover, the thermal decomposition kinetics of PEEK under 2% oxygen have shown that there can be a major change in the kinetic parameters even in the presence of low oxygen concentrations. Therefore, to go further in the investigation of the thermal stability of PEEK, the kinetics of its thermal decomposition in a more aggressively thermo-oxidative atmosphere (air), has been studied. The approach used unfolds in the following section.

IV.1.c. PEEK decomposition in air

Model free kinetic analysis of the decomposition behavior of PEEK in air has been reported by Vasconcelos *et. Al.* [86] in 2014. However, model free analyses assume that the decomposition is a single step process. It is clear from the TG and DTG curves of PEEK at different heating rates that the decomposition is a multi-stepped one (Figure 71).



Figure 71. TGA (left) and the corresponding DTG (right) curves of PEEK at 1 (black), 2 (red), 5 (blue), and 10 K/min (magenta), in air.

Indeed, at a heating rate of 10 °C/min, a first decomposition step is visible on the TG and DTG curve, corresponding to around 30 % of mass loss. After this, there is a slight stabilization for a few degrees before another sharp mass loss is recorded. This two-step phenomenon is visible on the TG and DTG curves at high heating rates but becomes less discernable at low heating rates. However, on the DTG curves, as compared to the TG curves, the multi-stepped decomposition behavior is clear. A first, minor step at the beginning of the decomposition is observed at 400 °C at 1 °C/min, and at around 500 °C at 10 °C/min. Under heating rates above 2 °C/min, two other major peak mass loss rates are visible. At 1 °C/min, the heating rate overlaps with the second decomposition step. However, a shouldering in the peak mass loss rate indicates that the two reactions are occurring in quick succession.

From the DTG and TG curves of PEEK under the different heating, we can deduce that the thermal decomposition of PEEK in air is underwent via at least three thermal decomposition steps. In order to have a deeper understanding on the nature of the decomposition steps occurring, the Friedman analysis of PEEK based on the TGA above was plotted (Figure 72).



Figure 72. Friedman analysis of PEEK using 4 different heating rates in air

The Friedman analysis (Figure 72) provided information on the different steps that may occur as well as the types of reactions occurring during these steps. The first peak on the right of the graph corresponds to the first decomposition step. When looking at the Friedman plots for heating rates above 1 K/min, two other peaks are visible after this step. This means that there are at least three steps in the kinetic decomposition mechanism of PEEK. The third peak is not clearly visible on the Friedman plot corresponding to 1 K/min because the two peaks are very close to each other and are overlapping, making one large peak. To confirm this, the activation energy plot from the same Friedman plot is shown on Figure 73.



Figure 73. Activation energy (black) and pre-exponential factor (red) plot for PEEK in air, obtained by Friedman analysis

The activation energy plot from the Friedman method (Figure 73) clearly shows that the activation energy is not constant throughout the PEEK's decomposition in air. A first step of the decomposition can be assigned to the beginning onset of the decomposition with an activation energy around 180 kJ/mol (conversion < 10%). After this, another step of decomposition, at about a quarter of the conversion is visible as a shouldering in the activation energy plot and a decrease in the activation energy with respect to the conversion. At 50% of conversion and forth, the activation energy remains relatively constant, suggesting that there is not further decomposition step until the final 10 % of conversion, whereby a small increase of activation energy is observed.

From the Friedman analysis, we can conclude that there are at least three major steps in the kinetics of the thermal decomposition of PEEK in air. However, to find out if there are any competitive reactions occurring during the thermal decomposition of PEEK in air, the activation energy of PEEK from the Friedman and OFW method were plotted on the same plot (Figure 74).



Figure 74. Activation energies calculated using Friedman analysis (black) and the Ozawa-Flynn-Wall method (magenta) in air

The activation energy plot obtained from the Friedman method is very different from that obtained by the OFW method. The major difference comes from the shape of the first and second step, suggesting that there are competitive reaction occurring during the thermal decomposition of PEEK in air from the second step onward. This should be taken into consideration when elaborating the kinetic model.

In order to have a proper kinetic model for the thermal decomposition of PEEK in air, it was essential that it was coherent with the decomposition mechanism of PEEK. We have seen the thermal decomposition of PEEK under inert atmosphere in the previous chapter. The onset of the decomposition was only slightly dependent on the atmosphere it was in. However, the presence of 20% of oxygen seems to have had an effect at low heating rates. Therefore, the model should be adapted so that it fits this difference. The model that was suggested is shown on Scheme 13 and is described hereafter.



Scheme 13. Kinetic model used to model the thermal decomposition kinetics of PEEK in air

Contrarily to the thermal decomposition of PEEK under nitrogen, the first step of the thermal decomposition in air comprises of an additional first step, whereby a small mass loss is recorded. This reaction step has a small contribution to the whole decomposition process but had to be taken into consideration for the kinetic model. This decomposition reaction probably corresponds to the thermo-oxidation of the crosslinked, graphite-like structure formed before any mass loss is recorded [87].

Following this step, a thermal decomposition similar to the thermal decomposition of PEEK under nitrogen was observed on the TG curves. This step was assigned to the formation of the char, which is formed by an autocatalytic reaction phenomenon. This is why an autocatalytic decomposition model was considered for this step. Indeed, the thermal decomposition of PEEK proceeds by random scission of the polymer chain, causing the release of reactive radicals. These radicals can further react with the unreacted polymer chain to further the decomposition process. The order of this reaction was optimized to 0.5, and the autocatalysis order was 1.6. This means that species released during the thermal decomposition play a bigger role in the kinetics of the decomposition than the initial product.

However, the comparison between the activation energy plots from the Friedman analysis and the OFW analysis suggested that there was possibly a competitive reaction occurring at this stage. Indeed, the presence of oxygen can cause the thermo-oxidation of the polymer, independently of the "concentration" of the polymer. On the other hand, the products that are formed after the thermo-oxidative decomposition leads to the formation of reactive species that can further cause the decomposition of the material.. This could also be translated by an autocatalytic effect on this step of the thermal decomposition of PEEK.

The third step of the thermal decomposition also involved competitive reactions (Figure 74). It involves the decomposition of the char that was formed in step two. However, unlike

under nitrogen, it is well known that the thermo-oxidative stability of charred structure is much less than its pyrolytic stability. Therefore, the activation energy for the decomposition of the char was much less. Therefore, two parallel Arrhenius reaction models were used to define the decomposition of the char.

The results of the aforementioned kinetic parameters are detailed in Table 16.

Step (reaction type)	1 (Fn)	2.1 (Cn)	2.2 (Cn)	3.1 (Fn)	3.2 (Fn)
Ea (kJ/mol)	169	110	39.9	100	20
Log(A) (log(1/s)	7.9	3.0	-2.3	3.5	-4.35
Reaction order	0.089	0.5	0.0	0.8	0
Kcat	-	1.6	1.4	-	-
Contribution	0.173	0.386	0.116	0.118	0.207

 Table 16. Kinetic parameters used in the model for the thermal decomposition of PEEK in air
 Image: Composition of PEEK in air

The TG curves from the kinetic parameters above were plotted with those from actual TGA. The resulting graphs are shown on Figure 75.



Figure 75. Best fit of the TG data for the three-step reaction models in Scheme 13, with the parameters given on Table 16. The curves represent the experimental data and the symbols represent the model

From a statistical perspective the correlation between the experimental and the simulated TG curves is 0.99970.

From the decomposition reactions that were used to model the thermal decomposition of PEEK in air, it can be noted that the autocatalytic nature of the first decomposition step is not present. This is explained by a thermo-oxidation reaction whereby the decomposition products do not contribute to further the decomposition. However, the subsequent decomposition reactions both involve an autocatalytic factor, both with non-negligible contributions (> 10 %). This suggests that there are reactive decomposition products that is formed during these reactions. These reactions are reminiscent of the char formation reactions that were attributed for the kinetic model for the thermal decomposition of PEEK under nitrogen. Finally, the last step of the thermal decomposition consists of two competitive reactions with a combined contribution of 0.325. This corresponds to the oxidation of the yet undecomposed char that is formed during the initial decomposition steps.

IV.1.d. Conclusion

The kinetic parameters for the thermal decomposition of PEEK under three different oxygen levels have been calculated. We have seen that the kinetic decomposition pathway adopted by PEEK is very different even in early stages of the decomposition. This means that despite the apparent independence on oxygen concentration that was postulated in the previous chapter (Chapter III.1.a.ii, page 127), the presence of oxygen does have a significant effect on the decomposition of PEEK.

Under nitrogen, the onset of the thermal decomposition is assigned to an autocatalytic decomposition mechanism. This is also the case for the onset of the thermal decomposition under 2% oxygen. However, in this case, oxygen brings about a competitive degradation reaction, also assigned to an autocatalytic decomposition reaction. Finally, under air, the first decomposition step involves another type of reaction. A small mass loss right at the onset of the decomposition suggested that the abundant presence of oxygen favored another initial decomposition. This was assigned to being a typical Arrhenius type decomposition.

The complexity of the subsequent decomposition reactions varied, depending on the atmosphere in which the polymer was. Indeed, the difference in abundance of oxygen gave way to different reaction pathways, whereby thermo-oxidation occurs.

The kinetics of the thermal decomposition of PEEK under different oxygen levels have provided insight on how it may behave under different areas in a fire scenario. A burning material usually undergoes pyrolysis in the absence of oxygen and a material subjected to an incident heat flux in a well-ventilated room under fire undergoes thermo-oxidative decomposition in air. However, in a less ventilated fire scenario, the thermal decomposition of the material occurs in oxygen depletion. Therefore, this investigation allowed for characterization of the kinetics of the thermal decomposition behavior of PEEK in a fire scenario.

In order to further the investigation to other high-performance polymeric materials, the kinetic parameters governing the thermal decomposition of PI was also studied and is discussed in the following section.

IV.2. Thermal Decomposition Kinetics of PI

Similarly to the investigation of the kinetic parameters for the thermal decomposition of PEEK, those of PI were also calculated under the three aforementioned atmospheres. The same strategy as for the investigation concerning PEEK was adopted for PI.

IV.2.a. PI decomposition in nitrogen

The TG curves and their corresponding DTG curves when PI is subjected to four different heating rates under nitrogen are shown on Figure 76.



Figure 76. TGA (left) and the corresponding DTG (right) curve of PI at 1 (black), 2 (red), 5 (blue), and 10 K/min (magenta), under nitrogen.

From the TGA plots of PI (Figure 76), it is clear that PI has a high thermal stability as hardly any mass loss is recorded until almost 500 °C, even under a low heating rate of 1 K/min. The temperature at the onset of the decomposition increases with increasing heating rate. It involves a sharp decomposition step, whereby around 30 wt% of mass loss is observed. This decomposition can be seen as the first peak on the DTG curve. After this peak, the mass loss rate decreases, but only to around 0.5 wt%/°C. this suggests that there is another step involved in the thermal decomposition of PI.

It can be noted that the maximum mass loss rate decreases with increasing heating rate. This suggests that the first decomposition step follows the same kinetic pathway. To further the understanding of the kinetics of the thermal decomposition behavior, the model free analysis (Friedman analysis) was performed on the TGA curves of PI at the different heating rates. The Friedman plot as well as the isoconversion lines corresponding to different conversions are plotted on Figure 77.

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Figure 77. Friedman analysis of PI using 4 different heating rates under nitrogen

From the Friedman analysis (Figure 77), it can be observed that the isoconversion lines to the right of the first peak has a gentler slope than the slope of the peaks. This means that the first decomposition reaction is accelerated. This is often the case in polymeric materials because their decomposition leads to the generation of radicals which are very reactive and contribute to the further decomposition of the material. For this reason, the first step of the thermal decomposition was assigned to an autocatalytic decomposition rate model (equation 6).

Moreover, the activation energy and pre-exponential factor based on the model free Friedman analysis is shown on Figure 78.



Figure 78. Activation energy plot for PI under nitrogen (left), obtained by Friedman analysis

From the two plots on Figure 78, it can be seen that the activation energy and the preexponential factor are relatively constant at the beginning of the decomposition process, until around 60% of conversion. After this, the activation energy increases rapidly from around 300 to around 1400 kJ/mol at 100% conversion. This means that there are at least two steps in the thermal decomposition of PI under nitrogen. Moreover, at around 90% conversion, there seems to be a slight change in the continuity of the curve, suggesting that there might be another step in the decomposition reaction. In order to check whether there are any competitive reactions occurring, the activation energies calculated from an Ozawa-Flynn-Wall curve was plotted on the same axes as the activation energies from the Friedman plot. This graph is shown on Figure 79.



Figure 79. Activation energies calculated using Friedman analysis (black) and the Ozawa-Flynn-Wall method (magenta) for PI under nitrogen

By comparing the evolution of the activation energies calculated from the two aforementioned methods, it can be seen that for the first 50% of the conversion, there is very little difference in activation energy. This means that there are not competitive reactions in the first step of the thermal decomposition. However, at higher conversions, we can see that the activation energies curves do not have the exact same shape, but the values are only slightly different.

From the model free analyses, we have seen that there are at least three steps in the thermal decomposition of PI under nitrogen. Additionally, the comparison of the activation energies from the derivative model free analysis (Friedman) and the integral model free analysis (Ozawa-Flynn-Wall), we have deduced that there are not any competitive reactions occurring during the thermal decomposition. Moreover, it was seen from both the activation energy plots that towards the end of the conversion, the activation energy of the thermal decomposition increases greatly.

These inputs are essential for the elaboration of a kinetic model for the thermal decomposition mechanism of PI. The model that was chosen is illustrated on Scheme 14 and explained in the subsequent paragraphs.



Scheme 14. Kinetic model used to model the thermal decomposition kinetics of PI under nitrogen

Moreover, the mechanism of the thermal decomposition that was detailed in chapter 3, the different reactions occurring during the thermal breakdown of PI under nitrogen is also known. The first step of the decomposition involves the random scission of the polymer chain. This corresponds to the first decomposition step, which is also the main decomposition step of the thermal decomposition. The kinetic model that was used for this step of the decomposition corresponds to an autocatalytic reaction (equation 6). Indeed, the random scission of a polymeric chain leads to the formation of reactive radicals that often take part in the subsequent decomposition of a material.

After the random scission of the polymeric chains, small gases such as ammonia, hydrogen cyanide, and methane were observed thanks to TGA-FTIR. The formation of methane and hydrogen cyanide probably comes from the secondary decomposition of aromatics that are formed during the char formation process. Indeed, at high temperatures, the char continues to strengthen and degrade, releasing hydrogen and low molecular weight products such as methane. This corresponds to part of the second step of the decomposition of PI under nitrogen.

Furthermore, the presence of hydrogen (which is assumed by the presence of methane), means that nitrogen containing moieties may be reduced to ammonia at very high temperatures. This explains the slightly delayed detection of ammonia in the TGA-FTIR, and corresponds to the third step.

Table 17 shows the kinetic parameters that were optimized for the decomposition model.

Step (reaction type)	1 (Cna)	2 (Fn)	3 (Fn)
Ea (kJ/mol)	277.768	369.820	410.149
Log(A) (log(1/s)	14.351	20.459	23.316
Reaction order	3.000	1.593	1.708
Kcat	0.377	-	-
Contribution	0.625	0.188	0.187

Table 17. Kinetic parameters used in the model for the thermal decomposition of PI under nitrogen

The last two steps correspond to extremely high activation energies, which is coherent with both the Friedman and the Ozawa-Flynn-Wall methods. However, the exact reactions occurring at such high temperatures are unknown. This is because the exact structure of the char formed during the initial decomposition is not perfectly known. However, we can safely mention that the 3-step reaction is coherent with the release of the decomposition products that were identified.

The first step of the decomposition was assigned to an autocatalytic decomposition, with an activation energy around 278 kJ/mol, a reaction order of 3.00 and an autocatalytic order of 0.377. This activation energy is coherent with the Friedman analysis Figure 78. The two subsequent reactions were modeled as Arrhenius reactions, with activation energies of 370 and 410 kJ/mol respectively. This corresponds to the high activation energy seen for the decomposition at conversions superior to 60%. These two reactions correspond to the slow decomposition of the char formed during the first step of the decomposition and each share around 20% of contribution to the whole mechanism.

Moreover, from Table 17, it can be seen that the first decomposition step, which corresponds to the autocatalytic step, is the one that has the highest contribution. The other two steps are also kinetically significant, with contributions of around 19 %

From the kinetic parameters in Table 17, the best fit model of mass loss with temperature was plotted along with the experimental TGA curves. The resulting graph is shown on Figure 80.



Figure 80. Best fit of the TG data for the three-step reaction models in Scheme 14, with the parameters given on Scheme 14. The curves represent the experimental data and the symbols represent the model

From the model that was adopted, the major decomposition reaction corresponds to the first step, with a contribution of 62.5 % in the model. However, the subsequent steps have a non-negligible contribution (18.8 %) to the model. This means that the char decomposition plays a major role in the thermal decomposition model of PI. Moreover, from a statistical point of view, the correlation coefficient of the model with respect to the experimental data was 0.99964.

Having the kinetics of the decomposition of PI under nitrogen in hand, our interest went to the effect that oxygen may have on kinetics of the thermal decomposition of PI. Therefore, the thermal behavior of PI under 2% oxygen was studied and is detailed in the next section.

IV.2.b. PI decomposition in 2% oxygen

The kinetic parameters of the thermal decomposition of PI under nitrogen have provided input on the kinetics of the pyrolysis of PI. However, under a fire scenario, the supply of oxygen can quickly become limited. Therefore, it is essential to understand the kinetics of the thermal decomposition of PI under low oxygen levels so as to simulate its decomposition pattern under the aforementioned fire scenario.

To do that, dynamic TGA was performed on PI at low oxygen levels at different heating rates. The resulting TG curves and their corresponding DTG curves of PI under 2% oxygen are shown on Figure 81.



Figure 81. TGA (left) and the corresponding DTG (right) curve of PI at 1 (black), 2 (red), 5 (blue), and 10 K/min (magenta), under 2% oxygen

Quite expectedly and similarly to the initial investigation of PI under different oxygen levels, PI remains stable up to a relatively high temperature of around 450 °C even at a heating rate of 1 K/min. From the TG curves it appears that there is only one decomposition step in the thermal decomposition of PI under 2% oxygen. Nevertheless, when looking at the DTG curves for heating rates corresponding to 2, 5, and 10 K/min, there seems to be at least two peaks for the thermal decomposition of PI. The absence of a visible second peak at the heating rate of 1K/min is assigned to the two decomposition steps occurring at similar temperature ranges.

Therefore, from the TGA and DTG curves, we can deduce that the thermal decomposition mechanism of PI is at least a two-step process. To confirm this, Friedman analysis was performed on the data from the above TG curves. The resulting plot is shown in Figure 82.

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Figure 82. Friedman analysis of PI using 4 different heating rates under 2% oxygen

The Friedman plot shows a small peak at the beginning of the decomposition, followed by another at around 50% conversion. Finally, another decomposition step is visible towards 100% conversion. This peak is not visible in the Friedman plot at 10 K/min. This may be because at the maximum temperature of the TG experiment, the mass loss was not total, suggesting that the reaction had not reached its completion. From these plots, we can deduce that there are at least three steps involved in the thermal decomposition of PI under 2% oxygen.

From this Friedman plot, the activation energies as well as the pre-exponential factor for the decomposition of PI was plotted with respect to the conversion (Figure 83). This is essential to obtain initial parameters for the modeling of the thermal decomposition of PI.



Figure 83. Activation energy plot for PI under 2% oxygen, obtained by Friedman analysis

From the activation energy plot based upon the Friedman analysis, it can be seen that at low conversion, the activation energy is relatively high (around 350 kJ/mol). This corresponds to the first step of the decomposition. However, as the material decomposes further, the activation energy decreases rapidly and is dependent on the conversion degree. This is assigned to the second step of the thermal decomposition. At conversions above 70%, the activation energy is still dependent on the conversion, but unlike the previous step, it seems to increase slightly. This is assigned to the third step of the decomposition.

Based on the two Friedman analysis plots, we have seen that the thermal decomposition of PI under 2% oxygen corresponds to at least three steps of decomposition. In order to have insight concerning eventual competitive reactions that might be occurring during the decomposition of PI, the activation energy based on calculations using Friedman analysis was compared to that based on the OFW method (Figure 84). Because of the difference in the approach for the two similar methods, the occurrence of competitive reactions is translated by a difference in activation energy for the same conversion.



Figure 84. Activation energies calculated using Friedman analysis (black) and the Ozawa-Flynn-Wall method (magenta) for PI under 2% oxygen

From the two activation energy plots, it can be seen that the global shapes of the two activation energy plots are relatively similar. Indeed, the activation energy increases for early conversions and then decreases. There is a slight difference in the activation energy for the first step of decomposition. However, the error is significant for the first step of the decomposition. It is therefore hard to conclude whether the competitive step occurs during the first step or later. As a result, the kinetic decomposition model was based on the understanding of chemical reactions occurring at the onset of the decomposition.

The model free analyses have provided insight on the number of steps that are involved in the thermal decomposition of PI. Using knowledge acquired from the thermal decomposition of PI in the previous chapter, a kinetic model for the thermal decomposition of PI under 2% oxygen is suggested (Scheme 15).


Scheme 15. Kinetic model used to model the thermal decomposition kinetics of PI under 2% oxygen

Similarly to the decomposition of PI under nitrogen, a three-step pathway was used to model the thermal decomposition of PI under 2% oxygen. However, in order to involve the thermo-oxidation reactions in the model, a supplementary step was required. From the TGA of PI under varying oxygen concentrations (chapter 3), it was seen that oxygen intervenes right at the start of the decomposition. Therefore, the thermo-oxidation step was added as a competitive reaction at the very first step of the decomposition model (step 1.2).

The optimized kinetic parameters for the thermal decomposition of PI under 2% oxygen are summarized in Table 18.

Step (reaction type)	1.1 (Fn)	1.2 (Fn)	2 (Cn)	3 (Fn)
Ea (kJ/mol)	349	353	62	99
Log(A) (log(1/s)	18.2	17.3	0.1	2.3
Reaction order	1.8	1.1	0.52	0.01
Kcat	-	-	1.69	-
Contribution	0.192	0.290	0.296	0.222

Table 18. Kinetic parameters used in the model for the thermal decomposition of PI under 2 % oxygen

The optimized parameters for the kinetic model fit well with the experimental TG curves (Figure 85). The activation energy for the two competitive reactions at the beginning of the reaction are of the same order of magnitude. One of the two reactions from the first step of the decomposition is assigned to the thermal decomposition of PI, while the other one is assigned to the thermo-oxidation of the polymer backbone.

Since thermo-oxidation usually results in the formation of carbon dioxide, carbon monoxide and water, no subsequent reaction is assigned after the reaction corresponding to the thermooxidation of the polymer backbone.

The second step is assigned to the subsequent thermal decomposition of the decomposition products formed during the initial thermal decomposition. Indeed, from the previous chapter, we have seen that the first decomposition of PI may lead to the formation of a char, or another crosslinked structure.

The formation of this structure is aided by the presence of radicals resulting from the initial decomposition reactions (step 1.1). Moreover, this structure may further thermally decompose into smaller structures. This leads to the formation of more radicals that can in turn participate in furthering the decomposition. Therefore, the second step of the decomposition of PI was assigned to an autocatalytic reaction type. This step has a relatively low activation energy because of the presence of radicals that are still lingering around the polymer after the first decomposition step.

The last reaction step corresponds to the thermo-oxidation of the remaining organic material and carbonaceous char.



Figure 85. Best fit of the TG data for the three-step reaction models in Scheme 15, with the parameters given on Table 18. The curves represent the experimental data and the symbols represent the model.

When comparing with the decomposition model under nitrogen, an additional competitive decomposition reaction is observed in the first step of the thermal decomposition model of PI under low oxygen concentration. This is because thermo-oxidation occurs right at the

beginning of the decomposition of PI, parallelly to pyrolytic decomposition. It is interesting to note that these two initial decomposition reactions have a significant contribution to the decomposition. Indeed, about 50 % of the model is assigned to the two initial steps. The other decomposition steps correspond to the char degradation and oxidation. Moreover, from a statistical point of view, the correlation coefficient between the experimental curve and the simulated curve based on the kinetic model is 0.99949., meaning that the model used to simulate the thermal decomposition of PI under 2% oxygen is consistent with the experimental TG curves.

To complete the investigation of the kinetics of the thermal decomposition of PI under different oxygen concentrations, the behavior of PI in air was also investigated.

IV.2.c. PI decomposition in air

After having investigated the thermal decomposition behavior of PI under low oxygen concentrations the kinetic of the thermal decomposition of PI in air was studied so that the effect of a highly thermo-oxidative atmosphere can be better understood. This also allows for the simulation of the degradation behavior when the material is subjected to heat in a well-ventilated environment. The presence of oxygen in air usually increases the extent to which a material decomposes when under thermal stress. Sometimes, oxygen can have a catalytic effect on the onset of the decomposition of a material.

Dynamic thermogravimetry was used to investigate the kinetics of the thermal decomposition behavior of PI in air. The TG curves of PI and their corresponding DTG curves at four different heating rates are shown on Figure 86.



Figure 86. TGA (left) and the corresponding DTG (right) curve of PI at 1 (black), 2 (red), 5 (blue), and 10 K/min (magenta), in air.

From the TG curves of PI in air, it can be seen that the thermal stability of PI is maintained until around 450 °C, whereby the onset of thermal decomposition is observed at the beginning of a mass loss process. The TG curves all appear to follow a single step. However, on the DTG curves, at high heating rates, a second peak, which is close to the first, is noticeable. This means that the kinetics of the thermal decomposition of PI in air occurs in at least two steps. In order to obtain further information regarding the number of steps and the types of reactions occurring during the thermo-oxidative decomposition of PI in air, the Friedman plot for the corresponding heating rates was plotted (Figure 87).



Figure 87. Friedman analysis of PI using 4 different heating rates in air

From the Friedman plot, an accelerated decomposition step can be distinguished as a first peak. The peak slope is steeper than the isoconversion lines. This suggests that the first decomposition step is accelerated, probably autocatalytic, as it was the case for the previous polymeric material studied. At higher heating rates (5 and 10 K/min) there seems to be another peak that is visible right after the first one. This confirms that there are at least two steps in the thermal decomposition of PI in air. it is therefore likely that at low heating rates, the two thermal decomposition steps are overlapping.

In order to see any eventual reactions that may be occurring during the thermo-oxidative decomposition of PI, the activation energy and log(pre-exponential factor) (calculated from the Friedman analysis), was plotted with respect to the conversion (Figure 88).



Figure 88. Activation energy plot for PI in air, obtained by Friedman analysis

The activation energy at the start of the conversion is relatively high at the beginning of the conversion (around 190 kJ/mol). It decreases until around 60% conversion where the activation energy is at around 130 kJ/mol. This means that there is another step in the decomposition of PI. At this point, and until almost 98 % conversion, there is little evolution in the activation energy. At 100% conversion, there is a high increase in activation energy. However, the error at this conversion is very high, therefore, it was not taken into consideration as a subsequent decomposition step.

The activation energy plot based on the Friedman method provided out the number of consecutive steps occurring during the thermo-oxidative decomposition of the material. To further the understanding of decomposition in terms of competitive reactions that may occur, the activation energy plot based on the Friedman method was compared with that based on the OFW method (Figure 89).



Figure 89. Activation energies calculated using Friedman analysis (black) and the Ozawa-Flynn-Wall method (magenta) for PI in air.

From the two activation energy plots on Figure 89, it can be seen that the two methods lead to very different activation energies in at around 50% conversion. This strongly suggests that there are competitive reactions occurring during the thermal decomposition of PI in air. It was therefore considered when elaborating the kinetic model for the thermo-oxidative decomposition of PI.

Based on knowledge acquired during the investigation of the thermal stability of PI and its thermal decomposition mechanism under nitrogen, we were able to take an attempt at defining a kinetic model for the thermo-oxidative decomposition of PI in air. The model is shown on Scheme 16.



Scheme 16. Kinetic model used to model the thermal decomposition kinetics of PI in air.

From Scheme 16, two major consecutive decomposition steps are illustrated. The first corresponds to the initial decomposition of PI, similarly to the thermal decomposition of PI

under nitrogen. It corresponds to the random scission of the polymer backbone. However, in the previous chapter, it was seen that the presence of oxygen tends to slightly decrease the thermal stability of PI at high temperatures. This translates into a lower activation energy for the onset of the decomposition. Additionally, the initial decomposition leads to the formation of reactive radicals which can take part in the scission of the initial polymer. This effect can be assigned to an autocatalytic type of decomposition reaction whereby the products increase the rate of the decomposition. During this step, rearrangement of the polymer backbone to form a crosslinked char structure was also hypothesized under nitrogen. This char is highly stable under inert atmosphere, but not under oxygen. This was evidenced by the TGA under different oxygen levels, whereby the second decomposition of PI was largely affected by the presence of oxygen.

It was therefore not unexpected to add a step whereby the thermo-oxidative reactions are occurring. This corresponds to step 2.2, which is assigned to an Arrhenius type reaction. Furthermore, while the material is being thermo-oxidized, there are also thermal decomposition that is on-going, via a similar mechanism as the first step. However, the initial structure of the polymer has changed, and so have the kinetic parameters for the decomposition step. Therefore, an autocatalytic type decomposition mechanism was assigned to this step.

The optimized kinetic parameters used in for the modeling of the thermal decomposition of PI in air are summarized in Table 19.

Step (reaction type)	1 (Cna)	2.1 (Cna)	2.2 (Fn)
Ea (kJ/mol)	181	122	112
Log(A) (log(1/s)	7.9	4.2	2.9
Reaction order	0.41	1.24	0.06
Kcat	0.73	0.97	-
Contribution	0.166	0.291	0.543

Table 19. Kinetic parameters used in the model for the thermal decomposition of PI in air

The activation energy for the first decomposition step is coherent with the activation energy calculated using the Friedman analysis for the first step (Figure 88). This first step of thermal

decomposition formed a charred structure and possibly a partially decomposed form of the polymer. Further thermal decomposition of this structure is modeled by reaction 2.1. This was assigned to a similar reaction as the first decomposition step. However, since the chains have already partially been broken, the activation energy is lower. Moreover, in the presence of air, the structure undergoes thermo-oxidation (modeled by reaction 2.2).

The simulated TG curves based on the kinetic model above as well as the experimental TG curves are shown on Figure 90.



Figure 90. Best fit of the TG data for the three-step reaction models in Scheme 16, with the parameters given on Table 19. The curves represent the experimental data and the symbols represent the model.

Contrarily to the kinetic model of the thermal decomposition of PI under 2% oxygen, the model in air does not have competitive reactions in the initial decomposition step. However, the autocatalytic nature of the reaction model suggests that there are reactive decomposition products that are released during that step, leading to the formation of a char as well as releasing oxidation products. Moreover, the other two decomposition reactions have been assigned to two thermo-oxidation reactions, each with a significant contribution as compared to the first step of the decomposition. Indeed, the decomposition of the char (step 2.2) and the further thermo-oxidation of the polymer (step 2.1) play a bigger role in the thermal decomposition than the initial char formation reaction (step 1). It is interesting to note that the thermo-oxidation of the char corresponds to a low order kinetic reaction model (reaction order = 0.06). This means that it is only slightly dependent on the "concentration" of the reactants.

The fitted curve seems to correspond well with the experimental curve. From a statistical point of view, the correlation coefficient between the experimental and the simulated curve is 0.99993.

IV.2.d. Conclusion

The kinetic parameters for the thermal decomposition of PI under three different oxygen levels have been calculated. We have seen that, from a kinetic perspective, the decomposition pathway adopted by PI during its thermal decomposition is significantly dependent on the oxygen concentration.

Under nitrogen, the kinetic pathway adopted during its thermal decomposition is relatively simple. However, the presence of a small amount of oxygen brings about a significant change in kinetic pathway adopted by the material during its thermal decomposition. Indeed, in the presence of a small concentration of oxygen, the decomposition pathway is much complexified, leading to a 3-step decomposition involving a competitive reaction at the initial decomposition step. Moreover, it was reported that the presence of oxygen increases the crosslinking that occurs in a material [87]. While this remark was justified for PEEK, extrapolating it to another highly charring polymer such as PI implies that a similar behavior may be expected. Therefore, a higher activation energy is observed for the thermal decomposition of PI under low oxygen concentration because a high crosslinking would have had occurred during the initial cross-linking reactions.

Under air, the activation energy for the onset of the decomposition is lower than under pyrolytic conditions. This is because the decomposition gases that are produced at the beginning of the decomposition are readily oxidized. A fast consumption of the decomposition gases pulls the kinetics towards the further decomposition of the material.

We have seen that from a kinetics perspective, the pathway adopted by PI during its thermal decomposition is highly dependent on the oxygen concentration. We have seen that low oxygen concentration leads to a higher crosslinking, leading to an increase in the activation energy of the onset of decomposition, but that in air, the crosslinking is taken over (for the most part), by thermo-oxidation. The difference in the kinetics of the thermal decomposition of PI has provided deep insight on the eventual behavior of the material under a fire scenario.

To further the understanding of the thermal decomposition kinetics of high-performance materials, those of a third high performance polymer: polybenzoxazole, were studied under the same conditions.

IV.3. Thermal decomposition of PBO

Having characterized the thermal decomposition kinetics of the two other polymeric materials, our attention was then focused on the characterization of kinetic parameters that govern the thermal decomposition of PBO under the different atmospheres aforementioned.

IV.3.a. PBO decomposition under nitrogen

As with the previous polymers, the first atmosphere in which the thermal decomposition of PBO was studied was nitrogen. The TGA and DTG plots corresponding to the four heating rates used for the calculation of the kinetic parameters of the thermal decomposition of PBO under nitrogen are shown on Figure 91.



Figure 91. TGA (left) and the corresponding DTG (right) curve of PBO at 1 (black), 2 (red), 5 (blue), and 10 K/min (magenta), under nitrogen

The exceptional thermal stability is once again appreciable from its TGA plots under nitrogen on Figure 91. There is no mass loss recorded until 600 °C at a heating rate of 1 K/min. The onset of thermal decomposition is higher as the heating rate increases, suggesting a positive activation energy. From the TGA plot, the first decomposition step appears to occur in one single step corresponding to a mass loss of around 30 wt%. Moreover, the DTG curve shows that the mass loss rate at high temperatures is not zero, meaning that there is at least one other step in the thermal decomposition of PBO under nitrogen.

The DTG of PBO share the same shape. The slight shift towards higher temperature of the peak of mass loss rate is also visible on the DTG curves. The mass loss rate is slightly lower as the heating rate increases.





Figure 92. Friedman analysis of PBO using 4 different heating rates under nitrogen

From the Friedman plot, only one decomposition can be seen. The isoconversion lines to the right of the peak have a slope that is close to that of the peak slope. This means that there is no acceleration or inhibition in the decomposition behavior of PBO under nitrogen. This is impressive given that usually, polymeric materials release reactive radicals that promotes further decomposition of the polymeric chains. Moreover, we know from the DTG curve (Figure 91) that there is at least a second step involved in the thermal decomposition of PBO under nitrogen. However, seeing as the DTG is relatively low at such a high temperature, it is likely that the activation energy was also very high for the eventual steps of the decomposition. To confirm this, the activation energy and the pre-exponential factor was plotted on the same graph (Figure 93).



Figure 93. Activation energy plot for PBO under nitrogen (left), obtained by Friedman analysis

From the activation energy curve shows that the thermal decomposition of PBO occurs with a relatively constant activation energy for the first 75% of the conversion. After that, the activation energy of the decomposition depends on the degree of conversion. Indeed, as the conversion nears 100%, the activation energy increases relatively quickly. This suggests that there is a second decomposition step in the kinetic mechanism of the thermal decomposition of PBO under nitrogen. To investigate eventual competitive reactions, the Friedman activation energy plot was compared with the Ozawa-Flynn-Wall activation energy plot (Figure 94)



Figure 94. Activation energies calculated using Friedman analysis (black) and the Ozawa-Flynn-Wall method (magenta) for PBO under nitrogen

The activation energies calculated using the Ozawa-Flynn-Wall method is very close to those calculated using the Friedman method. This means that it is unlikely that there are competitive reactions occurring during the initial steps of the thermal decomposition of PBO under nitrogen. A small difference in activation energy is visible towards 90% conversion, which could mean that there are competitive reactions at the end of the decomposition. However, the difference being still very small, and in order to have a minimum number of steps for a well fitted kinetic simulation, we did not involve any competitive reaction in the thermal decomposition of PBO under nitrogen.

The model that was used for the kinetic modeling of the thermal decomposition of PBO under nitrogen is shown on Scheme 17.



Scheme 17. Kinetic model used to model the thermal decomposition kinetics of PBO under nitrogen

From the thermal decomposition studies performed previously, it was seen that at the beginning of the decomposition, the major products that were generated during the early to mid-stage of the thermal decomposition of PBO under nitrogen corresponds to carbon dioxide and carbon monoxide. This was assigned to the random scission of the polymer chain. The formation of CO_2 was followed by a cross-linking reaction. However, it is unlikely that the cross-linking reaction is a kinetically significant one as compared to the random scission of the material. Additionally, the high remaining mass at 800 °C under inert atmosphere means that there is a large portion of the decomposition mechanism that is dedicated to the formation of PBO participate predominantly towards the formation of the char rather than subsequent chain stripping.

Furthermore, from the TGA-FTIR experiment that was performed on PBO under nitrogen, the generation of hydrogen cyanide, methane, and ammonia were observed at high temperatures. These small volatiles are reminiscent of the thermal decomposition of polyimide, whereby the charred structure formed during the first step of the degradation was further decomposed with the release of the same small molecules. This step of decomposition of the char was assigned a relatively high activation energy because it involved the release of small molecules from an already stable char.

Somewhat similarly to the final decomposition step of PI, the second decomposition step of PBO was assigned to the decomposition of the char, which releases the aforementioned gases. This step is a kinetically significant one as it was seen on the TGA and DTG curves (Figure 92) that a relatively low mass loss rate is observed despite being at high temperature (> 750 °C). Therefore, the second step of the thermal decomposition of PBO was assigned to a nth order Arrhenius equation (step 2, Scheme 17).

The kinetic parameters that were used for the kinetic model of the decomposition of PBO are reported in Table 20.

Step (reaction type)	1 (Fn)	2. (Fn)
Ea (kJ/mol)	280	519
Log(A) (log(1/s)	12	25.4
Reaction order	0.919	3.000
Contribution	0.49	0.51

Table 20. Kinetic parameters used in the model for the thermal decomposition of PBO under nitrogen

The activation energy used for the first step of the decomposition was 280 kJ/mol, which is close to the activation energy calculated using the Friedman analysis. Similarly, the pre-exponential factor for the first step of the thermal decomposition of $10^{12.3}$ is close to the one calculated Friedman analysis (10^{13}). Moreover, the activation energy rises quickly at towards the end of the conversion, which explains the high activation energy and pre-exponential factor for the second decomposition reaction.

The kinetic parameters from Table 20 allowed use to plot a best fit model TG. This is shown on Figure 95 along with the experimental TG curves.



Figure 95 Best fit of the TG data for the three-step reaction models in Scheme 17 with the parameters given on Table 20. The curves represent the experimental data and the symbols represent the model

The two stepped kinetic model that was used to simulate the thermal decomposition of PBO under nitrogen had relatively high activation energies. This explains its unusually high thermal stability. Moreover, the simulated TG models correspond closely to the experimental curves. Indeed, from a statistical point of view, a coefficient of correlation of 0.99950 is obtained between the simulated TG curves and the experimental ones. moreover, it is interesting to note that the first and second decomposition steps both have around 50 % contribution to the decomposition model. This means the decomposition of the char (second) step, is as significant a step for the thermal decomposition PBO as

IV.3.b. PBO decomposition under 2% oxygen

Similarly to the two previous polymeric materials, the kinetic parameters for the thermal decomposition of PBO under a low oxygen concentration (2%) was investigated. To do so, dynamic TGA was performed with PBO. The TG curves and their corresponding DTG curves are shown on Figure 96.



Figure 96. TGA (left) and the corresponding DTG (right) curve of PBO at 1 K/min (black), 2 K/min (red), 5 K/min (blue), and 10 K/min (magenta), under 2% oxygen

PBO is stable until around 550 °C whatever the heating rate used. Expectedly, the temperature at the onset of the thermal decomposition of PBO is higher when it is subjected to higher heating rates. From the TG curves, the thermal decomposition appears to occur in one step. At high heating rates (5 and 10 K/min), the decomposition is not total. This is clearly visible on the TG curves, whereby the residual mass at 800 °C is much higher than zero.

The DTG curve when PBO is heated at 1 K/min has only one peak. However, as the heating rate is increased, another peak is seen at higher temperature. This suggests that the decomposition of PEEK under 2% oxygen is at least a two-step process. The absence of the second peak at 1 K/min is assigned the two peaks overlapping each other.

In order to confirm this, the Friedman analysis of PBO under 2% oxygen was made for the different heating rates above (Figure 97).



Figure 97. Friedman analysis of PBO using 4 different heating rates under 2% oxygen

The isoconversion lines on the Friedman plot are slightly gentler than the first peak slope. This suggests that the first decomposition reaction is slightly accelerated. The isoconversion line at 98 % of the decomposition suggests that there is another step in the thermal decomposition of PBO under 2% oxygen. This is even more clearly visible on the activation energy plot which is shown on Figure 98.



Figure 98. Activation energy plot for PBO under 2% oxygen (left), obtained by Friedman analysis

The activation energy of the thermal decomposition of PBO under 2% oxygen is relatively constant until around 75 % of conversion. At higher conversions, the activation energy seems to increase sharply until the whole decomposition. This suggests that at least two steps are involved in the decomposition of PBO.

To identify the involvement of competitive reactions, the activation energy plot based on the Friedman method was compared with that based on the OFW method Figure 99. A slight difference in activation energy is observed at high conversions. However, it is not sufficient to suggest that there are competitive reactions occurring.



Figure 99. Activation energies calculated using Friedman analysis (black) and the Ozawa-Flynn-Wall method (magenta) for PBO under 2% oxygen

The model free analyses have allowed us to deduce that the thermal decomposition of PBO under 2% of oxygen involves two steps. We also acquired information regarding the occurrence of competitive reactions: there are not any. From these deductions, the pathway for the decomposition (summarized Scheme 18) comprises of two successive steps.



Scheme 18. Kinetic model used to model the thermal decomposition kinetics of PBO in 2% oxygen

From the thermal stability studies in the previous chapter, we have seen that oxygen plays a major role on temperature at the onset of the decomposition of PBO. It was suggested that oxygen has a catalytic role in the thermal decomposition of PBO. The first step of the thermal decomposition of PBO was attributed to the formation of a char. However, in the presence of oxygen, this char formation occurs at a much higher rate, and probably under a different mechanistic pathway promoted by oxygen.

Moreover, the cleavage of polymer chains leads to reactive radicals that can further react with other polymeric chains. Therefore, from a kinetics point of view, the first step of the decomposition of PBO under 2% of oxygen was attributed to an autocatalysis mechanism whereby the concentration of products plays a role in the decomposition mechanism.

The second step of the decomposition is attributed to the thermo-oxidation of the char that is formed. The carbonaceous structure formed during the first step of the decomposition is thermo-oxidized at high temperatures. This type of reaction is usually independent on the products formed (usually carbon dioxide, carbon monoxide, and water). Therefore, an Arrhenius type reaction was attributed to this step in the kinetic model.

The parameters used for the optimized modeling of the thermal decomposition of PBO under 2% oxygen is shown in Table 21.

Step (reaction type)	1 (Cna)	2 (Fn)
Ea (kJ/mol)	187	149
Log(A) (log(1/s)	8.0	5.4
Reaction order	1.1	2.4
Kcat	0.3	-
Contribution	0.115	0.885

Table 21. Kinetio	c parameters used	in the	model	for the	thermal	decomposition	of PBO	under 2	2% с	oxygen
	<i>P</i>			J		The second secon	-J			

The autocatalytic reaction (Cn-type) representing the first step of the thermal decomposition of PBO under 2% oxygen has an activation energy of 187 kJ/mol and a pre-exponential factor of $10^{8.1}$. These values are consistent with the model free analyses, whereby the first step of the thermal decomposition is usually the only one taken into consideration.

The second decomposition step corresponds to the oxidative thermal decomposition of the char formed in the first step. It is also likely that this step also involves the thermo-oxidation of some undecomposed polymer as well. The reaction was of order 2.4 and was attributed an activation energy of 149 kJ/mol and a preexponential factor of $10^{5.4}$ s⁻¹. Figure 100 shows the experimental curves as well as the simulated ones based on the data from Table 21.



Figure 100. Best fit of the TG data for the three-step reaction models in Scheme 18, with the parameters given on Table 21. The curves represent the experimental data and the symbols represent the model.

The kinetic model for the thermal decomposition of PBO under 2% has the same number of steps as for the model for the decomposition under nitrogen. The first difference lies in the autocatalytic nature and the activation energy for the first step of the decomposition leading to the char. This explains the lower decomposition temperature of the polymer in the presence of oxygen and the catalytic nature of oxygen in the decomposition. Similarly, the second decomposition step, which involves the thermo-oxidation of the char, has a much lower activation energy as compared to the second decomposition reaction under nitrogen. Moreover, it is interesting to note that the second decomposition reaction has a much higher contribution in the model, which has a more than acceptable fit with the experimental results. Indeed, from a statistical point of view, the correlation coefficient between the experimental curve and the model was 0.99983.

After having modelled the thermal decomposition of PBO under low oxygen concentration, the kinetics of its decomposition under air was also studied.

IV.3.c. PBO decomposition in air

The investigation of kinetic parameters for the thermal decomposition of PBO in air proceeded in the same manner as the previous ones. The TGA curves of PBO and their corresponding DTG curves are shown on Figure 101.



Figure 101. TGA (left) and the corresponding DTG (right) curve of PBO at 1 (black), 2 (red), 5 (blue), and 10 K/min (magenta), in air

The TG curves of PBO in air show that the material is stable until around 500 °C. At higher temperatures, a first mass loss step is visible. This mass loss corresponds to the first decomposition step of the material. At 1 K/min and 2 K/min, the first step can be clearly distinguished from the second one. There is a relatively abrupt change in the slope of both TG curves. At higher heating rates, the distinction is less easily made. This means that there are at least two steps in the thermal decomposition of PBO in air.

The DTG curves, on the other hand, tell another story. The first decomposition step is clearly visible as the peak with the highest mass loss rate on the DTG curves. At low heating rates, the second step is visible as a small, relatively constant mass loss rate at high temperatures. However, at higher heating rates (5 and 10 K/min), a third peak can be seen as a shouldering of the first major decomposition peak. This suggests that there is another step involved during the first mass loss process seen on the TG curves.

To further the understanding on the number of steps and the types of reactions that take place during the thermal decomposition of PBO in air, the Friedman plot corresponding to the different heating rates used for the TG analyses are shown on Figure 102.





Figure 102. Friedman analysis of PBO using 4 different heating rates in air

From the Friedman analysis, three steps can be deduced, corresponding to three different activation energies. The slope of the first peak (on the right) has a steeper slope than the isoconversion lines on it. This suggests that the first decomposition reaction is an accelerated one. It is likely that, from a kinetic modeling point of view, that it corresponds to an autocatalytic reaction. A small shouldering of the Friedman curve is discernable at high heating rates, suggesting that there is a second decomposition reaction. However, due to its proximity with the first decomposition, further information cannot be extracted from it. The isoconversion lines at high conversions suggest that there is another thermal decomposition reaction occurring at high temperatures. To confirm these hypotheses, the activation energy plot from these Friedman plots need to be analyzed (Figure 103)



Figure 103. Activation energy plot for PBO in air, obtained by Friedman analysis

From the activation energy plots based on Friedman analysis (Figure 103), it can be observed that the activation energy for the thermal decomposition of PBO in air is strongly dependent on the conversion. This suggests that the decomposition is relatively complex. However, we can see that there is a first activation energy that is relatively constant at low conversion degrees. After that, two small peaks are observed at 40% and 70% conversion. This suggests another step of decomposition. Finally, at high conversion (> 75%), the activation energy increases again, meaning that there is another step involved.

From the Friedman analysis, we have seen that there are at least three steps involved in the thermal decomposition of PBO in air. To further the understanding of the nature of these steps, the activation energy plot based on the Friedman analysis was plotted with the one based on the OFW analysis. The graph corresponding to the two plots are shown on Figure 104.



Figure 104. Activation energies calculated using Friedman analysis (black) and the Ozawa-Flynn-Wall method (magenta) for PBO in air

A difference in the activation energy from the two methods would suggest that there are competitive reactions occurring during the thermal decomposition. From Figure 104, it is clear that there are competitive reactions occurring as the shapes of the activation energy plots are very different from each other.

This input is invaluable for the development of the kinetic model for the thermal decomposition of PBO in air. However, in order to bring some physical sense into the mathematical equations, we need to go deeper into the investigation of the physico-chemical behavior of PBO under pyrolysis and relate it to what we have deduced from the aforementioned comments. The decomposition pathway that was chosen to model the kinetic parameters for the thermal decomposition of PBO in air is shown on Scheme 19.



Scheme 19. Kinetic model used to model the thermal decomposition kinetics of PBO in air

The thermal decomposition of PBO was studied in the previous chapter. It was deduced that oxygen may have a catalytic effect on the onset of the thermal decomposition of PBO. Therefore, similarly to the decomposition of PBO under low oxygen concentration, the first step of the for the kinetics of the thermal decomposition was assigned to an autocatalytic decomposition reaction whereby the benzoxazole rings are opened.

Moreover, it is also highly probable that the random scission of the polymer occurs during the decomposition of PBO. Contrarily to the thermal decomposition of PBO under nitrogen, the presence of oxygen hinders cross-linking reactions by reacting with some of the radicals formed during the thermal decomposition. This leads to the formation of highly reactive radicals, which can further react with the undecomposed polymeric chains. Therefore, the subsequent reaction is attributed to be of autocatalytic nature.

Moreover, from the OFW and the Friedman activation energy plots we have seen that there it is highly probable that competitive reactions are involved in the thermal decomposition of PBO in air. The last step of the thermal decomposition is therefore assigned to be two decomposition reactions occurring competitively. Indeed, after the first decomposition steps, it is likely that there are different types of reactions that may be occurring. The first being the simple thermo-oxidation of the charred structure formed after the first decomposition step. the other step corresponds to the further decomposition of the remaining chains, leading to reactive species, thus furthering the decomposition reaction. The thermooxidation reaction at high temperature is assigned to an Arrhenius type reaction (Fn), and the further scission of polymeric chains is assigned to another autocatalytic reaction (Cna).

The optimized kinetic parameters for the model on Scheme 19 are shown on Table 22.

Step (reaction type)	1 (Cna)	2 (Cna)	3.1 (Fn)	3.2 (Cn)
Ea (kJ/mol)	164	146	195	55.8
Log(A) (log(1/s)	6.43	5.7	7.4	0.5
Reaction order	0.2	1.0	0.7	2.2
Kcat	1.0	1.0	-	0.881
Contribution	0.108	0.193	0.471	0.228

Table 22.	Kinetic	parameters u	ised in	the	model	for the	thermal	decompositio	n of	PBO	in	air
		1				/		1				

The activation energy for the first step of the thermal decomposition (164 kJ/mol) is in accordance with the one obtained from the model free analyses. The low dependence on the initial concentration of the material (reaction order = 0.2) and high autocatalytic order (1.0) suggests that the initial decomposition reaction is driven by the reactivity of the decomposition products rather than the initial 'concentration' of the polymer. This is expected as the random scission occurs randomly.

Similarly, the second decomposition reaction is also an autocatalytic process. Expectedly, the rate of the decomposition is equally dependent on the initial products as it does on the reactants (reaction order and autocatalytic order both equal to 1). Unsurprisingly so, because the first reaction has led to the generation of reactive species which can both further the first and the second decomposition steps.

The competitive reactions occurring in the third step represent the final step of the thermooxidative decomposition. One whereby char-oxidation is taking place, and another which corresponds to the further decomposition of the remaining polymeric chains. The first corresponds to a simple Arrhenius kinetic decomposition model with an order of reaction of 0.7. It is interesting to note that this reaction has the highest contribution in the kinetic model that is proposed. This means that thermo-oxidation is the major reaction occurring, according to our model. Furthermore, the other competitive reaction is attributed to an autocatalytic decomposition model with an order of 2.2 and an autocatalytic order of 0.9, whereby the decomposition products take part in furthering the reaction. The physical sense of this decomposition model lies in the fact that cleaving the remaining polymer backbones leads to the formation of radicals which can aid in further cleavage the remaining polymer chain.

The model represented in Scheme 19 and the optimized kinetic parameters in Table 22 have allowed us to plot simulated TG curves for the heating rates that were used and visualize them with the experimental data. The corresponding curves are shown on Figure 104.



Figure 105. Best fit of the TG data for the three-step reaction models in Scheme 19, with the parameters given on Table 22. The curves represent the experimental data and the symbols represent the model.

The kinetic model for the thermal decomposition of PBO in air is more complex than those under nitrogen and low oxygen concentration. This is due to the higher concentration of oxygen in the atmosphere, meaning that a higher amount of thermo-oxidation can take place. The first step of the decomposition has a lower activation energy and a higher autocatalytic factor. The subsequent reaction is also an autocatalytic one whereby the decomposition reaction is still accelerated due to the presence of oxygen. The following step corresponds to two competitive reactions, both corresponding to the thermo-oxidation of the charred structure formed by the two initial steps. It is interesting to note that the thermo-oxidation steps are the major contributing reactions to the model. The model used fits well with the experimental curves. Indeed, from a statistical point of view, the correlation between the experimental and simulated TG curves is 0.99993.

IV.3.d. Conclusion

The kinetic parameters for the thermal decomposition of PBO under three different oxygen levels have been extracted through a model-based approach. The influence of oxygen on the thermal decomposition was very clear on both the onset and the subsequent decomposition steps involved in the thermal degradation of PBO.

Under nitrogen, PBO exhibited an exceptionally high thermal stability. This was evidenced by a high activation energy for the two steps involved in its thermal decomposition. However, a low concentration of oxygen decreased the activation energy by a large amount (-93 kJ/mol). A further decrease in the activation energy for the first step of the thermal decomposition is observed in air (-116 kJ/mol as compared to that under nitrogen). Therefore, a catalytic effect of oxygen is likely to occur when considering the thermal decomposition of PBO.

The subsequent decomposition reactions varied with the amount of oxygen. This is because of the involvement of the thermo-oxidative decomposition of the initial decomposition product. Indeed, thermo-oxidation is, in itself, highly dependent on the concentration of oxygen. This dependence was observable in the subsequent decomposition steps of the thermal decomposition of PBO under 2 % oxygen.

Globally, the kinetics of the thermal decomposition of PBO under different oxygen levels provided insight on the different kinetic decomposition pathways that the material would adopt in different areas pertaining to a fire scenario. Indeed, while the pyrolysis of the material is highly heat resistant, the thermo-oxidative stability of the material is much lower. A scenario involving the polymeric materials at different stages of a fire scenario (pyrolysis, oxygen poor, or air) can be easily simulated from these kinetic parameters.

IV.4. Conclusion

This chapter has been dedicated to the understanding and the evaluation of the kinetic parameters that govern the thermal decomposition of three high performance polymeric materials (PEEK, PI, and PBO) under three different oxygen levels. The first part of the analyses was based on model free considerations, whereby an understanding of the different steps and nature of the decomposition reactions were identified.

Moreover, thanks to the comprehension of the thermal decomposition mechanisms of the materials determined in chapter III, coupled with the information obtained from the model free analyses, we were able to design comprehensive kinetic models for the thermal decomposition of all the materials under each of the oxygen levels. This was of utmost importance to understand the impact that oxygen may have on the thermal decomposition behavior of highly performing polymeric materials. Indeed, because of the nature of the thermal solicitations to which a material is subjected in a fire scenario, it is essential to consider oxygen related implications in the thermal decomposition of the material, and thus complete the characterization of the three high performance materials that we have studied.

Furthermore, one of the objectives of this work being the conceptualization of fire retardants by acquiring base knowledge on the thermal and fire behavior of high-performance materials, which is the purpose of the next chapter. Indeed, previous work at the laboratory has incepted on a new class of fire retardants that promotes cross-linking of the polymer it is in under a fire scenario, thus mimicking the behavior of a high-performance polymer. This fire-retardant is called salen and will be discussed in the next chapte

V. Salen based complexes as Fire Retardants in PA6 and TPU

The highly envious thermal and fire properties of high-performance polymeric materials investigated in the previous chapters are evidence that it is possible for wholly organic material to resist to high temperatures and fire scenarios. By studying the modes of action that were adopted by those materials so that they behave in such a favorable manner under thermal stress and fire scenarios, insight regarding a new approach towards the fire retardancy of more common polymeric materials was sought, and somewhat found in the form of salen based fire retardants. While salen has been more or less established as a potential fire retardant in some polymeric materials, studying them with the input gathered from the thermal decomposition and fire behavior of high performance material can provide further perspectives as to how a small amount of an additive can enhance the fire performances of an otherwise mediocre material in terms of flame resistance. Therefore, this chapter aims at studying the effect of salen based fire retardants in two thermoplastics: polyamide 6 and thermoplastic polyurethane.

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With the aim of developing novel Fire retardants (FRs) with high efficiency and low toxicity, a class of FR has been developed at the laboratory in the form of N,N'-(bis salicylidene)ethylenediamine called **s1**) (salen, hereafter and *N*,*N*'-bis(4hydroxysalicylidene)ethylenediamine (salen(OH)₂, hereafter called s2) as well as their copper (II) complexes. They have proved to exhibit highly interesting fire properties in thermoplastic polyurethane (TPU) [4]. A study performed by Naik et. al. [44,89] has thoroughly investigated the decomposition mechanism of s2. It was demonstrated that under high temperature conditions, s2 has the ability to undergo a polycondensation reaction and crosslink, forming a thermally stable residue. In addition, the complexation of s^2 with copper revealed that the cation has the ability to increase its thermal stability thus increasing its degradation temperature. This particular reaction is reminiscent of the fire behavior of highperformance polymers that were studied in previous sections. When loaded with salen and its derivatives, TPU has shown an enhanced amount of char formation and a decrease in the peak of heat release rate in the mass loss cone experiment. This charring behavior was seen with PEEK in the chapter 3, whereby a low pHRR was obtained, partly thanks to its high char yield.

In order to better understand the fire behavior of the salen ligands as a fire retardants and develop new ones which could contribute enhancing the fire behavior of regular engineering polymeric materials so that the formulation of polymer/salen would mimic high performance materials, the effect of cation complexed to salen ligands was also investigated. The choice of the cation should influence the degradation mechanism of the FR as well as its fire properties and it is a promising route to designing new FRs. Since previous work had already started using salen in thermoplastic polyurethane (TPU), we have decided to focus our attention on the screening of other metallosalen (salen metal complexes) in order to determine their thermal stability and investigate their efficiency as FRs in the same polymer and to further the study to another engineering polymeric material: polyamide 6

Thermoplastic polyurethane (TPU) is widely known for having excellent mechanical properties. It shows high tensile strength, good wear abrasion resistance, good hydrolytic stability and excellent flexibility over a wide range of temperatures. For all these reasons, TPU is broadly applied in the plastic industry [90]. However, like most common plastics, because of its high flammability and its melt dropping during combustion, it has a reduced fire safety effect, thus greatly limiting its applications [91,92]. Therefore, in order to increase

the applicability of TPU, it is imperative to improve its fire safety with effective and environmentally friendly flame retardants.

Polyamide 6, on the other hand is an engineering polymer which also has a plethora of applications ranging from food packaging to transportation. Indeed, it has high tensile strength, fatigue resistance and toughness[15]. However, as most wholly organic polymeric materials, it has the drawback of being flammable[17]. Therefore, to extend the versatility of the applications of PA6, it is important to attribute flame retardant properties to this material.

The first part of this work will consist of presenting the synthesis and characterization of salen and metallosalens. Their thermal stability will also be evaluated so as to ensure that there is little or no degradation during polymer processing (usually around the melting point of the material). Their potential as flame retardants will also be evaluated via the MLC. This will provide insight on the possibility of making polymer/flame retardant additives as well as their eventual contribution in terms of thermal stability that it can bring to a polymer/salen system.

The second and third part of this section deals with the effect of salen and metallosalen on TPU and PA6. The thermal stability as well as the fire properties of the formulations will be evaluated.

V.1. Synthesis and Characterization of Salens and Metallosalens

V.1.a. Synthesis of Salens and Metallosalens

A range of salen based potential fire retardants were synthesized using facile one or twostep reactions. Figure 106 shows the two salen derivatives that were used as ligands for this work.



Figure 106. Structure of salen ligand s1 (left) and salen(OH)₂ (right)

Scheme 20 shows the reaction pathway towards the formation of the salen and salen $(OH)_2$ ligands. Salen, **s1** is the basic salen Schiff base, which corresponds to the condensation

reaction between two equivalents of salicylaldehyde and one equivalent of ethylenediamine. On the other hand, the salen(OH)₂, **s2** is obtained using two equivalents of 4-hydroxysalicylaldehyde and one of ethylenediamine. the reaction yields were particularly high with yields above 90 % for both salens.



Scheme 20. Synthetic pathway for the formation of salen s1 and salen(OH)₂ s2 [46]

The ligands were characterized using NMR spectroscopy (¹H, ¹³C, as well as heteronuclear coupling), InfraRed spectroscopy as well as mass spectrometry.

Furthermore, a selection of salen and salen(OH)₂ complexes (Figure 107 and Figure 108) were synthesized. Synthetic methods had to be adapted with respect to the sensitivity of the reactants that were used. The metals used were limited to first row transition metals (nickel, copper, manganese) and zinc [93]. cost. Most of the complexes afforded a relatively acceptable yield ranging from 40 % to 80 %. However, due to its high sensitivity to air, **s1-Mn** was not synthesized.



Figure 107. Metallosalen complexes (labelled s1-M) that were successfully synthesized



Figure 108. Metallosalen(OH)₂ complexes (s2-M) that were successfully synthesized

The synthetic pathway towards the synthesis of the salen-metal complexes is shown on Scheme 21. Metal acetates were used for the formation of all salen and salen(OH)₂ complexes.



Scheme 21. Synthetic pathway for the formation of metallosalens s1-M and metallosalen(OH)2 s2-M

Most of the complexes were characterized by NMR techniques (¹H and ¹³C). However, some of the metal ions that were used for the complexation reaction were highly paramagnetic, making their identification via NMR trickier. Therefore, IR spectroscopy and mass spectroscopy were also performed to characterize them.

The synthesized salen were to be formulated with TPU and PA6, which both have different processing temperatures. It was therefore of undeniable importance that the thermal stability of the salens be tested. Additionally, while industrial extrusion is mostly performed in air, the microextrusions that were performed in our laboratory was done under nitrogen atmosphere. It was therefore important to ensure that the thermal stability of the salens synthesized would withstand the high temperature under inert conditions and under thermo-oxidative atmospheres.

V.1.b. Thermal Stability of Salen and Metallosalen

V.1.b.i. Thermal Stability of salen **s1** and metallosallen **s1-M** under Pyrolytic Conditions

In order to ensure that the polymer remains intact when it is processed with the polymeric material, TGA was conducted under inert atmosphere. The TGA and corresponding DTG curves of salen and its corresponding metal complexes are shown in Figure 109 and the summary of the data is shown on Table 23.


Figure 109. TGA and corresponding DTG curves of salen (blue), salen-copper complex (s1-Cu) (wine), salen-nickel complex (s1-Ni) (dark yellow) and salen-zinc complex (s1-Zn) (turquoise) when subjected to a heating rate of 10 °C/min under nitrogen.

Under inert atmosphere, TG curves of **s1** show that there is a slow decrease in residual mass as from 150 °C to around 220 °C, after which a sharp decrease in residual mass is observed. This can also be observed on the DTG curve, whereby the mass loss rate increases slowly as from 150 °C and more rapidly at around 210 °C. After this, the mass loss increases rapidly until the MLR_{MAX} at 290 °C. temperature at the onset of the degradation (T_{95%}) corresponds to 219 °C. This corresponds to the first decomposition step of **s1**, whereby a mass loss of around 85 wt% is observed at 309 °C. This mass loss is followed by a slow, linear decrease mass corresponding to around 8 wt% from 309 to 800 °C. The residual mass at 800 °C is 7 wt%.

Somula	_	5	s1	
Sample	T5% [°C]	Tmax [°C]	MLR [%/°C]	Res [%]
s1	219	287	1.7^{1}	7
s1-Cu	322	345	4.8^{2}	40
s1-Mn	N/A	N/A	N/A	N/A
s1-Ni	363	424	1.7 ²	31
s1-Zn	386	405	0.4^{1}	58

Table 23. Thermogravimetric data of salen s1, and is metal complexes, s1-m under inert atmosphere at 10 °C/min

 $^{1.}$ MLR_{Max} occurs at the first step of the degradation

^{2.} MLR_{MAX} occurs at the second step of the degradation

The salen-copper complex **s1-Cu** shows a higher thermal stability than non-complexed salen. Indeed, the onset of the decomposition of **s1-Cu** occurs at 322 °C. A sharp degradation step is observed, starting at around 300 °C. The DTG curve shows two shouldering in the curve at 326 and 337 °C, suggesting that there is more than one step in its thermal decomposition. Moreover, the MLR_{MAX} is observed at 346 °C, corresponding to the largest mass loss. The residual mass of **s1-Cu** at 800 °C is 40 wt%. It is interesting to note that the residual mass is higher than that of the theoretical mass percentage of residual copper (19 wt%) that was complexed with the salen ligand. This high a residual mass suggests that a char is formed during the first steps of its thermal decomposition.

The salen-nickel complex **s1-Ni** has an even higher thermal stability than **s1-Cu**. Indeed, the onset of the decomposition (T_{95%}) is observed at 363 °C. It corresponds to a first step of degradation. Indeed, this is observed on the DTG whereby two peaks are visible. A first, at 368 °C with a MLR of 3 %/min, and another corresponding to the MLR_{MAX} (17 %/min) occurring at 425 °C. After these two steps of degradation, the mass loss rate is relatively low. A small mass loss (< 0.6 %/min) is observed from 450 to 800 °C. The residual mass at 800 °C is 31 wt%.

The salen-zinc complex **s1-Zn** exhibits the highest thermal stability among the five metallosalens that were synthesized. The onset of the decomposition is observed at 386 °C. It corresponds to a first step of degradation whereby a mass loss of around 14 wt% is observed. This step is associated to the MLR_{MAX} (3.5 %/min, 408 °C). It is followed by another mass loss step with a relatively low MLR that is close to zero. The residual mass at 800 °C is 59 wt%.

From the TG curves, it can be observed that the presence of a metal complexed to the salen ligand increases the onset of its thermal degradation. All four potential fire retardants have a non-zero residual mass at 800 °C. However, this residual mass is much higher when the ligand is complexed to a metal. It suggests that the presence of a metal on the ligand favors both the amount of char formed and the thermal stability of the char. Similarly to the thermal decomposition of s1-Cu, the residual mass at 800 °C does not correspond to the weight percentage of zinc in the complex (about 19 wt% of zinc in s1-Zn) For instance, in the case of s1-Zn, the first step of the decomposition which is assigned to the formation of the char occurs with a much lower mass loss (- 14 wt%) than non-complexed s1 (- 86 wt%). Similarly, mass loss corresponding to the char formation during the first step of the thermal degradation of s1-Cu (48 wt%) and s1-Ni (46 wt%) also correspond to a lower mass loss as compared to non-complexed s1. Moreover, the stability of the char is more different still. Indeed, mass loss rates after the first degradation step are higher for s1-Zn (0.9 %/min) and s1-Ni (0.6 %/min) than s1-Cu (approx. 0.2 %/min) and s1 (approx. 0.2 %/min). This suggests that despite **s1-Ni** and **s1-Zn** having a higher initial thermal stability under nitrogen, the carbonaceous structure formed during their first step of degradation is less stable than those formed during those of s1 and s1-Cu in pyrolytic conditions.

V.1.b.ii. Thermal Stability of s1 and s1-M in Air

The thermal stability of the synthesized potential flame retardants was also studied in an oxidative atmosphere through TGA. The same heating rate as for the measurements made under nitrogen were used. The TG and corresponding DTG curves of **s1** and its metal complexes are shown on Figure 110. The summary of the thermogravimetric data on the thermo-oxidative degradation of **s1** and **s1**-M is shown on Table 24.



Figure 110. TGA and corresponding DTG curves of s1 and its metal complexes in air at a heating rate of 10 °C/min

The TG curves of s1 and the corresponding metallosalens in air show that the decomposition occurs roughly in two steps. The first decomposition step can be assigned to the formation of a char (transient char), and the second whereby the char is thermo-oxidized at high temperature. However, the amount of char formed in the first step and the rate of decomposition of the char are different depending on which metal the s1 is complexed with.

Indeed, while the decomposition onset of **s1** is at 295 °C, those of the **s1-M** complexes are higher. Indeed, **s1-Cu** has a $T_{95\%}$ at 339 °C, **s1-Ni** at 350 °C and **s1-Zn** at 386 °C. Moreover, the first step of the decomposition corresponds to different mass losses for each additive. Indeed, the first step of the degradation of **s1** corresponds to a mass loss of around 70 wt% while the other complexes have a much lower mass loss after their first decomposition step.

			s1		
Metal complex	T _{5%} [°C]	T _{MAX1} [°C]	$T_{MAX2}[^{\circ}C]$	MLR [%/°C]	Res [%]
-	295	369	-	1.5 ¹	4
Cu	340	349	325	2.4^{1}	25
Mn	N/A	N/A	N/A	N/A	N/A
Ni	351	428	368	0.9^{2}	20
Zn	386	392	-	1.1^{1}	25

Table 24. Thermogravimetric data of salen s1, and is metal complexes, s1-m under thermo-oxidative atmosphere at 10 °C/min

^{1.} MLR_{Max} occurs at the first step of the degradation

 $^{2.}$ $\ MLR_{MAX}$ occurs at the second step of the degradation

The TG curves of **s1-Cu** and **s1-Ni** share the same mass loss during the first step of their decomposition (35 wt%). However, the second step of the decomposition is very different for the two species. Indeed, the TGA plot of **s1-Cu** exhibits a slow, gradual mass loss of around 40 wt%, leaving a residual mass of 25 wt% at 800 °C. The second decomposition observed on the TG curve of **s1-Ni**, on the other hand is much sharper and leaves a residual mass of around 20 wt%. This residual mass corresponds to the metallic oxides that are formed during the thermo-oxidation of the salen-metal complexes.

The most stable metallosalen among the 4 studied is **s1-Zn**. Indeed, the TG curve of **s1-Zn** shows that the first decomposition step corresponds to a mass loss of around 20 wt%, followed by a relatively slow degradation (DTG < 4 wt%/min) until 800 °C, whereby the residual mass is around 25 wt%.

V.1.b.iii. Thermal Stability of s2 and s2-M under Pyrolytic Conditions

Similarly to the investigation of the thermal stability of s1 and its corresponding metallosalens, that of s2 and the metallosalen(OH)₂ was also investigated under nitrogen. Figure 111 shows the TGA curve of s2 and its complexes under inert conditions and the summary of the data is shown on Table 25.



Figure 111. TGA and corresponding DTG curve of s2 (black), s2-Cu (red), s2-Mn (blue), s2-Ni (magenta), and s2-Zn (green) at a heating rate of 10 °C/min under nitrogen

The TG and corresponding DTG curves of s2 and its corresponding s2-M are shown on Figure 111. It can be observed that the decomposition onset of s2 (T_{95%}) takes place at 205

°C. It corresponds to a first decomposition step. It can also be seen that there are many small decomposition steps during the thermal decomposition of s2. This is further evidenced by the DTG curve of s2, whereby a major peak is observed at 205 °C, corresponding to a mass loss rate of 3.2 %/min, after which, two broad peaks are observed at 320 °C and 612 °C. These peaks are much lower in terms of DTG (approx. 1 %/min), but they evidence a slow mass loss that occurs throughout the TGA. The residual mass of s2 at 800 °C is 49 wt%.

The different steps in the thermal decomposition of s2 suggests that there is some char formation occurring. However, the char is not very stable since a significant mass loss is observed throughout the heating process.

Furthermore, not unlike the comparison between metallosalen and salen, the metallosalen(OH)₂ exhibit an enhanced thermal stability under nitrogen as compared to its uncomplexed counterpart. Indeed, the onset of the thermal decomposition of all four s2-M were higher than that of s2.

For instance, the metallosalen(OH)₂ **s2-Ni** shows the highest thermal decomposition onset (433 °C). It corresponds to a sharp mass loss of around 14 wt%. After this step, further decomposition occurs, as it can be seen on the TGA curve. This is even more noticeable on the DTG curve whereby a very high peak is visible at 433 °C (16 %/min), followed by other broad peaks at 500 and 558 °C corresponding to a mass loss rate of -3 and -2 %/min respectively. Indeed, after the first degradation step, a slow, continuous mass loss is observed until 800 °C, whereby the residual mass is 37 wt%.

Sample -			s2	
	T5%[°C]	T _{MAX} [°C]	MLR [%/°C]	Res [%]
s2	206	200	0.31	49
s2-Cu	345	345	0.3 ²	59
s2-Mn	371	550	0.1^{2}	63
s2-Ni	432	435	1.6 ²	37
s2-Zn	314	555	0.1 ²	60

Table 25. Thermog	ravimetric data o	f salen s2 , and is m	etal complexes, s2-m	under inert atmospl	here at 10 °C/mir
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^{1.} MLR_{Max} occurs at the first step of the degradation

^{2.} MLR_{MAX} occurs at the second step of the degradation

A similar decomposition behavior is observed on the TG curve of **s2-Cu**. Indeed, a sharp mass loss followed by a slower one is observed as temperature is increased. However, the onset of the degradation is recorded at a lower temperature (345 $^{\circ}$ C) and the residual mass at 800 $^{\circ}$ C is higher (59 wt%).

In the case of **s2-Mn** and **s2-Zn**, the thermal decomposition seems to start at a relatively low temperature. However, the mass loss rates of both species are relatively low. The onset of decomposition of **s2-Mn** and **s2-Zn** occurs at 371 °C and 314 °C respectively. The slow decomposition of these species is evidenced by the low values on the DTG curve, whereby the MLR_{MAX} does not exceed 1.1 %/min. Moreover, the residual masses at 800 °C of both **s2-Mn** (63 wt%) and **s2-Zn** (60 wt%) are relatively high. This suggests that a relatively stable charred structure is formed during the early decomposition stages of these species. This residual mass is higher than the proportion of metal that was present in the salen-metal complex (approximately 18 w%)

V.1.b.iv. Thermal Stability of **s2** and **s2-M** in Air

To further characterize the thermal stability of s2 and metallosalen(OH)₂, TGA was performed at a heating rate of 10 °C/min under oxidative atmosphere (air). This provides insight on the effect of air on the formation of a charred structure during its decomposition. The thermal stability of the char formed during the first thermal decomposition step was also evaluated using the same measurement. The TGA curves of s2 and s2-M in air are shown on Figure 112 and the summary of the data is shown on Table 26.



Figure 112. TGA and corresponding DTG curve of s2 (black), s2-Cu (red), s2-Mn (blue), s2-Ni (magenta), s2-Zn (green) when heated at 10 °C/min in air

The thermal decomposition of **s2** occurs in two major steps. The first, assigned to the formation of a char occurs at around 172 °C. A sharp mass loss is observed at this temperature (DTG = 13 wt%/min), followed by a transient char, which is oxidized at around 550 °C (evidenced by the second peak on the DTG curve of **s2**).

Metal complex –			s2		
	T _{5%} [°C]	T _{MAX} [°C]	T _{MAX2} [°C]	MLR1 [%/°C]	Res [%]
-	171	171 ¹	556	1.31	4
Cu	290	285 ¹	325	1.3 ¹	23
Mn	279	279 ¹	-	1.5^{1}	25
Ni	342	347 ¹	-	0.9^{1}	22
Zn	313	386 ¹	-	1.4^{1}	25

Table 26. Thermogravimetric data of salen s_2 , and is metal complexes, s_2 -m under thermo-oxidative atmosphere at 10 °C/min

^{1.} MLR_{Max} occurs at the first step of the degradation

 $^{2.}$ $\,$ $\,$ MLR_{MAX} occurs at the second step of the degradation

On the other hand, TGA plots of metallosalen(OH)₂, with the exception of that of **s2-Zn**, exhibit a single, sharp decomposition step at temperatures ranging from 300 to 400 °C. This decomposition step leads to a highly stable residue, as no further mass loss is recorded at higher temperatures. As for **s2-Zn**, a slow continuous decomposition of the complex, starting at the onset of the degradation on until 800 °C is observed on its TGA plot. It can

be inferred that the thermal decomposition pathway adopted by the zinc complex is different from the other metallosalen(OH)₂ counterparts. The residual mass for all three metal complexes is around 20 wt%, which roughly corresponds to the mass of metal oxide in the complex. This means that the organic part of the complex was completely degraded, leaving only the metal oxide as residue.

From the DTG curves of the **s2-M** complexes (except **s2-Zn**), it can be seen that there are actually two steps involved in their thermal decomposition. A sharp peak, corresponding to an initial mass loss, and assigned to the formation of a charred structure, followed by a broader peak, assigned to the decomposition of this structure. These two decomposition steps evidenced by the DTG curves show that the presence of a metal in the molecule has two effects on the thermal stability of the complex: firstly, the temperature at the onset of the decomposition increases (first, sharp DTG peak), and, secondly, the temperature for the second decomposition (second DTG peak) is lower than non-complexed s2.

V.1.c. Conclusion

The investigation of the thermal stability of s1, s2 and their corresponding complexes have shown that the presence of a coordination metal on a neat ligand improves most of the time the thermal stability of the ligand. This increase in thermal stability depends both on the coordination metal and the in base ligand. Moreover, the presence of a coordination metal showed that a higher residual mass is obtained with metal complexes of both s1 and s2.

Furthermore, it is also possible that the thermal decomposition pathway adopted by the complexes depends on the nature of the metal. Indeed, it was observed that the mass loss rate during TGA was very different whether the coordination metal used was zinc or nickel.

These different modes of thermal decomposition may influence both the thermal stability and the fire properties of a polymer with which it is formulated. Indeed, **s1**, **s2**, **s1-Cu**, and **s2-Cu** have been tested in thermoplastic polyurethane (TPU) before [24]. It was therefore a judicious approach to further the study of the effect of salen and metallosalen on this same polymer. Moreover, seeing as all the synthesized metallosalens and metallosalen(OH)₂ are stable at the processing temperature of TPU (180 °C), we are exempt of the issue of degradation of the additive during polymer processing.

V.2. Effect of Salen Derivatives on TPU

Previous work in the laboratory has reported that salen and its derivatives were efficient flame retardants on thermoplastic polyurethane [24]. In order to dig deeper on the effect of

salens and their metal complexes on the thermal stability and flame retardancy of TPU, this section will be dedicated to the investigation of the thermal and fire behavior of TPU formulations containing the salens and metallosalens characterized in the previous section. To do this, 10:1 weight ratio of TPU/salen were formulated and their thermal and fire properties were evaluated.

V.2.a. Thermal stability of TPU/salen and TPU/metallosalens

Before assessing the fire behavior of TPU/salen formulations, their thermal behavior was studied. Indeed, introducing a load in a material may either enhance or reduce the thermal properties of a material. Therefore, TGA was performed under nitrogen and in air for the formulations with TPU.

V.2.a.i. Thermal stability of TPU/salen and TPU/metallosalens under pyrolytic conditions

The TG curves of salen, **s1** and its corresponding metallic complexes under pyrolytic conditions are shown on Figure 113 and a summary of the TGA is shown on Table 27.



Figure 113. TGA curves (left) and corresponding DTG curves (right) of neat TPU (dotted, pink), TPU/s1 (blue), TPU/s1-Cu (dark red), TPU/s1-Ni (dark yellow), and TPU/s1-Zn (turquoise) when subjected to a heating rate of 10 °C/min under nitrogen, and a 10/1 wt% ratio of polymer/additive loading

From the TGA curve of neat TPU, the temperature at the onset of its thermal decomposition $(T_{95\%})$ can be read at 303 °C. the decomposition occurs in a single step. This is confirmed by the DTG curve of neat TPU.

In pyrolytic conditions (Figure 113), TPU/s1 shows a slight decrease of the thermal stability compared to neat TPU and TPU/s1-M complexes. Indeed, the decomposition of the TPU/s1 starts at 287 °C whereas neat TPU and the other formulations show an initial mass loss (95%) at a higher temperature of around 300 °C.

Table 27. Thermogravimetric data of salen TPU, TPU/s1, and is metal complexes, TPU/s1-M under inert atmosphere at 10 °C/min

Sample		s1		
	T _{5%} [°C]	T _{MAX} [°C]	MLR [%/°C]	Res [%]
Neat TPU	303	406 ²	1.4	5
s1	287	391 ²	1.2	7
s1-Cu	301	396 ²	1.1	9
s1-Ni	300	363 ¹	2.7	10
s1-Zn	297	3231	2.9	15

Chapter V- Salen based complexes as Fire Retardants in PA6 and TPU

 $^{1.}$ MLR_{Max} occurs at the first step of the degradation

^{2.} MLR_{MAX} occurs at the second step of the degradation

Moreover, even though the decomposition onset of TPU/s1-Zn and TPU/s1-Ni occurs at a slightly higher temperature, the mass loss step recorded on the TG curve is steeper than the other TG curves. This is more blatant when looking at the DTG curve, whereby a relatively high peak MLR is observed after the onset of the decomposition. In addition, the decomposition seems to be multi staged. Indeed, after the first decomposition, a non-zero DTG is observed on the DTG curve corresponding to both TPU/s1-Ni and TPU/s1-Zn. This means that after the first decomposition step, a small, slower step is recorded. The first step of the decomposition may be assigned to the formation of a char structure, which crosslinks further at high temperature. This hypothesis is strengthened by the increase in residual mass at 800 °C (15 wt% for TPU/s1-Zn, and 10 wt% for TPU/s1-Ni) as compared to neat TPU (5 wt%).

In more general terms, the presence of a 10:1 wt% of **s1** or **s1-M** does not greatly affect the temperature at the onset of the decomposition under nitrogen. However, the mode of decomposition does seem to be altered. This is noticed in the case of the zinc and nickel complexes. Moreover, the residual mass at 800 °C is generally higher compared to neat TPU. This suggests that the presence of a salen based additive may enhance the temperature stability of TPU.

As with **s1** and **s1-M** additives, the thermal stability of formulations containing **s2** and **s2- M** were tested under the same conditions.

Figure 114 shows the TGA and corresponding DTG curves of TPU/s1-M under pyrolytic conditions and Table 28 is a summary of the data regarding the TGA.



Figure 114. TGA curves (left) and corresponding DTG curves (right) of neat TPU (dotted, pink), TPU/s2 (black), TPU/s2-Cu (red), TPU/s2-Mn (blue), TPU/s2-Ni (magenta), TPU/s2-Zn (green) when subjected to a heating rate of 10 °C/min under nitrogen, and a 10/1 wt% ratio of polymer/additive loading.

TGA of TPU containing **s2** and its complexes show that they have similar thermal behavior to neat TPU in terms of the first decomposition temperature under nitrogen, which begins around 300 °C for every formulation. Moreover, there is a higher residual mass at 800 °C for the formulated samples as compared to that of neat TPU. The TG curve of TPU/**s2-Zn** shows the highest remaining mass at 800 °C (15 wt%). The TG curves of **s2-Cu** and **s2-Ni** show higher MLR than the other formulations.

Sama la		sl	l	
Sample	T5% [°C]	T _{MAX} [°C]	MLR [%/°C]	Res [%]
Neat TPU	303	406 ²	1.4	5
s2	298	407^{2}	1.4	9
s2-Cu	303	377 ²	2.1	11
s2-Mn	300	376 ²	2.0	11
s2-Ni	308	386 ²	2.7	7
s2-Zn	306	366 ²	1.4	15

Table 28. Thermogravimetric data of salen TPU, TPU/s2, and is metal complexes, TPU/s2-M under thermo-inert at 10 °C/min

^{1.} MLR_{Max} occurs at the first step of the degradation

 $^{2.}$ $\ MLR_{MAX}$ occurs at the second step of the degradation

However, the TG curve of TPU/s2-Zn shows that it exhibits an apparent single-step decomposition unlike the other formulations, which appear to decompose in two steps, similarly to neat TPU. The apparent single-step decomposition of TPU/s2-Zn is assigned to the overlapping of the two decomposition stages of the formulation. This is further evidenced on the DTG curve whereby a small shouldering is observed at 346 °C. The residual masses at 800 °C are significantly higher for all the s2-complex formulations

compared to that of neat TPU (as high as 50 wt% more in the case of TPU/s2-Zn). This suggests that there is the formation of thermally robust char during the first step of the degradation under nitrogen.

The presence of **s2** and its corresponding metal complexes does not seem to affect the temperature at which TPU thermally decomposes. However, the modes of decomposition seem to be affected by a few additives (mostly in the case of **s2-Zn**). Moreover, the presence of all additives seems to promote the formation of a more thermally stable char, as it is evidenced by the increased residual mass for the formulated samples as compared to neat TPU.

V.2.a.ii. Thermal Stability of TPU/salen and TPU/metallosalens in Air

It is known that during a fire scenario, the bulk of a burning material finds itself in near pyrolytic conditions, however, the previous section has shown us that thermo-oxidative degradation may occur in the presence of even a low concentration of oxygen. Moreover, polymeric materials that are only subjected to a high heat source (for instance, one that is not yet flaming, but is in the vicinity of a flame) may undergo thermo-oxidative degradation before itself flaming up. This is the case before ignition occurs in the mass loss cone experiment. Therefore, in order to have a deeper insight on the thermal stability of the TPU formulations studied, TGA was also performed in air, at the same heating rate as those performed under nitrogen. This is shown on Figure 115 and Table 29 is a summary of the data regarding the TGA



Figure 115. TGA curves (left) and corresponding DTG curves (right) of neat TPU (dotted, pink), TPU/s1 (blue), TPU/s1-Cu (dark red), TPU/s1-Ni (dark yellow), and TPU/s1-Zn (turquoise) when subjected to a heating rate of 10 °C/min in air, and a 10/1 wt% ratio of polymer/additive loading

The TG curves of TPU and TPU/s1-M, when the analyses are performed in air are very different from those performed under nitrogen (Figure 115). The thermo-oxidative

decomposition of TPU/**s1-M** occurs in a higher number of distinguishable steps as compared to their decomposition under inert atmosphere. This further evidenced on the DTG curve, whereby a number of peaks can be discerned. The first step corresponds to the formation of a transient char, which is oxidized at high temperature due to the presence of oxygen.

In air, TPU/s1 shows a much lower decomposition temperature (286 °C) at 5 wt% loss as compared to neat TPU (303 °C). This is further evidenced on the DTG curve of TPU/s1 whereby a non-zero mass loss rate is observed at temperatures as low as 200 °C (blue curve, Figure 115))However, the second degradation step shows that TPU/s1 has slightly more residual char than neat TPU ($M_{res} = 7$ % as compared to 5 % in neat TPU). s1

Sample		s1		
	T _{5%} [°C]	T _{MAX} [°C]	MLR [%/°C]	Res [%]
Neat TPU	312	376 ¹	1.5	3
s1	280	367 ²	1.2	4
s1-Cu	295	374 ²	1.1	4
s1-Ni	298	391 ²	1.1	2
s1-Zn	290	3121	2.3	5

Table 29. Thermogravimetric data of salen TPU, TPU/s1, and is metal complexes, TPU/s1-M under thermo-oxidative atmosphere at 10 °C/min

^{1.} MLR_{Max} occurs at the first step of the degradation

^{2.} MLR_{MAX} occurs at the second step of the degradation

Similarly, **s1-M** complexes show a first degradation step that is lower than that of neat TPU, ranging from 290 - 298 °C. The second step corresponds to the degradation of a transient char which decomposes at a higher temperature. In the case of TPU/**s1-Zn**, the first step occurs with a very high mass loss rate (30 wt%/min as compared to 15 wt%/min for neat TPU) and the second step occurs at a much higher temperature (495 °C) than all the others (< 460 °C). This could mean that there is the formation of a stable compound that remains thermally stable. Such a behavior is known to occur with the dihydroxy(salen) when it is subjected to a high temperature stress[44]. Apart from TPU/**s1-Ni** and **s1-Zn**, there is a slight increase in residual mass for all the formulations at 800 °C. The zinc and nickel based formulations have a similar residual mass at 800 °C, it remains a relatively low mass (<

5wt%) and is too small to have a meaningful impact on the thermal stability of TPU formulations

In the case of TPU/s1, no significant improvement or deterioration of the thermal stability of the TPU/additive system can be observed as compared to neat TPU. However, as it was the case for the TGA performed under nitrogen a different mode of decomposition is observed for TPU/s1-Zn and TPU/s1-Ni, whereby a rapid first step leading to the formation of char is observed. However, in air, this char is thermo-oxidized at high temperature. This char formation may have a protective role in a fire scenario. Indeed, char layers usually protect underlying material by limiting heat and mass transfer from the bulk of a burning material to the surface (flame). It must nevertheless be noted that in the scenario of a burning that there is very little thermo-oxidation that may occur. While the formation of this char under thermo-oxidative conditions holds promise, its ability to form and remain robust in a fire scenario also needs to be tried.

In the case of TPU/s1-Zns1-Zn, the char formed remains stable for a larger temperature range than the other formulations, suggesting that that char has the highest thermal stability.

TPU/s2 and TPU/s2-M were subjected to the same thermal stability measurements as its s1 counterparts. The TG and DTG curves are shown on Figure 116 and Table 30 is a summary of the data regarding the TGA.



Figure 116. TGA curves (left) and corresponding DTG curves (right) of neat TPU (dotted, pink), TPU/s2 (black), TPU/s2-Cu (red), TPU/s2-Mn (blue), TPU/s2-Ni (magenta), TPU/s2-Zn (green) when subjected to a heating rate of 10 °C/min in air, and a 10/1 wt% ratio of polymer/additive loading

Apart from the zinc-based formulation, the TG curves of TPU/s2 and TPU/s2-M formulations show similar behaviors as TPU/s1 formulations in air. The TGA plots of all the formulations exhibit a two-stage decomposition. The first degradation temperatures

range from 295 to 311 °C, with TPU/s2-Zn starting its degradation at the lowest (295 °C) temperature and that of s2-Ni being the highest (311 °C). The MLR are also relatively close to the MLR of neat TPU. However, in the case of s2, s2-Mn and s2-Zn, the TGA plots show that the second degradation of the formulations occurs at a higher temperature than the other formulations (> 500 °C). It is assigned to the ability of s2 to form thermally stable resins at high temperatures. The presence of these metal ions in the complex may catalyze this mechanism of resin formation and polycondensation making a greater amount of the thermally stable, cross-linked structure [24]. However, the other metals seem to favor a less thermally stable char.

Sample		sl	l	
	T _{5%} [°C]	T _{MAX} [°C]	MLR [%/°C]	Res [%]
Neat TPU	312	376 ¹	1.5	3
s1	303	384 ²	1.2	2
s1-Cu	302	370 ²	1.3	4
s2-Mn	307	388 ²	1.4	2
s1-Ni	311	378 ²	1.4	4
s1-Zn	295	3711	1.4	5

Table 30. Thermogravimetric data of salen TPU, TPU/s2, and is metal complexes, TPU/s2-M under thermo-oxidative atmosphere at 10 °C/min

^{1.} MLR_{Max} occurs at the first step of the degradation

^{2.} MLR_{MAX} occurs at the second step of the degradation

The biggest difference in the thermal behaviors of the different formulations comes at the third decomposition stage. Indeed, depending on the coordination metal on the additive, the second decomposition step corresponds to different mass loss rates on the DTG curves. For instance, the maximum mass loss rate for the second step of the decomposition of neat TPU, corresponds to a more or less sharp peak on the DTG peak at 508 °C. The peak corresponding to the third decomposition step of TPU/s2-Ni is much sharper and occurs at a lower temperature of 450 °C. conversely, that of TPU/s2-Zn, is relatively low and occurs at a slightly higher temperature (510 °C) than neat TPU.

The temperature and mass loss rates corresponding to this third step of the decomposition provide insight relative to the stability of the char formed during the first step of the decomposition. On this basis, we can infer that TPU/s2-Zn forms the most stable char after the first step of the decomposition.

The investigation on the thermal stability of TPU and its corresponding formulations has provided insight regarding the effect of loading the polymeric material by around 9 wt% of the additive. The temperature at the onset of the thermal degradation was only marginally affected by the presence of a load, whether TGA was performed under nitrogen or in air.

However, when the analyses were performed under nitrogen, the residual mass at high temperatures was significantly changed due to the presence of a salen or metallosalen. Indeed, the presence of a metallosalen tends to increase the residual mass at high temperatures. This may be assigned to a change in the decomposition pattern of the polymeric material, leading to a different structure at high temperature. The thermal robustness of the material depends on the coordination metal that was used for the salen/salen(OH)₂ based complex.

This thermal robustness was tested in a harsher thermal environment when it was evaluated in a thermo-oxidative environment. It was observed that the transient char formed during the first step of thermal degradation led to a more or less thermally resistant char. TPU/s2-**Zn** had the slowest mass loss rate at high temperature, suggesting that the residue formed after its first step of thermal decomposition is thermally stable.

Having acquired some thermal properties of the different polymeric materials studied, further investigation is required in order to properly characterize its behavior in high temperatures. Indeed, while we know that there are two steps involved in the decomposition of the formulations in air, we are still unaware of the heat contribution that the presence of the additive may bring in a fire scenario. The microscale combustion calorimeter may provide such information using a milligram scale test.

V.2.b. Microscale Combustion Calorimetry On TPU/salen

Seeing how the decomposition behavior of a formulation may vary upon addition of a small amount of additive, it was deemed worthwhile to study its combustion behavior using a microscale combustion calorimeter. This would provide information on the heat released during the decomposition of the material when it degrades in an inert atmosphere. This can provide valuable insight on its potential to sustain a flame in a fire scenario – the higher the peak of heat release rate, the greater the amount of combustibles released, therefore, the higher the potential of feeding a flame.

Microscale Combustion Calorimetry (MCC) was performed on both the flame-retardants and the formulated samples. This evaluation provides us with results regarding the specific



HRR, the temperature at which the peak heat release rate (pHRR) occurs as well as the THR. The results are summarized in Table 31.

2400



Figure 117. Corrected MCC curves of neat TPU (dotted, pink), TPU/s1 (blue), TPU/s1-Cus1-Cu (dark red), TPU/s1-Ni (dark yellow), and TPU/s1-Zn (turquoise) when subjected to a heating rate of 60 °C/min under nitrogen 10/1 wt%, and a ratio of polymer/additive loading

Figure 118. Corrected MCC curves of neat TPU (dotted, pink), TPU/s2 (black), TPU/s2-Cu (red), TPU/s2-Mn (blue), TPU/s2-Ni (magenta), TPU/s2-Zn (green) when subjected to a heating rate of 60 °C/min under nitrogen, and a 10/1 wt% ratio of polymer/additive loading

Figure 117 and Figure 118 show the MCC curves of TPU and its corresponding salen based formulations. The MCC curve of neat TPU shows that it has a peak heat release rate of 1535 W/g at 434 °C. Apart from s1 and s1-Ni, the MCC curves of every TPU containing s1-based additives show a decrease in the pHRR compared to that of neat TPU. The s1-Zn formulation has the lowest temperature (347 °C) at pHRR (Figure 117) and it also has the lowest total HR (Table 31). For the other s1-complexes, the pHRR occurs between 410 °C and 435 °C. The peaks exhibit different width at half height and have only one maximum. This broadness implies that the combustibles in the tested samples are released over a wide range of temperatures.

In the case of the formulations containing s2 and its complexes, the MCC curves of all the samples show a decrease in the pHRR (Figure 118) and THR (Table 31) compared to neat TPU. The lowest pHRR is observed on the PCFC curve of TPU/s1-Cus1-Cu (343 W/g), corresponding to a decrease of 73 % as compared to that of neat TPU. The lowest THR corresponds to the TPU/s2-Mn formulation with 38 kJ/g compared to 90 kJ/g for neat TPU (-58 %). It appears that additional peaks are observed before and after the pHRR. This multipeak phenomenon may correlate to the TG curves of the TPU/s2 and TPU/s2-M (Figure 116, page 277).

Sample	pHRR (W/g)	T (°C) @ pHRR	THR (kJ/g)
Neat TPU	1535	435	90
TPU/ s1	2659 (+ 73%)	431 (- 4 °C)	116 (+ 29%)
TPU/s1-Cu	763 (- 50%)	431 (- 4 °C)	52 (- 42%)
TPU/s1-Ni	1910 (+ 24%)	414 (- 21 °C)	65 (- 28%)
TPU/s1-Zn	594 (- 61%)	346 (- 89 °C)	33 (- 63%)
TPU/s2	608 (- 60%)	430 (- 5 °C)	54 (- 40%)
TPU/s2-Cu	408 (- 73%)	417 (- 18 °C)	42 (- 53%)
TPU/s2-Mn	756 (- 51%)	402 (- 33 °C)	38 (- 58%)
TPU/s2-Ni	808 (- 47%)	420 (- 15 °C)	39 (- 57%)
TPU/s2-Zn	680 (- 44%)	411 (- 24 °C)	46 (- 49%)

Table 31. Summary of the peak heat release rate, temperature at peak heat release rate and THR for the TPU/salen (10:1 wt%) formulations

In order to investigate further the decomposition behavior of the formulations, the MCC results were correlated to the TG curves i.e. the specific heat release rate as a function of residual mass. This allowed observing the evolution of the mass of the sample as well as the degree of decomposition at which there is a notable release of combustibles. This led to a representation of the amount of heat released with respect to the remaining mass of the samples (Figure 119 and Figure 120). The same scales were used for both sets of curves for comparison purposes.





Figure 119. HRR vs mass loss curves of TPU (dotted, pink), TPU/s1 (blue), TPU/s1-Cu (dark red), TPU/s1-Ni (dark yellow), and TPU/s1-Zn (turquoise) when subjected to a heating rate of 60 °C/min, and 10/1 wt% ratio of polymer/additive loading

Figure 120. HRR vs mass loss curves of neat TPU (dotted, pink), TPU/s2 (black), TPU/s2-Cu (red), TPU/s2-Mn (blue), TPU/s2-Ni (magenta), TPU/s2-Zn (green) when subjected to a heating rate of 60 °C/min, and 10/1 wt% ratio of polymer/additive loading

Except for that of TPU/s1-Zn, the HRR/mass-loss curves of TPU/s1 formulations (Figure 119) show an increase in HRR starting at around 60 % of residual mass. The HRR/mass-loss curve of the formulation containing TPU and s1 (blue) has a much higher peak HRR than neat TPU (dotted, pink). This suggests that most of the heat is released towards the end of the degradation of the samples and that there is a greater amount of combustibles released in TPU/s1 compared to neat TPU. The HRR/mass-loss curve of TPU/s1-Ni (dark yellow) sample shows a slightly broader peak than that of neat TPU. However, the overall shape of the curve is very similar to the neat TPU curve, suggesting that the degradation of these formulations is somewhat similar in terms of HRR. Regarding TPU/s1-Cu (dark red), the HRR/mass-loss curve shows a much broader range over which HRR is relatively low. This suggests that the pyrolysis of the TPU/s1-Cu releases combustible materials over a wider range of its mass loss during its degradation, but also at a smaller rate. The curve corresponding to TPU/s1-Zn shows a very different shape when compared to the others. Most of the heat is released at the beginning of its decomposition. After that, there is a relatively slow, continuous HRR until about 15 % residual mass.

In the case of neat TPU, there is a slow and continuous increase of the HRR until the peak of HRR is reached. The curves corresponding to TPU/s2 (Figure 120) formulations show erratic results. Most of the TPU/s2 begin to have a notable HRR at around 85 - 80 wt%. However, it is interesting to note that there seems to be a preliminary phase between 0 - 20% mass loss whereby there is a relatively stable heat release rate of approximately 100 - 150 W/g. This suggests that the early decomposition products of these formulations release non-combustible or hardly combustible products at the beginning of the pyrolysis.. The curve

corresponding to TPU/s2-Cu (Figure 120) formulation shows a very broad peak with a relatively low peak HRR. This shows that the release of combustibles occurs over a longer range of weight, suggesting that different decomposition products are released via a different mode of decomposition. It is also worth noting that there is, on average, more than 50 % decrease in the THR rate when the TPU/s2 complexes are tested with TPU in the PCFC.

From the combination of HRR/Temperature and HRR/mass-loss curves, it can be observed that TPU/s1-Cu and TPU/s2-Cu release low-combustibility volatiles over a wide range of their mass loss.

The TPU/**s1-Zn** formulation, on the other hand, exhibits an intriguing behavior in the sense that most of its combustibles are released at a very early stage of its pyrolysis. Moreover, it has shown a relatively low peak heat release rate (-63%) as compared to other **s1** based formulations.

Lastly, formulations of TPU and salen derivatives have shown that they can bring about a decrease in the HRR of the formulations by modifying the degradation steps of the formulations. This suggests that there would be a lower amount of combustibles released in a fire scenario. This strengthens the hypothesis that these additives may have some fire-retardant properties when they are incorporated in TPU. In order to verify this, a bench scale fire testing system (mass loss cone calorimetry) was used.

V.2.c. Fire behavior of TPU/salen

To investigate the fire behavior of the formulated polymeric materials, mass loss cone calorimetry was performed on (50 x 50 x 3) mm³ samples at a heat flux of 35 kW/m² and a separation of 25 mm from the heat source.

Figure 121 and Figure 122 show the MLC curves of the different formulations of TPU with salen and its derivatives under the aforementioned conditions.

The general behavior of every sample is relatively similar right after ignition. A sharp increase in the HRR is observed on the MLC curve. Also, most of the sample show, to some extent some swelling. This is possible due to the formation of a char on the surface of the material. It limits the mass transfer of combustibles to the upper surface of the material. However, depending on the robustness of the char formed, its thermomechanical integrity may be compromised at different times. Moreover, by inhibiting the release of inflammable

gases, the peak of heat release rate during the burning process of the material may also be decreased.



Figure 121. MLC curves of neat TPU (dotted, pink), TPU/s1 (blue), TPU/s1-Cu (dark red), TPU/s1-Ni (dark yellow), and TPU/s1-Zn (turquoise) when exposed to 35 kW/m² at 25 mm, and 10/1 wt% ratio of polymer/additive loading

Figure 122. MLC curves of neat TPU (dotted, pink), TPU/s2 (black), TPU/s2-Cu (red), TPU/s2-Mn (blue), TPU/s2-Ni (magenta), TPU/s2-Zn (green) when exposed to 35 kW/m² at 25 mm, and 10/1 wt% ratio of polymer/additive loading

With the exception of Zn based formulations, the HRR curves of all the samples showed a decrease in the pHRR compared to neat TPU. The data are summarized in Table 31.

The HRR plot of Neat TPU (dotted, pink) shows a pHRR at 277 kW/m² and a THR of 66.7 MJ/m². Two HRR peaks can be observed. The first step starts at the ignition whereby there is a steep increase in HRR. This increase peaks at around 176 kW/m² (147 s). After this, a slight decrease in HRR is observed until around 175 s. This is assigned to the formation of a char that protects the unburnt layer of the material and delays its decomposition. However, at around 200 s, another sharp increase in the HRR is observed. This suggests that the inflammable decomposition gases are eventually released despite the formation of the char. The peak HRR is reached at this step (at around 300 s) and corresponds to a heat release rate of 277 kW/m². A picture of the resulting residue is shown on Figure *123* (left). A charred residue can be seen in the center-part of the sample but most of the material



Figure 123. Residues of neat TPU (left), TPU/s1 (center), and TPU/s1-Cus1-Cu (right)

In the case of TPU/s1, the HRR curve shows no significant change brought about in the HRR values, neither in terms of pHRR nor in terms of THR. A small increase of the TTI is observed, suggesting that the char formed during the initial decomposition protects the underlying polymer for slightly longer.

TPU/s1-Cu and TPU/s1-Ni, behave differently as compared to neat TPU and TPU/s1. HRR curves exhibit only one peak occurring before that of neat TPU (250 s vs. 350 s). However, the value of pHRR is not significantly decreased compared to neat TPU (-1.8 %). A potential explanation for this behavior is that the char has a relatively low thermomechanical strength, causing it to break or not form at all. This can be observed on the photo of TPU/s1-Cu (Figure *123*). However, these formulations have a significantly lower THR as compared to neat TPU (-27.3% for s1-Cu and -22.2 % for s1-Ni). These results could be compared to the MCC results of the same formulations. It was noted that TPU/s1-Ni had a higher specific pHRR as compared to neat TPU (1910 W/g, +24 %). However, when it comes to the MLC test, the pHRR is only insignificantly lower. Similarly, the lower pHRR under the MCC would seem to be coherent with the lower pHRR under the MLC. However, the difference in the heat released is not as significant.

Sample	pHRR (kW/m ²)	THR (MJ/m ²)	TTI (s)
Neat TPU	277	66.7	69
TPU/s1	260 (-6 %)	65.5 (- 2 %)	92
TPU/s1-Cu	244 (-11 %)	48.5 (-27 %)	61
TPU/s1-Ni	256 (-7 %)	51.9 (-22 %)	66
TPU/s1-Zn	420 (+51 %)	54.3 (-18 %)	64
TPU/ s2	200 (-27 %)	50.5 (-24 %)	57
TPU/s2-Cu	187 (-32 %)	45.0 (-32 %)	43
TPU/s2-Mn	192 (-30 %)	47.3 (-29 %)	55
TPU/s2-Ni	251 (-9 %)	54.9 (-17 %)	69
TPU/s2-Zn	326 (+17 %)	52.4 (-21 %)	42

Table 32. Summary of pHRR and HRR values recorded during the MLC test of TPU and its corresponding salen formulations

MLC result for TPU/**s1-Zn** formulation showed a very high pHRR (420 kw/m²) as compared to neat TPU (+51.6%). This may correlate to TGA of TPU/**s1-Zn** which showed a drastic decrease in mass at a relatively low temperature (290 °C) therefore causing the rapid release of combustibles early during its decomposition under the radiative flux. A relatively sharp peak occurs quickly at the beginning of the test. It suggests that the sample degraded very quickly, releasing a lot of fuel and causing a high HRR, then forms a protective layer, which limited the release of energy. This char formation is from the decomposition behavior of the neat TPU, which, in itself is slightly charring (Figure *123*, left). Evidence of the char formation of TPU/**s1-Zn** can be seen in the picture taken after the MLC test (Figure 124). However, the char being relatively fragile, it did not keep its shape and collapsed. The high pHRR is assigned to the possibility that the presence of zinc catalyzed the degradation process of the formulation (as seen in the TGA) causing a rapid burning of the sample when it is subjected to an elevated temperature.



Figure 124. Residues of TPU/s1-Zn (left), TPU/s2-Mn (center) and TPU/s2-Cu (right).

Formulations of s2 and its complexes exhibit a lower pHRR and THR as compared to its s1 counterparts. Indeed, the HRR curve of TPU/s2 itself shows a pHRR of 200 kW/m² which is about 28 % lower than that of neat TPU and 23% lower than that of TPU/s1. This could be correlated to the fact that s2 has the ability to form thermally stable cross-linked charred structure (polyphenol) at high temperature [4].

The HRR as a function of time curve of neat TPU, **s2** and **s2-M** formulations are relatively similar immediately after ignition. There is the formation of a char which inhibits the decomposition of the sample. In the case of **s2** and **s2-M** formulations, this char is remains intact for a longer time. This results to a plateau that is observed in the HRR curves of TPU/**s2-Cu** and TPU/**s2-Mn**. It also explains the lower pHRR of these samples (pHRR < 200 kW/m², as compared to neat TPU with a pHRR at 277 kW/m²). Indeed, the shapes of the HRR curves of these two formulations are consistent with HRR curves of materials that exhibit charring when they are burnt [94]. These observations suggest that the cross-linking ability of **s2** is maintained when the ligand is complexed with Cu²⁺ or Mn²⁺ [4]. Moreover, The HRR curves of TPU/**s2-Cu** and TPU/**s2-Mn** show the lowest pHRR and THR of all the formulations. The HRR values are close to each other and are consistent with PCFC results. Indeed, when compared to neat TPU, they showed a relatively low pHRR both in the PCFC test (-56 % for Cu and -51 % for Mn as compared to neat TPU) and in the MLC test (-32.5 % for Cu and -30.7 % for Mn).

As with TPU/s1-Zn, the HRR curve of TPU/s2-Zn shows a higher pHRR compared to neat TPU. (+17.7 %). However, the s2-Zn formulation induces a lower pHRR than TPU/s1-Zn. This may be due to ability of s2 to form a cross-linked polyphenolic structure in the polymer matrix, forming a protective thermally stable layer, thus decreasing the pHRR[44]. The zinc cation may increase the rate of formation of the cross-linked structure, as it was observed on the MLC samples. However, because these bond formations are rapid (as seen with the steep mass loss rate on the TGA curve) and exothermic, it could explain the exceedingly high pHRR as compared to neat TPU.

Furthermore, these results have shown that there is no distinct correlation between MLC and PCFC results. Indeed, considering that after the MCC tests, the most promising sample as a fire retardant was the TPU/s1-Zn formulation. However, upon performing MLC, it was seen that among all the samples tested, TPU/s1-Zn has the highest pHRR, making it a mediocre candidate as a FR.

V.2.d. Conclusion

The thermal stability of TPU formulations are hardly affected by the presence of the additives. Indeed, the temperature at the onset of the thermal decomposition remained within 10% of that of neat TPU. However, the presence of a coordination metal on the additives seems to have an effect on the charring behavior of the formulations that were made. This was evidenced by the higher temperature at which the second stage of the decomposition starts in air (with a TGA). Indeed, **s1-Zn** and **s2-Zn**, despite having a steeper mass loss rate at the initial decomposition, also forms a more stable structure at its end. This structure remains stable for a larger temperature range as compared to neat TPU and other formulations. This suggests that the presence of a zinc-based additive may enhance the stability of the char formed during the first stage of the thermal decomposition of the polymer.

Moreover, some formulated samples have shown that they may have some positive effect on the flame retardancy of the TPU. This was evidenced by a lower pHRR of the formulated samples as compared to that of neat TPU. Moreover, all the samples measured have shown that the THR when they are burning beneath a 35 kW/m² heat source is less than that of neat TPU. Indeed, with the exception of the TPU/s1 formulation, all the other formulations exhibit a THR which is at least 15% lower than that of neat TPU.

Furthermore, it is known that fire retardants may behave differently depending on the polymeric material it is used in. It was therefore deemed appropriate to further the study of the effect of a select few of the previously used potential flame retardants on another polymer.

V.3. Effect of Salen Derivatives on PA6

As mentioned, salen and its derivatives have shown that they may potentially improve the fire behavior of TPU. However, the results obtained, despite not being completely insignificant, may be different if the FR are used in another polymeric material. Indeed, seeing as the fire-retardant mode of action of salen and its derivates is based on the formation of a char, only little effect was bound to be observed on a non-charring polymeric material. Therefore, in order to further the fire-retardant effect of salen on a material, a slightly more charring polymeric material was used: PA6.Since s2-Cu has demonstrated a potential fire-retardant effect on TPU, it was also tested on PA6. Moreover, in order to check the catalytic effect that zinc may have when it is incorporated in PA6, s2-Zn was also used as an FR. Therefore, this section will deal with three possible candidates as a fire-retardant on PA6: s2 (uncomplexed ligand), s2-Cu, and s2-Zn.

V.3.a. Thermal stability of PA6/**s2**, PA6/**s2-Cu**, and PA6/**s2-Zn** on PA6 Since the presence of an additive on a polymeric material may impact the thermal properties of a material, the thermal stability of PA6 and its corresponding formulations were evaluated

using thermogravimetric analyses in pyrolytic conditions and in air.

V.3.a.i. Thermal stability of PA6/**s2**, PA6/**s2-Cu**, and PA6/**s2-Zn** on PA6 under nitrogen

Figure 125 and Figure 126 show the TGA and DTG curves of PA6 and its corresponding formulations under pyrolytic conditions. Table 33 is a summary of the data regarding the TGA of PA6 and its corresponding salen metal complexes.



-25 PA6-Neat -20 PA6/s2 DTG (%/min) PA6/s2-Cu PA6/s2-Zn -15 -10 -5 100 200 300 400 500 600 700 800 Temperature (°C)

Figure 125. TGA curves of neat PA6 (dotted, olive), PA6/s2 (black), PA6/s2-Cu (red), and PA6/s2-Zn when subjected to a heating rate of 10°C/min under nitrogen, and a 10/1 wt% ratio of polymer/additive loading

Figure 126. DTG curves of neat PA6 (dotted, olive), PA6/s2 (black), PA6/s2-Cu (red), and PA6/s2-Zn when subjected to a heating rate of 10°C/min under nitrogen, and a 10/1 wt% ratio of polymer/additive loading

The TGA curve of neat PA6 (olive, dotted) shows that the temperature at the onset of the degradation occurs at 401 °C. The decomposition appears to occur in a single step whereby the polymeric material is completely degraded over a small range of temperature. The maximum mass loss rate (23 %/min) can be observed on the DTG curve, and is recorded at 454 °C.

From the TG curve of the formulations, it can be seen that the onset of the degradation generally occurs at a slightly lower temperature (between 370 -375 °C). However, the mass loss rates of the formulated samples are lower than that of neat PA6. One major difference in the thermal decomposition behavior is observed on the TG and DTG curves of PA6/s2-Zn, whereby the maximum mass loss rate occurs at a lower temperature 413 °C as compared to the other formulations (approximately 456 °C).

Table 33. Thermogravimetric data of salen PA6, PA6/s2, PA6, s2-Cu and PA6/s2-Zn under nitrogen at 10 °C/min

Sample		Sź	2	
	T _{5%} [°C]	T _{MAX} [°C]	MLR [%/°C]	Res [%]
Neat PA6	400	454	2.3	1
s2	370	457	1.6	7
s2-Cu	375	451	1.6	10
s2-Zn	375	413	1.9	16

 $^{1.}$ MLR_{Max} occurs at the first step of the degradation

 $^{2.}$ $\ MLR_{MAX}$ occurs at the second step of the degradation

The residual masses at 800 °C are also different from one formulation to another. Neat PA6 leaves hardy any residue at 800 °C. However, the presence of **s2**, **s2-Cu**, and **s2-Zn** seems to have an effect on the residual mass at high temperature. Indeed, a higher mass at 800 °C is recorded for the loaded polymeric material, the highest being with **s2-Zn** (16 wt%).

The TG curves under pyrolytic conditions have provided insight on the thermal stability and some decomposition behavior that can be expected from them. However, during a fire scenario, the burning environment is not only relatable to pyrolytic conditions (e.g. thermo-oxidation of the material upon heating before ignition). Therefore, the TGA of PA6 and its corresponding salen formulations were also performed in air.

V.3.a.ii. Thermal stability of PA6/**s2**, PA6/**s2-Cu**, and PA6/**s2-Zn** on PA6 in air

Figure 127 and Figure 128 show the TGA and corresponding DTG curves of PA6 and its formulations when they were heated in air at a heating rate of 10 °C/min. Table 34 is a summary of the data regarding the TGA.



Figure 127. TGA curves of neat PA6 (dotted, olive), PA6/s2 (black), PA6/s2-Cu (red), and PA6/s2-Zn when subjected to a heating rate of 10°C/min in air, and a 10/1 wt% ratio of polymer/additive loading

Figure 128 DTG curves of neat PA6 (dotted, olive), PA6/s2 (black), PA6/s2-Cu (red), and PA6/s2-Zn when subjected to a heating rate of 10°C/min in air, and a 10/1 wt% ratio of polymer/additive loading

The TG curves of PA6 and its formulated samples show that there are two steps during their thermo-oxidative decomposition. The first step of the decomposition can be assigned to the formation of a charred structure (formation of a transient char), and the second step can be assigned to the decomposition of the char that is formed.

The temperature at the onset of the thermo-oxidative decomposition of neat PA6 is measured at 375 °C. That of the other formulations are recorded at 350 °C (PA6/s2), 362 °C (PA6/s2-Cu), and 366 °C (PA6/s2-Zn). The decomposition temperatures are within 10 % of each other, suggesting that there is only a minor decrease in thermal stability when comparing with the neat material.

Somula	s2			
Sample	T5% [°C]	$T_{MAX} [^{\circ}C]$	MLR [%/°C]	Res [%]
Neat PA6	377	445	1.5	0
s2	350	445	1.5	0
s2-Cu	362	435	1.3	0
s2-Zn	366	414	1.5	0

Table 34. Thermogravimetric data of salen PA6, PA6/s2, PA6, s2-Cu and PA6/s2-Zn under thermo-oxidative atmosphere at 10 °C/min

 $^{1.}$ MLR_{Max} occurs at the first step of the degradation

 $^{2.}$ $\ MLR_{MAX}$ occurs at the second step of the degradation

However, the amount of char formed during the first step of the thermo-oxidative decomposition is different depending on the additive that was used. Indeed, the first decomposition step on the TGA curve of neat PA6 leaves at around 15 wt%, but that of PA6/s2-Zn leads to a charred structure corresponding to around 26 wt%.

This means that if the decomposition behavior is similar in air, in a fire scenario, the presence of the zinc based would form a char more quickly. This can protect the underlying material by limiting heat and mass transfer to the flame.

V.3.b. Microscale Combustion Calorimetry on PA6

Since the release of volatiles also occurs relatively quickly, it might mean that the heat released during the early decomposition of the material generates a high amount of combustibles. To verify the heat released during the combustion of the thermal decomposition products of PA6 and its corresponding formulations, MCC was performed on them.

Figure 129 shows the MCC curves corresponding to PA6 and the PA6 based formulations. The data are summarized in Table 35.



Figure 129. MCC curves of PA6 (olive, dotted), PA6/s2 (black), PA6/s2-Cu (red), and PA6/s2-Zn (blue), and a 10/1 wt% polymer//additive loading.

The MCC curve of neat PA6 shows that the heat release rate is close to zero until around 375 °C, whereby an increase in heat release rate is recorded. The pHRR is recorded at 468 °C and corresponds to a value of 847 W/g. The MCC curves of PA6/s2 (black) and PA6/s2-Cu (red) show that the pHRR is very close for the two formulations (approx. 660 W/g). Similarly, the temperature at the peak of heat release rate are also close to each other (452 and 458 °C). The MCC curve of the PA6/s2-Zn formulation shows a very different behavior as compared to those corresponding to the other formulations. Indeed, the pHRR occurs at a lower temperature than the other formulations (417 °C, as compared to 455 and 468 °C for the other formulations and neat PA6 respectively). However, the pHRR value (586 W/g) is also the lowest among all the other PA6 formulations. In addition, another peak is observed in the MCC curve at 468 °C.

The presence of **s2-Zn** seems to bring about a very different decomposition behavior on PA6. Despite the pHRR occurring at a lower temperature, its value is 31 % lower than that of neat PA6. Moreover, the two steps in the thermal decomposition is clearly visible on the MCC curve. The first step is assigned to the release of volatile products that is essential for the formation of the carbonaceous char. Since the second peak of the HRR corresponds exactly to the pHRR of neat PA6, we have deduced that the second step corresponds to the thermal decomposition of uncharred structure, leading to the release of similar volatile products as neat PA6. However, since the cross-linking reaction has taken place in the first decomposition step, the amount of "neat PA6" left is lower. Therefore, the second peak of heat release rate is much lower than that of neat PA6 simply because the amount of material

left to thermally degrade and release heat is less. This is also evidenced by the lower THR during the combustion of the pyrolyzates corresponding to the thermal decomposition of PA6/s2-Zn as compared to that of neat PA6.

Additionally, the presence of **s2** and **s2-Cu** seems to have an influence on the pHRR of PA6 when tested using the MCC. According to our previous study, it might be assigned to the crosslinking phenomenon that occurs during the thermal decomposition of the material [24]. This causes a densification of the polymer matrix, causing less thermal breakdown to occur, thus leading to a lesser release of volatile and combustible decomposition products.

Table 35. Summary of peak of heat release rate, temperature at peak heat release rate and the THR for the PA6/salen formulations

Sample	pHRR (W/g)	T (°C) @ pHRR	THR (kJ/g)
Neat PA6	847	467	47
PA6/s2	661	458 (- 9 °C)	51 (+ 9%)
PA6/s2-Cu	660	452 (- 15 °C)	47 (0%)
PA6/s2-Zn	586	417 (- 50 °C)	37 (- 21%)

The THR during the MCC test on PA6, PA6/s2, and PA6/s2-Cu are relatively close to each other. However, the THR of PA6/s2-Zn is 21% lower than that of neat PA6.

In order to investigate further the decomposition behavior of the formulations, the MCC results were correlated to the TG curves i.e. the specific heat release rate as a function of residual mass. This allowed observing the evolution of the mass of the sample as well as the degree of decomposition at which there is a notable release of combustibles. This led to a representation of the amount of heat released with respect to the remaining mass of the samples (Figure 130).



Figure 130. HRR vs mass loss curves of PA6 (olive, dotted), PA6/s2 (black), PA6/s2-Cu (red), and PA6/s2-Zn (blue) when subjected to a heating rate of 60 °C/min, and a 10/1 wt% polymer//additive loading

From the HRR vs mass loss curve, it can be observed that the onset of the release of combustibles start early in the decomposition of PA6 and all the other formulations. In the case of neat PA6, the HRR increases steadily until around 30 % of mass loss. After this, the heat release rate of the thermal decomposition products decreases until the maximum decomposition. PA6/s2 and PA6/s2-Cu also release an increasing amount of combustibles in the first 20 % of the mass loss. After that, the heat release rate decreases until the end of the decomposition. The HRR/mass loss curve of PA6/s2-Zn shows that the release of combustibles occurs at an even earlier stage of the decomposition of the material. However, the peak of heat release rate reached is slightly lower than the other formulations. This suggests that the first decomposition step of all the formulations is the one that causes the release of most combustible materials. Consequently, we can further infer that the first decomposition is indeed the process whereby rearrangement of the polymer structure into a char can occur.

While a slight decrease in HRR and, in the case of PA6/s2-Zn, in THR is observed, the actual fire behavior of PA6 and its corresponding formulations also need to be studied. This will be explored in the next section; whereby the fire performance of PA6 and its salen based counterparts were evaluated using the mass loss cone calorimetry.

V.3.c. Fire behavior of PA6/salen

To investigate the fire behavior of PA6 and its corresponding formulations, the MLC test was used on samples of $(100 \times 100 \times 3) \text{ mm}^3$ samples with an incident heat flux of 50 kW/m^2

and a separation of 35 mm from the heat source. The conditions here are different from the test performed on the TPU sample because of the various inconveniences posed by the fire behavior of PA6. Indeed, the samples tested have shown a high amount of swelling, therefore a higher separation (25 mm for TPU vs 35 mm for PA6) was used. However, despite the higher separation, the swelling was still too significant. This caused the polymeric material to touch the igniter of the mass loss cone calorimeter, leading to non-repeatable results with an incident heat flux of 35 kW/m². Therefore, we decided to use a higher incident heat flux (50 kW/m²) to increase the rate of decomposition and, as such, cause an earlier ignition time, before observing significant swelling.

Figure 131 shows the MLC curve of PA6 and its corresponding formulations when they were tested under an incident heat flux of 50 kW/m^2 , separated by 35 mm. the critical values for the test are summarized in Table 36



Figure 131. MLC curves of neat PA6 (olive, dotted), PA6/s2 (black), PA6/s2-Cu (red), and PA6/s2-Zn (blue)

The MLC curve of neat PA6 shows that there is no heat released until ignition (at 45 s). After ignition, there is a rapid increase in the HRR, peaking at 498 kW/m² (121 s). The HRR then decreased sharply for the next 100 s, then at an increasingly lower rate until flameout at 474 s. The THR during the MLC test was 65 MJ/m². The HRR curve of PA6/s2-Cu has a similar shape to that of neat PA6. Although it has a slightly lower ignition time (38s), the pHRR is slightly lower (469 kW/m²) and also occurs in less time (107 s) as compared to neat PA6. However, the THR measures for PA6/s2-Cu is lower (53 MJ/m²) than neat PA6. Concerning the PA6/s2 formulation, while the time to ignition is longer (76 s) than neat

PA6, the pHRR is higher (596 kW/m² vs 512 kW/m²). This is achieved shortly after ignition, whereby a sharp increase in HRR is observed. After this, the HRR decreases sharply at first, then slowly until flameout at 596 s. The THR is close to that of neat PA6. PA6/s2-Zn has an entirely different shape than the other formulations. IAfter ignition, there is a rapid increase in HRR until the pHRR at 72 s (226 kW/m², - 56 % as compared to neat PA6). This pHRR is followed by a slow decrease in pHRR until flameout at 551 s.

pHRR (kW/m²) Sample TTI (s) THR (MJ/m²) Neat PA6 51 512 65 PA6/s2 76 596 (+17%) 63 (- 3%) 469 (- 8%) PA6/s2-Cu 38 53 (- 18%) 29 PA6/s2-Zn 226 (- 56%) 50 (-23 %)

Table 36. Summary of the MLC test results on the different PA6 formulations under 50 kW/m² and 35mm separation

The general behavior before ignition of the PA6/salen based formulations are similar (Figure 132). Indeed, the first observation made was the formation of a charred layer on the surface of the material. This corresponds to the initial decomposition of the material. Moreover, since the incident heat flux on the material is still relatively significant, the material continues to decompose thermally, causing the release of decomposition gases. This caused a swelling of the material because the volatile decomposition products could not escape through the surface due to the protective char layer that is formed. However, as the pressure builds up, the gases are eventually released, and the gases ignite. It is worth noting that this behavior was not observed in the case of neat PA6.



Figure 132. Pictures taken of neat PA6 (top left, green), PA6/s2 (top right, black), PA6/s2-Cu (bottom left, red), and PA6/s2-Zn (bottom right, blue) during the MLC right before ignition.

After ignition, a steady burning is observed for all the samples (Figure 133). In the case of PA6/s2 the surface of the material seems to remain intact during the initial burning process. However, we believe that the flame is fed by fuel coming from the bulk of the material. Eventually, the char ends up collapsing, causing a steady release of combustible volatiles to feed the flame. Moreover, a similar behavior is observed in the case of the MLC of PA6/s2-Cu.


Figure 133. Pictures taken of neat PA6 (top left, green), PA6/s2 (top right, black), PA6/s2-Cu (bottom left, red), and PA6/s2-Zn (bottom right, blue) during the MLC 5 s after ignition.

However, the protective layer lasts less time, and a steady release of gases can be observed via the formation of gas bubbles on the surface of the material, suggesting that the protective char formed is not thermally strong enough to withstand the incident heat, causing it to break, thus maintaining a steady influx of combustibles to sustain the fire. PA6/s2-Zn on the other hand does not exhibit this behavior. Instead, the formation of a char is observed, which is clearly visible 60 s after ignition of the sample (Figure 134).



Figure 134. Photo of PA6/s2-Zn 60 s after ignition when subjected to 50 kw/m².

Despite taking longer to catch fire, the fire performance of PA6/s2 is worse than that of neat PA6 because of the high pHRR during burning. The longer ignition time of PA6/s2 may be due to the protective layer that is formed during the initial decomposition stage. This layer seems to keep volatile combustibles from escaping and reaching the igniter. However, after a while the pressure buildup is sufficient to break the charred layer, causing a sudden release

of a large quantity of volatiles. As a result, they are ignited and, upon burning, cause a drastic increase in pHRR. A similar phenomenon is observed with PA6/s2-Cu. However, the accumulation of gases lasts less time as the material ignites much faster. This means that the amount of combustibles released upon the breakage of the charred layer is less than that released for the PA6/s2 sample. Therefore, a lower pHRR is achieved when comparing with PA6/s2.

On the other hand, despite having a much lower ignition time than the other tested samples, PA6/s2-Zn also has more than 50 % lower pHRR values. This suggests that the decomposition of PA6/s2-Zn releases a lower amount of combustibles (confirmed by the lower pHRR measured using the MCC). This can be accounted for by the fact that the there is a higher amount of charring that is visible on the sample. This means that the presence of s2-Zn has led to the formation of a carbonaceous product that is less likely to feed the flame with combustibles.

In order to better understand the reasons behind the difference in HRR corresponding to the formulations, Py-GCMS was performed on PA6 and its salen based formulations. The sample was heated for one minute under flash pyrolysis conditions (700 °C) and the volatile gases that were evolved during this decomposition was separated by a GC column and analyzed using mass spectrometry.



Figure 135. Total Ion Chromatogram (TIC) of neat PA6 (green), PA6/s2 (black), PA6/s2-Cu (red), and PA6/s2-Zn when subjected to a flash pyrolysis at 700 °C under helium.

Figure 135 shows the total ion chromatograms (TIC) of PA6 and the three salen-based formulations when they were subjected to a flash pyrolysis at 700 °C.

The TIC of all the samples show a major peak at around 20 min (circled in blue), which has been identified as caprolactam. Two other major peaks that were common for all the formulations and neat PA6 are those having a retention time of around 35 min (encircled in red). They were attributed to a linear dimer which has depolymerized leaving a nitrile end group. Hexenenitrile and hexanenitrile (green) were also detected at major decomposition products for every sample.

However, when looking at the TIC of neat PA6, there are several decomposition products that are observed with a retention time ranging from 20 to 35 min. These decomposition products correspond mostly to small linear amides with a nitrile end-group on one end. These low molecular weight decomposition products probably contribute to the high heat release rate of PA6 during the mass loss cone calorimetry test.

On the other hand, when looking at the TIC for the same range of time (20 - 35 mm) for the salen based formulations, it can be observed that the relative intensities of the peaks at are much lower as compared to those on the TIC of neat PA6. This suggests that in the presence of salen in the polymeric material, there is a lesser amount of these small combustibles.

Moreover, a higher proportion of (2E,4E)-hexa-2,4-dienenitrile and 2-oxocyclopentane-1carbonitrile was observed on PA6/s2-Zn as compared to the other formulations and neat PA6 (brown square, Figure 135). This evidences that there is the formation of poly alkenes alongside the formation of caprolactam. The presence of polyalkenes suggests that high temperature poylmerisation may occur at high temperature leading to a crosslinked structure. This also suggests that instead of the entirety of the thermal decomposition products releasing the combustibles, some of them leads to the formation of a cross-linked structure, as it was physically observed on the PA6/s2-Zn sample during the MLC test. This thermal decomposition products led to the thermal decomposition of PEEK whereby the thermal decomposition products led to the formation of a highly crosslinked, thermally robust structure.

V.3.d. Conclusion

We have seen that under inert atmosphere, temperature of the onset of the thermal decomposition PA6 is hardly affected by the presence of approximately 10 wt% of salen. However, the residual mass at high temperatures led to believe that there was an enhancement in their stability as compared to neat PA6. This could be explained by an increased crosslinking occurring during the thermal decomposition, aided by the presence of salen(OH)₂ derivatives, which is known to aid in the cross linking of PA6 [4].

This enhanced high thermal stability was even more evidenced when PA6 and its salen counterparts were subjected to high temperature under thermo-oxidative atmosphere. It also brought light upon the thermo-oxidative stabilities of the transient char that is formed during the first step of the decomposition. Unfortunately, the transient char did not seem to be stabilized by the presence of the salen derivatives. Indeed, the three fire-retardants that were tested seemed to have a transient char that decomposes at relatively close temperatures to each other.

Moreover, while the study on combustion behavior of the formulated samples have previously shown that the presence of a salen based additive may affect the combustibility of the decomposed products, this was not entirely the case for PA6/salen formulations. Indeed, the HRR results measured remained relatively close to that of neat PA6. However, insight regarding the decomposition behavior of PA6/Zn was obtained. Indeed, while the peak of heat release rate of PA6/s2-Zn was around 20 % less than that of neat PA6, we were also able to see two different pHRR. This means that there are at least two steps in the

thermal decomposition of PA6 whereby combustibles are released. These two steps are assigned to first, the crosslinking reactions taking place within the polymeric material, and secondly, the "regular" decomposition of the material.

However, despite having a lower pHRR under the microscale combustion calorimetry test, the actual fire behaviors of the formulated samples were less conclusive. Indeed, the MLC curve of PA6/s2 shows that it has a higher pHRR than neat HRR. This may be due to the sudden release of a large amount combustibles after flaming up, leading to a high heat release rate.

PA6/s2-Cu on the other hand showed no improvement as compared to neat PA6 in under the fire test. Indeed, the peak of heat release rate was only marginally lower than that of neat PA6. However, the test did show a significant decrease in the THR (-18 % as compared to neat PA6).

Finally, the most promising fire retarded PA6 among the three fire retardants that were used was PA6/s2-Zn. Despite it having a much lower ignition time, the pHRR was more than 50 % less than neat PA6. This low pHRR was assigned to the charring that is observed during the burning process. Indeed, when the surface of the material chars, it limits the amount of fuel that is released to feed the fire. Moreover, it was also observed by Py-GCMS that the thermal decomposition of PA6/s2-Zn generates other molecules than neat PA6. This suggests that the small molecules could have been used for the formation of the charred structure.

In order to confirm this, further structural and chemical analyses need to be performed on the charred structure of the material. In addition, a more in-depth analysis of the decomposing PA6/s2-Zn needs to be made in order to have a better insight as to the thermal decomposition mechanism and the synergy it seems to bring to the fire performances of PA6.

V.4. Conclusion

Several potential fire retardants have been synthesized and characterized. It was observed that the presence of a metal on both salen and salen(OH)₂ impropriated a higher thermal stability in the complex formed as compared to the non-complexed molecule. This high thermal stability meant that they could be incorporated into polymeric materials without any decomposition on their part.

Salen, salen(OH)₂, and their corresponding complexes were thus incorporated in two polymeric materials: thermoplastic polyurethane (TPU) and polyamide 6, (PA6) and their thermal stability and fire performances were evaluated.

While the presence of a fire retardant in TPU did not have a major impact on the temperature of the onset of the thermal decomposition under inert conditions, the presence of the additive improved the residual mass at the end, suggesting that their presence led to a thermally enhanced char. This char, depending on the coordination metal used in the salen/salen(OH)₂, had different thermal stability under thermo-oxidative conditions. It was noted that TPU/s1-Zn and TPU/s2-Zn led to the char with the highest thermal stability, but it also was the formulation with highest decomposition speed. This is a two-way sword in the sense that the polymeric material would decompose much quicker, leading to a higher release of combustibles, however, once the first decomposition step has formed the char, the remaining material is more thermally robust.

However, the fire retardancy of the polymeric materials told a different story. Indeed, the zinc based salen complexes showed the higher pHRR when they were tested under 35 kW/m^2 under the mass loss cone calorimeter. None of the **s1** based fire retardants shows significant improvement on the fire retardancy of TPU. However, copper and manganese-based formulations held promise as fire retardants, but further fire tests need to be performed to understand their fire behavior.

Similarly to the TPU based formulations, the presence of salen in PA6 formulations had little or no effect on the temperature at the onset of the thermal decomposition of PA6. However, the residual mass at high temperature of the formulated samples was systematically higher than that of neat PA6. The TGA analyses in air evidenced that the thermal decomposition of PA6 and its corresponding salen based formulations followed at least a two-step process. The two-step decomposition of the PA6/s2-Zn was further evidenced using the MCC.

Mass loss cone calorimetry performed on PA6 showed that the presence of **s2-Zn** in the PA6 matrix had the greatest influence on the fire behavior of the tested samples. Indeed, the time to ignition of the PA6/**s2-Zn** sample was the lowest among all the formulations tested. Despite this being a drawback, it should be noted that the peak of heat release rate when PA6/**s2-Zn** was tested under the cone calorimeter at 50 kW/m² was more than 50 % lower than that of neat PA6.

This chapter has provided preliminary thermal and fire behavior of a new class of fire retardants. We have seen that depending on the material that is being tested, the flame-retardant behavior of the same fire retardant may have a negative effect on the fire properties of the material. It is therefore necessary to test a novel fire retardant in all its possible applications.

However, it is also important to dig deeper into the mechanisms in which the flame retardancy works. In the case of PA6/s2-Zn, the fist hypothesis is that there is an enhanced charring that is favored by the presence on s2-Zn in the material. However, further chemical and physical tests need to be performed in order to finish this study.

Conclusion and Outlook

Conclusion

This work has been dedicated to the study of the thermal and fire behavior of highperformance polymeric materials with the aim of acquiring the required insight to design smart fire retardants that would act as such high-performance materials when subjected to heat and fire. It also involved the testing and evaluation of such a potential fire retardant: salen, its derivatives, and its metal complexes.

To achieve this, an in-depth literature review on the thermal decomposition and fire retardancy of polymeric materials in general allowed for the understanding of the factors that govern the thermal stability and fire performance of a polymeric material. A literature review concerning a range of high-performance polymers was performed. These involved polymeric materials which possess high thermal and fire resistance, most of which were aromatic polymers. From this, due to their extremely enviable thermal and fire properties, three polymeric materials were chosen to be studied further: polyetheretherketone (PEEK), polyimide (PI), and polybenzoxazole (PBO).

These materials were tested in thermally demanding environments using TGA, under different oxygen levels in order to simulate different aspects of a fire scenario.

Under inert conditions, the three high performance polymers decomposed at high temperatures (above 550 °C), and yielded more or less 45 wt% of char. It was observed that the temperature at the onset of the decomposition has a varied dependence on the oxygen. Under 2% oxygen, the decomposition temperature of PEEK and PI is close to their decomposition temperature under nitrogen (less than 3 °C difference). However, for PBO, the temperature at the onset of the decomposition is 35 °C lower in 2% oxygen as compared to the onset of its decomposition under nitrogen. This means that the effect of oxygen on the onset of the thermal decomposition was more significant for PBO than for PEEK and PI, which showed a lower difference in thermal decomposition onset.

Moreover, the gases evolved during the thermal decomposition of these polymers were identified using TGA-FTIR and Py-GC/MS, allowing us to elucidate their decomposition pathway when subjected to thermal stress under inert conditions. The high cross-linking potential of all three materials was brought to light. It explained the high residual masses at

high temperatures when the materials were heated under nitrogen. Indeed, the highly aromatic background of the high-performance polymeric materials studied allowed for the formation of a dense crosslinked structure under high temperature, leading to the formation of a robust, stable char under inert conditions. However, as it is known, this char is thermo-oxidized in the presence of oxygen. This means that in a fire scenario whereby the materials themselves are not flaming but are under a high enough radiative heat flux in the presence of oxygen, they are likely to completely degrade due to thermo-oxidation.

To confirm this, the kinetic parameters for the thermal decomposition of the highperformance materials in the three above-mentioned atmospheres were calculated using a model-based simulation. From them, the activation energies pertaining to the first step of the decomposition were compared. It was observed that the presence of oxygen (even 2%) in the atmosphere decreases the activation energy. Moreover, the kinetic decomposition pathway adopted when the materials are heated under nitrogen, 2% oxygen, or air were also different from each other. It can be concluded that the onset of the decomposition temperature is more dependent on the oxidative nature of the atmosphere than it was assumed by the TG analyses, whereby the temperature at the onset of the decomposition were very close, whatever the atmosphere (with the exception of PBO)

In order to further the fire characterization of PEEK and PI under a fire scenario, they were subjected to a mass loss cone (MLC) calorimetry test. This allowed for the understanding of the heat released when PEEK and PI are subjected to high incident heat fluxes (50 and 60 kW/m²). Under the MLC, PEEK swells by a large amount, which can be explained by its crosslinking potential coupled with the inert decomposition gases evolved during its thermal decomposition. A relatively low peak of heat release rate is observed as compared to common engineering polymers (< 125 kW/m² when subjected to either 50 or 60 kW/m²), thus evidencing a high fire performance. PI, on the other hand, did not swell as much. However, it did exhibit an outstanding fire performance whereby no flaming was observed when subjected to 50 kW/m². A small flame is observed at 60 kW/m², but the peak of heat release rate remains astonishingly low (< 30 kW/m²), despite the high incident heat flux.

From the decomposition studies of PEEK, we have explained that its ability to form a char and simultaneously release non-flammable gases such as carbon monoxide may lead to the swelling of the char. The graphite-like char keeps its structure and acts as a barrier, preventing mass transfer from the polymer bulk to the surface, and heat transfer from the surface to the bulk. This protective layer of char is what impropriates such an enviable fireresistant trait to PEEK.

As for PI, the thermal decomposition products correspond to a high amount of carbon dioxide and carbon monoxide, meaning that the flammable decomposition gases are diluted by the non-flammable ones. This means that the concentration of combustibles is not high enough for the material to ignite. Moreover, like the thermal decomposition of PEEK, a dense char is also formed during the thermal decomposition of PEEK. Therefore, both the dilution of the combustibles in the gas phase, and the protection of the underlying material by the formation of a dense char protect the material and gives it excellent fire performances under both 50 and 60 kW/m².

The last step in our strategic design consisted of evaluating a fire retardant that could alter the fire behavior of a common polymer such that it acts as a high performance one when subjected to thermal stress and/or fire scenario. To achieve this salen, its derivatives, as well as some metal complexes (**s1**, **s2**, and their complexes with copper, nickel, manganese, and zinc) were formulated with a neat polymeric material under a low loading (10:1 weight ratio). Two polymers were used: thermoplastic polyurethane (TPU) and polyamide 6 (PA6).

Concerning the fire retardant, it was observed that the presence of a coordination metal increased the temperature at the onset of its thermal decomposition as well as its residual mass at high temperature. It is likely that the material itself forms a crosslinked structure when it is subjected to elevated temperature[44].

The salen complexes formulated with TPU were heated under nitrogen and in air and their fire properties were evaluated using MLC at 35 kW/m². There was no enhancement in thermal stability where the onset of the decomposition is concerned. However, with the exception of the zinc-based formulations, neither the salens nor the salen complexes showed a significant difference in the decomposition temperature. The zinc-based formulations, on the other hand, decomposed much quicker than the others under nitrogen. This means that the presence zinc in the material increases the rate of thermal decomposition, perhaps by catalyzing it.

As a result, the zinc-based formulations were the ones showing the poorest fire behaviors under the mass loss cone at 35 kW/m². Indeed, MLC curves of both zinc-based formulations (TPU/s1-Zn and TPU/s2-Zn) showed a sharp increase in pHRR right after ignition. Similarly, none of the s1 based formulations showed any significant improvement in the fire

behavior of TPU. However, among the other formulations, TPU/s2, TPU/s2-Cu, and TPU/s2-Mn showed lower pHRR and may hold a promise as a fire retardant in TPU.

Furthermore, when the salen based fire retardants were formulated with PA6, little or no effect was observed on the temperature at the onset of the thermal decomposition of PA6. However, their residual masses at high temperature were higher than that of neat PA6. A two-step decomposition was observed.

Similarly to the TPU/salen formulations, the fire performances of PA6 were evaluated using the mass loss cone calorimetry under 50 kW/m². Contrarily to the TPU/salen formulations, the zinc-based formulation showed a significant decrease in the pHRR. Indeed, the pHRR was lowered by more than 50%. This was attributed to the char formed during its initial decomposition, that led to the protection of the underlying polymer. This prevents the underlying material from undergoing extensive thermal decomposition that could release a high amount of fuel to a fire. Therefore, while the actual mechanism of the thermal decomposition behavior and the fire retardancy of the zinc based salen is not yet known, it has shown that it can have some form of mimicry of a high-performance material when it is subjected to a fire scenario.

In summary, the study of the high-performance material has provided insight on how a highly thermally stable and fire-resistant material reacts when subjected to high heat and fire scenarios. Understanding the kinetics of the thermal decomposition of these materials have also showcased the effect that oxygen may have both on the decomposition pathway and the activation energy for the thermal decomposition of the materials. Additionally, from the insights acquired through the study of the high-performance materials, a potential fire retardant was tested and its potential as a high-performance material imitator under fire conditions were evaluated. While the potential as a fire-retardant is present in salens, it also opens up a world of possible high-performance material mimicking fire-retardants.

Outlook

Seeing how this work is a multi-faceted one, it is obviously laced with several outlooks, coming from the various topics approached while they were being unfurled.

The first strategy adopted for the design of novel fire retardants was based on the study of fire properties and thermal behavior high-performance material. While the study of the thermal decomposition under inert atmosphere provided invaluable insight pertaining to the pyrolytic behavior of the polymeric materials, the exact reactions that are occurring under slightly oxidative atmospheres are not perfectly known. Despite the reasonable inferences made during the unfolding of this work, a deeper knowledge of the thermo-oxidative degradation of these materials can provide a clearer and more concrete view on their behavior in different fire scenarios. Moreover, a more complete decomposition pathway due to thermo-oxidative degradation would also heighten the understanding of the fire behavior that these materials exhibit when they are subjected to a fire scenario. This can also strengthen the hypotheses made for the analyses of the kinetics of the thermal decomposition of the high-performance materials. Moreover, to complement the study of high-performance polymers, a wider range of polymeric materials would provide a deeper insight on their enviable properties. By studying the decomposition and fire behavior of other materials, it could be possible to define structure/property relationships on the fundamental aspects of a polymeric material that impropriates high temperature and fire properties to it.

Furthermore, having observed a significant improvement in the fire performance of some salen-based fire retardant, it would be interesting to go further in this direction. This can be achieved by screening of a wider range of salen based derivatives and their complexes, and by furthering their application to a wider range of polymeric materials such as polyurethanes.

By testing the fire retardants on different polymeric materials, a deeper understanding of the fire retardancy of the synthesized additives will be reached, leading to a more adapted applicability on commonly used polymers. Indeed, as salen is a thermally triggered fire retardant, its action will depend on the nature of the polymer it is used with. This means that further decomposition and fire characteristics of the polymer/FR formulations need to be investigated in order to extract data as to how fire and decomposition behaviors of the materials evolve with the presence of the additive. In doing so, a deeper understanding of the thermally triggered fire retardant will be achieved and its adaptability to novel polymeric materials can be envisaged.

Additionally, by investigating a wider range of salen-type molecules as fire retardants, the thermally triggered nature of the fire retardant can be further understood. Indeed, we have seen that when complexed with a metal, the salen/metal complex shows an enhancement in its thermal stability. However, an improvement in the fire properties was not always observed. Therefore, bringing different structural changes in the base salen molecule and its corresponding complexes will provide a larger platform for the investigation of its versatility as a fire retardant.

Ultimately, it can be of interest to dig deeper into the unification of the two major aspects that were investigated in this work, that is, high performance polymeric materials and salens. Indeed, as a fire retardant, salen has shown that it has the potential of acting as a high-performance polymeric material when subjected to elevated temperatures. By having a more profound insight on the thermal decomposition of high-performance polymeric materials coupled with a thorough understanding of the thermally triggered fire retardant (salen), it might be possible to develop novel smart fire retardants which would act as a high-performance polymeric material in a fire scenario.

All in all, this work has been the first step towards a novel, backwards approach to fireretard common polymers. However, with the ever-increasing progress in the field of chemistry, it is almost always possible to go even further to find the perfect fire retardant.

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Annex – Technical data sheets of polymeric materials

TPU Elastolan C85A and PA6 S-27 BL Natural (Solvay)

Typical Properties of Elastollan®	ASTM Test Method	Units	Typical Values
All the physical properties reported here are measured on injection molded samples. Properties of sheet or film samples of this product are also available upon request.			
Specific Gravity	ASTM D 792	g/cm ³	1.19
Shore Hardness	ASTM D 2240	Shore A or D	85A
Taber Abrasion	ASTM D 1044	mg loss	25
DIN Abrasion	DIN 53516	mm ³ loss	25
E-Modulus	ASTM D 412	psi	3000
Flexural Modulus	ASTM D 790	psi	3600
Tensile Strength	ASTM D 412	psi	6000
Tensile Stress at 100% Elongation	ASTM D 412	psi	1000
Tensile Stress at 300% Elongation	ASTM D 412	psi	2200
Ultimate Elongation	ASTM D 412	%	590
Tear Strength	ASTM D 624, Die C	lb/in	620
Compression Set 22h at 70°C 22h at 23 °C	ASTM D 395 "B"	% of original deflection	35 25
Glass Transition temperature*	BASF Analytical Method	°C	-40
Vicat Softening Temperature	ASTM D 1525	°C	110
DMA Softening Temperature	BASF Analytical Method	°C	100

*Measured with Dynamic Mechanical Analysis (DMA). DMA profile is available upon request. Above values are shown as typical values and should not be used as specifications.

PA6 S27 BL Natural (Rhodia)

Property	Nominal Value	Unit
Relative viscosity in H ₂ SO ₄ (ISO 307)	2.70	
Viscosity index in HCOOH	140	ml/g
Relative humidity	< 0.2	%
Residual monomer	< 0.8	%
Specific gravity	1.13	g/cm ³
Tensile strength at yield	85	N/mm ²
Tensile strength at break	55	N/mm ²
Elongation at break	> 50	%
Flexural modulus	3000	N/mm ²
Notched Charpy Impact	4.5	kJ/m ²
Melting point	222	°C

PEEK Ketron 1000 (Quadrant Engineering Plastic Products)

Physical properties (indicative values)

PROPERTIES	Test methods	Units	VALUES
Colour	-	-	natural (brownish
			grey) / black
Density	ISO 1183-1	g/cm ³	1.31
Water absorption:			
 after 24/96 h immersion in water of 23 °C (1) 	ISO 62	mg	5 / 10
	ISO 62	%	0.06 / 0.12
- at saturation in air of 23 °C / 50 % RH	-	%	0.20
 at saturation in water of 23 °C 	-	%	0.45
Thermal Properties (2)			
Melting temperature (DSC, 10 °C/min)	ISO 11357-1/-3	°C	340
Glass transition temperature (DSC, 20 °C/min) - (3)	ISO 11357-1/-2	°C	- · · ·
Thermal conductivity at 23 °C	11 4	W/(K.m)	0.25
Coefficient of linear thermal expansion:			12/23
 average value between 23 and 100 °C 	8.5	m/(m.K)	50 x 10 ⁻⁶
 average value between 23 and 150 °C 	-	m/(m.K)	55 x 10 ⁻⁶
 average value above 150 °C 	(US)	m/(m.K)	130 x 10 ⁻⁶
Temperature of deflection under load:			<<
- method A: 1.8 MPa	ISO 75-1/-2	°C	160
Max. allowable service temperature in air:			
- for short periods (4)		°C	310
- continuously : for min. 20,000 h (5)		°C	250
Min. service temperature (6)	3 . €5	°C	-50
Flammability (7):			\sim
- "Oxygen Index"	ISO 4589-1/-2	%	35
 according to UL 94 (1.5 / 3 mm thickness) 	-	•	V-0/V-0
Mechanical Properties at 23 °C (8)	0		
Tension test (9):	1	Va	7 10
 tensile stress at yield / tensile stress at break (10) 	ISO 527-1/-2	MPa	115/-
- tensile strength (10)	ISO 527-1/-2	MPa	115
- tensile strain at yield(10)	ISO 527-1/-2	%	1000
- tensile strain at break (10)	ISO 527-1/-2	%	17
- tensile modulus of elasticity (11)	ISO 527-1/-2	MPa	4300
Compression test (12):		1.4	1
- compressive stress at 1 / 2 / 5 % nominal strain (11)	ISO 604	MPa	38 / 75 / 140
Charpy impact strength - unnotched (13)	ISO 179-1/1eU	kJ/m ²	no break
Charpy impact strength - notched	ISO 179-1/1eA	kJ/m ²	3.5
Ball indentation hardness (14)	ISO 2039-1	N/mm ²	210
Rockwell hardness (14)	ISO 2039-2	70-	M 105
Electrical Properties at 23 °C			
Electric strength (15)	IEC 60243-1	kV/mm	24
Volume resistivity	IEC 60093	Ohm.cm	> 10 '*
Surface resistivity	ANSI/ESD STM 11.11	Ohm/sq.	> 10 ¹³
Relative permittivity ε _r : - at 100 Hz	IEC 60250	-	3.2
- at 1 MHz	IEC 60250		3.2
Dielectric dissipation factor tan δ: - at 100 Hz	IEC 60250		0.001
dissipation factor lan 6 - at 1 MHz	IEC 60250	-	0.002
Comparative tracking index (CTI)	/IEC 60112	-	150

Note: 1 g/cm³ = 1,000 kg/m³; 1 MPa = 1 N/mm²; 1 kV/mm = 1 MV/m.

Polybenzoxazole (Zylon, Toyobo)

Physical Properties	Metric	English	Comments
Density	1.54 g/cc	0.0556 lb/in ^s	
Moisture Absorption at Equilibrium	2.0 %	2.0 %	at 65% RH
	3.5 %	3.5 %	at 90% RH
Mechanical Properties	Metric	English	Comments
Tensile Strength, Ultimate	5800 MPa	841000 psi	
Elongation at Break	3.5 %	3.5 %	
Tensile Modulus	180 GPa	26100 ksi	
Tenacity	3.71 N/tex	42.0 g/denier	
Thermal Properties	Metric	English	Comments
Decomposition Temperature	650 °C	1200 °F	
Oxygen Index	68 %	68 %	

Some of the values displayed above may have been converted from their original units and/or rounded in order to display the information in a consistent format. Users requiring more precise data for scientific or engineering calculations can click on the property value to see the original value as well as raw conversions to equivalent units. We advise that you only use the original value or one of its raw conversions in your calculations to minimize rounding error. We also ask that you refer to MatWeb's terms of use regarding this information. <u>Click here</u> to view all the property values for this datasheet as they were originally entered into MatWeb's terms of use regarding this information.

Electrical Properties	
Dielectric constant @1MHz	3.4
Dielectric strength (kV mm ⁻¹) 22
Dissipation factor @ 1kHz	0.0018
Surface resistivity (Ohm/sq)) 10 ¹⁶
Volume resistivity (Ohmcm) 10 ¹⁸
Mechanical Properties	
Coefficient of friction	0.42

Polyimide Cirlex Cl (GoodFellow)

Mechanical Properties	
Coefficient of friction	0.42
Elongation at break (%)	8-70
Hardness - Rockwell	E52-99
Izod impact strength (J m ⁻¹)	80
Tensile modulus (GPa)	2.0-3.0
Tensile strength (MPa)	70-150

Physical Properties		
Density (g cm ⁻³)	1.42	
Flammability	V0	
Limiting oxygen index (%)	53	
Radiation resistance	Good	
Refractive index	1.66	
Resistance to Ultra-violet	Poor	
Water absorption - over 24 hours (%)	0.2-2.9	

Thermal Properties	
Coefficient of thermal expansion ($x10^{-6} \text{ K}^{-1}$)	30-60
Heat-deflection temperature - 1.8MPa (C)	360
Lower working temperature (C)	-270
Specific heat (J K ⁻¹ kg ⁻¹)	1090
Thermal conductivity @23C ($W\ m^{\text{-1}}\ K^{\text{-1}}$)	0.10-0.35
Upper working temperature (C)	250-320