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***Spécialité* : Molécules et Matière Condensée**

par

Dr. Maude JIMENEZ

Elaboration de matériaux fonctionnels - Approche par procédés de traitement de surface

Soutenu le 14 juin 2013 devant la Commission d'Examen suivante :

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Garant	**Prof. Serge BOURBIGOT** *Ecole Nationale Supérieure de Chimie de Lille*

“Learn from yesterday, live for today, hope for tomorrow. The important thing is not to stop questioning.”

A. Einstein

Acknowledgments

My first thanks go to Prof. Serge BOURBIGOT and Prof. Michel TRAISNEL for having welcomed me as assistant professor in the team and giving me the opportunity to take part to very interesting projects. I am especially grateful to them for their trust and guidance experienced these last years, which, combined with their continuous and stimulating participation, kept me highly motivated and enthusiastic. My sincere thanks also go to Prof. Sophie DUQUESNE, who provided me with the best scientific and moral support I could ever have desired. I also thank Prof. LEGRIS and Prof. LEFEBVRE for having me welcomed in the UMET laboratory and ISP team, Jean GRIMBLOT and Bernard FONTAINE for having me welcomed in ENSCL and Prof. BENCHIBOUN, Prof. MAZZAH and Prof. BOUSSEKEY for having me welcomed in the IUT and having trusted me to teach chemical engineering to our students.

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Contents

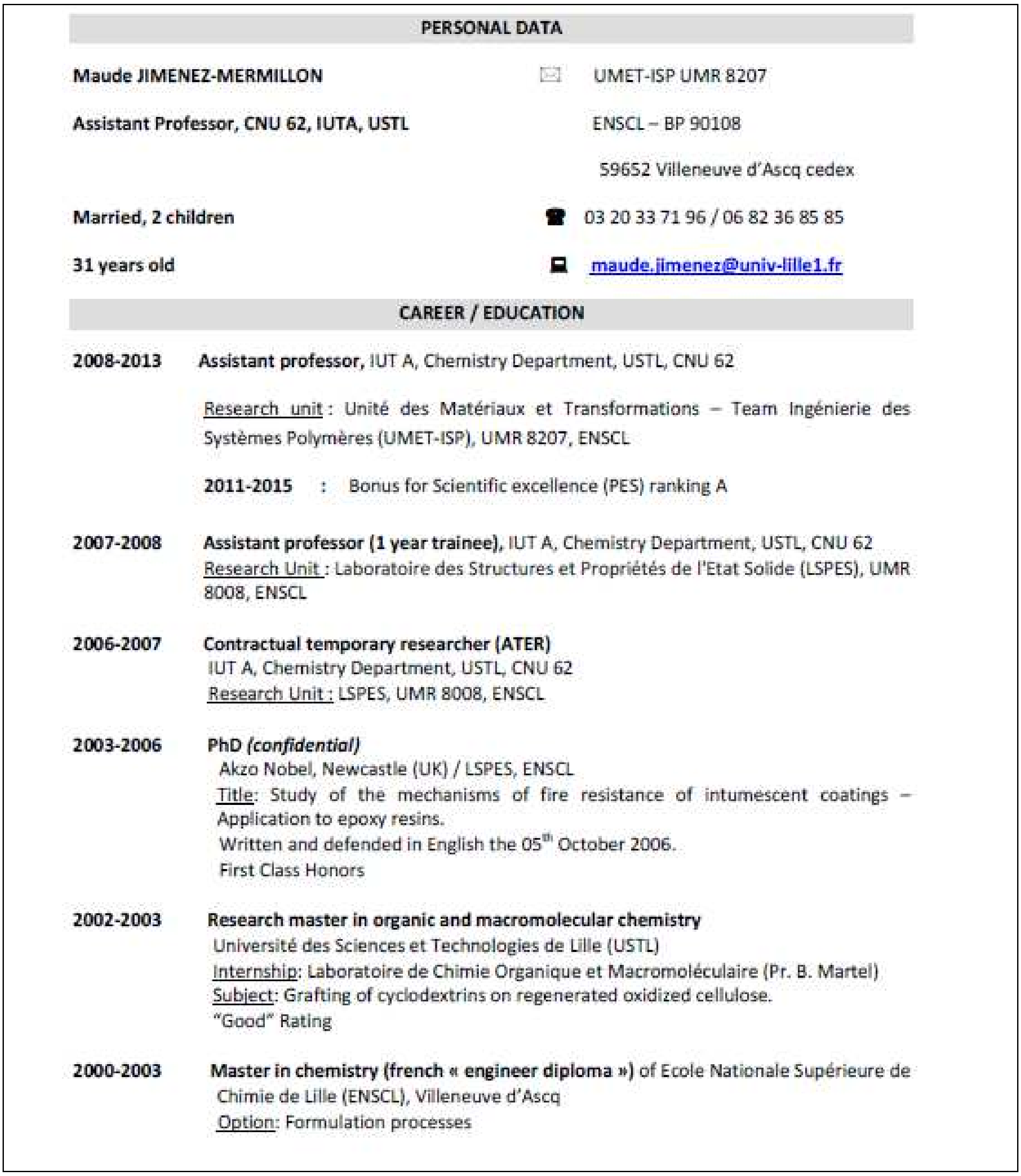
Abbreviations index

AES : Auger Electron Spectroscopy
ANR : Agence Nationale de la Recherche
APP : Ammonium Polyphosphate
APTMS : Aminopropyltrimethoxysilane
ATER : Attaché Temporaire d'Enseignement et de Recherche
ATG : Thermogravimetric Analysis
BLG : Beta Lactoglobulin
BPEI : Branched Polyethyleneimine
BSE : Back-Scattered Electrons
CNRS : Centre National de la Recherche Scientifique
CNU : Conseil National des Universités
CP : Cross-Polarization
CPER : Contrat de Projet Etat Région
CRP : Centre de Recherche Public
CVD : Chemical Vapor Deposition
DBD : Dielectric Barrier Discharge
DMVP : Dimethyl vinylphosphonate
EDS : Energy-dispersive X-ray spectroscopy
ENSCL : Ecole Nationale Supérieure de Chimie de Lille
EPMA : Electron Probe Micro-Analyzer
FCE : Fonds de Compétitivité des Entreprises
FEDER : Fonds Européen de Développement Régional
FR : Fire Retardant
FSI : Flame Spread Index
FTIR-ATR : Fourier Transform Infrared Spectroscopy Attenuated Total Reflectance
FUI : Fonds Unique Interministériel
GF : Glass Fiber
GWFI : Glow Wire Flammability Index
HMDSO : Hexamethyldisiloxane
HPASMC : Human Pulmonary Artery Smooth Muscle Cells
HPMEC : Human Pulmonary Microvascular Endothelial Cells
HRC : Heat Release Capacity
HRR : Heat Release Rate
IFR : Intumescent Fire Retardant
INRA : Institut National de la Recherche Agronomique
ISO : International Organization for Standardization
ISP : Ingénierie des Systèmes Polymères
IUT : Institut Universitaire de Technologie
LbL : Layer-by-Layer
LCOM : Laboratoire de Chimie Organique et Macromoléculaire
LOI : Limiting Oxygen Index
LSPES : Laboratoire des Structures et Propriétés de L'Etat Solide
M : Melamin
MA : Meta-Aramid
MAS : Magic Angle Spinning
MAUD : Matériaux et Applications pour une Utilisation Durable
MCC : Micro Combustion Calorimeter
MCF : Maître de Conférences

MLC : Mass Loss Calorimeter
NMR : Nuclear Magnetic Resonance
NW : Non Woven
OTI : On Track Innovation
P : Phenolic
PA : Polyacrylate
PA : Polyamide
PAA : Polyacrylic acid
PC : Polycarbonate
PECVD : Plasma Enhanced Chemical Vapor Deposition
PES : Prime d'Excellence Scientifique
PET : Polyethylene Terephtalate – Polyester
PIGP : Plasma Graft Induced Polymerization
PLA : Polylactic Acid
POSS : Polyhedral Oligomeric Silesquioxanes
PP : Polypropylene
PRAS : Plateforme Régionale d'Analyse de Surface
PW : Practice Work
RF : Radiofrequency
RFGD : Radio-Frequency Glow Discharge
R-LP-PECVD : Remote-Low Pressure- Plasma Enhanced Chemical Vapor Deposition
SDI : Smoke Development Index
SE : Secondary Electrons
SEM : Scanning Electron Microscopy
TEM : Transmission Electron Microscopy
TEP : Triethylphosphate
THEIC : Tris-(2-hydroxyethyl) isocyanurate
THR : Total Heat Release
TMDSO : Tetramethyldisiloxane
ToF-SIMS : Time of Flight Secondary Ion Mass Spectrometry
TSR : Total Smoke Release
TTI : Time to Ignition
UL : Underwriter Laboratories
ULS : Ultra Light System
UMET : Unité des Matériaux et Transformations
UMR : Unité Mixte de Recherche
USTL : Université des Sciences et Technologies de Lille
VPD-AP-DBD : Vapor Polymerization Deposition - Atmospheric Plasma- Dielectric Barrier Discharge
VTF : Vertical Flame Testing
XPS : X-Ray Photoelectron spectroscopy

Preamble

This manuscript aims at discussing the research topics I have developed during and since my PhD thesis and also presents the research works I have been co-supervizing. Before describing these topics, I will however briefly present in **Figure 1** my personal data, background and career and I will then detail my teaching and research activities.



PERSONAL DATA

Maude JIMENEZ-MERMILLON
Assistant Professor, CNU 62, IUTA, USTL

Married, 2 children
31 years old

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CAREER / EDUCATION

2008-2013 **Assistant professor,** IUT A, Chemistry Department, USTL, CNU 62
Research unit : Unité des Matériaux et Transformations – Team Ingénierie des Systèmes Polymères (UMET-ISP), UMR 8207, ENSCL
2011-2015 : Bonus for Scientific excellence (PES) ranking A

2007-2008 **Assistant professor (1 year trainee),** IUT A, Chemistry Department, USTL, CNU 62
Research Unit : Laboratoire des Structures et Propriétés de l'Etat Solide (LSPES), UMR 8008, ENSCL

2006-2007 **Contractual temporary researcher (ATER)**
IUT A, Chemistry Department, USTL, CNU 62
Research Unit : LSPES, UMR 8008, ENSCL

2003-2006 **PhD *(confidential)***
Akzo Nobel, Newcastle (UK) / LSPES, ENSCL
Title: Study of the mechanisms of fire resistance of intumescent coatings – Application to epoxy resins.
Written and defended in English the 05th October 2006.
First Class Honors

2002-2003 **Research master in organic and macromolecular chemistry**
Université des Sciences et Technologies de Lille (USTL)
Internship: Laboratoire de Chimie Organique et Macromoléculaire (Pr. B. Martel)
Subject: Grafting of cyclodextrins on regenerated oxidized cellulose.
"Good" Rating

2000-2003 **Master in chemistry (french « engineer diploma »)** of Ecole Nationale Supérieure de Chimie de Lille (ENSCL), Villeneuve d'Ascq
Option: Formulation processes

Figure 1. Personal data, background and career

After my PhD (2003-2006) carried out in partnership with Lille University and Akzo Nobel in Newcastle (UK), dedicated to the study of the mechanism of action of an intumescent thick epoxy based coating designed to protect steel structures in hydrocarbon fires, I got a position as “ATER” (contractual assistant professor) in 2006 in Lille University (IUT, chemistry Department).

I was then officially established as assistant professor in 2008 in Lille University (IUT, chemistry department). In the IUT (a 2 years program to become assistant engineer), I have been and I am currently teaching fluid dynamics (Semester 1), heat transfers (S2), chemical engineering unit operations (S3) and reactors (S4). I am also the pedagogical supervisor of the process engineering hall in the IUT and I am in charge for extensive renovation and for maintenance of this building (100 k€ investments since 2008). I am also in that frame responsible for teaching coordination and training of teachers from other departments.

I also have been co-supervising since 2007 a bachelor’s degree (Chemical and Pharmaceutical Industries), option PTSFRF (Surface Treatment Processes and Formulation of Functional Coatings), and I am currently responsible for the demand of habilitation of a professional bachelor’s degree entitled « Advanced processes and materials » in Lille University, for an opening in September 2014.

All my teaching activities and responsibilities are further detailed in the **Annex 1** of this manuscript.

I was meanwhile affected as researcher in UMET (Unité Matériaux et Transformations) laboratory, in the ISP (Ingénierie des Systèmes Polymères) team, and more precisely in the “Reaction and resistance to fire of materials” group.

The **Figure 2** presents the organization of UMET laboratory (**Figure 2a**) and the four topics developed in the “Reaction and resistance to fire of materials” group (**Figure 2b**).

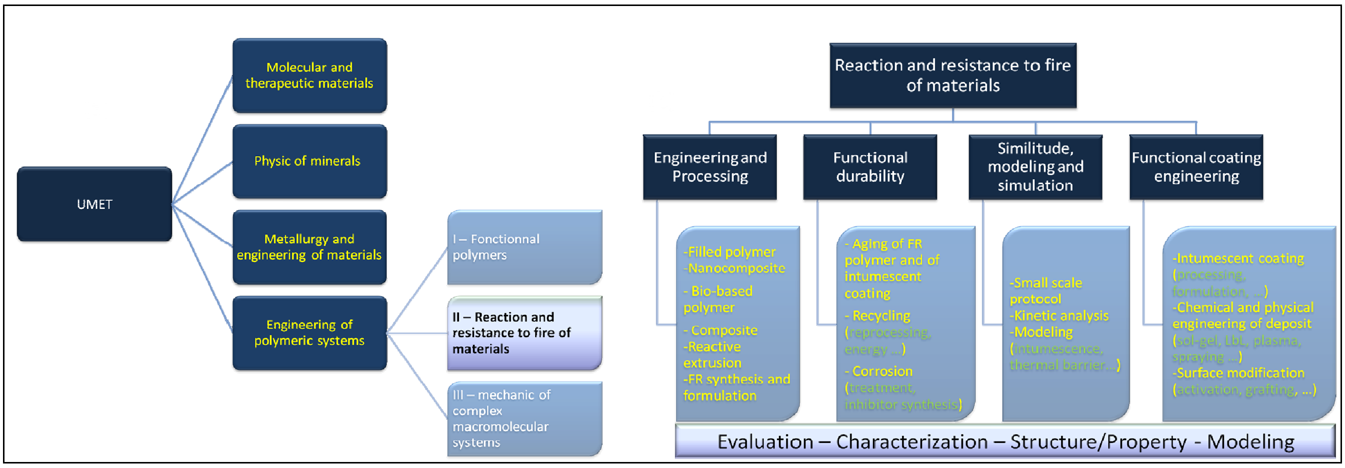

Figure 2. Presentation of UMET-ISP research unit (a) and reaction and resistance to fire of materials group thematic (b)

I will briefly discuss in the following part the topics I am developing in the group, as well as some of the projects associated.

The main topic I have been involved since I have been hired is the "**Functional coating engineering**". It consists in developing surface modification processes and elaborating functional coatings through the implementation of various surface treatment processes in the laboratory. The main objective is to provide fire resistant and/or fire retardant properties to different kinds of materials (steel, polymers and textiles) through these processes.
My first research interest is dedicated to the study of **thick intumescent coatings** to protect various subtrates.
During my PhD period, I first studied a **thick** epoxy based **intumescent coating** applied on steel to protect offshore platforms against hydrocarbon fires. I characterized the coating in terms of **fire-resistance** [1] and I then established the mechanism of action of this coating under rapid heating [2]. I developed an experimental methodology combining various small scale tests [3] allowing the prediction of the behavior of an intumescent coating in industrial large furnace tests. I finally implemented in the group a "high-throughput" small scale test which showed excellent correlations with industrial furnaces [4] and I developed a model for the numerical simulation of intumescence using a commercial finite element code (Comsol Multiphysics). **This PhD allowed to input in the group the topic entitled "Similitude, modeling and simulation"**. These last years, I had the opportunity to continue to work on this topic by participating to the development of a small scale furnace mimicking at reduced scale the large scale industrial furnace tests. We are still carrying this test development and we are now recognized at an international level for these small scale tests developments. Meantime, I also worked on the development of kinetics of degradation models allowing the simulation of the thermal degradation behavior of intumescent coatings in various fire scenarios [5].

Intumescent coatings are usually applied on wood and steel. I however have successfully extended the use of some **intumescent coatings onto various plastic materials** [6-9], by implementing a surface pre-treatment of the polymer before the coating application. It is the first time that this concept was published in the 'reaction fire' field. We further developed this concept through an industrial partnership with Rhodia (2007-2010) to reach enhanced fire retardant applications for electronic equipment [co-supervision (50%) of the PhD of H. Gallou, supervized by C. Jama (50%)]. During this project, a novel concept, combining the incorporation of a small percentage of fillers in the bulk and a thin layer of intumescent coating was recently patented [10] and published [11, 12]. A particular interest was dedicated to the study of the mechanisms of action of the intumescent coating in presence of the polymeric substrate, without and with fire retardant fillers incorporated in the bulk.

Both these concepts are efficient to protect polymers or textiles, however to be efficient intumescent coating thicknesses are sometimes too high compared to the material thickness. To further develop the "functional coating engineering" topic in the group, and particularly the development of thin coating processing - which is currently the best (and sometimes the only) option for protecting thin polymer films or textile materials - I also decided to develop a "**thin film coatings" topic** in the group. Various ways existing to deposit thin films on materials, we mainly focused these last years on the use of plasma coatings and Layer-by-Layer (LbL) deposition treatments.

Our team invested in 2006 in low pressure radiofrequency (RF) cold plasma treatment chambers and we managed to graft-polymerize phosphorus containing precursors by PIGP (Plasma Induced Graft Polymerization) on textiles to fire retard them. However, this process, although efficient to reach the desired properties, is a wet and multi-step process. This is why we meantime developed the use of a dry process, the Remote - Low Pressure - Plasma Enhanced Chemical Vapor Deposition (R-LP-PECVD) technology, to fire retard polymers. The concept of using PECVD to fire retard polymers had already been developed by S. Bourbigot and C. Jama (1999-2000), and in the frame of H. Gallou PhD (2010), we intended to achieve enhanced fire retardant performances for electrical applications using this technique. Unfortunately PECVD treatment was not efficient enough to meet some of the severe criteria imposed to electronic equipment. This is why, similarly to the protocol previously developed for the use of intumescent coatings, we managed to partly reach these objectives by combining a small amount of fillers incorporated in the bulk and a very thin organosilicon film deposited by PECVD on the surface. This concept was also recently patented [13] and published [12].

I then successfully extended the use of PECVD technology on high performance textiles, in a FUI project (Textherm, managed by S.Duquesne and S. Bourbigot), in partnership with the companies Alstom transport, Duflot and Kermel, consisting in developing innovative light thermal screens based on textile structures for automotive, rolling stock and airplanes [14].

We thus developed these technologies, first for fire retardant purpose, and also meantime for various applications (functional glasses, biomaterials, heavy metals remediation…) developed in collaborations with academic teams (Lille 2 University, Mines de Douai, ENSAIT, IFTH, Monastir University) and industrial partners (Arc International, Saverglass, Arcelor Mittal, INRA, Baudelet, Clayrton's, AGC Glass) through public projects (Drawspeedglass, Atmosverre, Fansbamed, young researchers project, Depoltex) and private collaborations. All these collaborations and the papers associated [15-23] are further detailed in the **Annex 2**, but they will not be presented in this manuscript.

R-LP-PECVD and RF cold plasma treatments are however discontinuous processes and industrial applications on large samples usually require continuous treatments. This is why we oriented the thin functional coatings topic to methods allowing the modification of a surface at atmospheric pressure. For example, I currently co-supervise at 50% a PhD student [(K. Apaydin) directed by S. Bourbigot (50%)], in collaboration with the CRP H.Tudor in Luxembourg in the frame of a FNR project entitled FRCoatings (2011-2014). This project aims at investigating the efficiency as flame retardant systems of coatings obtained by Layer-by-Layer (LbL) deposition [24] and by Dielectric Barrier Discharge (DBD) atmospheric plasma assisted deposition on thermoplastics and textiles (process input by F. Hilt, PhD in Luxembourg, 2011-2014). Meantime, we have recently invested in atmospheric plasma treatments (ULS and ULD from AcXys technology) and I am currently transfering the low pressure cold plasma processes developed in the group into atmospheric plasma processes, which could be implemented "in line".

During the development of these topic dedicated to the development of surface treatments (thin or thick films), I have noticed, whatever the couple substrate/coating, the great importance of the phenomena occurring at the material surface (aging, fouling) or at the interface (adhesion, delamination…), appearing when the sample is stored, when it is submitted to external constraints (UV, temperature, moisture…) or when it is in contact with a liquid. These phenomena are of high importance, as they prevent the functional durability of the coating and they must be taken into account when a coating - whatever the coating process- is developed. This is why I have started to develop further this topic in the incoming years, which is part of the **"functional durability" topic** in the laboratory.

In this mind, I started in 2011 to study the aging of intumescent coatings applied on steel and on polymers, submitted to UV light and temperature constraints [25] and submitted to immersion in water and salted water [26]. Surface analysis techniques such as Electron Probe Micro Analysis, Scanning Electron Microscopy etc. were of great help to understand these aging mechanisms.

This issue concerning functional durability can also be applied to completely other topics than fire retardancy. For example, I had the opportunity to evaluate interactions between the microstructure of a stainless steel surface and milk proteins put together in contact in a heat exchanger. I am still currently investigating in partnership with G.Delaplace from INRA and A.Allion from Arcelor Mittal this "fouling" phenomenon, which is preventing the functional durability of materials when put in contact with a liquide. In that frame, we recently developed, in partnership with the "Plateforme

Régionale d'Analyse de Surface" (PRAS) of Lille University, the use of extreme surface analysis techniques (e.g. XPS, ToF-SIMS, AFM) to analyze this fouling phenomenon on nano-thick fouling layers [PhD G.Alogaili (2011-2014), that I co-supervise at 50% with M.Traisnel] [27, 28]. To support the development of this topic, I have submitted in 2013 an ANR young researcher project on that subject, which is currently being reviewed.

To summarize, I mainly developed these last years three main research topics in the group: (i) the study of thick intumescent coatings that I started during my PhD and extended further to polymeric materials; (ii) the processing of functional thin films applied to polymer films and textiles, and (iii) the study of the functional durability of materials and surface treatments which is an emerging topic in the group. Some projects (detailed list in **Annex 2**) supporting these research topics have allowed me since 2006 to co-supervize 6 PhD students (3 current students and 3 defended theses), 5 Post-Doc students and 11 master students. A detailed list of these students is presented in the **Annex 3**. They contributed to the redaction of papers in peer-reviewed international journals, to patents and to communications and posters as well. The **Table 1** summarizes the number of papers published these last 8 years and the communications associated. A detailed list is presented in the **Annex 4**.

Table 1 : Number of papers and communications since 2005

Peer-reviewed papers in international journals	20 (14 as first author) 3 under revision 4 submitted
Patents	2
Technical papers	6 (5 as first author)
Oral communications with peer-reviewed proceedings	18 (5 as speaker)
Oral communications (no proceeding)	27 (9 as speaker)
Invited conference (as speaker)	5
Posters with peer-reviewed proceedings	8
Posters (no proceeding)	11

These last years, I also had the opportunity to co-organize some events, such as an EPMA seminar day in the ENSCL in 2008. I also was the main supervisor of the organization of a young researcher symposium in 2005 (around 80 attendees), entitled SAJEC2005 (Sigma-Aldrich Jeunes Chercheurs) that took place in Lille University. I also participated to recruitment jurys of research engineers and I am regularly asked to review some papers in peer-reviewed international journals (about 15 papers reviewed per year). These activities are further detailed in the **Annex 5** of this manuscript.

To conclude this preamble about my research activities, I can summarize the various competences I have acquired these last years through these three main research topics (thick coatings, thin films and functional durability) in **Figure 3**.

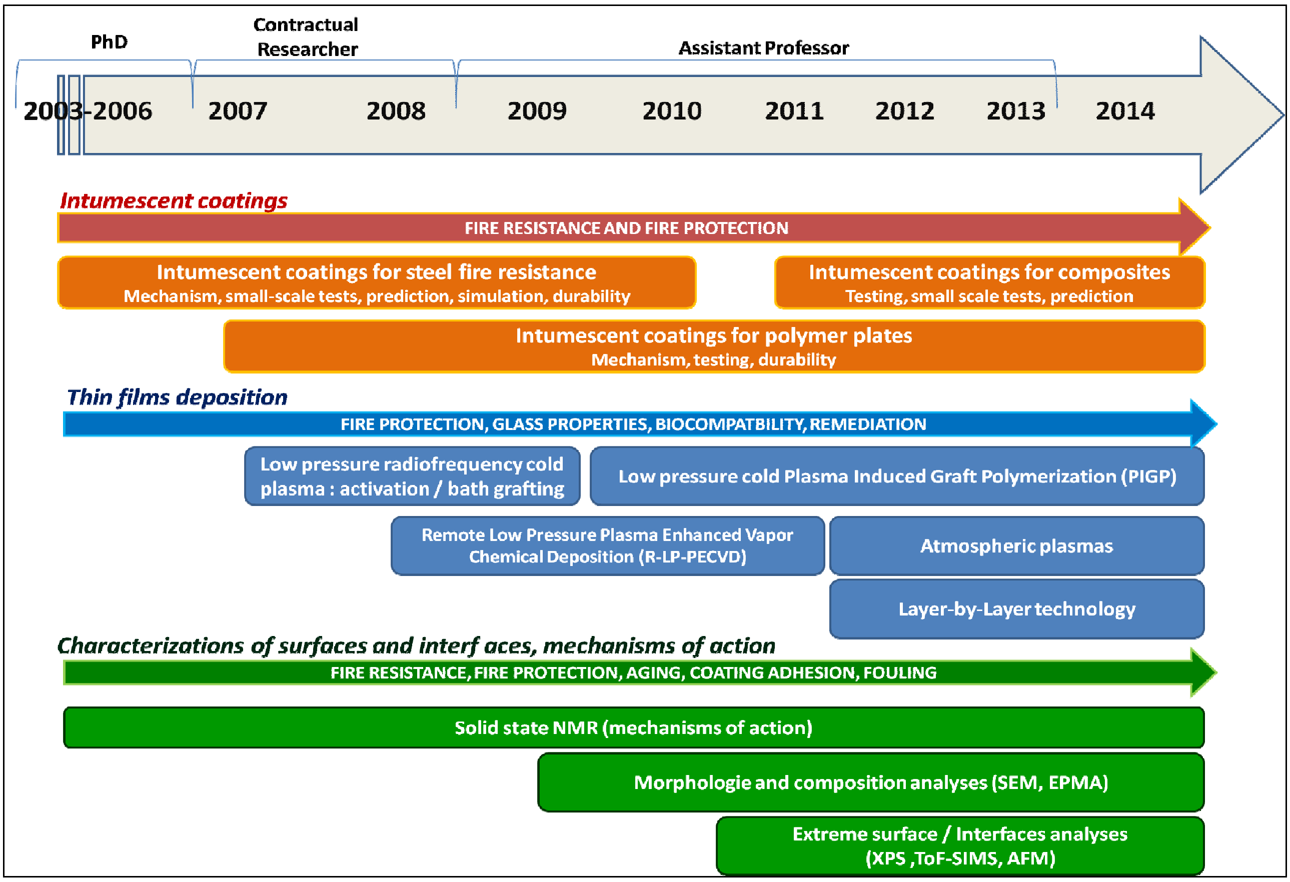

Figure 3. Schematic diagram of the competences acquired

The next part of this manuscript consists in a general introduction on the main topics I am developing in the lab: functional coating engineering and on the topic I aim at developing: functional durability of materials and coatings.

General Introduction

Raw materials, such as metals, polymers, textiles and glasses possess their own properties (mechanical, physical…) which are mainly determined by the bulk chemistry and morphology of the material.

To give a material certain functional properties (e.g. anti-corrosive, UV-resistant, anti-bacterial, flame retardant etc.) different pathways can be followed, such as the reactive approach, the bulk approach and the surface treatment approach.

The **Figure 4** presents these different pathways applied to give functional properties to various materials.

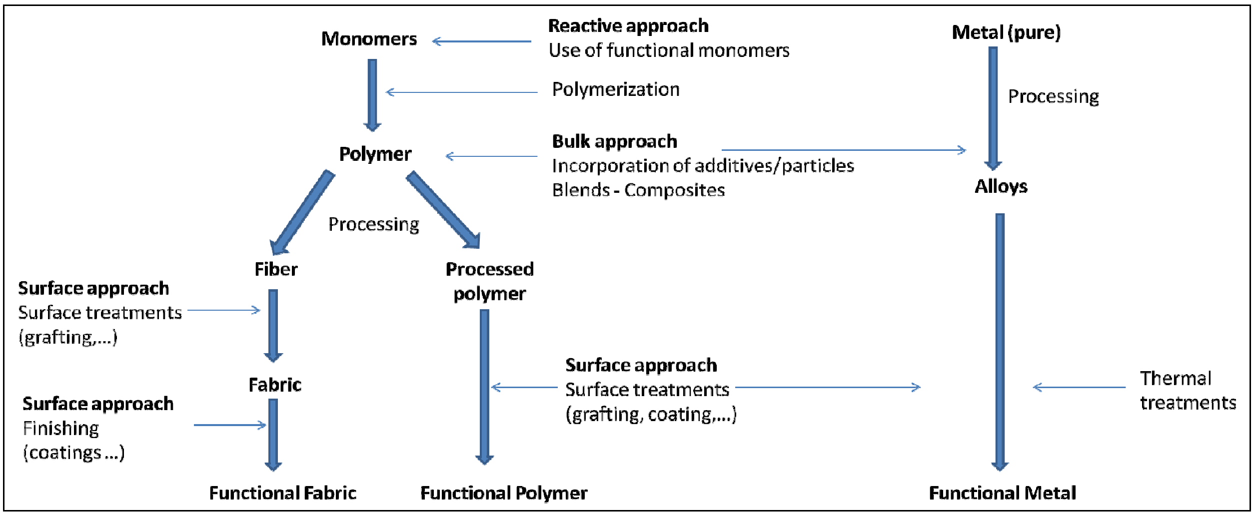

Figure 4. Different ways to fire retard polymers, textiles and metals

For a polymer-based material, the first solution ("Reactive approach") consists in the chemical modification of the monomer, leading to a polymer matrix or fiber in-situ functionalized. This technique is very efficient, but it is not easy to conduct on an industrial scale with most thermoplastic polymers, it can be rather expensive and so it is not commonly used.

In the second approach ("Bulk approach"), the polymer can be blended with fillers or active species, extruded and processed. These kinds of treatments are usually efficient to reach the functional property desired; however the bulk properties of the material are modified in terms of mechanical and physical properties, and unfortunately usually in the wrong way.

One way to overcome this issue (third solution) is to partly or completely replace these bulk treatments by surface modifications or surface coatings that would allow reaching the desired properties without affecting the material bulk. This is the "Surface approach".

For other kinds of materials, such as metals for example, similar solutions exist to provide specific properties: bulk treatments (e.g. alloys, incorporation of specific fillers) and surface treatments (e.g. organic coatings, conversion coatings, corrosion inhibitors, etc.).

During and since my PhD, I have mainly considered the third proposed approach, i.e. the surface modification of different materials, such as steel, glass, various polymers and textiles. In that frame, the material's surface properties are of major importance: if a material surface does not have the desired properties for a particular application, then undesirable surface events can lead to failure of the material and the device or system containing it. Examples of such failures include: (i) delamination of an adhesive bond; (ii) permanent staining of a fabric; (iii) fouling of membranes/steel plates with proteinaceous films; (iv) bacterial growth, etc.

It is also important to realize that the surfaces of normal, i.e. "as fabricated" materials often do not have the same compositions as the bulk phase. This can be due to the adsorption of contaminants from the surrounding environment (e.g. oils, soils, bacteria…), desorption of impurities and surface active compounds from the bulk phase (e.g. lubricants added as process aids) for polymeric materials, oxidation or hydrolysis of surface groups and preferred molecular orientation of surface groups (e.g. to minimize surface free energy). These effects often occur unevenly across a surface area, in "spots", "islands" or "domains". Surfaces can also have local physical defects, such as scratches, which can be an issue in some applications.

Therefore it is necessary to modify the materials surfaces, whether merely to clean them or to modify them physically, chemically, mechanically or biologically, in order to control the subsequent surface interactions and responses which are required for any particular application. The main methods that can be used to modify a material surface and /or to provide a functional property are listed hereafter (non exhaustive list).

- Physico-chemical methods
    - ➢ Treatment with active gases and vapors, or radiations
        - o Active gas or accelerated ion treatments (e.g. etching, functionalization using Radio-Frequency Glow Discharge (RFGD), flame treatment, corona discharge, Dielectric Barrier Discharge, atmospheric plasmas, ion beam; ion implantation, etc.)
        - o Cross linking of surface molecules (e.g. RFGD, ionizing radiation, UV…)
        - o Deposition of polymers from active gases and vapors (e.g. plasma polymerization, chemical vapor deposition, flame spray, etc.)

    - Solution treatments or bulk phase desorption
        - Solution deposition of polymers and amphiphiles (e.g. functional coatings, surfactants, layer-by-layer deposition, Self-Assembled Monolayers, Interpenetring polymer networks, …)
        - Desorption of surface active compounds from bulk (e.g. desorption of surfactants from bulk to surface)
        - Chemical treatments to modify surface groups (e.g. oxidize, sulfonate, phosphate, chlorinate…)
        - Chemical conjugation of molecules to surface groups (e.g. silanating agents…)
    - Combination of both kinds of treatments (active gases and solution)
        - Graft Polymerization (e.g. initiation by ionizing radiation, UV, Ozone, plasma treatments, followed by polymerizations)
        - Patterns or domains of the above (e.g. microlithographic techniques)

- <u>Mechanical methods</u>
    - Roughening, Polishing (e.g. from nano-rough to porous surfaces)
    - Micromanipulation (e.g. using Atomic Force Microscopy probes)
- <u>Biological methods</u>
    - Physical adsorption of biomolecules (e.g. proteins, peptides, drugs, lipids, etc.)
    - Chemical conjugation of biomolecules to surface groups
    - Cell seeding and growth

I have tried to develop in UMET some of the techniques presented in the paragraph above to provide to steel, glass[1], polymers or textiles some functional properties without affecting the bulk properties of the materials.

As the “reaction and resistance to fire of materials” group mainly aims at developing and studying fire-retardant products, my first main topic in the group consisted in developing the use of coatings and of various surface treatment processes to fire protect steel, polymers and textiles. This manuscript is thus divided into four main chapters, describing the development of my research topics

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[1] *All the work that was carried out on glass substrates will however not be presented in this manuscript, as it is strictly confidential.*

previously described in the preamble, i.e. (i) thick intumescent coatings applied for fire resistance of steel (Chapter 1) and for fire retardancy of polymers (Chapter 2); (ii) thin functional films applied on polymer films and textiles (Chapter 3) and (iii) functional durability (Chapter 4).

In **the first chapter** of this manuscript, I will present the work carried during my PhD (2003-2006) on the study of **thick epoxy based intumescent coatings applied on steel** against hydrocarbon fires. In this chapter, I will present the coating characterization in terms of fire-resistance efficiency, then the mechanism of action of the coating will be described, and finally the development of a small scale test allowing to predict the behavior of the coating in various fire scenarios will be presented. The further developments induced by my PhD in the topic "similitude, modeling and degradation" of the group will be also briefly presented.

In the **second chapter** I will describe how we achieved to extend the use of the intumescent coatings - usually applied to protect metals (as shown in the chapter 1) - to the **fire protection of thin polymer samples** (Polycarbonate, Polypropylene, Polyamide 6,6). Polymers are usually fire retarded by incorporating fillers directly into the bulk. However, thin films are not easy to fire retard by this way. Moreover, from an industrial point of view it is more interesting to fire retard these materials after they have been processed, as it allows (i) keeping the bulk properties; (ii) customizing the material; (iii) possibly developing multifunctional materials. This is why we extended the concept of intumescent coatings to these thin polymer films. These polymer surfaces are however not favoring adhesion of coatings: plastics are in fact composed of non-polar, long-chain molecules, their surfaces have little free energy, and are essentially inert. Unlike high energy materials (such as metals and ceramics), plastics lack of available bond sites offered by charged ions distributed over the surface. Without this molecular attraction, liquids fail to wet the surface, resulting in poor adhesion and coverage. This is why **surface pre-treatments** such as flame treatments were considered to be carried out prior to coating application, thus promoting the adhesion and enhancing the fire retardant properties. It will also be shown in this chapter that intumescent coatings are however sometimes not sufficient enough to meet severe criteria required for example in the case of high performance electrical applications: this is why we developed a novel concept, consisting in **combining the incorporation of a small amount of fillers in the bulk with a thin intumescent coating layer on the surface**, which allows reaching high fire protection. Fire retardant mechanisms involved when these two approaches are combined will also be described. Further developments and perspectives, consisting in applying these intumescent coatings on **composites** (composites skin materials and foam-cores) and developing accurate small scale fire testing, will be also presented.

The intumescent coatings applied in the Chapter 2 need however a certain thickness (100-200 µm) to be efficient and can thus also modify some properties (e.g. visual, mechanical…) of very thin films or textiles when applied on both sides of these materials. In the **third chapter** I will thus describe some **surface treatment processes** that are currently being developed to fire retard thin films or textiles by **very thin coating layers**. The processes used are (i) low pressure cold plasma processes and (ii) atmospheric coating processes. In a first place, two different low pressure cold plasma processes were tested to bring fire retardant properties to textiles and polymer plates:

- **Radio frequency low pressure cold plasma** induced graft polymerization, consisting in grafting an unsaturated monomer on a textile using a low pressure cold plasma treatment.
- **Remote Low Pressure Plasma Enhanced Chemical Vapor Deposition** used for the deposition on polymers and textiles of thin dielectric films and passivation films like silicon oxides.

Since it is easier for industrial processability issues to work at atmospheric pressure than at low pressure, complementary treatments are currently developing, such as:

- **Vapor Polymerization Deposition assisted by a Dielectric Barrier Discharge**, a very recent versatile and promising technology, which allows the deposition of a wide variety of organic monomers onto a polymer at atmospheric pressure without degrading the polymeric substrate.
- **Layer-by-Layer deposition**, consisting in alternating deposition of polyanions and polycations on a solid substrate leading to the formation of polyelectrolyte multilayer films.

All these processes lead to promising results, allowing improving the fire retardant properties of polymers and textiles through very thin coating layers. Further developments in this topic will consist in using the most promising processes to fire retard polymeric open-cells foams.

In the first chapters, various functional coating processes (intumescent coatings, plasma and LbL treatments) have been used or developed. However, the functional durability of these coatings has not been investigated, although it is of major importance. **The last Chapter (Chapter 4),** that could be entitled “functional durability”, is devoted to the issues associated to the coatings and surface treatments previously described. One major **issue associated to materials and coatings is aging**. Different aging conditions (light exposure, temperature, moisture, salt spray, immersion…) can very rapidly decrease the functional properties of a material or of a functional coating. Two examples will be described in this manuscript: the suspected physical aging of intumescent coatings applied on polymer substrates will be investigated, and the chemical aging of a thick epoxy based intumescent coating will be evaluated as well. The literature being quite poor in this field, an important incoming work is needed in this topic, which has to be carried out on plasma coatings, on LbL coatings and on intumescent coatings, to identify the different aging mechanisms involved in the loss of functional properties, and to try to develop some solutions to overcome these aging issues, such as for example the use of thin top coats, the encapsulation of sensitive fillers, etc.

Another **issue** associated to the loss of functional properties of a material or of a coating is **fouling**: fouling is generally defined as the unwanted formation of thermally insulating materials or deposits from process fluids onto surfaces. As the surface is then covered with contaminants, it usually loses its functional properties. It is then of primary importance to understand the mechanisms of fouling deposition at the surface to then try to find solutions to prevent it. In this chapter, some results obtained during investigations at a nanoscale of dairy fouling on stainless steel surfaces will be presented.

I will start this manuscript by a chapter summarizing the research work carried out during my PhD (2003-2006) on the use of intumescent coatings applied to improve the steel fire resistance.

Chapter 1- Fire resistance of steel substrates by intumescent coatings

This work has been done in the frame of my PhD (2003-2006), carried out in partnership with Akzo-Nobel, Newcastle (UK). 4 papers were published during the PhD period [1-4] and further work led to two other papers in the following years [5, 29].

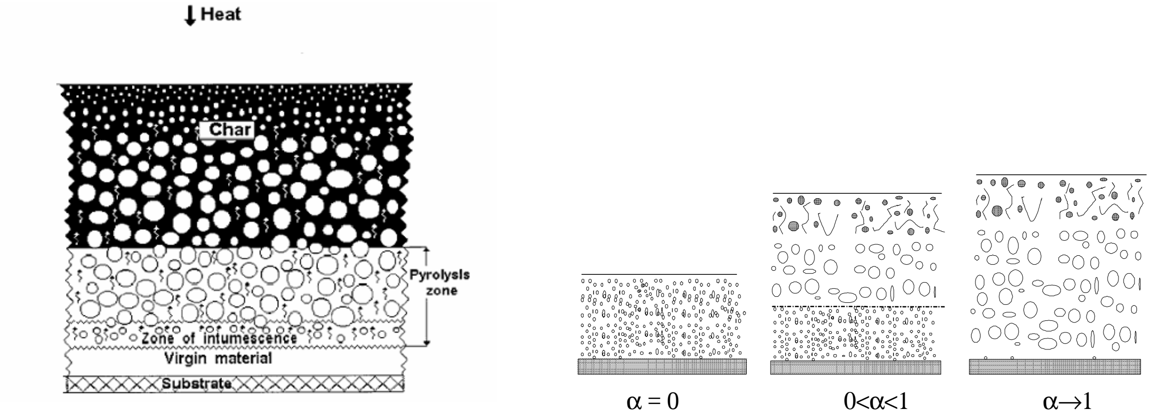
The word "intumescence" comes from Latin "intumescere" which means "to swell up". It describes well the behavior of an intumescent material. When heated beyond a critical temperature, it begins to swell and then to expand. It was first reported by L.J. Gay-Lussac in 1821 in the case of the flame retardancy of textiles [30]. In 1934, a German patent (extended to the USA in 1938) claimed the flame retardancy of wood using a mixture of diammonium phosphate and formaldehyde [31]. It is reported the formation of a swollen char layer upon heating (**Figure 5**) protecting wood but the word 'intumescence' is not used in the text. The first comprehensive paper was published in the early 70s by H. Vandersall and it gives the basics of intumescence [32]. It was stated that the ingredients of intumescence are mainly composed of an inorganic acid or a material yielding acidic species upon heating (e.g. phosphate), of a char former (e.g. pentaerythritol) and of a blowing agent that decomposes at the right temperature and at the right time to enable the blowing of the system (e.g. melamine). Intumescent coatings have had a large increase in use, as a method of passive fire protection for steel protection [32, 33] over the past few years.

Figure 5. Intumescent coating protecting a steel plate

They must resist to fire and avoid its passage and/or that of gaseous products of combustion. They appear similar to a paint finish, and remain stable at ambient temperature. However, in case of a fire, coatings expand to many times their original thickness resulting in the formation of an insulating foam-like layer or 'char' which protects the substrate.

The formation of an intumescent char is a complicated process involving several critical aspects: chemistry (charring), rheology (expansion phase, visco-elasticity of char) and thermophysic (limitation of heat and mass transfers) [34].

The intumescence process results from a complex succession of **chemical reactions** that have to occur in an adequate sequence [35-37]. Upon heating, the polymeric binder begins to soften. The heat also leads to a release of an inorganic acid (for example phosphoric acid coming from ammonium polyphosphate). The acid reacts with a carbon source (such as for example polyol) leading to a carbonization of the system. Gases coming from the decomposition of the blowing agent or of the system enable the carbonaceous material to expand. At a final stage, solidification of the foamed char, through cross-linking reactions and condensation occurs. The chemistry involved in the development of the intumescent process is thus a major concern when dealing about those systems. The intumescence process resulting from a combination of charring and foaming at the surface of the substrate (**Figure 6**), the physical aspects of the intumescent systems are also an important task of investigation.



(a) **(b)**

Figure 6. Schematic view of an intumescent coating with its different zones (a) and its development as a function of the conversion degree α (b)

The charred layer acts as a physical barrier which slows down heat and mass transfers between gas and condensed phases. The formation of an effective char occurs via a semi-liquid phase, which coincides with gas formation and expansion of the surface. The **viscosity of the degraded matrix in the blowing phase** is, as a consequence, a critical factor [34]. The **mechanism of expansion** resulting from the low diffusion of gaseous degradation products through the carbonaceous material and/or from bubbles growth has to be clearly identified as well. Another significant aspect of intumescent formulations is the **mechanical strength** of the intumescent char. In the conditions of a fire, char destruction can proceed not only by means of ablation and heterogeneous surface burning but also by means of an external influence such as wind, mechanical action of the fire or convective air flows. The mechanical stability of the intumescent char thus depends both on the structure and porosity of the foamed intumescent material. To summarize, not only the chemistry of an intumescent system has to be characterized, but also physical parameters such as viscosity, expansion and mechanical resistance of the char. A methodology to bind the fire resistant properties of intumescent coatings with their chemical and physical properties has been input in the group during this PhD and is presented in the next sections.

I-1 Characterization of the performance of an intumescent fire protective thick coating

Intumescent coatings have been used in the field of the fire protection of steel structures since a long time. In this area, intumescent materials are classified as either thick or thin coatings. The first class is usually based on epoxy resins and contains agents that intumesce upon heating. They are available as solvent free systems that allow application of up to 8-10 mm per coat. These films are particularly efficient in case of hydrocarbon fire and jet fires scenario. Thin intumescent films were introduced as early as the 1930's [32] and are used for protection from cellulosic type fires. They are generally available as solvent or water based systems and applied by spray or brush roller as thin film up to 3 mm. They typically use thermoplastic acrylic based resin systems, and they respond rapidly and intumesce quickly when undergoing a cellulosic type fire environment.

I-1.1 Industrial furnace tests

Required levels of protection are normally specified in terms of **time** and **temperature** on the basis of one or more criteria, which may include statutory requirements, design considerations and insurance cost implications. It can vary from a few minutes to several hours but it usually takes the form of 15 minutes increments. The duration is established by a time rating which is determined by testing in accordance with an approved standard.

The standards depend on the kind of fire the material should resist. There are two main categories of fires: the cellulosic or wood fire, and the hydrocarbon fire (**Figure 7**).

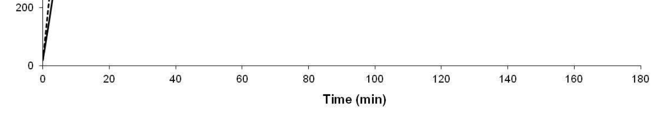


Figure 7. Main standard fire test curves

The hydrocarbon test curve (UL 1709), which is the one used when steel is protected by intumescent coatings, is meant to duplicate or be indicative of the rapid temperature rise seen when an hydrocarbon fuel such as oil or natural gas burns: the temperature rises rapidly to 900°C within 4 minutes and significantly higher overall temperatures are reached (between 1100°C and 1200°C). It is now a common test method for high risk environments such as petrochemical complexes and offshore platforms. A comparison of temperature versus time curves for different coating compositions allow a comparison of the efficiency of these different coatings during the intumescence process. Furnace tests, in which the temperature response on the backwall of the coated substrate is monitored, are used to measure the heat resistance.

The test presented in this manuscript (**Figure 8**) is a demonstration test (OTI 95 634) and the specification is to burn a given volume of propane (0.3kg/s) at a given heat flux (200-250 kW/m²) and at a given distance (1 m) from the test piece. The burning conditions fit as close as possible the ramp of temperature of a hydrocarbon fire heating curve (UL 1709).

Figure 8. Large industrial furnace test

Thermocouples are attached to the backside of the coated plates. The plates are mounted vertically in the furnace door and burnt (**Figure 9**) until the thermocouples attached to the backside of the plates reach a temperature higher than 400°C. 400°C is chosen as “failure temperature”, corresponding to the failure temperature of loaded steel. This test produces temperature versus time curves and characterizes the heat protective effect of the different coatings in a hydrocarbon fire.

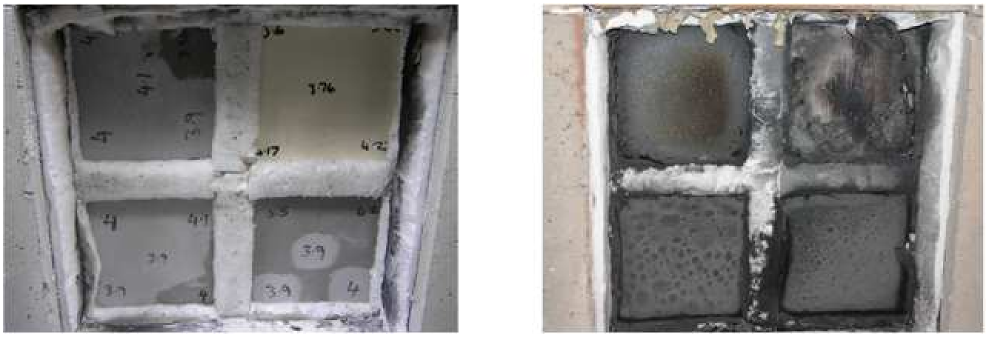


Figure 9. Four steel plates coated, before and after the test (front surface of coating pictured)

I-1.2 Characterization of intumescent coatings using industrial furnace test

The efficiency of different intumescent formulations designed to protect steel in the case of hydrocarbon fire was evaluated using the furnace test previously described. The model coating we investigated during this PhD was based on a thermoset epoxy-amine resin system into which fire retardant agents, boric acid and ammonium polyphosphate derivative had been incorporated [1]. The aim was to evaluate the behavior of the thermoset resin containing - or not - the additives.

Figure 10 shows the evolution of temperature as a function of time on the backside of the steel plates coated with the different thermoset based formulations according to the UL1709 test.

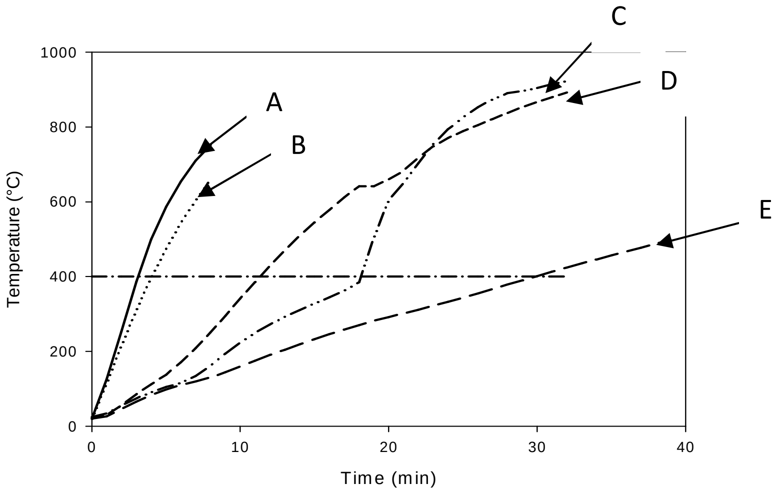


Figure 10. Evolution of temperature on the back side of a steel plate of different intumescent coatings.

As mentioned earlier, 400°C was chosen as limited temperature. The time to reach this temperature in the case of the steel plate covered with the virgin thermoset resin (curve B) is close to the one in the case of the steel plate alone (curve A). As expected, it implies that the thermoset resin does not provide any protective effect. This organic resin can in fact easily initiate or propagate fire, because it can decompose to yield volatile combustibles when exposed to heat. For this reason flame retardants have to be added into the polymer. Ammonium Polyphosphate (APP) is a high molecular weight chain phosphate. It is an interesting component because it can be used both as acid source and blowing agent: it is a source of phosphoric acid which speeds up the formation of carbonaceous char and of NH_3 which improves the swelling [38-40]. When coated APP is added to the thermoset resin (curve C), an improvement in performance is observed (time to reach 400°C of 11 min compared with 5 min for the uncoated steel). Intumescence and charring take place, but the char falls off the plate before the end of the experiment (change of slope at 610°C). Borax ($Na_2B_4O_7$,$10H_2O$) and boric acid are well established as flame retardants and zinc borates have emerged as a replacement for antimony oxides in halogenated fire retardant polymers [32, 41]. Addition of boric acid (curve D) to the resin also leads to improved performance, the time to reach 400°C is increased to 18 min. Development of intumescence is also observed, however the char falls off the plate (rapid change of slope at 400°C) (**Figure 11**).

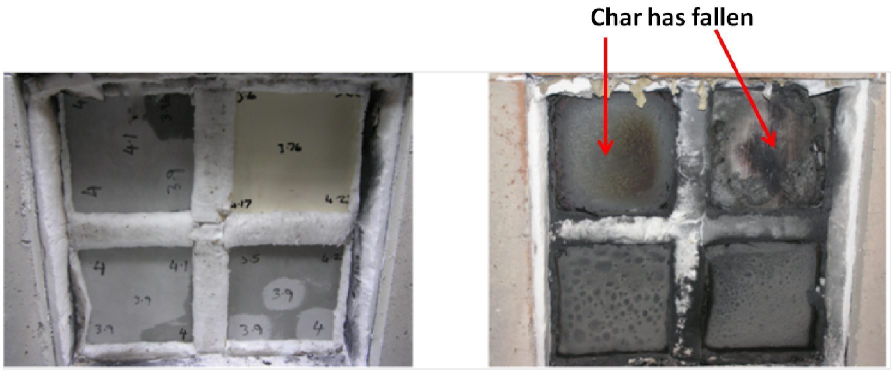


Figure 11. Four steel plates coated, before and after the test (front surface of coating pictured)

These falls could be explained by a loss of adherence of the coating on the plate, and/or by a loss of cohesion of the char or also by the effect of gravity, since the tests are carried out vertically. The best result is obtained when both the coated APP and boric acid are added to the resin (curve E). The time to reach 400°C increases up to 29.5 min and the char adheres to the plate. **These results clearly evidence that the combination of coated APP and boric acid is required to obtain high performance level.** In order to better understand those phenomena, a study of the interactions between both components was then carried out.

I-2 Toward a better understanding of the mechanism of action of intumescent coatings

I-2.1 Chemical approach

As mentioned earlier, the intumescent coating studied is based on a thermoset epoxy-amine resin system into which fire retardant agents, boric acid and an ammonium polyphosphate derivative have been incorporated.

I-2.1.a Degradation mechanisms of boric acid and the coated APP

Boric acid turns by dehydration into boron oxide between 140°C and 200°C, leading to a hard and high thermally stable residue. The amount of residue is high, which can be an important parameter in the formulation of an intumescent coating. As boric acid releases water and forms a hard glass, it can play the role of blowing agent, providing a "glue" to hold the combustion char together and thus providing structural integrity to the char.

The **coated APP** used in this study is a blended mixture of ammonium polyphosphate (APP), which is a high molecular weight chain phosphate, containing a significant amount of nitrogen and phosphorous [42] and tris(2-hydroxyethyl)isocyanurate (THEIC). THEIC is a carbonization agent in the intumescent system and may be a synergist (P/N) as previously reported in the literature [43].

Various analyses results [2] lead to the following mechanism of degradation of APP coated with THEIC (**Figure 12**):

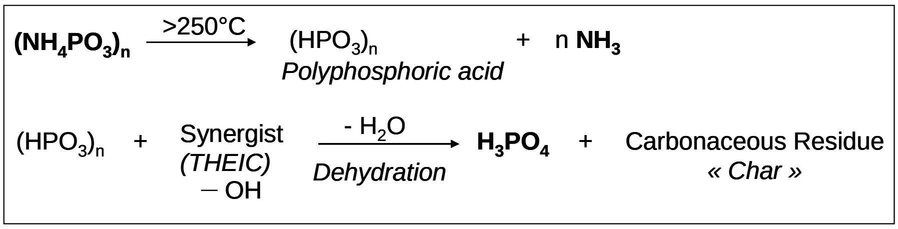


Figure 12. Formation of phosphocarbonaceous species in presence of THEIC

Phosphocarbonaceous species are formed by reaction between the degradation products of APP and THEIC. As a consequence, the nitrogenated agent has a strong catalytic effect on the degradation of APP. It is interesting to notice that coated APP is an acid source (there is creation of phosphoric acid), a blowing agent (due to the release of ammonia) and also a carbonization agent (the THEIC contains atoms of carbon, which provide a char when heated). As a consequence, coated APP constitutes intrinsically an intumescent system.

Coated APP and boric acid used as individual component can both play a significant role in the mechanism of intumescence. However, the large scale furnace tests showing a great improvement when both APP and boric acid are incorporated in the coating, the study of the potential interactions between these two components using Thermogravimetric analyses (TGA) (not shown here) and a solid state nuclear magnetic Resonance (NMR) approach has thus been carried out.

I-2.1.b Evidence of interactions between APP and boric acid: a solid-state NMR approach

The char can be analyzed by FTIR, X-Ray diffraction and solid state NMR. All these techniques have been investigated in the laboratory, but to our mind the most relevant one is solid state NMR, which allows investigating amorphous materials. This technique has been developed in the laboratory these last 15 years and shows great potential in the understanding of reaction mechanisms in intumescent coatings [2, 44-49]. In this study, the main components of interest in the coating and char were Carbon, Phosphorous and Boron, which are relatively easy to study using solid state NMR spectroscopy (respectively ^{13}C, ^{31}P and ^{11}B NMR).

Figure 13 presents the ^{11}B solid state NMR spectra of the boric acid and of the mixture boric acid / coated APP heat treated at 450°C and those results are compared with the spectra of boron oxide and borophosphate. The spectra show unambiguously that a reaction takes place between boric acid and coated APP, or between the degradation products of these compounds.

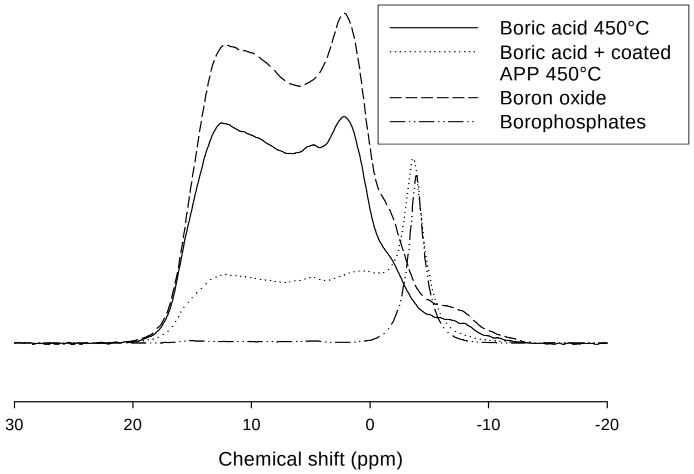


Figure 13. ^{11}B solid state NMR spectra of boric acid mixed with coated APP at 95 and 450°C

The spectrum of the mixture of boric acid and coated APP heated at 450°C exhibits a peak at δiso= –3 ppm which can be assigned to crystalline borophosphate. It demonstrates that the APP and/or phosphoric acid released when coated APP degrades effectively reacts with boric acid and/or boron oxide to yield borophosphate [50],[2]. At 450°C, residual boron oxide can be distinguished on the spectrum.

The APP/H_3BO_3 mixtures as mentioned above have also been examined using ^{31}P solid state NMR (not presented) leading to the same conclusions.

However, considering only the results obtained at 450°C does not enable to determine if borophosphates are formed through a reaction between boric acid and coated APP or between the degradation products of these compounds. In order to determine at which temperature borophosphate is formed, the mixture of boric acid and coated APP was treated at four other temperatures: 95°C, 150°C, 250°C and 300°C (**Figure 14**) and analyzed by ^{31}P NMR.

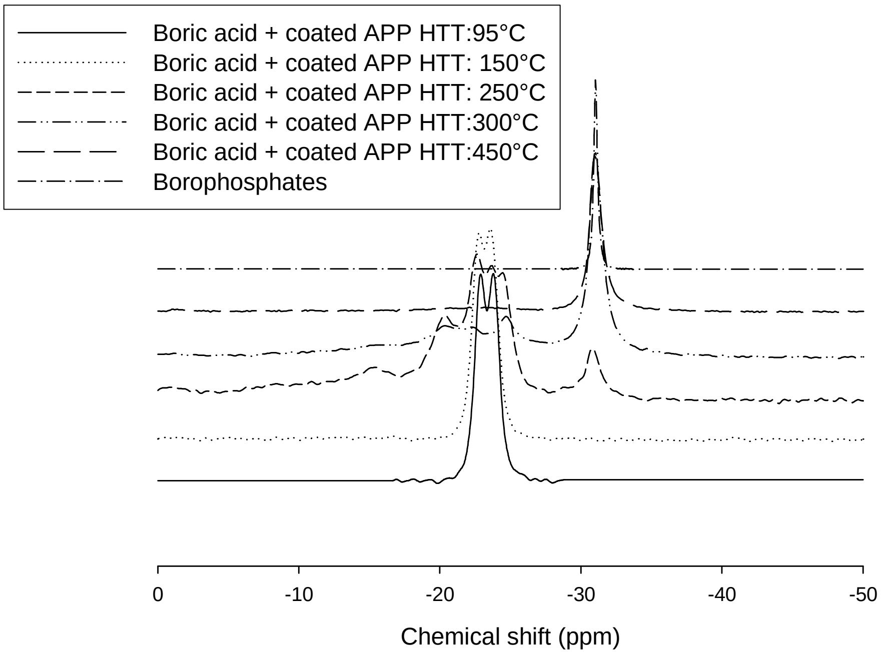


Figure 14. ^{31}P NMR of a mixture of boric acid and coated APP treated at five different temperatures.

The peak corresponding to borophosphate appears in the spectrum at 250°C, i.e. when all the boric acid has turned into boron oxide and the coated APP is turning into phosphoric acid. A broad band between -18 ppm and -27 ppm is observed for the heat treatment at 300°C, which can be assigned to polyphosphoric acid having different levels of cross-linkings.

At 450°C, only crystalline borophosphate and boron oxide glass remain. It means that the reaction yielding borophosphate is a reaction between the degradation products of boric acid and coated APP.

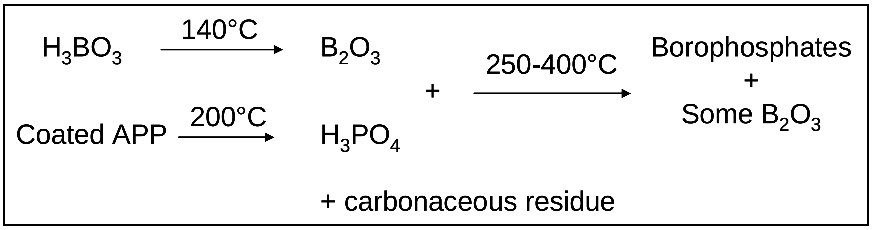


Figure 15. Scheme of reaction of creation of borophosphates

The **Figure 15** explains why it is important to add some THEIC to the APP: coated APP degrades earlier (about 200°C) than pure APP (about 300°C). This allows a rapid production of phosphoric acid, and so a possible reaction at low temperature (250°C) between this component and boron oxide.

As a consequence, the following criteria may be defined:

- **The release of the acid source must occur at relatively low temperatures, particularly below the decomposition temperature of the char former (in our case the coated APP and the thermoset resin).**
- **It is necessary that the carbon source reacts with the catalyst at a lower temperature than that at which thermal decomposition occurs.**
- **Blowing agents must decompose at the proper temperature and should release copious quantities of gaseous materials. The “proper” temperature will depend on the system in which they are used. Blowing should occur after the melt forms but before the char hardens.**

The interactions between boric acid and coated APP have been investigated, but the interactions of the thermoset resin (the binder) with boric acid and coated APP on the development of the intumescent system have to be analyzed as well. These interactions are identified and described in the following section.

I-2.2 Influence of the binder: a multiscale experimental approach

An intumescent coating is working well when there is high char yield and high expansion, when the viscosity during the degradation of polymer is not too high or too low so that the mixture can swell, when the char created has enough mechanical resistance to resist both the fire and external stress and when the char shows good adhesion to the steel plate during burning. The idea was to combine different experiments such as thermogravimetric analyses, visco-elastic measurements and “torch tests” to try to evaluate all the relevant parameters (chemical interactions, expansion, viscosity, mechanical resistance and adhesion) to completely characterize the intumescent formulation and develop a multiscale approach that could be further used for the development and investigation of any intumescent coating.

I-2.2.a Thermal stability

The thermogravimetric analyses carried out in controlled air and temperature conditions give an overview of the degradation process of a coating in thermo-oxidative conditions and an idea of the reactivity between the components [51]. The weight loss is plotted against the temperature, and at the end of the TGA it is possible to have a look at the char to see if effective intumescence occurs.

To investigate the potential interactions between additives in the thermoset resin, the difference of weight loss between experimental and theoretical TG curves (Δ(T) curves) is presented for the three mixtures in **Figure 16**. The Δ(T) curves allow us to show a potential increase or decrease in the thermal stability of the polymeric matrix related to the presence of one or every additive [37], i.e. boric acid and coated APP in our case. When the experimental curve is higher than the theoretical one (or when the difference weight loss curve is positive), the loss of weight is lower than expected, showing that the reactivity of the resin with the additive leads to a thermal stabilization of the materials. If the experimental curve is lower than the theoretical one (or when the difference weight loss curve is negative), the reactivity of the resin with the additive leads to a thermal destabilization of the materials.

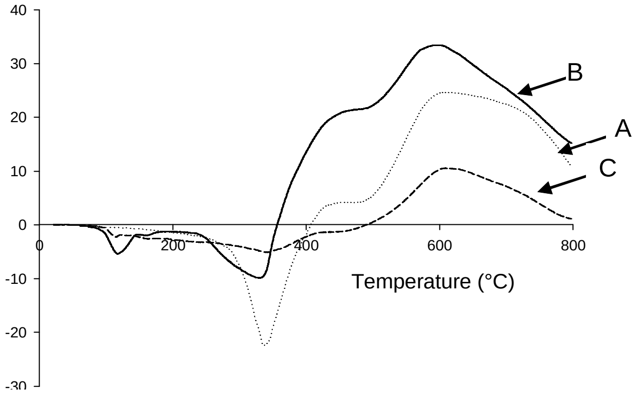


Figure 16. Curves of weight differences (difference between experimental curves and calculated curves)

The comparison of the experimental curve with the calculated curve for the mixture A (thermoset resin containing APP derivative) shows an important decrease of about 20 % in the thermal stability between 300 and 400°C. This destabilization suggests a reaction between the additive and the polymeric matrix leading to the formation of volatiles. An increase in thermal stability is then observed from 500 to 800°C with an increase of 10 % compared to the result expected if no reaction happened. The chemical interactions between the two components lead to the formation of a high thermal stability material.

The Δ(T) curve for mixture B (epoxy resin containing boric acid) shows that the two steps corresponding to the dehydration of boric acid occur at lower temperature when incorporated into the epoxy resin and that chemical interactions between the two components lead to the formation of a high thermal stability material.

The Δ(T) curve for the mixture C (epoxy resin containing boric acid and APP derivative) evidences that the chemical interactions between the three components lead to the formation of a thermally stable material between 350 and 800°C but the residue at 800°C of the final products is as predicted.

To try to link the chemical reactivity of the system (observed by TGA) with the development of the intumescent foam, visco-elastic measurements were then carried out and the results are described in the next section.

I-2.2.b Visco-elastic measurements

The formation of an effective char occurs via a semi-liquid phase, which coincides with gas formation and expansion of the surface [41]. Gases released from the degradation of the intumescent material, and in particular from the blowing agent, have to be trapped and to diffuse slowly in the highly viscous melt degraded material in order to create a layer with "appropriate" morphological properties. If the degraded matrix has a too low viscosity, rapid diffusion of gases will take place and these ones will not be trapped in the coating and escape to feed the fire. As reported earlier, the viscosity of the degraded matrix in the blowing phase is, as a consequence, a critical factor [52, 53].

The rheological studies were based on the use of a unique apparatus, the Thermal Scanning rheometer TSR Rheometric Scientific ARES-20A, in a parallel plate configuration (**Figure 17**). This apparatus allows an original approach of the study of the physical behavior of an intumescent coating, as both the complex viscosity and the swelling can be simultaneously measured as a function of temperature and/or time.

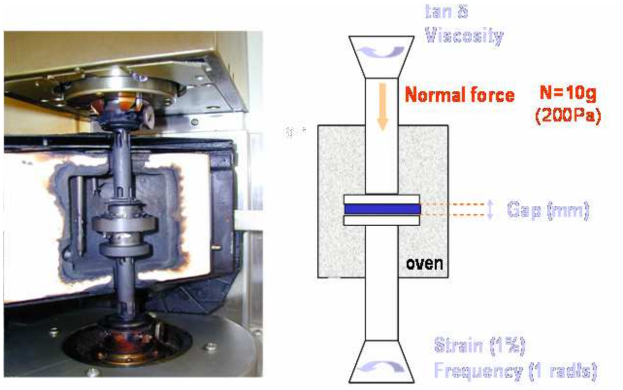


Figure 17. Dynamic visco-elastic measurements

Figure 18 (Figures (a) and (b)) compares **the expansion** and **complex viscosity** of the four formulations, the virgin thermoset resin (A), the thermoset resin mixed with boric acid (B), the thermoset resin mixed with coated APP (C) and the thermoset resin mixed with both Boric acid and coated APP (D).

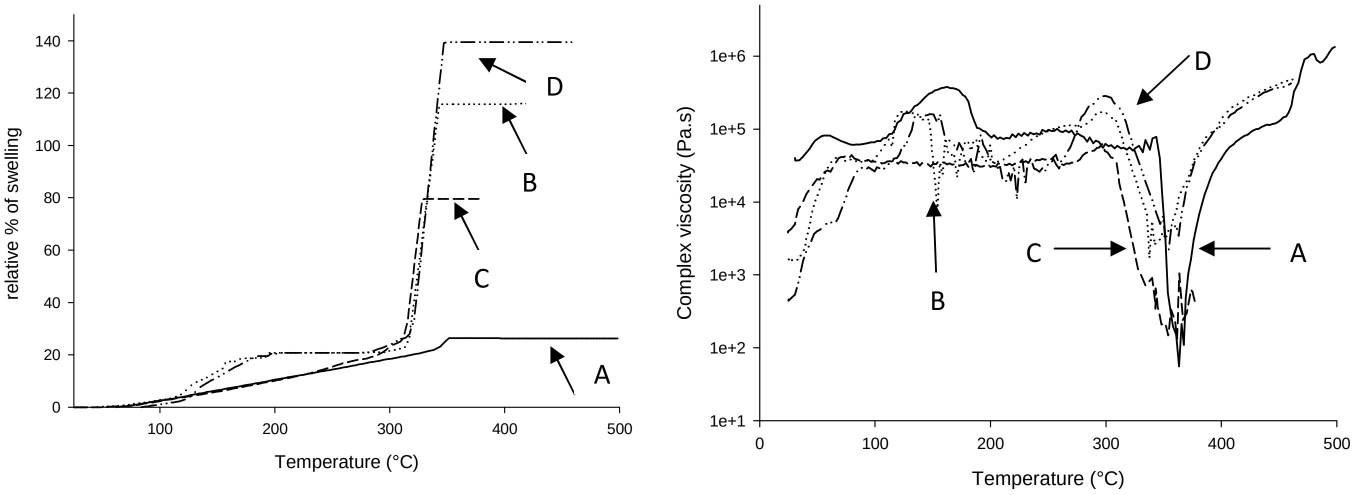


Figure 18. (a) Expansion of the sample (b) Complex viscosity

For the four coatings, the viscosity remains reasonably steady until 300°C. From 330 to 350°C it decreases very rapidly to then increase again quite rapidly until 400°C at higher temperatures a further slow increase in viscosity is observed.

This increase of viscosity after 400°C can be attributed to a carbonization process, the liquid phase disappears and a highly condensed char structure is produced.

For the thermoset epoxy resin (A), the peak of decrease of viscosity corresponds to the main step of degradation of the resin, which loses 90% of its mass between 300 and 460°C. When boric acid is added to the resin (mixture B), the viscosity shows a decreasing peak but over a larger range of temperature [300-400°C] compared with [330-380°C] in the case of the resin alone. Moreover, the minimum viscosity is higher than that of the epoxy resin and there is an important expansion of the coating (about 120%). The boric acid acts as an intumescent agent. It is proposed that the formation of B_2O_3 due to the dehydration of the boric acid leads to the formation of a "glass-like" material which increases the viscosity of the melt (compared with the unmodified resin) and prevents the gaseous decomposition products escaping to feed the flame.

When the coated APP is incorporated into the resin (mixture C), the viscosity decreases in a similar way to the resin alone, but over a larger temperature range [300-500°C]. The TG analyses (not presented) also evidenced a degradation at a lower temperature when APP is added to the thermoset resin. During its degradation, as said earlier, APP forms phosphoric acid [54] which leads to a decrease in melt viscosity due to the formation of a liquid phase. In addition, the released acid catalyzes the degradation of the epoxy resin, leading to degradation at lower temperature. Expansion of the thermoset resin is significantly improved when the APP derivative is added. The APP additive degrades to yield ammonia above 200°C. There is a good correlation between the temperature of the onset of degradation observed by TG and temperature at which the expansion starts (T=300°C in both cases). The expansion is attributed to the evolution of volatile degradation products, which are trapped in the structure. APP incorporated into the resin leads to intumescence, even if the residue obtained at 500°C is unfortunately extremely light and crispy. This, together with the non-controlled release of ammonia, leads to variable expansion results.

The presence of both boric acid and the APP derivative in the thermoset resin (mixture D) leads to a higher expansion (140%) and the main peak of viscosity is similar to the peak corresponding to mixture B. The presence of the APP derivative does not seem to influence significantly the rheological behavior of mixture B. The residue obtained is solid and dense. The conditions are favorable to allow slow diffusion of the gaseous degradation products and effective intumescence. This phenomenon, together with a thermally stable char structure provides effective protection.

To summarize, it is noteworthy that swelling starts at about 300°C, suggesting that the expansion takes place because of the relatively low viscosity of the char combined with the release of volatile degradation products. It is also observed that all the mixtures that contain boric acid exhibit a lower decrease in viscosity. As a consequence, boric acid plays a key role in the intumescent behavior of the coating, acting both as an intumescent agent and char reinforcer. Finally, as the peak of viscosity of the mixture thermoset resin + boric acid + APP derivative is the smallest, the swelling is the highest because the char can accommodate the stresses due to the internal pressure created by the evolving gases.

However, an important parameter that also has to be taken into account is the mechanical properties of the char. If the char is destroyed when subjected to external perturbations such as explosion (e.g. BLEVE [Boiling Liquid Evaporating Vapor Explosion], Jet fire) or wind turbulence, the coating will not provide effective protection of the steel structure.

I-2.2.c Mechanical strength of the char

In the stabilization phase of an intumescent structure, the change in the viscosity of the charred material under stress may explain the loss of the protective character of the intumescent shield. Indeed, if the shield becomes too hard, the creation and propagation of cracks leading to a rapid degradation of the material occurs. If a char has a good structural, morphological and heat insulative properties but is easily destroyed under a mechanical action, its efficiency is totally lost in the turbulent regime of combustion.

A consideration of the mechanical stability of intumescent char appeared first in the technical literature in discussions about the nature of bonds which provide char stability [55-57].

Berlin et al. [58] for example used a "Structurometer ST-1", developed at the Moscow State Food Academy, to measure the force required to destroy the char [59]. The samples were first pyrolysed and then a destructive force was applied to the sample. It was concluded that one of the main factors influencing the mechanical stability is the char porosity: the smaller the pore size the better the char strength.

A similar method was developed in our laboratory at Lille University [60] in recent years, using the Thermal Scanning Rheometer. The main interest of our approach is that the measurement of the destruction force is made directly after swelling of the sample, at high temperature, working as an "in situ" experiment.

Mechanical resistance is evaluated using a different test protocol than in the case of measurement of swelling and complex viscosity: at t=0s, the sample of controlled thickness is put into the furnace and heated to 500°C without applying any strain (the upper plate is not in contact with the sample) as shown in **Figure 19**. This allows the sample to intumesce without any constraint. The upper plate is then brought into contact with the intumesced material and the separation between the plates is reduced linearly at a controlled rate.

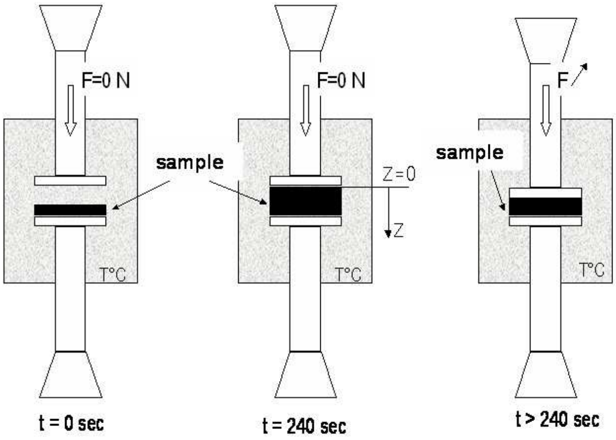


Figure 19. Measurement of the char strength

The force is followed as a function of the gap between the two plates.

Figure 20 presents the destruction force of the carbonaceous char plotted against the distance between the plates for the following mixtures at 500°C: the thermoset resin (A), the thermoset resin + coated APP (B), the thermoset resin + boric acid (C) and the thermoset resin mixed with both boric acid and coated APP (D).

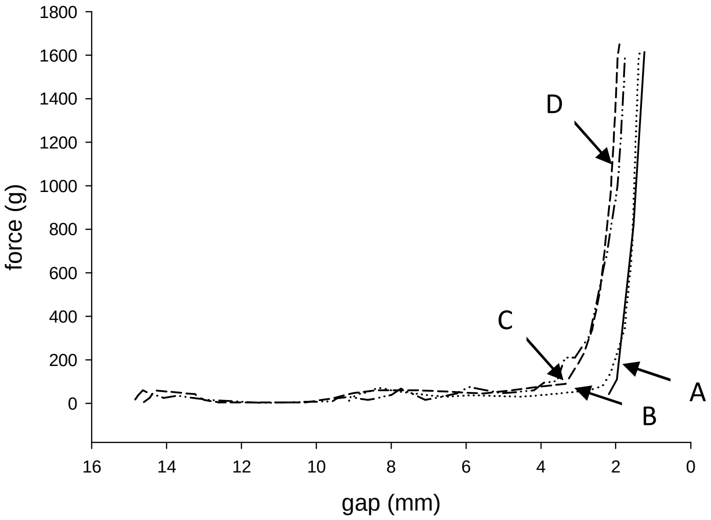


Figure 20. Mechanical resistance at 500°C of different formulations

The curves corresponding to mixtures A and B are not very different: the char is not resistant and a very weak force is sufficient to destroy it. It is only when 1 mm of residue remains that the force increases, and this is due to the fact that the residue has been strongly compressed.

The curves corresponding to mixtures C and D give the same results at the beginning: a very weak force is sufficient to destroy the char. But the force begins to increase earlier than in cases A and B, there is a difference of about 2 mm, which means that the char is harder. It appears that the presence of boric acid, and particularly the formation of boron oxide, provides better mechanical resistance. We can however not conclude from these experiments if borophosphates show a better effect than boron oxide on the mechanical resistance of the char, as there are only slight differences between the curves obtained for the thermoset resin mixed with boric acid and thermoset resin mixed with boric acid and coated APP.

I-2.2.d Adhesion of the char

In order to further investigate the behavior of the intumescent char and to try to understand why certain chars did not remain stuck to the plate, Bunsen burner tests, or “torch tests” (**Figure 21**) were carried out. In all cases, no deformation of the substrate (steel plate) has been observed.

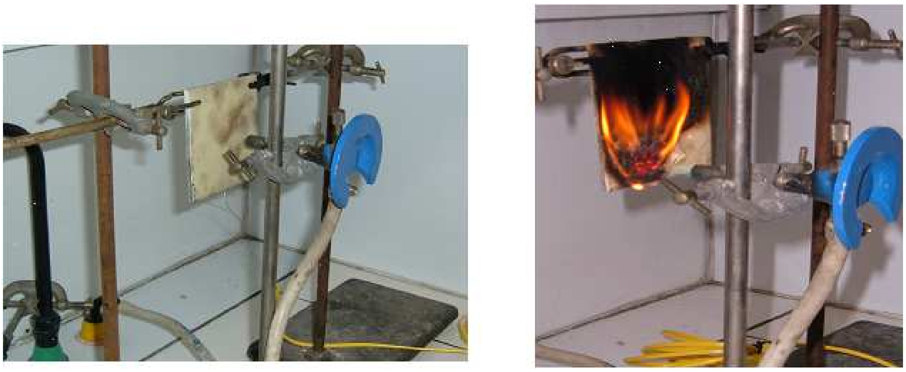


Figure 21. Pictures of the small scale test using a Bunsen burner, before and during the test.

Three plates were evaluated: thermoset resin + boric acid, thermoset resin + APP derivative, thermoset resin + boric acid + APP derivative. The pictures of the residues obtained are shown on **Figure 22**.

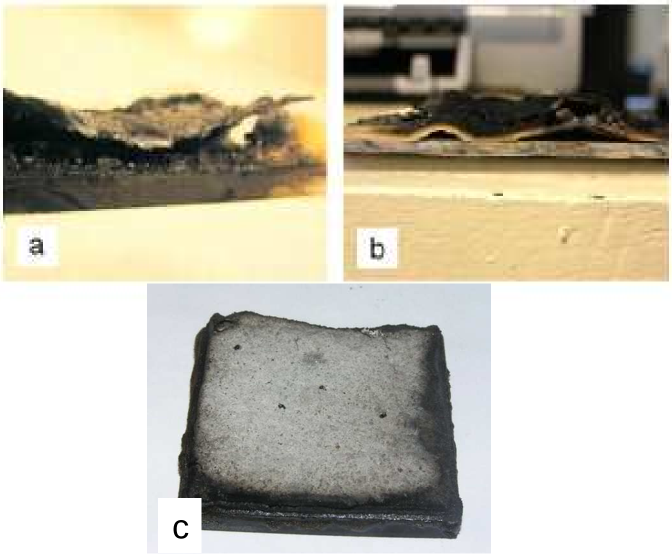


Figure 22. Residues obtained after the torch test (a): thermoset resin + coated APP, (b): thermoset resin + boric acid, (c): thermoset resin + coated APP + boric acid.

The char of the thermoset resin + coated APP does not adhere to the plate because it is light and crumbly. However, as some coating remains on the plate, cohesive rather than adhesive failure appears to occur. It suggests that phosphates promote adhesion of the coating on the plate[61], and that the detachment of the char is mostly due to the structure of the char.

On the contrary, the char developed by the combination of thermoset resin + boric acid does not adhere on the plate but shows a high hardness, due to the boron oxide glass formed.

The char developed by the ternary system thermoset resin + boric acid + coated APP does not fall off the plate. It seems that this char combines the positive effect of phosphates promoting adhesion to steel and of borates which produce a very hard char. Considering the interactions existing between the products of degradation of boric acid and coated APP, borophosphate seems to promote both the adhesion and hardness of the intumescent coating. Borophosphate does not melt before 1200°C, whereas boron oxide melts between 300 and 700°C and turns into a series of suboxides. This also could explain why the intumescent formulations containing a lot of boron oxide form a less efficient protective layer: as the mixture melts until 700°C, the intumescent development is not homogeneous, and this, combined with the too high hardness of the glass, could also explain why the char falls off the plate.

To summarize, the additives interact with the thermoset resin to increase its thermal stability and also favor the adhesion between the coating and the steel plate. Considering the previous conclusions on the mixture boric acid + coated APP, it can be stated that borophosphates created upon heating lead to these improved properties. The degradation of the resin at about 350°C creates an important decrease of viscosity. Boric acid seems to be the key additive to reduce this

fall of viscosity: in fact it turns by dehydration into boron oxide, a low melting glass; the matrix formed traps the gases, and this enables a high expansion and the formation of a char that presents a good mechanical resistance. The best result however is obtained when both additives are combined into the resin: there is a small decrease of viscosity at 350°C, a high expansion and the char has an appropriate mechanical resistance and adherence.

The mechanism of action of the coating being elucidated, a further objective was to find some ways to predict the intumescent coatings behavior in a fire. The first idea was to examine whether the performance in large scale industrial fire tests could be correlated with the parameters of the intumescent coating measured using the previously described laboratory analyzing tools (visco-elastic measurements, char yield, mechanical strength). The analysis of possible correlations between the intrinsic parameters of intumescent coatings and their efficiency was carried out using a "Principal Component Analysis" approach.

A second approach consisted in developing novel small scale and high throughput tests to allow rapid screening of formulations [48] and accelerate the research on new and more efficient intumescent formulations. In fact, furnace tests are very expensive and panel preparation is time consuming; moreover only a few panels can be tested in one day.

These two approaches are discussed in the following part.

I-3 Prediction of the behavior of an intumescent coating in a fire

I-3.1 Correlations with small scale and large furnace tests

This section deals with the possible correlations between the identified parameters obtained using the analyses commented above and the industrial furnace tests carried out on a certain number of coatings. Six key parameters have been selected from our previous experiments and discussion:

The industrial furnace test gives two parameters: (i) The time of failure and (ii) the expansion of the coating, obtained at the end of the test.

Thermogravimetric analysis (TGA) gives the char yield at 800°C after a temperature ramp of 10°C/min.

The experiments using the rheometer give three parameters: (i) the complex viscosity about 330°C, corresponding to the degradation of the thermoset resin. It is at that time that the swelling occurs, so it is at that time that the viscosity evolution is the most important. (ii) the expansion calculated at 500°C after a dynamic ramp temperature of 10°C/min; (iii) the mechanical resistance of the char (i.e. the relative gap (%) corresponding to the beginning of the maximum increase of the normal force).

As six parameters are considered, 5 axes should be defined. The new coordinates of the different parameters on these axes can then be calculated (not shown here) [4].

It is then possible to draw 10 correlation circles, corresponding to combinations between the different axes (axes 1/2, 1/3,…, 4/5). Considering the correlation circle presented in the **Figure 23**, it can be assumed that the data of “remaining mass” and “expansion in the furnace” are correlated, just as “Expansion in rheometer” and “time of failure”, or also “mechanical resistance and complex viscosity”.

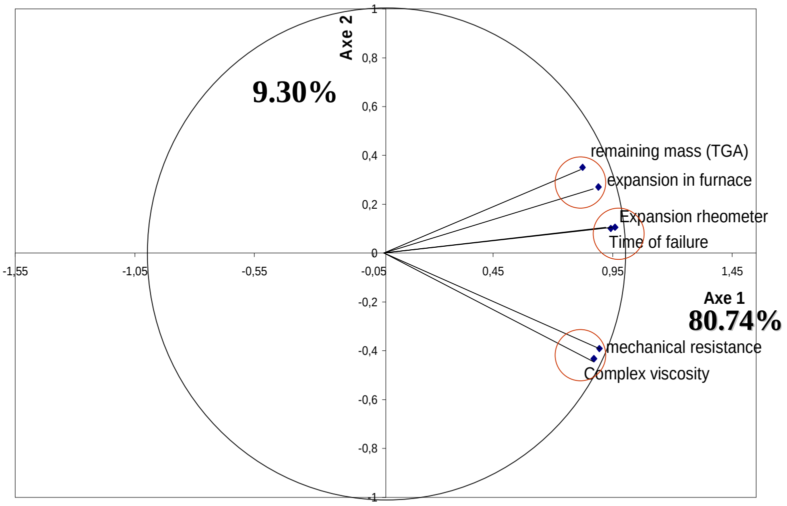


Figure 23. Main correlation circle

To confirm these possible correlations, the corresponding linear regressions have been calculated. **Table 2** presents all the regression coefficients R obtained between the different experiments.

Table 2. Summary of the correlation coefficients calculated.

	time of failure	complex viscosity at 330 °C	residual weight at 800 °C	expansion in rheometer	expansion in furnace
time of failure	1				
complex viscosity at 330 °C	0.7397	1			
residual weight at 800 °C	0.7312	0.6256	1		
expansion in rheometer	*0.8667*	*0.8101*	*0.829*	1	
expansion in furnace	*0.9088*	0.6155	0.6834	*0.8693*	1
mechanical resistance	*0.8167*	*0.9088*	0.5914	0.7932	0.7085

The values in italics correspond to the formulations for which R > 0.8. Seven excellent correlations are observed: (i) correlation between the expansion in the furnace and the expansion in the rheometer; (ii) correlation between the expansion in the furnace and the time of failure in the furnace; (iii) correlation between the expansion in the rheometer and the time of failure in the furnace; (iv) correlation between the expansion in the rheometer and the complex viscosity at 330°C; (v) correlation between the mechanical resistance and the complex viscosity at 330°C; (vi) correlation between the expansion in rheometer and residual weight at 800°C; (vii) correlation between the mechanical resistance and the time of failure in the furnace.

Considering then all the correlation coefficients obtained from the PCA, it can be concluded that two kinds of correlations, summarized in **Figure 24** exist: direct and second order correlations.

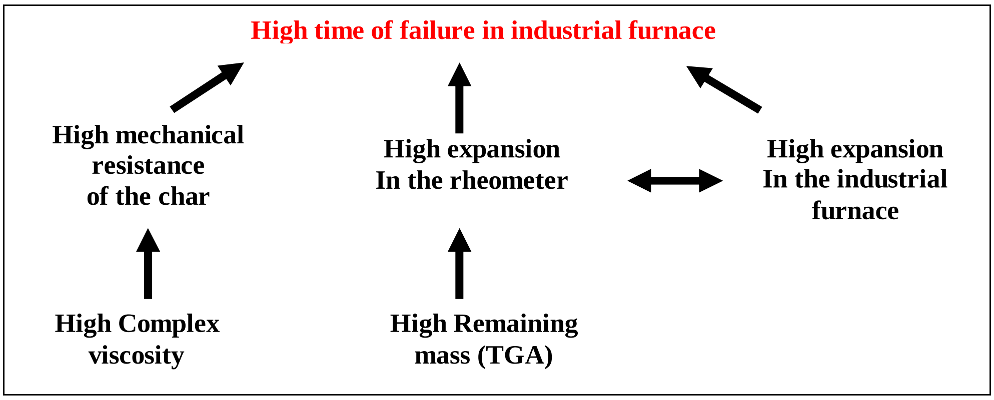


Figure 24. Correlations between the different parameters.

The most important objective is to reach a high time of failure in big furnaces. **Figure 24** shows three direct correlations with this parameter. The first one concerns the mechanical resistance of the char which is very well correlated with the time of failure. It means that, in the case of this coating, if a high mechanical strength is measured using the rheometer, a high time of failure should be obtained, which means a high efficient intumescent coating. This result confirms that the heat insulative properties of the char directly depend on its structural and morphological properties. The expansion of the char both in the rheometer and in the furnace is also directly linked with the time of failure. It means that the insulation will be more efficient if the char swells a lot. This is not surprising, as an important amount of char will prevent too important heat transfers. However, in some cases, for example cellulosic coatings, the result can be slightly different: in fact, if the coating sometimes expands too much, the char created can be too light and not stable, whereas a coating which will expand less but which is more resistant to stress will better protect the substrate [51].

These results are interesting because they suggest that all the experiments made with the rheometer are strongly correlated to those obtained in the industrial furnace. It means that the resistance of the char and its expansion are reliable parameters to evaluate in a first approach the behavior of intumescent epoxy based coatings in a real fire.

The other correlations presented are “second order” correlations, which are not directly linked to the furnace tests results. For example, the complex viscosity taken at 330°C and corresponding to the degradation of the polymer matrix is also correlated with the mechanical resistance. It means that if the complex viscosity is high at 330°C, the mechanical resistance will be high: it confirms that if the viscosity is too low, easy diffusion of gases takes place, the gases will not be trapped but rather escape to feed the flame, leading to a poorly mechanical resistant char. The second correlation concerns the char yield in thermogravimetric analyses linked to the expansion in the rheometer. If there is a high expansion, it means that the amount of char will be important, which is essential to have an efficient thermal barrier.

Aim was to propose to researchers in coatings development a panel of small scale analyses which could help to predict the behavior of the coating in big industrial furnaces. The rheometer has been proven to be a powerful tool, as it allows carrying out two types of experiment (mechanical resistance and expansion) which results are directly linked to the results of industrial tests. These results are essential to be used as preliminary tests in research, because they permit optimizing much more rapidly and at very low cost the formulations. The selected formulations will be then progressed to full scale furnace testing, saving both time and money.

The combination of small scale analyses described previously led to very interesting correlations. However, there is no quantitative evaluation of the heat barrier effect of the coating, which is a crucial parameter in a fire retardant formulation. Our purpose in the following section is to present the development of a high throughput small scale test permitting a rapid evaluation and prediction of the heat barrier effect of intumescent coatings when exposed to an external heat flux.

I-3.2 Development of a high-throughput small scale test

- **Test description**

The aim is here to evaluate the efficiency of the intumescent coating in terms of heat transfer. As in the case of large furnace tests, time/temperature profiles are measured on the back of a coated steel plate.

In our test the heat source is a heat radiator supplied by Saint Gobain (France). Steel plates are the same as those used in the industrial test. About 1 mm of the intumescent coating is applied on the surface of the steel plate. A coating resistant to 800°C and having a constant emissivity of 0.92 is applied on the non-heated side of the steel plates. The constant emissivity of the backside of the plate allows accurate measurement of the surface temperature of the plate using an infrared pyrometer. The infrared pyrometer is positioned at a constant distance from the steel plate and the IR beam is pointed on the centre of the plate. It detects the temperature on the non heated face of the steel plate and registers the time / temperature curve on a computer. The whole system is placed into a box to avoid air flow effect in the fume cupboard: aim is to reduce the convective and chimneys effects.

In this experiment no “failure temperature” is considered since the heating temperature never reaches 1200°C as in the large furnace. This test is mostly used by comparing the temperature obtained after 20 minutes for one formulation to the virgin steel plate or to the reference formulation. The experimental device is presented in **Figure 25**.

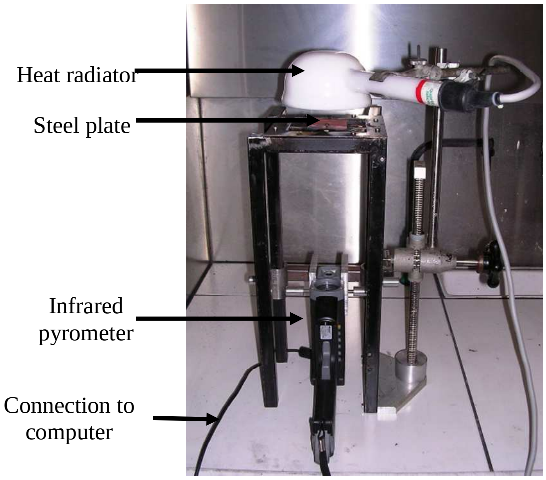


Figure 25. Presentation of the small scale test.

The small scale test is very stable and repeatable. The reference curve is the temperature versus time curve obtained for the virgin steel plate black coated on its non heated face.

- **Correlations with the industrial furnace test**

Different intumescent formulations were studied using heat radiator and large furnace tests, in order to compare the obtained results. Three different types of formulations were tested: the first type was constituted of the three basic intumescent epoxy based formulations (IF1: thermoset resin + coated APP, IF2: thermoset resin + boric acid, IF3: thermoset resin + coated APP + boric acid) which are compared to the confidential reference coating (IF 8). The second series of tests were carried out on three intumescent epoxy based mastics (IF12, IF13, IF14), also compared to the commercial formulation (IF8). The final tests were carried out on three unknown cellulosic coatings (IFA, IFB, IFC), which were also tested in a large furnace using the cellulosic heating curve. The purpose was to validate the test under different conditions for various coatings.

The **Figure 26** compares the temperature versus time curves obtained during industrial furnace tests (a) and our lab-scale test on IF1, IF2, IF3 and IF8 (b).

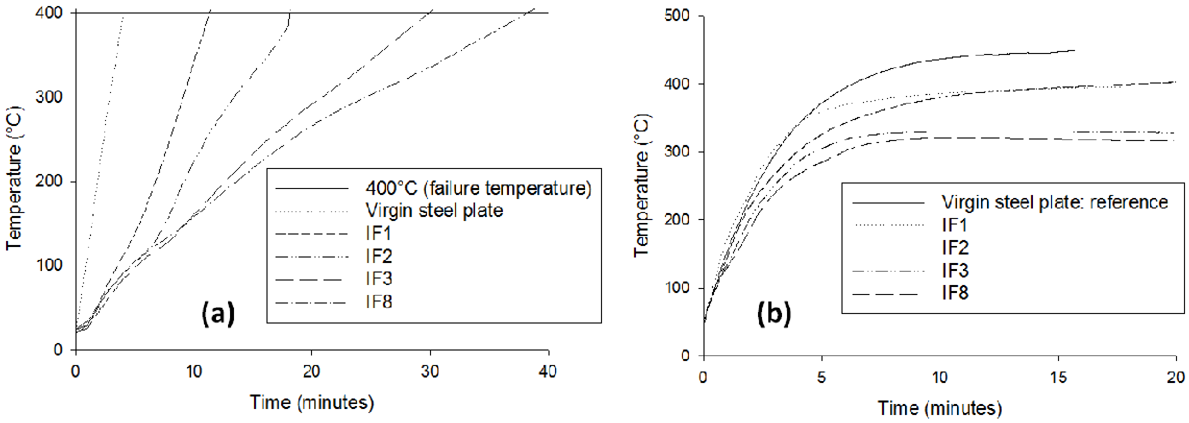


Figure 26. (a) temperature versus time curves in large scale furnace compared to (b) temperature versus time curves using heat radiator test.

The parameter taken into account is the time to failure, namely the time when the steel temperature reaches 400°C. The materials exhibit very different behaviors: the most efficient coating is IF8 (time of failure of about 40 minutes) while the worst one is IF1 (time of failure of 10 minutes).

During the heat radiator test, an important increase of temperature occurs at the beginning of test (from 0 to 350 s) in all cases, but after 450 s the temperature remains quite steady. It is interesting to compare the temperature at the end of the experiment: the best performance is obtained when the temperature increases slowly during initial heating and when the smallest temperature is reached at the end of the test. In this case the curves are quite well distinguished, the best formulation is also IF8 with a temperature of about 320°C reached after 1200s, and the worst one is still IF1, which reaches about 400°C in 1200s.

The ranking of results obtained after 1200s in the heat radiator test and at 400°C in the furnace tests are summarised in **Table 3**.

Table 3. Ranking of results obtained for tests on intumescent formulations (1=>best result)

	Heat radiator test	Big furnace test
IF1	4	4
IF2	3	3
IF3	2	2
IF4	1	1

The correlation is excellent and so, the heat radiator test appears to be a very good tool to carry out an initial assessment of how a coating might perform in a hydrocarbon fire. Another interesting facet of the heat radiator test is that it is possible to look at the texture of the resultant char to estimate its mechanical resistance.

A second series of tests was carried out on four different intumescent mastics: IF8 (confidential formulation), IF12, IF13 and IF 14 [4]. The curves will not be presented in this manuscript. However, as in the earlier study, the correlation between the two tests is excellent, with the same ranking of coating performance obtained. It is thus possible to conclude that the heat radiator test can be used to effectively rank the efficiency of intumescent mastics.

However, as mentioned earlier, there are not only intumescent epoxy mastics in the fire protection coating market: two main kinds of coatings exist, the thick film intumescent coatings (mastic) and thin film intumescents (cellulosic coatings). The next section will examine whether the heat radiator test can also be used to study cellulosic intumescent coatings.

➢ Test validation on unknown cellulosic intumescent coatings

Testing of cellulosic coatings is different from testing intumescent mastics: the hydrocarbon fire curve is replaced by the standard cellulosic fire curve (**Figure 7**). During this test, coatings are applied on steel plates or on beams and columns, which are put inside the furnace and the standard cellulosic fire is applied to them. As these coating are not designed to be applied on heavily loaded components, 500°C is taken as “failure temperature”, with the corresponding “time of failure”.

Three commercial cellulosic coatings (IFA, IFB and IFC) have been evaluated using the heat radiator and furnace tests. This is a “blind test” as nothing is known about the composition of the coatings tested. The temperature versus time curves are not presented in this manuscript, but the **Table 4** clearly shows that correlation between the two tests is excellent, with the same ranking of coating performance obtained.

Table 4. Ranking of results obtained for intumescent cellulosic coatings (1=>best result)

	Heat radiator test	Big furnace test
IFA	1	1
IFB	3	3
IFC	2	2

Figure 27 summarizes the correlations between the two tests by plotting the time of failure at 400°C in the furnace test and the temperature obtained after 15 minutes during heat radiator test.

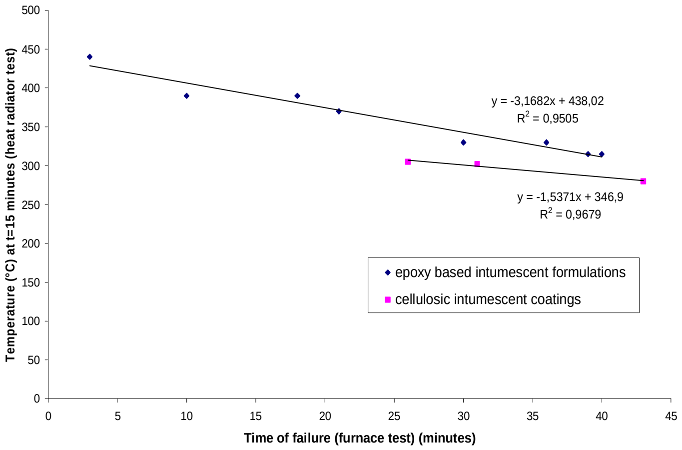


Figure 27. Correlation between the time of failure in furnace test and the temperature after 15 minutes during heat radiator test.

Very good correlation coefficients are obtained by linear regression both for epoxy based and cellulosic intumescent systems. The result can be surprising as the furnace test consists mainly in a convective flux whereas the heat radiator is a radiative heat source. But even if the heating ways are different, the results are well correlated.

To summarize these results, a reliable high throughput test has been developed in the laboratory in order to evaluate the heat barrier effect of different intumescent formulations. This is a small size, rapid and low cost test, easy to use, showing great repeatability and allowing rapid screening of thick and thin film intumescent formulations. It is a very interesting preliminary tool for the development of new intumescent coatings as it can avoid the requirement to carry out large furnace tests on many coating formulations. Only the promising formulations are then submitted to full scale furnace testing.

I-4 Further developments and perspectives

The development of a panel of small scale tests allowing predicting the behavior of an intumescent coating in a hydrocarbon fire opened the door to a topic dedicated to small scale protocol development. The “heat radiator” test was a very simple test, and even if it showed excellent correlations with the large furnace tests, we aimed these last years at developing small scale furnace tests mimicking the large scale furnace test but at a reduced scale.

A small scale test [62], mimicking the large furnace tests that can be found in different industries was developed in the laboratory by Y. Paul during his CNAM project and further optimized by P. Bachelet (Engineer in the group) and B. Gardelle (PhD student, 2010-2013). The test is presented on **Figure 28**.

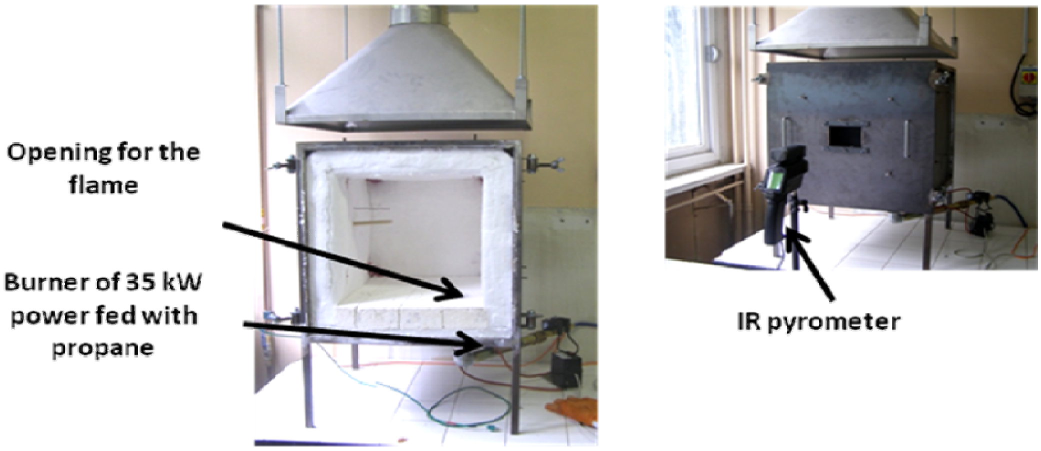


Figure 28. Small furnace test developed to mimic the UL1709 large scale furnace test

There is a burner of 35kW fed with propane. The sample is put into the furnace door, with the coated side inside the furnace. An infrared pyrometer is used to register the temperature at the backside of the steel plate. The backside of the plate is covered with a black heat resistant coating allowing maintaining a constant emissivity (similar approach as that developed for the heat radiator test). The experimental UL1709 curve obtained fits quite well the standard curve (**Figure 29**).

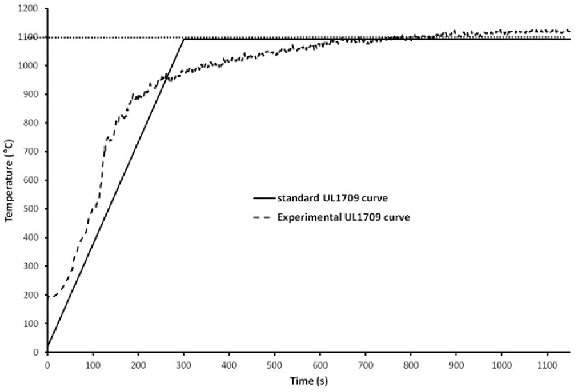


Figure 29. Comparison between the standard UL1709 curve and the experimental one

First temperature versus time results give promising results. The curves obtained are currently being correlated with large furnace tests.

Further work has to be carried out to continue to develop and enhance this test and to correlate the results obtained with industrial furnace tests. For example, a similar apparatus allowing testing larger plates (20*20 cm²) or a furnace equipped with a window allowing looking at the intumescent coating behavior are currently being developed in the group, opening the door to great possible enhancements as they will allow taking into account both the temperature versus time curves, the adhesion and the mechanical resistance of the char.

The development of a panel of lab scale analyses correlated with industrial furnace tests has been proven to allow the rapid testing of a large number of formulations and an accurate prediction of their behavior in a hydrocarbon fire. It will facilitate the testing of a lot of novel and promising ingredients inside the intumescent formulations, but it is also an important step in the development of modeling and simulation tools, as it is easier to define and establish degradation models (kinetic analysis) and models of heat transfers in an intumescent coating using small scale tests.

Both these approaches have thus been considered in the years following my PhD thesis.

For example, the thermal behavior of an intumescent coating under pyrolysis has been modeled and simulated using kinetic analyses approaches [5]. According to the analyses, the degradation of the formulation could be modeled using four successive reactions (A → B → C → D → E) with Avrami-Erofeev functions [73] (**Figure 30**).

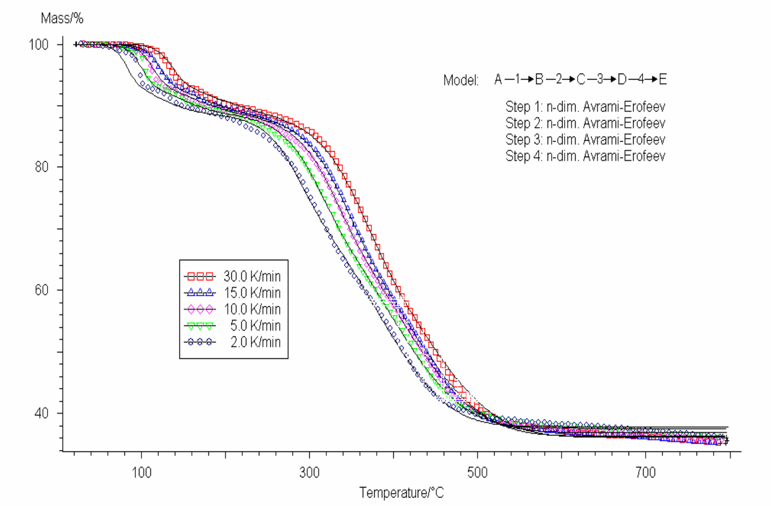


Figure 30. Experimental (dots) and simulated (line) TG curves of intumescent formulation.

Among the classical types of global kinetic models, Avrami-Erofeev and n-th order functions are often used to describe the degradation of polymers [74]. Here, the Avrami-Erofeev function was chosen because it gave the highest quality of fit, compared to the use of n-th order functions.

Our model fits the experimental TG curves extremely well. It should be emphasized that it has a formal character, but no information on the chemistry can be obtained from TGA data only. The true reactions of the system are too complex [2] to be characterized in any fundamental way, so the reactions are described as pseudo species which are themselves complex materials or a mixture. The kinetic parameters associated to the model are presented in **Table 5**.

Table 5. Computed kinetic parameters of the pyrolysis of the intumescent formulation.

Step n°	Log (A) (A: s^{-1})	E (kJ/mol)	Dimension n
1	5.3	54.5	1.85
2	3.7	49.6	0.55
3	6.3	97.9	1.02
4	14.7	221.9	0.23

The first two steps of degradation of the intumescent coating correspond to the degradation of boric acid in boron oxide. The activation energies are weak, this fits the usual activation energies of boric acid, which are comprised between 40 and 70 kJ/mol.

We then compared experimental and simulated curves in pyrolytic conditions at 50, 150 and 180°C/min and we managed to obtain a very good agreement between experimental and simulated curves (**Figure 31**).

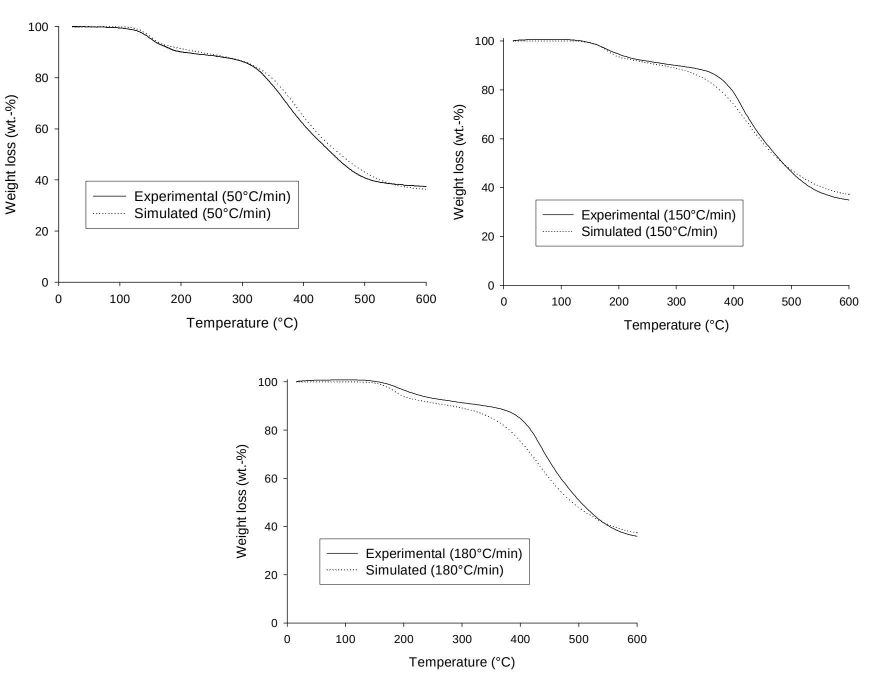


Figure 31. Comparison between simulated and experimental degradation curves at 50, 150 and 180°C/min.

The predictive curve at 180°C is somehow different from the experimental curve than in the case of the curves at 150 and 50°C/min. It can be explained by the fact that it is a quite high heating rate, and in the case of an intumescent system, the more the heating rate increases, the more rapidly the char swells: the char is less homogeneous, the heat transfers are accelerated and thus the degradation rate of the coating increases. However, even if this difference is particularly clear between 20 and 600°C, the residue at 800°C seems experimentally to be quite independent of the degradation rate. The small difference observed might come from different facts: maybe competitive reactions, due to a high heating rate, begin to appear; or maybe in this range of high heating rates the TG itself has some limitations in measurement, due to the difference of heat transfer. However these differences are not significant and that is why it can be assumed that the model established is accurate. This means that our approach can be used to model the thermal behavior and the pyrolytic degradation of the intumescent formulation whatever the scenario.

The last step of the study was to try to implement in the software the hydrocarbon fire test curve. The heating steps of the hydrocarbon curve were decomposed and linearized, the heating rate of the first step was thus shown to be about 770°C/min. The degradation curve was then simulated by the software using our model. The predicted char yield at 1200°C was about 40%. This simulation was finally validated by experimental results obtained during industrial furnace tests: the steel plates covered with coating were weighed before and after furnace tests. The mean of the results obtained for eight experiments shows a char yield of about 45%, and this result fits well our prediction [5].

This means that it is also possible in a first approach to evaluate the degradation behavior of the coating in a real fire, which, combined with other small scale tests, allows to avoid to carry out too many industrial furnace tests which are very expensive and time consuming. Moreover, the model established allows determining the main kinetics parameters of the pyrolysis of the intumescent formulation. These parameters can be further used in a global approach consisting in modeling heat transfers in an intumescent coating. A first approach of modeling of heat transfers has been carried out using the "heat radiator test" as model and the commercial software COMSOL Multiphysics v.3.2 as modeling tool. The first model we developed combines ALE (Arbitrary Lagrangian Eulerian) method, created for moving boundaries with the heat transfer and Navier-Stokes equations. This allows the modeling of a layer of an intumescent coating which swells up when heated (**Figure 32**): the temperature of the coating can been modeled at different times and plotted against the expansion.

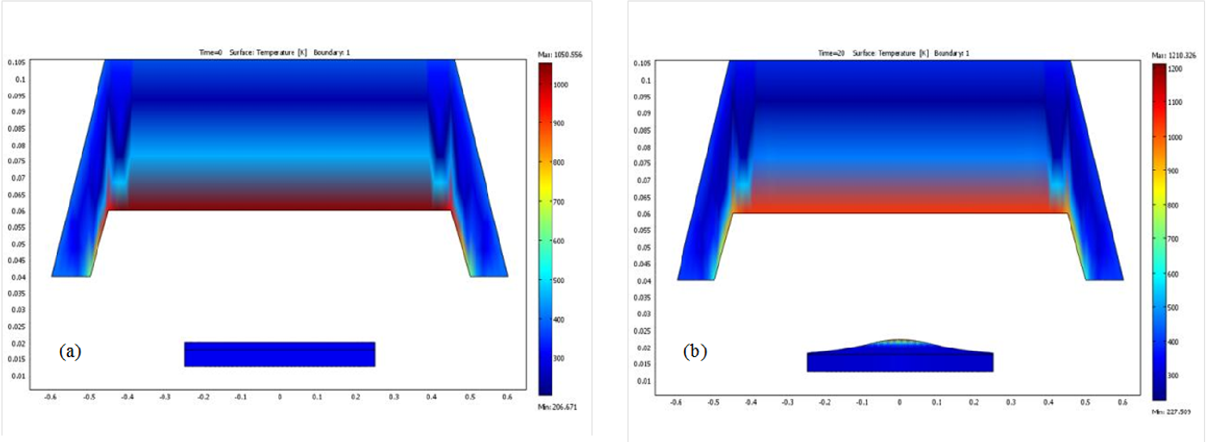


Figure 32 (a) and (b). Two-dimensional model simulating the expansion and heat transfers inside a layer of intumescent coating (at t=0 and t=500s).

The preliminary results are interesting and show the gradients of temperature inside the expanded layer; but the model still needs to be enhanced in a future work, by adding the steel plate inside the model and by taking into account the porosity and the characteristics of the char, such as porosity, kinetics of degradation, density and internal pressure. My colleagues S. Bourbigot and F. Samyn are currently developing this modeling topic on various intumescent coatings and I will be associated to this development in the frame of an industrial funded project on the modeling of the degradation behavior of composites (protected by an intumescent coating) in a fire.

The objectives of the work presented in this first chapter were –to summarize - both academic and industrial:

- **Investigation of the mechanisms of degradation of a thick epoxy based intumescent formulation and of the interactions occurring between the main ingredients.**
- **Design of new small-scale tests and development of a panel of lab scale analyses allowing an improved comprehension of the intumescence phenomenon and also allowing the prediction of performance of different intumescent coatings in a hydrocarbon fire.**
- **Simulation by mathematical models of the kinetics of degradation of the intumescent coating that could be extrapolated in different fire conditions.**

The research results and methodologies developed during and after this PhD thesis allowed to input and to start in the group the topic entitled "Similitude, modeling and simulation". We are now a team recognized at an international level for these small scale tests developments and we

intend to further develop modeling tools in the incoming years. Some of these small scale tests applied to foams and composites will also be presented in the Chapter 2.

As shown in the first chapter, intumescent coatings are usually designed to protect steel structures against fire. We the decided to investigate if this concept could be applied in some extent to fire retard polymeric materials, as described in the following Chapter 2. In fact, polymeric materials are easily flammable and contribute actively to the fire. They are usually fire retarded by incorporation of additives (e.g. intumescent fire retardant (IFR) additives) in the bulk, resulting in an intumescent foam. Our idea was to apply an intumescent coating on thermoplastics to improve their reaction to fire and to protect them instead of incorporating the IFR into the bulk. It presents a priori several advantages: it does not modify the intrinsic properties of the materials, e.g. the mechanical properties, and it is easily processed and it should be recyclable.

In the incoming second chapter, the concept of applying intumescent coatings on thermoplastics, developed in the laboratory, will be described and validated on polypropylene and polycarbonate. The improvement of this concept for industrial applications requiring very high performances against fire (e.g. electrical applications) will then be described and the mechanisms involved will be explained. Finally, the perspectives of development of this concept on composites will be rapidly presented.

Chapter 2- Fire retardancy and protection of polymeric substrates by intumescent coatings

This work first started by internal development in the laboratory [6-8], and was then supported by the CIFRE PhD of H.Gallou (2007-2010) [11, 12], funded by Rhodia Company, France. This work led to one patent [10]. The concepts elaborated are now extended to other kinds of materials [9] and will be further developed in the incoming years.

II-1 Concept

The main way to fire retard plastics is right now a **bulk treatment, i.e. the use of flame retardants and stabilizers directly blended within the polymer** [63]. This well working approach tends however to some limits: usually important amount of additives are needed to be efficient, which creates three major problems: first, the migration of the additives from the bulk to the surface of the polymer forms a non uniform compound after a while. Secondly, because of the weak interaction between the additives and the polymer matrix, weak or “fragile” points are formed in the matrix which decrease the mechanical strength of the specimens [64-66]. And finally industrials intend to reduce the thickness of their samples, involving processing issues because of the high amount of fire retardant additives. There is also nowadays a tendency to avoid the very efficient halogenated compounds on account of their potential secondary effects, such as corrosive fumes and highly toxic compounds which are emitted during burning. An emerging problem is also the recyclability of fire retarded polymers which is problematic, particularly in electrical devices.

In recent years, IFR additives have attracted a great attention in the flame retardancy of polymers [55, 67, 68] to replace these halogenated components. The main problems associated with these IFR systems can however be the moisture sensitivity and poor compatibility with polymer matrix. For example, melamine phosphate, commonly used as carbonization catalyzing agent, is easily attacked by moisture [69]. When it is for example blended with PP, the exudation of the additives leads to a decrease in the properties of the PP composites not only in terms of flame retardancy but it also affects mechanical and electrical insulating properties.

The chemical modification of the macromolecule is another method to make fire retarded polymeric matrices [70]. This technique is not easy to conduct on an industrial scale with most thermoplastic polymers, and can be rather expensive and so is not commonly used.

The third approach, developed in our group, consists in **applying an intumescent coating on the polymer surface**, instead of incorporating the IFR into the bulk. This is an attractive alternative method as it allows concentrating the fire retardant properties onto the polymer surface (where the flammability occurs) and thus allows preserving the bulk properties of the material.

This is a brand new approach: very few studies have investigated the use of intumescent coatings on plastics. Intumescent coatings are worldwide used for steel [71] and wood [72], some studies have been carried out on textiles with the back coating of phosphorous containing formulations [73, 74] but only one previous study in our laboratory has shown an interest to apply an intumescent coating on Polypropylene composites [75]. One issue however encountered by the use of coatings can be the bad adhesion of the coating onto the polymeric substrate, and particularly when waterborne coatings are used. Different ways, such as corona treatments, cold plasma and more recently atmospheric plasma, exist to improve the compatibility between a substrate and a coating [76]. Flame treatment [77] is also a well-established, low cost and rapid method to improve adhesion. Passing the flame over a surface leads to an increase in surface energy and wettability, respectively, thus enabling a good contact between the fluids used for decoration of the surface. This novel concept, consisting in combining both an intumescent coating and a treatment allowing the improvement of adhesion onto a plastic, offers a new pathway to fire retard plastics. We thus decided to validate this concept [7] on two polymers: polypropylene and polycarbonate.

II-2 Concept validation on Polypropylene and Polycarbonate

Polypropylene (PP) and polycarbonate (PC) were selected as two different matrices since one is a non-polar polymer whereas the other one is not.

Both these polymers are good examples representative of the limits of actual bulk treatments. PP is widely used in many fields, such as building, automotives, electronic and electric industry. It is highly combustible and needs to be flame retarded. Until last years, halogen-containing compounds, alone or in conjunction with antimony trioxide, were the main flame retardants for PP [78]. Phosphorus and nitrogen based compounds, as well as metal hydroxides constitute now a rapidly growing group of flame retardants which are in the focus of public interest concerning environmental friendly chemicals. Metal hydroxides [79], mainly magnesium hydroxide and aluminum hydroxide, are commonly used in the flame retardancy of polymers due to their low toxicity and cost. But usually more than 60 wt-% loading of metal hydroxides is required in PP to obtain efficient flame-retardant properties, and such high loading levels lead to a great decrease in the mechanical properties of the filled polymer materials [64-66].

Same kind of observations can be done for the Polycarbonate (PC): PC is known for its transparency and it exhibits excellent mechanical strength, good electrical properties and is widely used in a

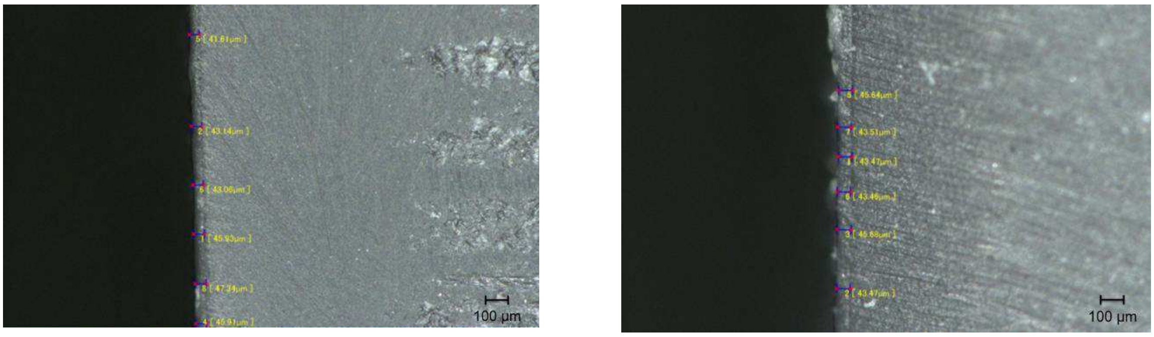
variety of fields such as for example electric and electronic machinery, automobiles, architecture. The aim to meet safety criteria in these various applications is to develop a PC based component which is an efficient flame retardant system, which prevents dripping during fire and which allows maintaining the mechanical and optical properties of PC. Polycarbonate resin is also usually fire retarded by incorporation of a flame retardant during processing. The most common flame retardants used were bromine-based e.g. decabromodiphenyl ether [80]. Another way is to add a relatively large amount of phosphorous based flame retardants (10-30 wt%.). However, these phosphorous based additives can lower the impact strength of the PC or yellow it in high-temperature or high-humidity conditions. Sodium and potassium perfluoroalkanesulfonic [81] acids were found effective in amounts well under 0.05-0.5%, but these components are still halogenated compounds. Some recent works have described the development of fire retardant PC combined with polymethylphenylsilsesquioxane spheres [82], but mechanical resistance issue still remains.
In the following part, in order to validate the concept of plastic protection by an intumescent coating, the results, in terms of both adhesion and fire barrier, of the application of a waterborne transparent intumescent varnish (Pyroplast HW100, Rütgers Organics, unknown formula) on flamed polypropylene (PP) and polycarbonate (PC) samples are presented.

Before applying the intumescent coating on the polymer substrates, the surfaces of the samples were treated with a flaming apparatus and this flame treatment was optimized. The coatings were then applied using a semi-industrial spraying machine from CLID (Lille, France). The adhesion of the coating was thus evaluated on PC and PP using the “Tape” test and classified following the ASTM D 3359-02 standard (best classification 5B, worse 0B).

The adhesion of the varnish on flame treated PC achieves the best classification (5B) demonstrating a good adhesion between the coating and the substrate. The adhesion test of virgin coated flame treated PP shows a slightly worse adhesion compared to PC since the sample is classified 4B. The adhesion improvement is explained by the fact that flaming treatment allows both the oxidation and the cleaning of the surface: the water contact angle decreases for both polymers, showing that the wettability of the samples increases. The standard deviation is very small, proving that the flame treatment is homogeneous. Some reactive functions such as hydroxyl functions are created on the sample surface [83], which allow a better compatibility with the coating and thus a better adhesion of the coating.

In order to investigate the effect of the thickness of the coating and to determine the optimized thickness that permits achieving satisfactory fire performances, the spraying time was varied during the deposit. The thickness of the coating was evaluated using an optical microscope and **Figure 33** presents, as an example, the results obtained for a spraying time of 3 sec.

It can be observed that, whatever the matrix, the thickness of the coating is homogeneous along the sample. Several observations were done and a classical statistical calculation gives that for a spraying time of 3s, the thickness was equal to 42+/-5 µm.



(a) (b)

Figure 33. Optical picture of the cross-section of a coated PC (a) and PP (b) for a spraying time of 3 sec.

Figure 34 reports the limiting oxygen index (LOI) of PP and PC versus the coating thickness. The LOI is the minimum concentration of oxygen, expressed as a percentage, that supports the combustion of a polymer: the higher the value, the better the flame retardant (FR) properties of a sample.

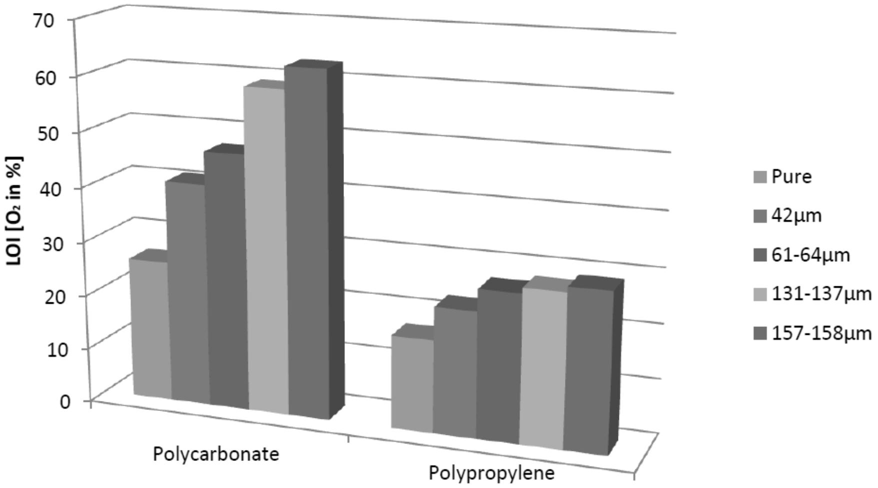


Figure 34. LOI versus coating thickness for PC and PP

It is observed that higher values were obtained for PC compared to PP in both cases (virgin and coated materials). This difference makes sense since the behavior of both materials against fire is very different. Whereas PC chars when exposed to a flame, PP melts and burns vigorously after ignition. Lyon and al. [84] compared the flammability of various polymers, including PP and PC using different techniques. They studied the char yield of PP and PC in micro-scale calorimeter and they reported values of respectively 0 and 23wt.-%. On the other hand, total heat released by combustion of volatile fuel from PP is reported equal to around 43kJ/g against around 20kJ/g for PC. It thus demonstrates that the flammability of PC and PP are different and then it is not surprising to observe differences in their FR properties.

LOI value of virgin PC is 26 vol.-% and increases to 41 vol.-% for a 42µm coating and up to 63 vol.-% for 157µm. The LOI of virgin PP is 18 vol.-% and increases from 23 vol.-% up to 29 vol.-% when the thickness increases respectively from 42 to 158 µm. In both cases, an improvement of the FR properties of the materials is observed with the coating thickness. Those results demonstrate that the use of an intumescent coating to improve the FR properties of PP and PC is efficient.

Table 6 reports the UL94 rating for both 0.8 mm and 1.6 mm thick samples. UL 94 is a plastic flammability standard widely required in the field of electric and electronic equipment. The rating varies from V0 for low flammable material (burning stops within 10s on a vertical specimen; drips of particles allowed as long as they are not inflamed) to NC (non-classified - burning time is higher than 30s on a vertical specimen and/or the material burns totally).

Table 6. UL94 rating versus coating thickness for PC and PP (NC: Not Classified)

Substrate	Coating Thickness (µm)	UL94 rating (0.8 mm bars)	UL94 rating (1.6 mm bars)
PC	0	V2	V2
	42	V0	V0
	61	V0	V0
	131	V0	V0
	157	V0	V0
PP	0	NC	NC
	42	V2	NC
	64	V2	V2
	137	V2	V1
	158	V1	V0

As observed in the case of LOI, better properties are obtained in the case of PC compared to PP. Indeed, whereas for PC, V0 is achieved for both 0.8 and 1.6mm thick samples and whatever the thickness of the intumescent coating, V0 is only achieved in the case of PP for 1.6mm bar and 158µm thick intumescent coating. Similarly to what discussed previously, this difference could be explained by the burning behavior of the virgin matrix. Indeed, since PC is a highly viscous and charring material, when the material is exposed to the flame, low deformation of it occurs and thus the intumescent char layer could act as a protective coating. In the case of PP at the opposite, when the material degrades, its viscosity sharply decreases and drops are observed. In that case, the development of the intumescent coating is not fast enough to avoid the increase in temperature of the substrate and thus the melting of the PP. The specimen highly deforms and the intumescent char cannot totally follow this deformation. As a consequence, mass and heat transfers can occur between the flame and the substrate resulting in low FR performance. However, it is noteworthy that achieving a V0 rating in the case of PP is not an easy task and thus the results obtained for 158 µm thick intumescent coating are very encouraging.

Finally, Mass Loss Calorimeter (MLC) was also used to evaluate the FR properties of the coated PC and PP. This equipment is identical to that used in oxygen consumption cone calorimetry (ASTM E-1354-90), except that a thermopile in the chimney is used to obtain heat release rate (HRR) rather than employing the oxygen consumption principle. Our procedure involved exposing specimens (coated face) in horizontal orientation. External heat flux of 50 kW/m² was used for running the experiments. This flux corresponds to common heat flux in developed fire scenario. A distance of 55 mm was used to allow the expansion of the intumescent coating. The mass loss calorimeter was used to determine the heat release rate (HRR). When measured at 50 kW/m², HRR is reproducible within ±10%.

HRR and its maximum value (Peak of Heat Release Rate, PHRR) can be used to characterize the hazard represented by a material regarding its contribution to fire and can provide information on fire size and fire growth rate: the lower the HRR, the better the fire performance.

HRR curves as a function of the time are reported respectively for PC and PP in **Figure 35** and in **Figure 36**.

Similarly to the results obtained for the two other fire testing methods, the FR performance of coated materials are better in the case of PC compared to PP. In particular, it is observed that for PC, when a thickness of 61µm or higher is used, no ignition of the material occurs and thus the HRR remains close to zero.

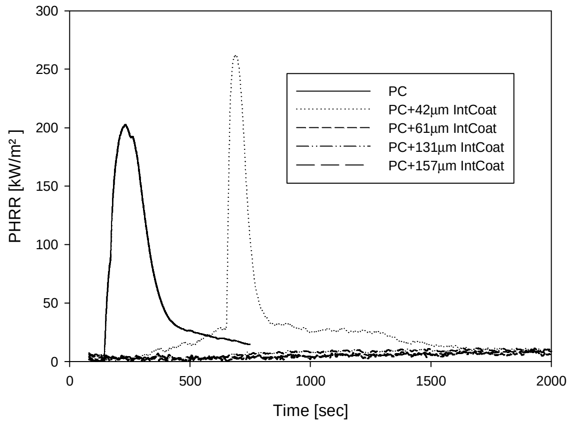


Figure 35. HRR versus time for PC and coated PC versus coating thickness (IntCoat: Intumescent Coating)

For a thickness of 42µm, a peak is observed with a slightly higher PHRR value compared to virgin PC (260 kW/m² versus 200 kW/m²) but the peak is observed at higher time (720s versus 230s). This is well correlated with the time to ignition (TTI) that is around 140s for virgin PC and around 650s for PC coated with 42µm of intumescent varnish. It could thus be assumed that when the plate was coated with 42µm of intumescent varnish, intumescence develops, leading to the formation of a protective layer but this layer is too thin and fragile. Just before ignition, the protective layer breaks, maybe because of internal pressure leading to the release of the degradation products of PC that were previously trapped by the intumescent coating and ignition occurs. As a consequence, it leads to rapid ignition of these gases and their combustion leads to a slightly higher PHRR.

In the case of PP, the results are very different because in all cases, ignition was observed and a peak corresponding to the combustion of the material occurs.

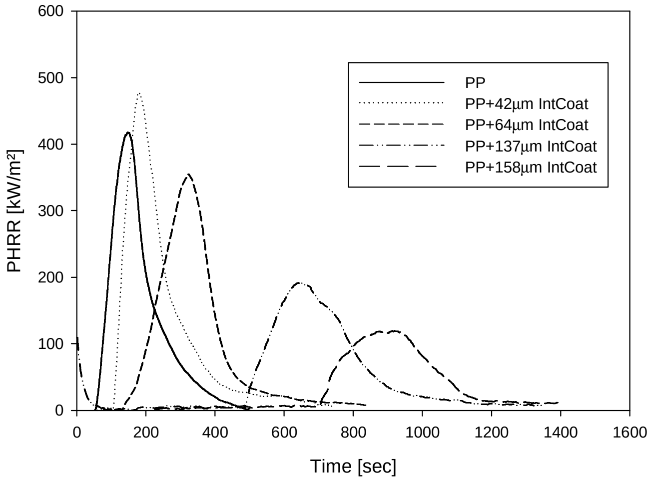
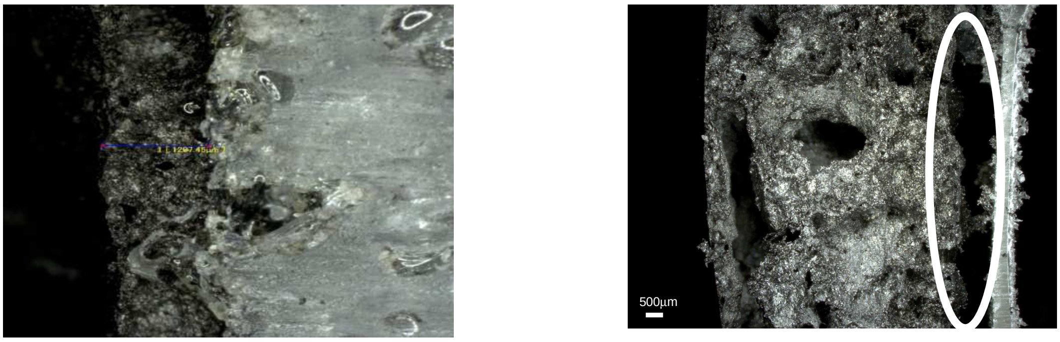


Figure 36. HRR versus time for PC and coated PC versus coating thickness (IntCoat : Intumescent Coating)

The TTI increases with the coating thickness whereas the PHRR decreases. Indeed, pure polypropylene ignited after 56 s and reached a maximum heat release rate of 420 kW/m². The 42 µm thick coated PP ignited after 107 s and reached a heat release value of 477 kW/m². This value is a bit higher than for pure polypropylene and similar explanation as in the case of PC is proposed. For the 64 µm thick coating, the PHRR was slightly lower than for virgin PP (355 kW/m²). For 137 and 158µm coating thickness, PHRR are respectively equal to 188 and 118 kW/m².

From those results, it can also be concluded that a minimum thickness of 158µm is required to achieve satisfactory results (UL94 V0 rating, high LOI, low PHRR value and high TTI) in the case of PP whereas 64µm is the minimum thickness for PC. PP and PC behave in complete different manners when exposed to fire. Indeed, it was previously mentioned that PP melts before burning whereas PC, which is a highly viscous material, does not (only softening is observed). Thus, the cohesion between the protective layer and the polymer during the MLC test is lower. As a consequence, degradation gases (fuel) may escape leading to the ignition of the material.

In order to confirm the protective mechanism of the intumescent coating and to better understand the role of the polymer matrix, MLC experiments were stopped after characteristic times of the combustion. The sample was thus taken out from the heat source (conical heater) and quickly covered to stop oxygen supply leading to fast flame suppression. Collected residues were analyzed using digital optical microscope and examples of results are presented in **Figure 37**.



PC-60s

PP – 600s

Figure 37. Digital pictures of cross-section of the 64µm coated PC and 158µm coated PP after respectively 60 and 600sec exposure at MLC (50kW/m²)

It can be observed from these pictures that in the case of PC, the intumescent paint remains stuck to the polymer matrix and thus can play its protective role. If we observe the samples after longer combustion time (results not shown), the only difference is in the thickness of the intumescent coating. Residue collected at the end of the MLC test still shows some unburned PC. In the opposite, considering PP, just before ignition (at t=600sec), some void (showed as white ellipse on the picture PP-600s) is observed between the intumescent paint and the polymer matrix. It could be observed that this big bubble between the matrix and the coating increases in size up to the break of the intumescent coating that leads to release of fuel and thus to the ignition of the material. At the end of the test, no remaining virgin PP was observed.

Our concept of polymer fire protection by applying an intumescent coating was thus validated for both PP and PC, with somehow better results obtained in the case of PC, which is a charring polymer. In the frame of a PhD thesis in partnership with Rhodia company (PhD H.Gallou, 2010), we then tried to extend this concept on Polyamide 6,6 (PA6,6) for the fire protection of electrical and electronic equipment. We will see in the following section that this concept presents however some limitations for high performance electrical applications. This is why a novel concept, combining a small amount of fillers incorporated in the bulk and a thin intumescent coating layer, has been developed and is also presented in a further section.

II-3 Concept limitation for high performance electrical applications

PA6,6 filled with glass fibers (PA6,6-GF) is used in many industrial fields such as housing materials, transport or electrical engineering applications. Due to its chemical composition, this polymer is easily flammable. As far as the main applications concern electrical and electronic equipment, its flame retardant properties become an important requirement. The most discriminating tests are LOI, UL94 and GWFI (Glow Wire Flammability Index).

The GWFI test (IEC 60695-2 standard) is used to simulate the effect of heat that might arise in malfunctioning electrical equipment. Test results provide a way to compare the ability of materials to extinguish flames and their ability not to produce particles capable of spreading fire. The glow wire is heated via an electrical resistance. A test specimen is held for 30s against the tip of the glow wire with a force of 1 N. The product is characterized by the highest temperature (for a test specimen), at which one of the following conditions are fulfilled: flames or glowing of the test specimen extinguish within 30 s after removal of the glow-wire and there is no ignition of the wrapping tissue placed underneath the test specimen; or there is no ignition at all of the test specimen.

The aim was in this example to obtain high LOI values, V0 rating at UL94 test for 1.6mm or 0.8mm thick samples and a validation at 960°C of the GWFI.

The usual way to fire retard PA6,6-GF consists in incorporating a high loading of fire retardant additives. We showed in a recent work [12] that a minimum amount of 23% of aluminium diethylphosphinate Exolit OP1230 (AlPi) (**Figure 38**) incorporated in bulk during PA6,6-GF extrusion process allows reaching these requirements.

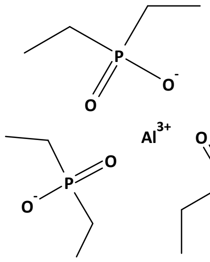


Figure 38 : Formula of aluminum diethylphosphinate (AlPi)

In fact, we observed that the incorporation of only 8% of AlPi allows obtaining good fire properties. Indeed, even if V0 rating at UL94 is not achieved, the sample, which is not classified at 5%, shows a V1 rating for 8% of additives (extinction time superior to 10s and dripping of polymer). Moreover, it validates the GWFI at 960°C. The V0 rating however is only obtained when 23% of additives are added, which is an important amount that modifies the intrinsic properties of the polymer such as its mechanical properties.

We thus evaluated the FR performance of an intumescent coating (the same as the one previously described for PP and PC) on virgin PA6,6-GF substrates. A flame treatment before coating spray was carried out in order to obtain a 5B rating at the adhesion test. We observed that LOI and UL94 rating achieve satisfactory performances whereas GWFI is only 750°C (**Table 7**) which is not sufficient for use as Electrical and Electronic Equipment.

Table 7: Flame retardant performances of PA66-GF coated with 100µm of varnish

	LOI (vol.-%)		UL-94		GWFI
Sample thickness	0.8 mm	1.6 mm	0.8 mm	1.6 mm	1mm
PA6,6-GF + 100µm varnish	52	54	V-0	V-0	750°C

This is why it was decided to test the combination of bulk and surface treatments by incorporating a very low amount of AlPi in PA6,6-GF and by coating it with the 100µm thick coating.

II-4 Novel concept: combination of bulk and surface treatments

In that case, the AlPi content in the PA 6,6-GF was fixed at 5wt.-%. Indeed, it was previously reported [12] that for PA6,6-GF 5% AlPi , the material is not classified at UL94 and presents a low LOI value (26 vol.-%). However, considering the intumescent coating as surface treatment, it was demonstrated that both UL94 and LOI can be sharply improved (V0 rating and LOI higher than 50vol.-%). That is why 5% AlPi - and not 8% - was chosen in this case.

The flame retardant properties obtained when the 5% AlPi added in the bulk and the 100µm of intumescent varnish are combined are presented in the **Table 8** and compared with the PA6,6-GF + intumescent varnish and PA6,6-GF - 23% AlPi which is the optimized formulation considering the bulk approach.

Table 8: Flame retardant performances of PA6,6-GF-5% AlPi - 100µm intumescent coating (IntCoat) compared to other formulations

	LOI (vol.-%)		UL-94		GWFI
Sample thickness	0,8 mm	1,6 mm	0,8 mm	1,6 mm	1 mm
PA6,6 GF - IntCoat	52	54	V0	V0	750
PA6,6GF - 5%AlPi -IntCoat	**63**	**65**	**V0**	**V0**	**960**
PA6,6 GF -23% AlPi	42	44	V0	V0	960

The addition of 5% AlPi to the formulation combined with the 100µm thick coating allows increasing the LOI to very high values (63-65 vol.-%), keeping the V0 ranking for samples of 0.8 mm and 1.6 mm thickness and validating the GWFI test at 960°C. It has to be highlighted that the results in terms of LOI are even better than those obtained with the formulation loaded with 23% of AlPi.

To summarize, an interesting formulation to be used as electrical and electronic equipment could be defined as a combination of 5% of aluminum phosphinate and 100µm thick intumescent varnish. The LOI is the highest (63-65 %), the sample is V0 rated at both 0.8 and 1.6mm and this material validates the GWFI test at 960°C. The interest of this new approach, which has been patented [10] and published [12], might be to combine two different mechanisms of action: a condensed phase mechanism through the formation of an intumescent barrier and the gas phase action of AlPi which releases phosphorus-based radicals. The concept consisting in combining two mechanisms of action in a bulk approach has already been developed by Braun et al. [85] and by Gallo et al. [86, 87] who obtained synergistic effects by combining in Poly (1-4 butylene terephtalate) (PBT) AlPi respectively with melamine cyanurate and metal oxides. The combination of AlPi and intumescent fire retardants in the bulk has also recently been reported by Yi et al. [88] who incorporated in an acrylonitrile-butadiene-styrene copolymer (ABS) ammonium polyphosphate and other additives such as AlPi. Again, a synergistic effect was observed. In our novel approach, we however apply the intumescent fire retardants as a coating on the sample surface and not in the bulk as in the previous published papers. We could have thought the AlPi action would be inhibited by the presence of the intumescent coating; on the contrary, it plays a complementary effect, particularly for LOI and GWFI test. It seems that when the intumescent barrier is crossed, the AlPi takes over from it and releases the species allowing protecting the polymer at 960°C. This is why a particular attention was paid to the possible mechanisms of action taking place during burning in these different situations.

II-5 Mechanisms of action involved during burning

In flame retardancy, the most significant chemical reactions interfering with the combustion process can take place in the condensed and/or gas phases.

In the condensed phase different types of reactions can take place. Among them, the flame retardant can lead to the formation of an isolating carbon layer (char) on the polymer surface. A polymer flame retarded by intumescence is essentially a special case of a condensed phase mechanism. The activity in this case occurs in the condensed phase and radical trap mechanism in the gaseous phase appears to be not involved.

In a gas phase, such as reported in the case of the AlPi, the radical mechanism takes place: the highly energetic radicals ($H^\cdot$, $OH^\cdot$) are trapped by different radicals (e.g. $PO^\cdot$) in the case of phosphorus based compounds. The exothermic processes which occur in the flame are thus stopped, the system cools down, the supply of flammable gases is reduced and eventually completely suppressed.

The concept developed previously was thus to combine a mechanism in condensed phase (intumescent coating) and a mechanism in gaseous phase (AlPi). First of all, the mechanisms of both systems were investigated separately and then a possible mechanism of action when AlPi is combined with the intumescent coating could be discussed.

In order to investigate the mechanism of action of the intumescent paint and of the combination AlPi/intumescent paint, some Mass Loss Calorimeters (MLC) experiments were stopped at characteristic steps of combustion (**Figure 39**) and the residues collected were analyzed by solid state NMR. This experiment is thereafter called “shutter test”.

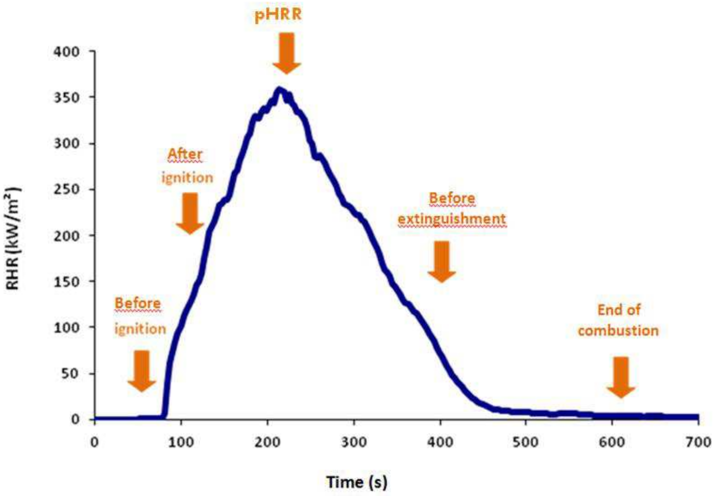


Figure 39. Representation of the characteristic steps of the cone calorimeter analysis investigated.

The samples were analyzed by ^{31}P, ^{27}Al and ^{13}C solid state NMR before ignition, after ignition, at the PHRR, before extinguishment and/or at the end of the combustion. Three samples were analyzed at different combustion times: PA6,6-GF filled in with 23%AlPi, PA6,6-GF covered with 100µm of intumescent coating and PA6,6-GF filled in with 5% AlPi and covered with 100µm intumescent coating.

The mechanism of action of aluminum diethylphosphinate (AlPi) in PA6,6-GF has been already detailed by U.Braun et al. [89] and F.Samyn et al. [90]. They established that both thermal and hydrolytic polymer decompositions take place during burning, and that phosphinates vaporize during both steps of degradation of the PA6,6-GF, without showing particular interaction in condensed phase with the polymer matrix. Our NMR results (not presented here, see [11]) are consistent with this decomposition model. At the end of the combustion, ^{13}C NMR confirms that a char is obtained. ^{31}P NMR shows the degradation of the phosphinates during combustion, with the apparition of some aluminophosphates in amorphous form at the end of the combustion. The ^{27}Al spectrum confirms these observations, with a very low signal corresponding to aluminophosphates appearing at the end of the combustion. **Figure 40** summarizes the decomposition mechanism of the PA6,6-GF AlPi.

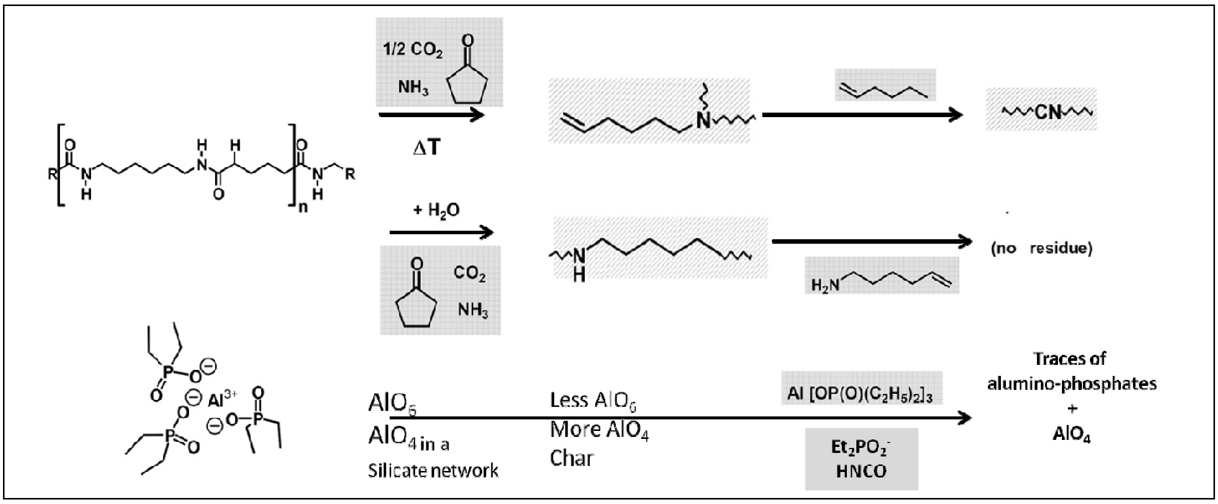


Figure 40. Decomposition mechanism of PA66-GF 5%AlPi [7]

On the other hand, it was shown that when PA6,6-GF plate was coated with the intumescent coating, a protection of the substrate occurs. Indeed, ^{13}C NMR analyses (not presented here) show that PA6,6-GF is only partially degraded during the MLC experiment since the signals corresponding to the aliphatic fragments of PA6,6-GF are retrieved in the bulk part at the end of the combustion, which is not the case for non protected PA6,6-GF. However, the signals obtained during degradation of both the coating and the polymer plate being similar, it is not really possible, using only ^{13}C NMR, to determine if some interactions exist between the polymer and the coating.

^{31}P NMR however demonstrates that the intumescent coating and the polymer are “mixed” together during burning, since the phosphorus species are detected both in the bulk and in the surface layer. Indeed, the ^{31}P NMR signals of the coated PA6,6 during burning present the same signals (Q_0 and Q_1 sites [91])[2] for both the bulk and the surface.

In that case, as the virgin PA6,6-GF does not contain any phosphorus, it is clear that during burning one part of the virgin polymer begins to degrade and is mixed with the semi-viscous intumescent system. In some way, it may be assumed that the polymer becomes fire retarded in bulk during burning thanks to the intumescent coating applied on it. ^{31}P NMR analyses also give some clues about the mechanism of degradation of the intumescent coating. Indeed, even if the intumescent

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[2] *Depending on the number of the bridging oxygen the phosphate tetrahedra can be described as Q_i, where i represents the number of the bridging oxygens and can have a value of 0, 1, 2, 3. Such notation was first used by Lippmaa, and is widely accepted in the literature for describing structures of phosphates and silicates. A framework built up with Q_3 denotes a fully polymerized structure, while Q_2 unit gives only a two-dimensional structure based on chains or rings. Q_1 means two tetrahedral connected by a corner and Q_0 means isolated tetrahedra. Q_0 units are characteristic for orthophosphate structures.*

coating used is a commercial product, it was demonstrated that when degraded formation of ortho and pyrophosphate (both aliphatic and aromatic) should be suspected. This is often observed when studying degradation of intumescent coatings [2].

Figure 41 summarizes the supposed mechanism of action of the intumescent coating on the PA6,6-GF.

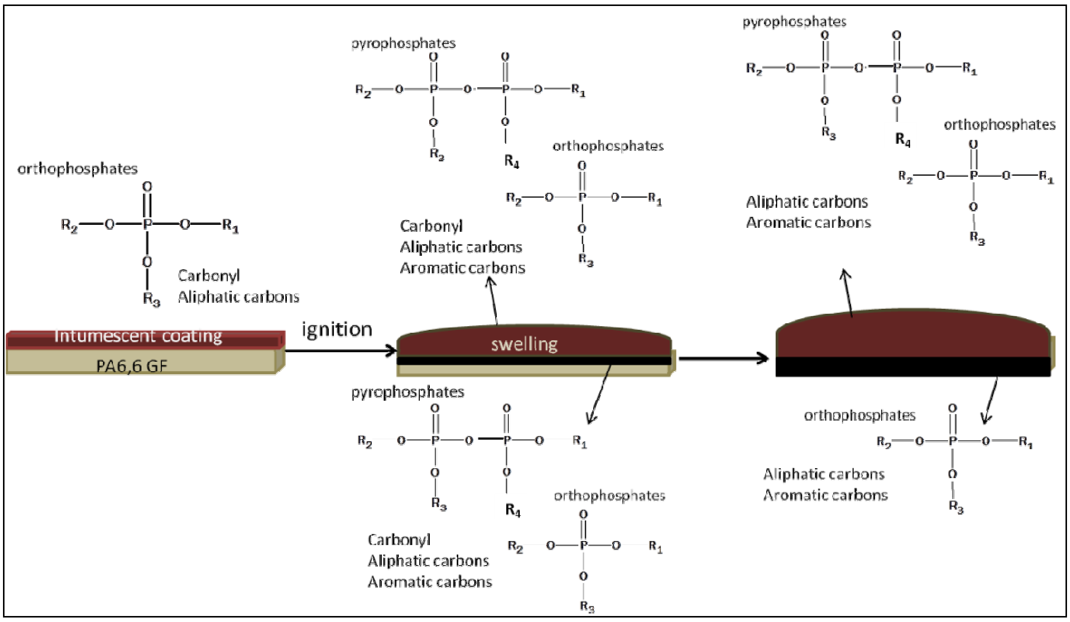


Figure 41. Mechanism of action of the intumescent coating on the PA6,6-GF

Finally, the main objective was to explain the improvement of the fire retardant properties of the material when both the bulk and the surface treatments are combined. Indeed, in that case, the GWFI test shows great improvement: GWFI is validated at 750°C for PA6,6-GF IntCoat, at 850°C for PA6,6GF 5%AlPi whereas it is validated at 960°C when both approaches are combined. The AlPi clearly has an influence on the GWFI test as with only 5% AlPi in polymer bulk the GWFI is validated at 850°C. These differences can first be explained by the test configuration: the test specimen is held for 30s against the tip of the glow wire with a certain force. It means that the specimen penetrates inside the intumescent coating layer and when it has crossed this barrier it penetrates inside the polymer. If the polymer is not intrinsically protected it will burn and the intumescent coating will no longer be efficient. This is a first explanation but we wanted to demonstrate if interactions between the intumescent coating and AlPi occur or not. That is the reason why the chemistry of the system was investigated during combustion.

^{13}C NMR analyses show that similarly to what observed for PA6,6-GF coated with the intumescent coating, a protective behavior of the intumescent coating is obtained. Indeed, the PA6,6-GF also only partially degrades during the cone calorimeter experiment since aliphatic structures are maintained in the material, up to the end of the test.

^{31}P NMR spectra however show some differences in presence of AlPi: the peaks characteristic of AlPi are as expected observed in the bulk material but an additional peak appears after ignition at -30 ppm, corresponding to the presence of alumino-phosphates. This peak only appears at the end of the combustion in the PA6,6-GF 5%AlPi spectrum. It could thus be assumed that the presence of the intumescent coating leads to the condensation of the sublimated AlPi in the pores of the structure that allow its further degradation up to the formation of aluminophosphates. This phenomenon is confirmed by ^{27}Al spectra: at the end of the combustion, signals corresponding to $AlPO_4$ structures are observed in the bulk. Moreover, it is interesting to observe that after ignition, peaks characteristic of the ^{31}P species coming from the intumescent coating are observed in the bulk materials. It thus confirms that similarly to what observed when PA6,6-GF is used as a substrate, both materials are mixed together when burning.

It is therefore assumed that the intumescent coating acts as a barrier for the gaseous products produced from the degradation of AlPi. Aluminophosphates are formed during burning, these species migrate and are trapped inside the coating char. The presence of aluminophosphates stabilizes the char and might allow a better protection of the underlying substrate. The **Figure 42** summarizes the different mechanisms involved.

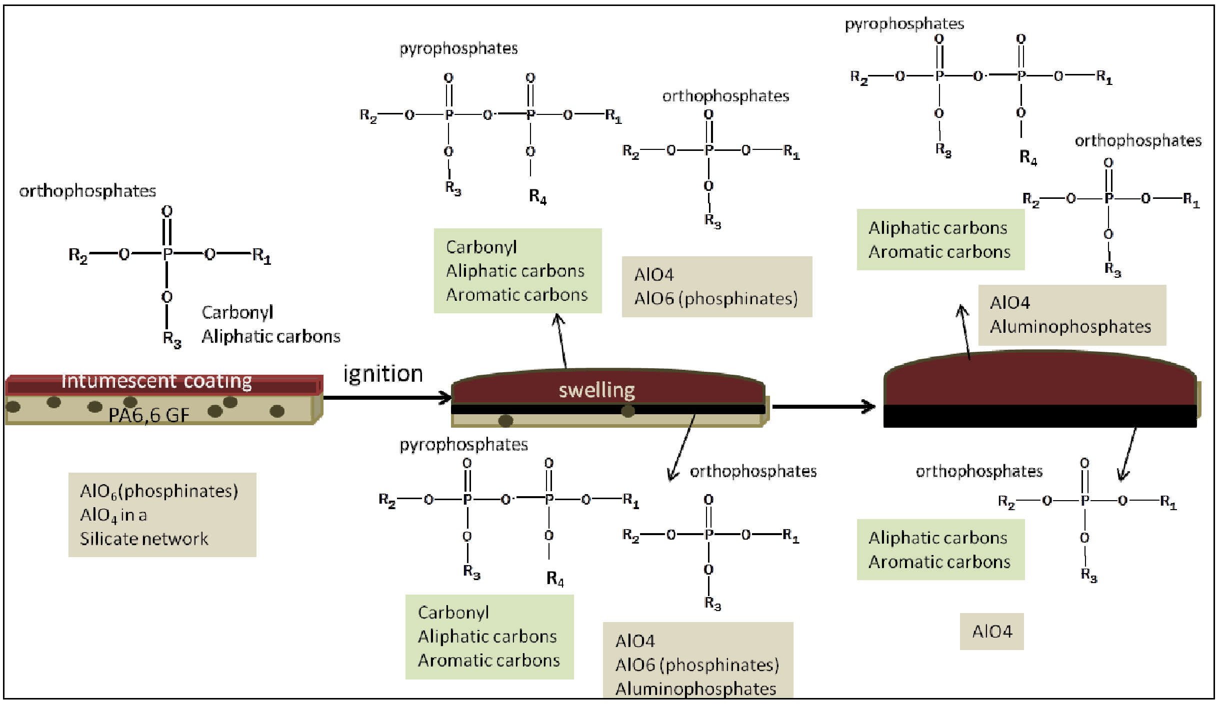


Figure 42. Mechanism of action of the intumescent coating on the PA6,6-GF containing 5% AlPi.

The interest to combine this kind of bulk treatment and the intumescent coating would then be double: the gases released by the AlPi are trapped in the intumescent coating and this could favor the swelling but also lead to a stabilization of the intumescent coating since aluminophosphates are formed and thus the protective barrier is more stable.

To summarize, the first objective was to describe the mechanism of action of an intumescent coating on PA6,6-GF. It is interesting to notice that, as in Chapter1, it was again proven in this part that solid state NMR is a powerful tool to establish mechanisms of action of fire retardant agents both in bulk and surface treated materials. It was in fact evidenced characterizing the material by ^{13}***C,*** ^{31}***P and*** ^{27}***Al solid state NMRs at different combustion times of MLC test that during burning one part of the virgin polymer begins to degrade; this viscous degraded polymer is then mixed with the semi-viscous charring intumescent layer. In some way, during burning, the polymer is fire retarded in bulk thanks to the intumescent coating applied on it. The second objective was to investigate the potential synergy between the gas phase fire-retardant mechanism of AlPi and the condensed phase fire protective mechanism of the intumescent coating to explain the enhanced fire-retardant properties (e.g. GWFI validated at 960°C). Using the same NMR techniques, the interest to combine the bulk treatment in low amount and the intumescent coating was evidenced to be twice: the AlPi cannot completely sublimate because of the protective coating and is probably condensed inside the intumescent structure pores. As it is trapped in the condensed phase, it then degrades into aluminophosphates, increasing the thermal stability and thus the heat barrier efficiency of the expanded char layer.***

In the previous sections, the efficiency of intumescent coatings to protect various polymer plates (PP, PC, PA6,6) has been demonstrated, with some limitations for particular applications, which have been successfully overcome by the development of a concept combining bulk and surface treatments. The efficiency of both methodologies (simple coating or bulk/coating combination) being validated for three completely different polymers, we might assume that they should work for any kind of polymer. We thus recently decided to extend this concept development to other kinds of polymeric materials, i.e. composites.

II-6 In-development perspectives: application to composites

The use of composites in civil engineering structural components is increasing day by day due to their light weight, high specific strength, and stiffness properties [92]. A sandwich-structured composite is a special class of composite materials that is fabricated by attaching two thin but stiff skins to a lightweight but thick core (**Figure 43**).

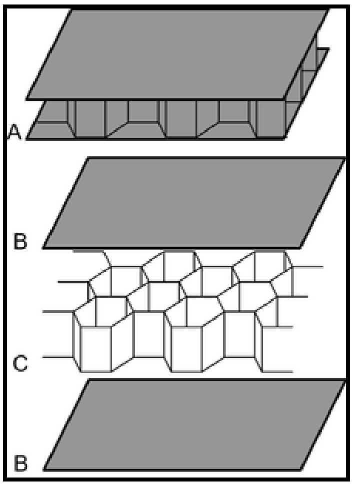


Figure 43. Diagram of an assembled composite sandwich (A), and its constituent face sheets or skins (B) and foam core (C).

Laminates of glass or carbon fiber-reinforced thermoplastics or mainly thermoset polymers (unsaturated polyesters, epoxies...) are widely used as skin materials. Sheet metal is also used as skin material in some cases. The core material is normally a low strength material, but its higher thickness provides the sandwich composite with high bending stiffness with overall low density. Open- and closed-cell-structured foams like polyvinylchloride, polyurethane, polyethylene or polystyrene foams, balsa wood, syntactic foams, and honeycombs are core materials commonly used. Open- and closed-cell metal foams can also be used as core materials.
The core is bonded to the skins with an adhesive or with metal components by brazing together.

In the following example, we consider a foam-core material, and particularly polyethylene terephthalate (PET) core-composite lightweight foams used for making the ceiling of railway stations which will be built in Saudi Arabia (railway stations for high speed train). Building codes and regulations require materials exhibiting low flame spread and low smoke generation.

Following our approach on the application of intumescent coatings on polymeric substrates, commercial intumescent paints were selected to provide fire resistance to those PET composite foam-cores.

The composite to be tested is a PET foam block (ARMAform, Armacell Benelux SA) covered with glass woven fabrics (Gurit) impregnated by an epoxy resin (Ampreg 21FR, Gurit).

Different commercial intumescent coatings were selected, including epoxy-based [Chartek8 of International Paint (C8) and Firetex M93 of Leigh’s paint], polyester-based [Polycor 2330 BR, Cray

Valley] and latex-based [Avicoat FS/DS of Arabian vermiculite, Intuflam of Lurie and Pyroplast ST200 of Rutgers Organics] resins. A mass of 1kg of wet paint per square meter was applied (**Figure 44**).

Figure 44. PET foams coated with the intumescent coating Avicoat

II-6.1 Fire testing

The associated fire test (**Figure 45**) is the Steiner Tunnel (ASTM E-84) [93]. It is referenced as a method to assess flame spread and smoke density and is a mandated test for our materials. It is the primary test method for evaluating resistance to fire of interior finish materials.

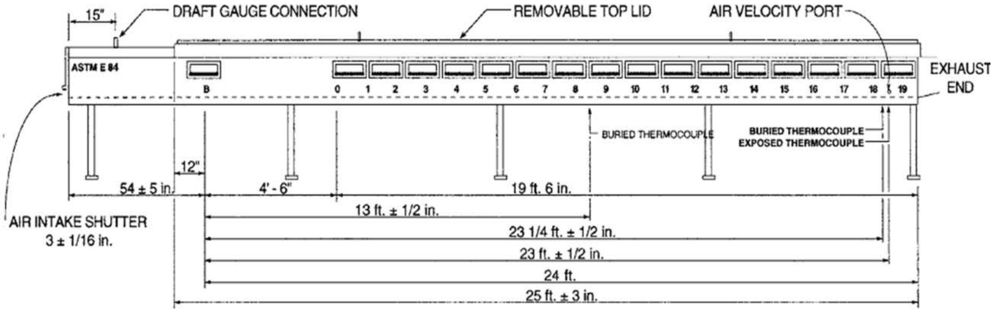


Figure 45. Schematic view of the Steiner tunnel according to ASTM E84

The apparatus consists in a tunnel-like enclosure measuring 8.7 × 0.45 × 0.31 m^3. The test specimen is 7.6 m long and 0.46 m wide and is mounted in the ceiling position. It is exposed at one end, designated as the burner end, to a 88-kW (5000-Btu/min) gas burner. There is a forced draft through the tunnel from the burner end with an average initial air velocity of 1.2 m/s. The measurements consist of flame spread over the surface and smoke obscuration in the exhaust duct of the tunnel. The test duration is 10 minutes, flame spread is determined visually through windows built into the tunnel and an optical cell mounted at the tunnel exhaust measures smoke density. A flame spread index (FSI) is calculated on the basis of the area under the curve of flame tip location versus time. The FSI is 0 for an inert board, and is normalized to approximately 100 for red oak flooring. A smoke developed index (SDI) is calculated on the basis of the area under the light obscuration versus time curve, and is equal to 100 for red oak flooring.

Since the Steiner tunnel test requires approximately 4 m² of material, it is often not practical to use an experimental approach to develop products that have to meet specific test performance requirements. The test is not suitable for quality control and/or for the screening or development of new materials for the same reason. Moreover, this test is time consuming and of high cost. To address this problem, a number of correlations and models have been developed to predict Steiner tunnel test performance on the basis of data from a small-scale test such as the cone calorimeter [94].

In the pursuit of our approach to make small scale tests (cf. Chapter 1 of this manuscript) to support the topic “simulation, degradation and modeling” in the group, we have developed a mini Steiner tunnel for evaluating intumescent formulations.

II-6.2 Mini Steiner Tunnel development

To make fast evaluation of the PET foam core composites protected by the different intumescent paints, we have developed a ‘mini’ Steiner tunnel (reduction of the Steiner tunnel at 1/8 scale) which is fully described in **Figure 46**. Temperatures as a function of time are measured during the test using 6 thermocouples (hereafter called Th.x with 1≤ x ≤6); small windows permit to follow flame spread and smoke is collected in the chimney to measure its opacity with a smoke density analyzer including a halogen light (**Figure 47**).

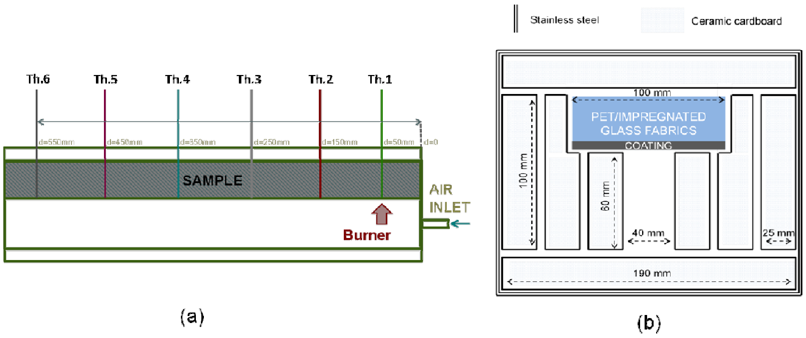


Figure 46. (a) Schematic view of the lab-scale Steiner tunnel and (b) its internal construction (side view)

Figure 47. Light beam / Exhaust end adapter on the top of the mini Steiner tunnel chimney

II-6.3 Intumescent coated PET foam cores fire testing

Using the lab-scale Steiner tunnel previously described, the potential benefit of using commercial intumescent coatings for improving the resistance to fire of PET foam-based composite was investigated. The screening of these various intumescent coatings are presented in the following section.

II-6.3.a Screening of intumescent coatings using the "mini" Steiner tunnel

The temperature versus time curves (only curves of thermocouples 4 are presented on **Figure 48**) are very promising and allow us to discriminate the different coatings.

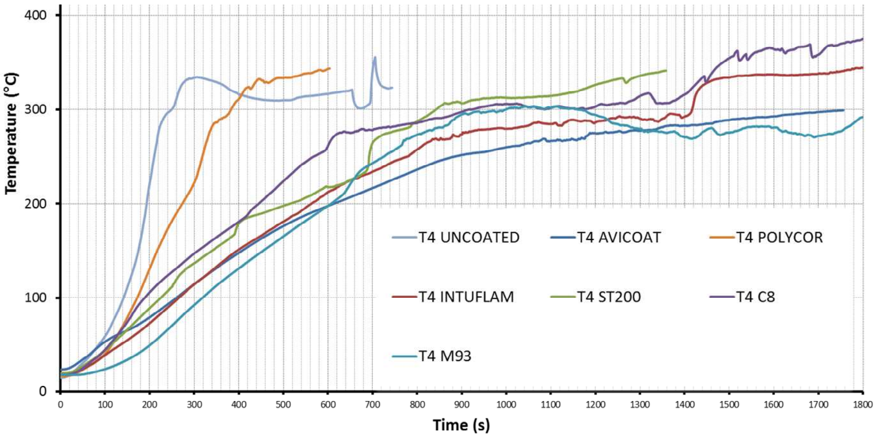


Figure 48. Temperature (thermocouple 4) as a function of time in the mini Steiner tunnel

Avicoat and Intuflam give the best barrier properties. Avicoat can be presented as the most efficient coating since it gives the best results on Th.1, Th.4 and Th.5 and it is the second best on Th.2 and Th.6.

Visual observation of the residues indicates that not all the coatings have developed an intumescent structure. Avicoat and Intuflam do not swell but they provide the best performance forming a non-expanded char at the surface. In our conditions, thermal constraint is not high enough to make the material to expand. At the end of the test, it is observed that the PET foam is well protected by Avicoat (large part of PET foam remains intact) (**Figure 49**) which indicates that the efficiency of this coating is quite high.

Figure 49. Residue of PET foam protected by Avicoat in the mini Steiner tunnel

Regarding the good results obtained with Avicoat in terms of fire barrier properties, a specimen coated with this reference was then tested under large scale ASTM E84 conditions in the evaluation center of Intertek in Elmendorf-USA. The Avicoat coating was about 700 µm thick and it exhibited good adhesion to the composite when evaluated by the ASTM D3359B test. In the following section, the results obtained during this large scale test are presented and possible correlations between these results and those obtained by our small scale test are then investigated.

II-6.3.b Correlations with large scale Steiner Tunnel test

The description of the specimen after testing indicates that a charred aspect is observed on 85% of the total length (**Figure 50-a**). Then, a discoloration occurs. The picture of a section of the specimen however clearly shows that no intumescent phenomenon occured during the test. The observation of the sample tested on the small scale tunnel also shows a charred aspect without intumescent phenomena; the coating is just distorted and cracked (**Figure 50-b**).

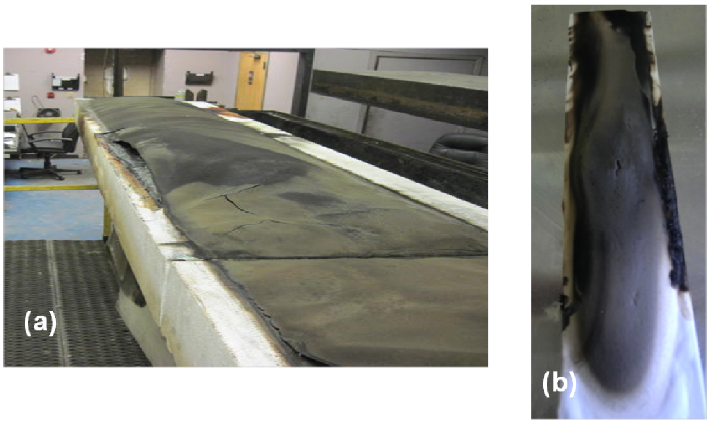


Figure 50. (a) Avicoat coating protecting PET foam after the large scale Steiner tunnel and (b) after the lab-scale Steiner tunnel test

These results suggest that, on the one hand, the standard conditions are reproduced: the results of the small scale test can be extrapolated for the evaluation of the thermal barrier effect (temperature versus time curves). On the other hand, the thermal constraints seem to influence the behavior of the coating as follows: the convective constraint (flame) and the conditions of the tunnel test lead to no intumescence, only to the formation of a crust. It is noteworthy that Avicoat paint exhibits an intumescent behavior (large expanded and foamed char) when undergoing an external heat flux during a cone calorimetry experiment (external heat flux of 50 kW/m²).

II-6.4 Prediction of Steiner Tunnel test performance

According to ASTM E84, there are three classifications for the fire resistant materials: Class A for products with FSI ≤ 25, Class B for products with 25 < FSI ≤ 75, and Class C for products with 75 < FSI ≤ 200. For all classes the SDI cannot exceed 450. Class A products are generally permitted in enclosed vertical exits. Class B products can be used in exit access corridors, and Class C products are allowed in other rooms and areas.

At the small scale, PET foams coated with Avicoat are classified A since FSI and SDI are 8 and 150 respectively. On the contrary, the same product is not classified at the large scale since FSI and SDI are 15 and 550 respectively but it is noteworthy that flame spread is extremely low. Nevertheless, the shapes (sigmoid shape) of the SDI and FSI curves look similar indicating the small scale test can capture the fire behavior of the intumescent PET foams developed at the large scale (**Figure 51** and **Figure 52**).

In the case of FSI, flame spread starts almost at the same time (160s vs. 180s) but it remains slower at the small scale (maximum is reached at 350s at the large scale compared to 600s at the small scale) (**Figure 51 (a) and (b)**).

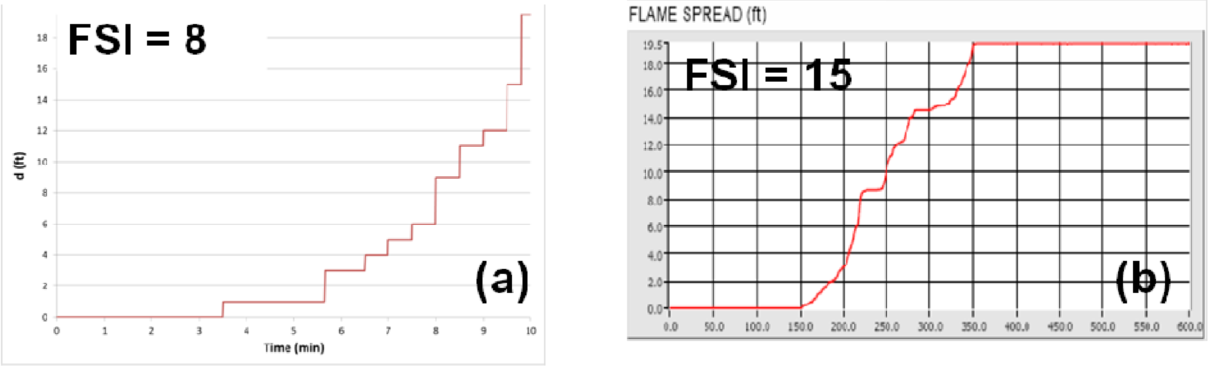


Figure 51. Flame spread as a function of time measured at the small (a) and large scales (b).

In the case of SDI, the main step of smoke obscuration increase starts at shorter times at the large scale (200s) compared to the small scale (320s). The smoke opacity maximum is also higher at the large scale (90%) compared to the small scale (50%) (**Figure 52 (a) and (b)**).

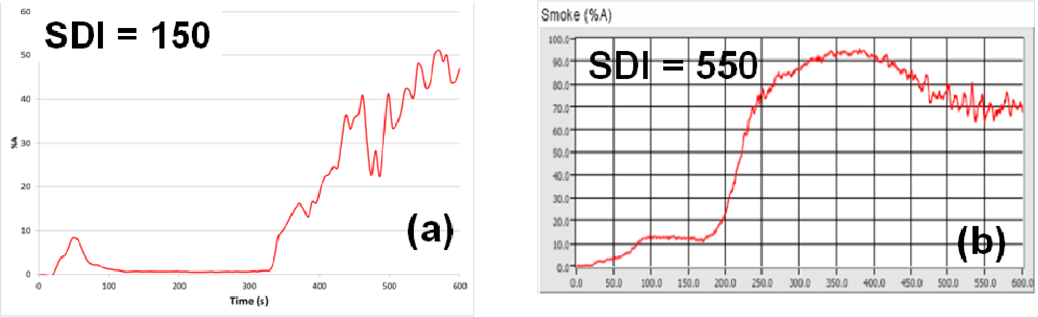


Figure 52. Smoke opacity as a function of time measured at the small (a) and large scale (b).

The comparison of the results measured at the small and large scales is encouraging because the mini Steiner tunnel can capture the fire behavior of an intumescent material at the large scale (similar residues and similar SDI and FSI curves).

At this time, the experimental device developed can however not predict accurately the classification of the evaluated materials but the screening at the small scale permits to select the best materials. It needs further improvement to make accurate prediction. The power of the burner must be increased as well as air velocity in the tunnel to get similar fire spread and so, acceptable FSI could be expected. The SDI is too low because of the extraction which should be adjusted and/or the design of our chimney should be redrawn to permit more accumulation of smoke. We intend to pursue these recommendations in the near future.

We thus demonstrated in this section that intumescence is an efficient method for fire protection of structural foam core composites. Small scale test developed (Steiner tunnel) shows acceptable correlation with the large scale test even if further improvements have to be done. When appropriately designed, this approach will be very useful to make the 'high throughput' development of intumescent coatings protecting composites. Moreover, we recently started to collaborate with an industrial partner on the improvement of fire retardancy of carbon fiber-epoxies composite skins by applying an intumescent coating onto them. During this project, various intumescent coatings will be applied on the composite skin structure, and the obtained materials will be tested to fire using a specific fire test that will also be developed in the frame of this project.

As it was demonstrated in this second chapter, the application of commercial intumescent coatings on polymer plates and composites is efficient to protect them, although sometimes a combination between bulk treatment and coating is needed to meet severe criteria.

However, the tendency is now to decrease the materials thicknesses, and thin polymer films (0.8 mm, 0.4 mm) and textiles have to be flame retarded for various applications. Intumescent coatings are efficient, but the thickness applied can be too high compared to the film thickness. Surface modifications by thin films coatings (physical [95] or chemical [96] treatments) seem to be an attractive method to address this issue, as it would allow concentrating in thin coated layers the fire retardant properties onto the polymer surface and would thus allow preserving the bulk properties of the thin material. Many methods currently exist to deposit thin coatings layers on various substrates (metals, textiles, polymers) based on different concepts (e.g. sol-gel coatings, plasma coatings, layer by layer deposition, "grafting from" and "grafting to" polymerizations, etc.) which could be used to provide fire retardant properties to materials, and particularly to thin polymer films and textiles. The following Chapter 3 will present the results we obtained using Layer-by-Layer deposition and cold plasma technologies to fire retard polymers and textiles.

Chapter 3- Fire retardancy and protection of polymer films and textiles by thin coatings

The topic developed in this chapter was carried out in the frame of internal work and through various collaborations (PhD A. Vannier, 2007 - Flexifunbar Project, Textherm Project (2009-2011), PhD H.Gallou, 2010 - CIFRE Rhodia and PhD K. Apaydin (2011-2014), FRCoatings Project and led to three papers [12, 14, 24] and one patent [13].

Polymer based substrates can be divided in two categories: bulk polymer and textiles. We showed in the last section that it is possible to protect polymer plates by intumescent coatings. However these coatings are usually classified as “thick” materials and this can be an issue for certain applications, and particularly on thin polymer films (e.g 0.4 mm thickness). Fire retardancy of bulk polymers by thin film coating deposition is a very recent approach that is currently being developed in research institutes. Only few techniques exist to manage to deposit very thin films on polymer surfaces: some very recent research papers detail the use of Layer-by-Layer (LbL) deposition, which consists in alternating deposition of polyanions and polycations on a solid substrate leading to the formation of polyelectrolyte multilayer films [24, 97, 98]. Some papers from 1999-2001 also detail the use of a low pressure cold plasma to deposit some organosilicon thin layers onto polymer plates [99, 100]. The current intensive development of cold plasma technologies (low pressure and atmospheric plasmas) thus gives the opportunity to develop innovative treatments in this field and some of them will be further presented in this chapter.

Meanwhile, only few solutions exist to achieve persistent fire retardancy of textiles and it is even more problematic when textiles made from fibers of natural origin such as cellulose fibers (cotton for instance) are concerned. Indeed, for this type of fibers, the fire retardant property can only be conferred by means of a surface treatment of the material. Among all textile fibers, cotton is the most commonly used in domestic applications (clothes, beddings, furniture, wall-hangings, etc.). However, it is also one of the most flammable materials (LOI 18.4%). The current commercial solutions existing (e.g. Proban®, Pyrovatex®) also present several disadvantages, such as the need of specialist ammonia cure units for Proban® and formaldehyde release for Pyrovatex® [101]. It is thus of primary importance for public safety to find ways to render this material less flammable and of course, in a most economically and environmentally friendly manner. Recently, LbL deposition and cold plasma treatments were also sucessfully applied on cotton textiles as well as on thermoplastic fabrics with promising results in terms of fire retardancy and the use of these technologies will be reviewed in the following sections.

In this chapter, the effect of various surface treatments such as Layer-by-Layer deposition and cold plasma treatments on the fire protection of polymer films and/or textiles will thus be presented. Low pressure wet and dry plasma treatments (Plasma Induced graft Polymerization and Remote Low pressure Plasma Enhanced Chemical Vapor Deposition) will be described, and preliminary results using a continuous in-development atmospheric plasma treatment (Vapor Polymerization Deposition assisted by a Dielectric Barrier Discharge) will be presented.

III-1 Fire retardancy of polymeric films and textiles protected by Layer-by-Layer thin coatings

The LbL technique was discovered in 1966 by Iler [102] and developed by Decher et al. [103] in the 90's. Nowadays, this popular technique is widely used in various fields such as drug delivery [104, 105], anti-reflection [106, 107], electrochromic [108-110], oxygen barrier [98, 111-117] and it is only in recent years that this technique has been considered to design flame retardant coatings [98, 118-126]. Li et al. [118] have been the first to study the flammability of coatings made from branched polyethylenimine (BPEI) and Laponite clay designed by LbL deposition on cotton fabrics. It was shown by vertical flame testing (VFT) that the clay coating delays the degradation of the cotton by providing a sheath-like ceramic barrier. Also using the LbL method, Carosio et al. investigated two systems to enhance fire stability of PET substrates [122, 123]. For example, one of these systems based on colloidal silica nanoparticles leads to an increase of TTI of 45 %, a decrease of the PHRR of 20% and is able to prevent incandescent melt dripping of PET fabric. More recently, several groups of researchers developed, using LbL, an intumescent flame retardant system [98, 125-129] which is generally made of the four ingredients described in the Chapter 1: a carbon source, an acid source, a swelling agent and inorganic fillers to reinforce the char layer [33]. The first work dealing with an intumescent flame retardant coating built up by LbL was realized by Li et al. [125]. They demonstrated the effect of (poly(allylamine)(PAAm) - polyphosphate (PSP)) nanocoatings on the fire retardant properties of cotton. They showed that these coatings reduce the PHRR, THR, after-flame time, afterglow and increase the char formation as a function of the number of bilayers deposited. Laachachi et al. [98] elaborated an intumescent system including poly(allylamine chloride) (PAH), montmorillonite and PSP on Polylactic acid (PLA) thin films. The (PAH-clay) with and without PSP films were elaborated using classical LbL method with an additional step consisting in diffusing PSP into the multilayer films prepared. The cone calorimeter results displayed an improvement of fire properties of the PLA substrate coated with $(PAH\text{-}MMT)_n$ assembly. Recent studies were meanwhile carried out by Carosio et al. [126], Alongi et al [127, 128] and Laufer et al [129] using e.g.

combinations between ammonium polyphosphate (APP) and chitosan or silica to improve the reaction to fire of cotton or polyester-cotton blends [126].

Looking at these research works, it can be observed that most of them were carried out on natural textiles, some were tested on synthetic textiles and only a few were tested on polymer thin films, such as PLA [98] or PC [97]. The aim of the work currently carried out in collaboration with CRP Tudor Luxembourg (PhD student K.Apaydin) is thus to fire retard various polymeric substrates, such as polyamide-6 (PA6) thin films (0.5 mm thick), by the LbL methodology.

In this example, PA6 was coated with a flame retardant film, made from polyallylamine (PAH) (polycation) and montmorillonite (MMT) (polyanion), elaborated by Layer-by-Layer (LbL) technique (**Figure 53**) [24].

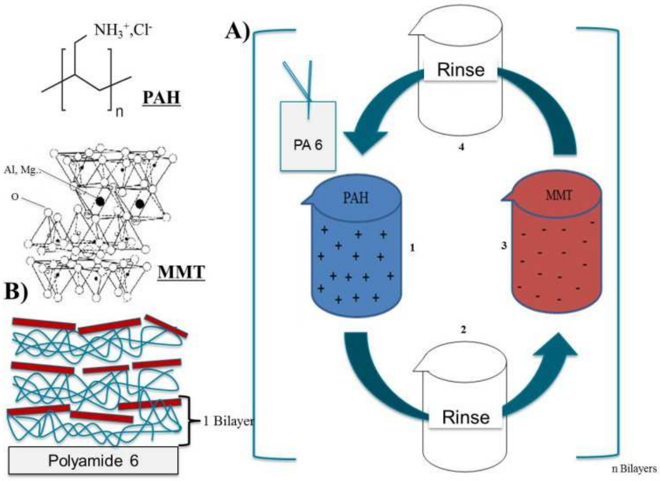
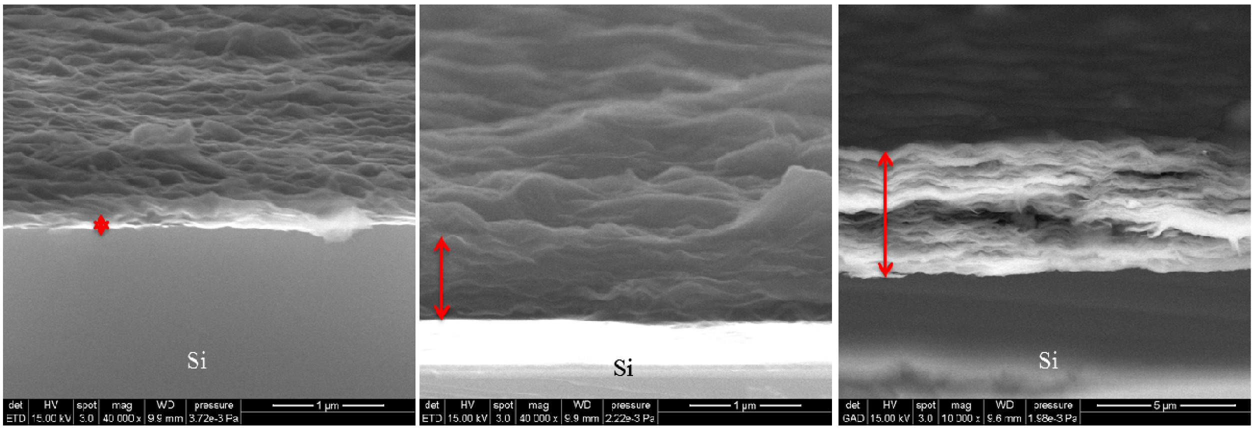


Figure 53: A) Schematic representation of layer-by-layer deposition. Steps 1-4 were repeated until the desired number of bilayers and B) a cross-sectional representation of the obtained assemblies.

The (PAH-MMT)$_n$ assembly (with n the number of bilayers deposited) exhibits an exponential growth regime. At n = 20 bilayers deposition of PAH and MMT, the film reaches a considerable thickness of ~ 5 µm with the alignment of MMT in the direction parallel to the substrate.

Scanning Electron Microscopy (SEM) analyses of the cross-section (**Figure 54**) and Atomic Force Microscopy (AFM) analyses display a regular and continuous morphology of the obtained films.



n =5 BL **n =10 BL** **n =20 BL**

Figure 54 : SEM (SE) cross section of 5, 10 and 20 BL coated samples

Thermogravimetric analyses (not presented here, see [24]) show that the presence of $(PAH\text{-}MMT)_n$ films at 10 and 20 bilayers enhances the thermal stability of the polyamide substrate. Cone calorimetry evidences excellent reaction to fire of the material since PHRR is decreased by more than 60% in the presence of 20 bilayers of PAH-MMT film in comparison with uncoated PA6 (**Figure 55a)**.

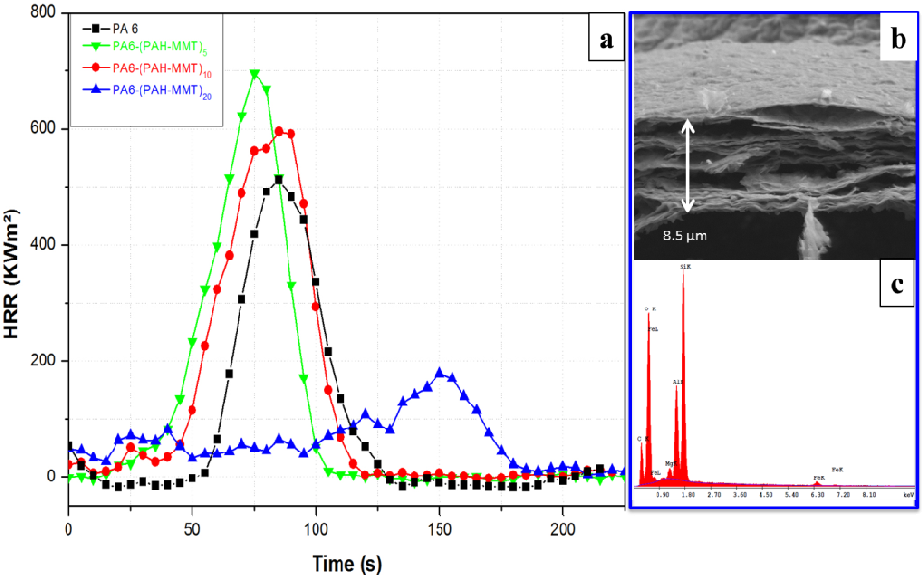


Figure 55: Heat release rate curves as a function of time for coated and uncoated PA6 samples (a), cross section image (b) and EDS (c) of 20 BL film residue after burn testing.

The pictures of the residues after cone calorimeter test are presented in **Figure 56**.

Figure 56: Images of the residues of virgin polyamide 6 (A), and PA6 + 5BL (B), 10BL (C) and 20BL (D) coatings after burn testing.

No residue is observed for the uncoated polyamide 6. However, at 5 BL the presence of a residue is present in small amount, contrary to the 10 and 20 BL films where an organic carbonaceous layer is formed at the surface of the substrate. Nevertheless cracks (circled in red in **Figure 56**) are detected for the 10 BL coating, which might explain the poor results obtained with the cone calorimeter. These cracks could be at the origin of the increased standard deviation of PHRR. Furthermore, only the 20 bilayers films form a continuous char layer without defects and the thickness of the coating at the end of the combustion test is twice higher than that of the initial thickness (**Figure 55b**). The clay platelets are aligned parallel to the substrate, which probably provide good mechanical and barrier properties to the coating. Moreover the elements revealed by EDS analysis show that this protective layer is mainly constituted of inorganic expanded MMT (**Figure 55c**). Indeed, under the external heat radiation the PAH trapped in the clay releases ammonia which leads to the swelling of the char layer formed. The foam tends to isolate heat and oxygen from the fuel source and thus favors fire extinguishment. According to these results, it appears that the samples which exhibit the best fire performances is the $(\text{PAH-MMT})_{20}$ coatings.

This work thus proves that it is possible, using an appropriate system (e.g. PAH-MMT in this case) with the adequate number of bilayers (20 BL), to successfully fire retard a thin polymeric film (PA6) with a very thin coating layer (5µm) by LbL deposition. A mechanistic study of the fire retardant action of this system is currently carried out to fully understand why this system is so efficient.

Other systems are also currently being investigated on polymer films and textiles, such as for example PAH-PSP systems, which have been successfully applied on polymer thin films and on thermoplastic textiles.

As mentioned earlier, other treatments also exist to deposit thin coatings onto bulk polymer and textile substrates. Among all the different kinds of surface treatments (wet or dry), the cold plasma technique is one of the processes allowing to graft covalently small functional groups as well as macromolecular compounds, using various technologies. In the next section, some of these processes, wet (PIGP process) or dry ones (R-LP-PECVD and VPD-AP-DBD) will be presented to fire retard polymer films and textiles.

III-2 Fire retardancy and protection of polymeric substrates by thin plasma-polymer coatings

III-2.1 Plasma Induced Graft Polymerization

Plasma technologies offer a way of achieving the means of developing novel nanocoatings having the desired thermal shielding effects. Shi for example has demonstrated that low pressure, radiofrequency discharge plasma treatment of a number of surfaces including poly(ethylene terephthalate) in the presence of gaseous (CF_4/CH_4) leads to flame retardation [130]. Later studies in which ethylene-vinyl acetate copolymers were plasma-exposed for times up to 15 minutes followed by immersion into acrylamide gave very high yields of surface grafted poly(acrylamide) and LOI values approaching 24vol% at 47vol% grafting levels [131, 132]. We developed in 2006 during A.Vannier PhD (FP6-Flexifunbar project) - at the same time than Tsafack et al. team [133, 134] - a process allowing to reduce the flammability of cotton and cotton/polyester textiles. The protocol consisted in the simultaneous grafting and polymerization of acrylate monomers bearing phosphate groups on the surface of the textile by a low pressure cold plasma treatment.

The polymerization of the monomers was induced by means of an inert gas (argon plasma). Plasma induced radicals on polymer surface permit reactions for surface modification such as graft and/or block copolymerization [133, 135]. This is called the *plasma grafting*. In that case, the plasma is employed only to activate the surface of the material. The grafting step of a polymer for instance is performed afterwards in a separate step in a solution containing the monomer either by heating or by using UV or γ radiations. Activation of the surface and simultaneous grafting and polymerization of a non-volatile monomer can also be performed in a single work-step in the plasma chamber: this is called the *plasma-induced graft-polymerization (PIGP)*. This method is of considerable practical interest. A scheme of an experimental procedure for an inert-gas plasma-induced graft-polymerization of monomers on a textile is presented in **Figure 57**.

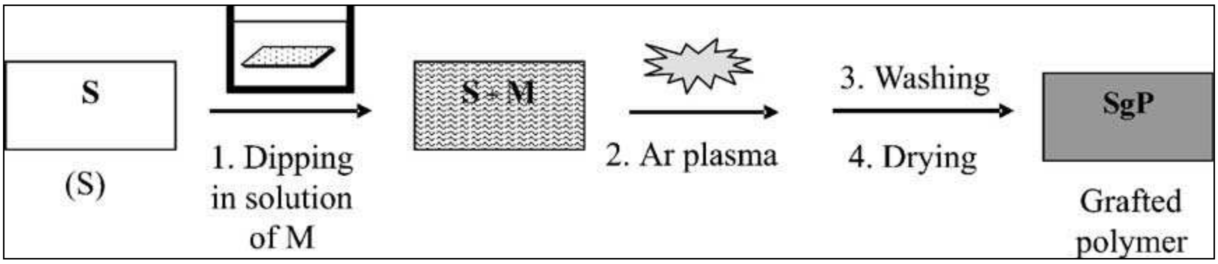


Figure 57 : Example of experimental procedure for an inert-gas plasma induced graft-polymerization of monomers [133]

In step (1), the fabric samples (S) are immersed at room temperature in a solution containing the monomer (M), a photo-initiator and eventually a cross-linking agent. After the removal of the excess of the solution, the substrate is submitted in step (2) to an inert gas plasma for a certain time. Finally, the sample is washed in step (3) and dried in step (4). By using this procedure, the aim is to induce in one step simultaneously the grafting and the polymerization of various monomers using an inert gas plasma. The desired properties are achieved by creating covalent bonds between the substrate and the growing polymer at the surface. This plasma-induced graft-polymerization (PIGP) procedure is a “grafting from” polymerization pathway, meaning that active sites (ionic and radical ones) are created at the polymer surface and used to start the polymerization of a functional monomer. An unsaturated monomer containing e.g vinyl, allyl or acryloil functions can be fixed through this method using plasma or radiations. It is however difficult, using this technique, to control the architecture in an efficient manner, i.e. the number and size of grafted chains.

We aimed at grafting a supposedly fire retardant polymer on the surface of a textile in order to get fire retardant properties. The polymer chosen was the polyethylene methacrylate phosphate, containing phosphorous and a vinyl function, allowing its fixation on the textile by graft copolymerization. The principle of the experiment was to coat the surface of the textile by the monomer (ethylene glycol methacrylate phosphate) (**Figure 58**) and then to induce the polymerization by plasma (PIGP).

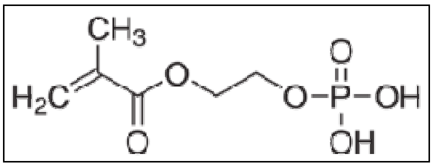


Figure 58 : Ethylene glycol methacrylate phosphate monomer

Previous treatments were applied to the textiles, such as de-oiling or desizing (according to its starch content) and activation/cleaning by argon plasma pre-treatment. The coated textiles were then tested using LOI in order to check the fire retarding properties of the grafted polymer. The various experiments carried out are represented in **Figure 59**.

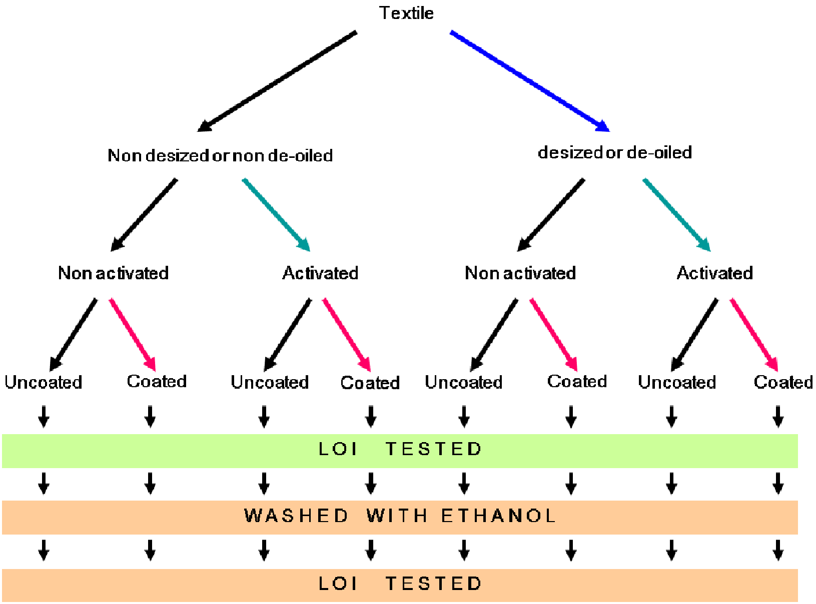


Figure 59 : Diagram of the different experiments carried out

Three different textiles were tested: (i) pure cotton; (ii) 44% Polyester (PES)-56% cotton; (iii) 65% PES - 35% cotton; and the LOI results were compared before any further washing (**Figure 60**). Grey data correspond to uncoated samples and black data correspond to the coated samples.

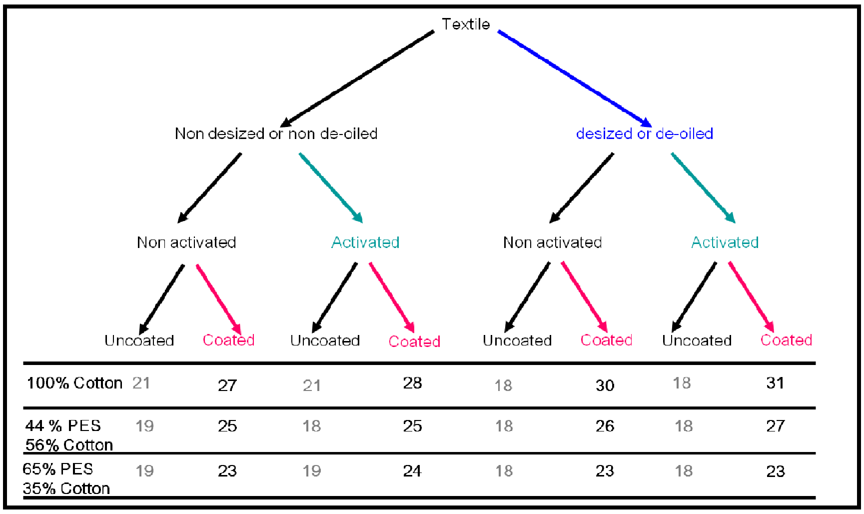


Figure 60 : LOI results of the treated textiles before any washing

There is practically no difference between a sample activated and a non-activated one. The activation might be important in term of grafting but does not, by itself, affect the fire behavior of the materials.

As soon as the textile is coated with the phosphorus based polymer, the LOI values increase from 23 up to 31. We note that the more cotton in the textiles, the higher the LOI values. This phenomenon could be attributed to the carbonization process of the cotton when burning, which is not the case of PES.

Finally, the textiles were washed with ethanol and tested again by LOI to check the grafting durability. In the **Figure 61** , the grey values correspond to the non coated samples, the black ones to the grafted and not washed samples and the blue ones to the grafted and washed samples.

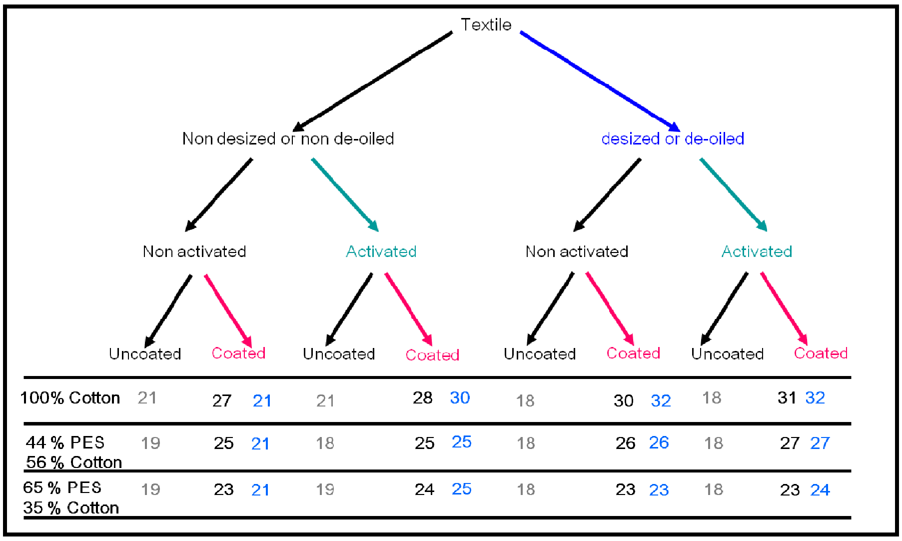


Figure 61 : LOI results of the treated textiles after ethanol washing (30 min.)

It appears that, whatever the textile, when it has not been pre-treated with de-oiling/desizing or plasma activation, the LOI decreases, meaning that the grafting is not durable and that the polymer is partially or totally removed from the textile. It also shows that the argon plasma pre-treatment is as efficient as desizing/de-oiling to clean the textile, without using enzymes or solvents.

In the case of desized/de-oiled or activated textiles, or both, the grafting is efficient, the polymer remains on the surface of the textile and the LOI values remain quite stable. In the case of the cotton however, the LOI value increases. This is possibly due to the elimination of some remaining monomer.

A complementary study was carried out by varying the monomer concentration in the impregnation bath. The results obtained (examples in **Table 9**) show that the higher the monomer concentration, the better the LOI value.

Table 9 : LOI results depending on the monomer concentration (values obtained for 44%PES-56% cotton textile)

Concentration g.L^{-1}	**0**	**10**	**50**	**150**	**300**
LOI (%O_2)	**19**	**19**	**20**	**23**	**25**

In order to obtain interesting fire performance a minimum monomer concentration of 150g.L^{-1} is required. Best results are obtained with 300g.L^{-1}. However it is important to note that the aspect of the textile changes when the polymer is grafted on it. The stiffness of the textile is sharply affected by the surface treatment. The more polymer is coated on the textile, the less flexible the textile.

This work demonstrated that fire retardants can be efficiently grafted by PIGP process on the surface of a textile and provide enhanced fire retardant properties, even after washing. The desizing/de-oiling step can be also advantageously replaced by a cleaning/activation process of the surface using the plasma technology. The use of the PGIP process is thus promising and I am currently using it to try to fire retard open-cell foams as it is quite an issue to fire retard these materials by bulk treatments.

Other cold plasma technologies however exist, avoiding the multi-step approach of the PIGP process and also preventing from using solvents or bathes. In these "dry" technologies, the plasma can be put in contact with volatile organic, organosilicon or organometallic compounds which lead to the deposition of a thin polymer film on the surface of a material. One of these techniques, called LP-

*PECVD (Low-pressure Plasma Enhanced Chemical Vapour Deposition) (**Figure 62)** allows deposition at low temperatures, which is often a critical parameter.*

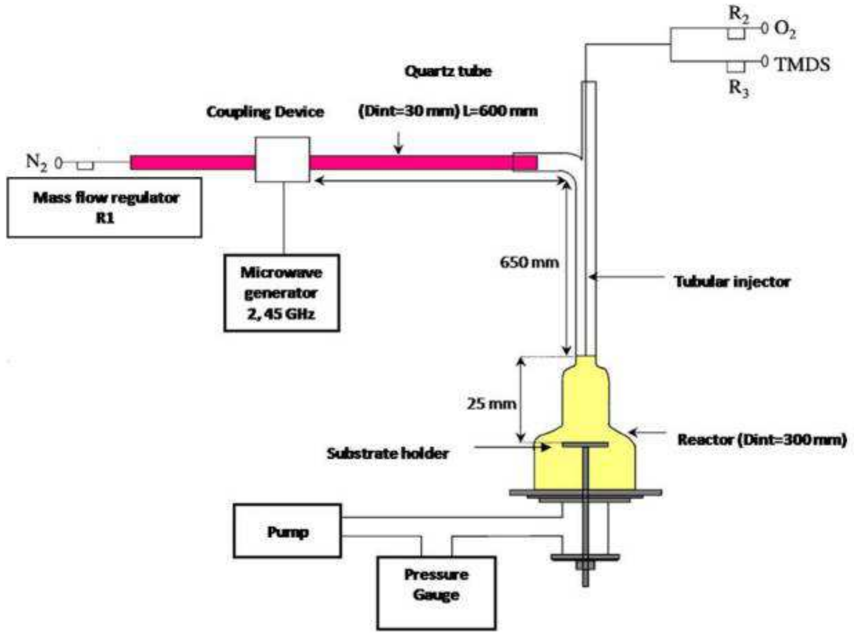


Figure 62 : Experimental scheme of the lab Remote LP-PECVD process

LP-PECVD is mainly used for the deposition of dielectric films and passivation films like silicon oxide or nitride layers at low temperature. It can be also used for SiC layers of poly-Silicon deposition. Remote LP-PECVD is also used, which is similar to LP-PECVD except that the substrate is not directly in the plasma discharge region, which allows processing temperatures near to room temperature.

The next section presents two possible applications of this technology to fire retard fabrics and polymers.

III-2.2 Remote Low Pressure Plasma Enhanced Chemical Vapor Deposition

III-2.2.a Application on textiles

High performance and high temperature resistant fibers have been developed to answer specific needs in different fields such as aerospace, biomedical, civil engineering, construction, protective apparel, transportation, geotextiles and electronic area. Each of these fibers exhibits a combination of properties which allows it to fill a niche in the upper end of the high performance fiber spectrum. The resistance to heat and flame is one of the main properties of interest for determining the working conditions of the fibers [136]. We aimed at achieving protecting for 700s a metallic substrate from heat and/or fire using specific nonwoven (NW) textiles functionalized by cold plasma treatment

(Textherm project). The bottom of the metallic substrate must not go beyond 235°C in 700s and the NW must not flake off, crack or ignite. Potential applications are the protection of plastic parts from heat source in an engine compartment of automobiles for example.

In the first place the efficiency of some high performance nonwovens (meta-aramide (MA), polyacrylate (PA), phenolic (P) and melamin (M) based NW fabrics) was evaluated in terms of thermal stability and heat resistance by combining thermogravimetric analyses and the "heat radiator test" developed in our laboratory [4]. This small size test, as mentioned in the Chapter 1 of this manuscript, had been developed in order to carry out rapid screenings of the heat barrier efficiency of intumescent formulations protecting steel plates. This test also allowed demonstrating the heat barrier efficiency of Carbtex NW [137] on steel substrates and that is why it was decided in this study to apply the same technique on other high temperature resistant NW. In this study, most of the "heat resistant fibers" were shown not to be very efficient to protect an aluminum plate after 700s of heating under a radiative heat source. As emissivity is one of the main parameters involved in the Stefan Boltzmann law, controlling the radiative heat transfers, the main idea was then to try to change the emissivity of the surface to improve the heat resistance of the fibers under a radiative heat source. The second idea was to modify the NW fabric by forming a thermally stable coating onto their surface. A protective material combining both effects should be very efficient to protect the aluminum plates.

Some previous works of other teams have demonstrated the efficiency of such plasma treatments for fire retardancy purpose. A review written by Morent et al. provides a very interesting overview of non thermal plasma treatments of textiles [138]. Some works showed the efficiency of the deposition of thin film protective coatings on fibers or textiles [139, 140]. Li et al. [141] reported the modification of ultra-high-strength polyethylene (UHSPE) fibers through allylamine plasma deposition; Aragi et al. [142] explained how to deposit a titanium nitride coating on Kevlar while more recently Kilic et al. [143] managed to both increase water repellency and decrease vertical flame spread of polyamide and cotton fabrics using plasma polymerization of HMDSO.

In this study, a cold remote nitrogen plasma process (**Figure 62**) was applied on NW fabrics using a TMDSO (Tetra Methyl Di Siloxane) precursor in order to coat them with an organosilicon thin film. This film was then characterized using ^{29}Si solid state NMR, Scanning Electron Microscopy (SEM) and Electron Probe Microanalysis (EPMA). The heat resistance of the NW fabrics was finally evaluated using the heat radiator test.

Some of the results, published in [14] obtained are presented in the following part.

➢ Coating characterization

Due to the diversity and non-selectivity of the CVD reaction, the ^{29}Si NMR spectrum (**Figure 63**) of the deposit shows a multitude of peaks of different intensities, including the presence of M, D, T and Q groups, detailed in the **Table 10** with the corresponding chemical structures [144].

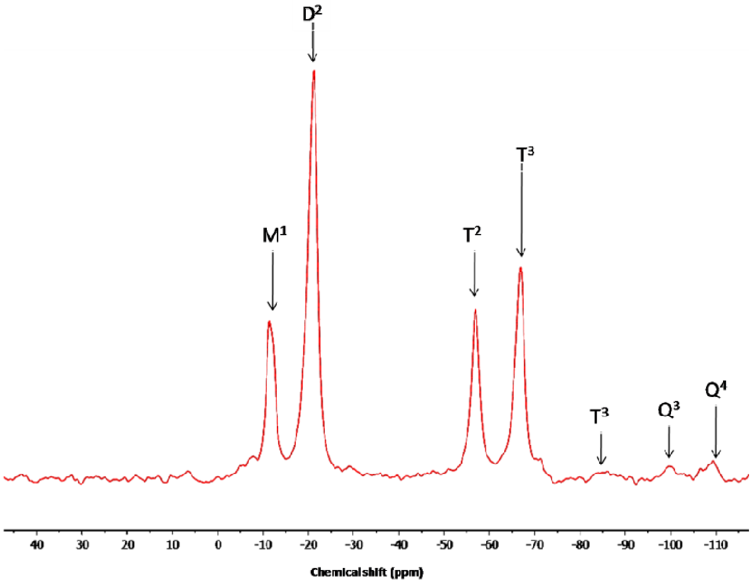
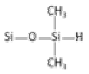
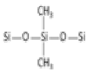
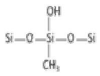
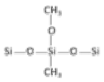
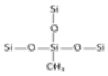
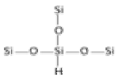
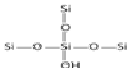
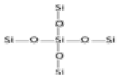


Figure 63 : ^{29} Si NMR spectrum of the organosilicon coating using TMDSO as precursor. *in a Mn structure, M means that only one O is linked to the Si nuclei, with n the number of Si linked to the Oxygen. D is used for two Si-O bonds, T in the case of a ternary structure and Q for a quaternary structure

Table 10 : List of ^{29}Si NMR peaks with their experimental chemical shifts and assigned structures

Chemical shift (ppm)	-11	-21	-58		-66	-84	-100	-109
Assignment	M^1	D^2	T^2		T^3		Q^3	Q^4
Structure								

The TMDSO-based film contains M^1, D^2, T^2, T^3, Q^3 and Q^4 groups. The peak at -11 ppm (M^1) reflects the precursor structure (TMDSO) (**Figure 64**), showing that the polymerization is incomplete.

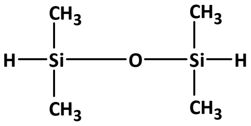


Figure 64 : TMDSO structure

The most oxidized configuration (Q) seems to be in weak proportions compared to M, D and T configurations.

The morphology of the deposit on a fiber was then observed by SEM analyses. On **Figure 65**, PA fibers, non coated (a) and coated (b), are compared.

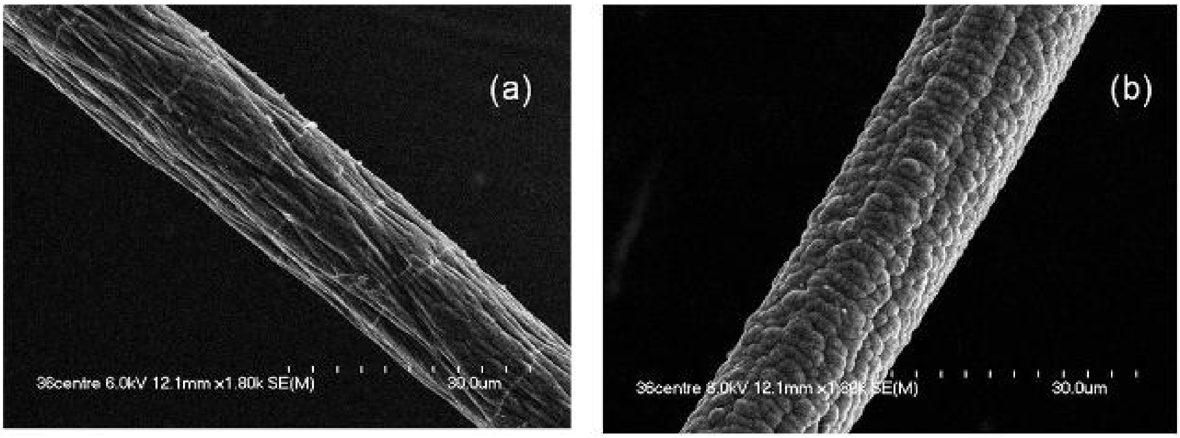


Figure 65 : SEM pictures (SE) of a virgin fiber (a) and a coated fiber (b)

The coating appears homogeneous and shows a typical cauliflower-like structure of a TMDSO plasma polymer, with a coarse roughness [140, 141]. The fiber is entirely coated with the polysiloxane deposit. A cross-section of the coating around PA fibers was also investigated by SEM. The SEM picture is shown on **Figure 66** at different magnifications.

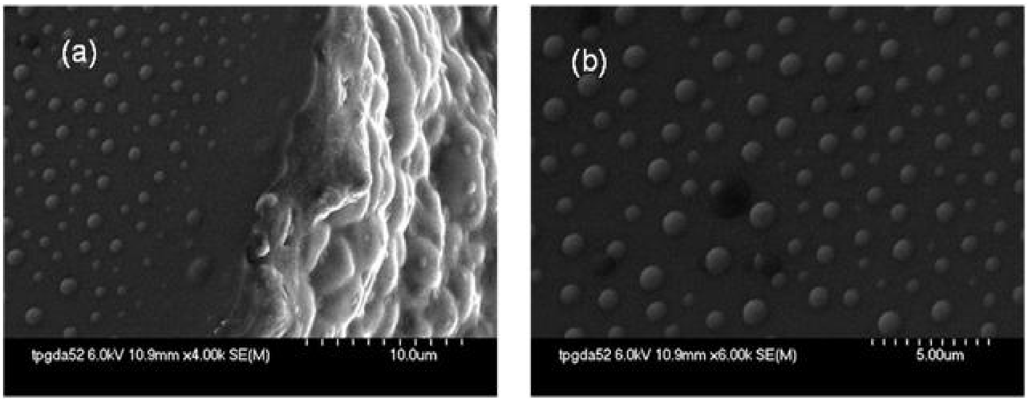


Figure 66 : SEM pictures (SE) of a cross-section of a polysiloxane coated fiber (Magnification 4000 (a) and 6000 (b))

As observed on **Figure 66** the coating is dense and relatively homogeneous, but it contains some “particles” dispersed inside. It can be assumed, that these “particles” consist in non-polymerized TMDSO which has not reacted and has been trapped into the polysiloxane structure.

In order to confirm this hypothesis, EPMA analyses were performed on this sample. X-Ray mappings are shown on **Figure 67** for Si, C and O elements.

White color corresponds to the highest concentrations whereas black corresponds to the lowest concentrations.

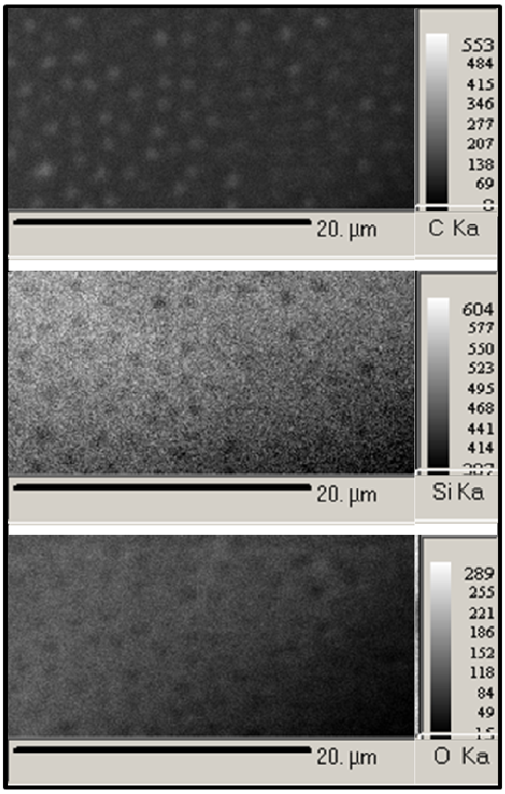


Figure 67 : C, Si and O X-Ray mappings (EPMA) of the cross section of the polysiloxane coating

The particles are clearly visible on the pictures: they contain more Carbon, less Si and less O than the rest of the coating. This result, correlated with the chemical structures obtained by NMR, evidences that the particles are composed of non-polymerized TMDSO.

It can be concluded from these characterizations that the plasma polymer obtained consists in a variety of polysiloxanes, including some monomer, trapped in the polymerized structure. However, the coating is homogeneous and completely surrounds the fibers of the NW fabric surface.

The next step consisted in testing the coated NW fabrics under the heat radiator test in order to determine if their behavior under a radiative source is improved compared to the virgin NW fabrics.

- **Fire testing**

The MA, PA, M, and P based NW fabrics were thus tested on an aluminum plate (reference) for 700 s under the heat radiator. The temperatures reached after these 700s are compared for the non treated and treated fabrics (**Table 11**).

One other interesting facet of the heat radiator test is that it is also possible to look at the texture of the resulting formed residue to estimate its mechanical resistance. It is a major advantage since these “high temperature resistant” fibers should also resist external stresses.

The **Table 11** presents the temperature reached by the backside of the aluminium plate after 700 s of testing for the non treated and treated fabrics. It shows as well the aspect of the fabrics after heat radiator test without plasma pre-treatment, after cold plasma treatment, and after heat radiator test with plasma pre-treatment.

Table 11: Temperature and aspect of the non treated and treated NW fabrics after heat radiator test.

Fiber	**Temperature after test (non coated fabrics) (°C)**	**Non coated Fabrics after heat radiator test**	**Coated fabrics**	**Temperature after test(coated fabrics) (°C)**	**Coated Fabrics after heat radiator test**
MA	252			234	
PA	275			225	
M	235			235	
P	280			240	

The polysiloxane coating seems to have a large influence on the behavior of the NW fabric under a radiative heat source. In the case of MA, PA and P NW, the temperature measured after 700s decreases of respectively 18°C, 50°C and 40°C when the samples are coated. The temperature after 700s is the same for non coated and coated M based fibers (235°C). Looking at the pictures, it is however clear that the structural integrity of the NW fabric is maintained, no cracks are observed and the polymer is less degraded. The polysiloxane coating particularly greatly improves the heat resistance of the P based NW fabric: the non coated NW fabric was efficient for only 50s whereas the coated one reaches a stable temperature (240°C) after 700s of heating. As in the case of the M NW fabric, the polysiloxane coating contributes to maintain the structure integrity of the sample and to avoid its shrinkage.

In all cases, the surfaces show a weak degradation, the coating seems to protect the surface fibers as the deposit is still visible after 700s of exposition. The white powdering char observed for PA non coated NW fabric is not observed when the NW is coated. In the case of PA, M and MA based NW fabric, no degradation of the surface is observed (no brittle char nor cracks appear).

These phenomena can be due to a lower thermal conductivity and to a lower surface emissivity (e.g. by the color which remains white): the lower surface temperature in presence of the polysiloxane coating could be explained by the “re-emission” of some radiations. But there might also be a mechanical influence of the coating layer, as it was shown to completely and homogeneously surround the fibers.

The coated fibers were thus characterized by SEM after testing with heat radiator in order to determine how the polysiloxane coating behaves under a radiative heat flux (**Figure 68**).

The result is interesting: the fibers are still coated with a “crusty” layer, which does not adhere to them but simply surrounds them.

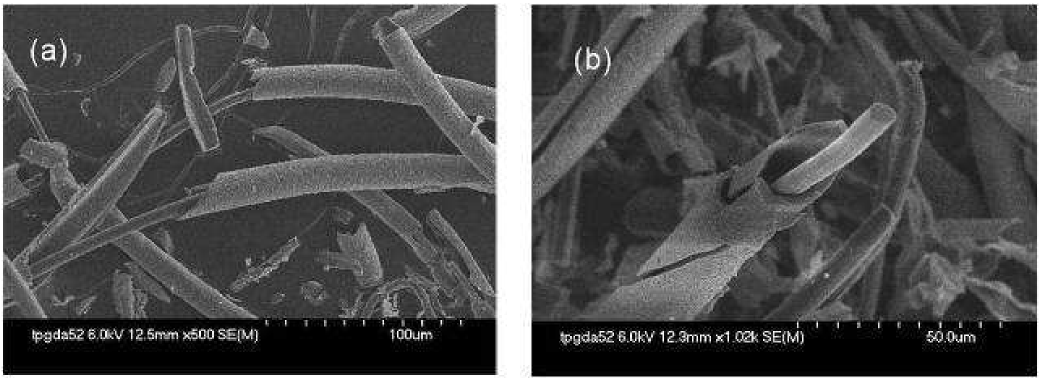


Figure 68: SEM pictures (SE) on coated and heated PA fibers

The structure obtained is very homogeneous with a coarse roughness on the surface as observed before heat exposure. These analyses confirm that the polysiloxane coating which surrounds the fibers turns into a ceramic like protective layer under heating, which still insulates and protects the fibers, preventing their degradation and though the degradation of the entire NW fabric. The structural integrity of the fabric is thus maintained.

Some NW fabrics, not very efficient to protect an aluminum plate after 700s of heating under a heat radiative flux, were coated using R-LP-PECVD with a protective material consisting in a silica-like structure of low emissivity and low thermal conductivity [14]. This plasma polymer consists in a variety of polysiloxanes. The coating is homogeneous and completely surrounds the fibers of the NW fabric surface. After heat radiator test, the structural integrity of the NW fabric is maintained when fibers are coated, no cracks are observed and the polymer that composes the fiber is less degraded. The polysiloxane coating surrounding the fibers turns into a silica-like protective layer under heating, which insulates and protects the fibers, preventing their degradation and though the degradation of the entire NW fabric. This study thus proved the efficiency of the R-LP-PECVD treatment to protect fabrics against a radiative heat flux.

Another example, using R-LP-PECVD for protecting polymer plates against fire, is presented in the next section.

III-2.2.b Application on polymer substrates

The same R-LP-PECVD technique was applied to fire retard polymer plates. The aim was to try to flame retard PA6,6-GF substrates by plasma-polymerized thin films for electrical applications. This work was carried out during the project for Rhodia Company already presented in Chapter 2 of this manuscript, consisting in fire retarding PA6,6-GF plates by a thin intumescent coating layer. The objectives are thus the same as already presented (high LOI, V0 rating and GWFI test validated at 960°C). The use of R-LP-PECVD process to deposit a thin film on Polyamide-6 (PA-6) substrates was already proven in the laboratory to improve the resistance to fire of this polymer [99, 100]. The coatings were obtained from polymerization of 1.1.3.3-tetramethyldisiloxane (TMDSO) monomer mixed with oxygen during the process. They formed a thermal barrier that decreased the rate of heat release of coated Polyamide-6. Same kind of results were reported with PA6,6 substrates and hexamethyldisiloxane (HMDSO) monomer [145].

The aim in this work was thus first to evaluate the effect of a thin polysiloxane layer (using TMDSO precursor) deposited on the PA6,6-GF and to compare it to the PA6,6-GF fire retarded in bulk with 23 wt.-% of AlPi.

➢ Polysiloxane coating on Polyamide 6,6 substrates

To realize the deposits, different treatment conditions leading to different coating thicknesses were compared using the R-LP-PECVD process described earlier (**Figure 62**).

The influence of different parameters (O_2, N_2 and TMDSO flow rates, distance injector/substrate, power, time of pre-treatment and treatment) on the thickness of the polysiloxane deposit was first investigated. The different conditions led to four different coating thicknesses: 1.2 µm, 2.6 µm, 6.8 µm and 11.7 µm.

The surfaces obtained were then characterized in terms of wettability, thickness and adhesion of the deposit compared to the reference (pure PA6,6-GF). The water contact angle increases in all cases, meaning that the surface becomes more hydrophobic than the untreated PA66-GF. According to the tests, contact angles of the treated samples remain constant whatever the thickness of the coating, meaning that the chemical species formed on the surface are similar and that the deposit is homogeneous.

Figure 69 illustrates the adhesion of the organosilicon film observed after tape test (ASTM D3359-B) by optical microscopy. The thicker the film is, the worse the adhesion. This is attributed to the fact that when the thickness of the coating increases, the deposit tends to delaminate.

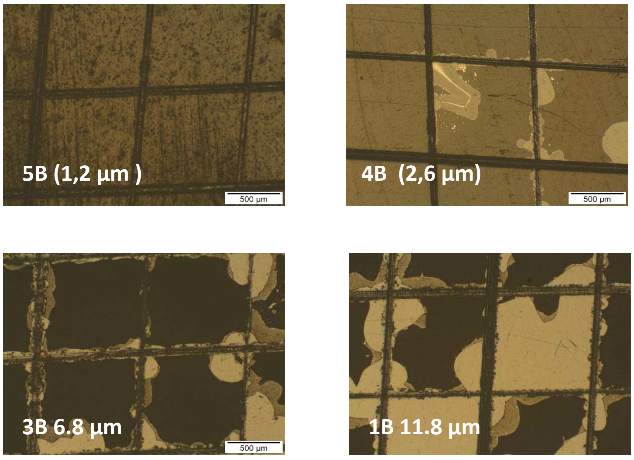


Figure 69 : Illustration of adhesion of coating by optical microscopy

Flame retardant performances of the films deposited on PA6,6-GF were then evaluated using LOI, GWFI, UL94 and MLC measurements. None of the samples was classified at UL94 test and none of them validated the GWFI test as well. However, even if the GWFI test of treated PA66-GF was not validated, it has to be noted that a thin protective silicon barrier was formed during the first seconds of the test but once this layer cracked, the sample burnt completely as it did not contain a fireproofing agent in its formulation to stop the flame spreading.

Table 12 compares the LOI values for coated PA6,6-GF samples to the non coated PA6,6-GF (thickness of 1.6 mm).

Table 12: LOI values versus the thickness of the film deposited on PA66-GF

Thickness (µm)	0	1.2	2.6	6.8	11.7
LOI (%)	21	27	29	36	34

The LOI value of the coated PA66-GF is improved: it increases as soon as the film thickness reaches 1.2 µm. A maximum value of 36% is obtained for a film thickness of 6.8 µm. Then it decreases to 34% for a film thickness of 11.7 µm. This might be due to the poor adhesion of the coated layer for this thickness (**Figure 69**). Therefore, the coating allows improving the fire retardant properties of the PA66-GF according to this test. **Figure 70** shows test specimen at LOI and LOI+1 as a function of the coating's thickness, compared to virgin PA6,6-GF.

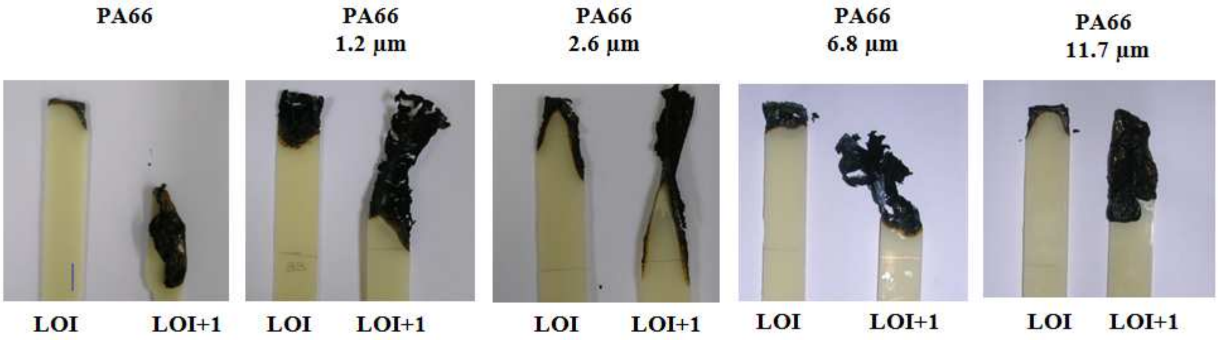


Figure 70. Illustration of LOI for treated PA66-GF

In the value of oxygen concentration corresponding to the LOI, the combustion stops quicker after inflammation and the sample burns only on a height of less than 1 cm. When the oxygen concentration corresponds to LOI+1, the material degrades faster, producing a large amount of carbonaceous residue which shows weak mechanical resistance. However, the behavior of plasma treated PA6,6-GF sharply differs from the one of virgin PA6,6-GF. A thin protective silicon crust is formed on the surface of the PA66-GF when the material is treated, which prevents the dripping of the sample. This might explain the increase of LOI as soon as 1.2µm of deposit is coated.

HRR curves (not shown here, see [12]) of untreated PA66-GF and coated PA66-GF were also obtained by MLC. Treated samples ignite approximately at the same time than the untreated PA66-GF. Further to this ignition, a thin white film is formed at the surface of the material. This structure is not particularly effective because it does not cause reduction of the HRR in regard to the untreated polymer. However, the curve profile is not exactly the same as that of PA6,6-GF profile: the plasma coating shows a small protective effect after ignition (appearance of a peak between 100 and 150s) which disappears when the thin layer cracks.

To summarize, a thin layer of polysiloxane coating shows some effectiveness in the first minutes of fire but it is too thin to have a long-time effect. This is why, as in the case of PA6,6-GF covered with an intumescent coating, a combination between a low amount of fire retardant additive (in bulk) and the R-LP-PECVD treatment was investigated.

- **Combination between bulk treatment and R-LP-PECVD treatment**

The fire retardant properties (UL94) of PA6,6-GF including AlPi and treated with the organosilicon film are compared to those of PA6,6-GF treated with the organosilicon film in **Table 13**. It is observed that the combined approach (the use of a fire retardant additive at low loading and the surface treatment) allows providing enhanced fire performances. The PA6,6-GF containing 8% of AlPi and coated with a thickness of 11.7µm leads to a V0 classification at the UL94 test and validates the GWFI test at 960°C.

Table 13: UL94 classification vs. the thickness of the film deposited on PA6,6-GF and PA6,6-GF 8%AlPi

Thickness (µm)	0	1.2	2.6	6.8	11.7
PA6,6-GF + plasma	NC	NC	NC	NC	NC
PA6,6-GF 8% AlPi + plasma	V1	V1	V1	V1	**V0**

Looking at **Table 13**, it can be noticed that the best fire retardant behavior (V0 rating) is obtained for a film thickness of 11.7 µm onto PA66-GF 8%AlPi surface. During the test, the structure of the polymer leads to the formation of a protective layer which is reinforced by the polysiloxane coating.

The coating of a thin film (11.7 µm) of polysiloxanes on PA 6,6-GF fire retarded with a low amount of AlPi (8%) shows an improvement of the classification at UL 94 test. In theory, this experiment

gives interesting results when the coating is thick enough, although adhesion issues can also interfere. Even if low-pressure cold plasma technique seems not really adapted for big panels, it could however be interesting for industrials to apply it on small pieces, as this technique is well adapted to small dimensions. However, even if this concept was recently patented by Rhodia [13], we did not test yet the application of such process on three-dimensional complex shape panels and it is thus not possible to extrapolate if the coating will homogeneously cover and adhere on the whole sample.

R-LP-PECVD seems to be a promising approach, however it is a discontinuous method, not adapted for big panels and moreover energy and time consuming. This is why plasma coatings obtained at atmospheric pressure were considered to overcome these issues. The next section details some preliminary results obtained using an atmospheric plasma technology recently input in Luxembourg research institutes (PhD K.Apaydin and F.Hilt).

III-2.3 Atmospheric plasma process

Atmospheric plasmas are in-development processes, mostly applied onto textiles by now, which show an emerging interesting potential to achieve flame retardant properties, as shown in a recent review [101]. Very recent work carried out by Horrocks et al. has led to a patented process [146] [147] in which atmospheric plasma treatment is performed. The authors demonstrated that the flash fire resistance of both pure cotton, flame retarded cotton and poly(meta-aramid) fabrics can be improved by a threefold surface treatment. First, the fabric surface is activated by plasma. Then, functionalized clays are dusted on the fabric. A plasma polymerized layer based on HMDSO is finally deposited on the surface. They have shown that the presence of clay on the surface of cotton led to an increase of the TTI value during the combustion in cone calorimeter. The PHRR values decreased from 119 to 113 for HMDSO only, 109 for clay-only and 99 kW/m^2 for HMDSO/clay samples immediately following plasma treatment [146]. It is known that both polysiloxane and clay can create a thermal and oxygen barrier between the coated polymer and the heat, thus preventing degradation volatile compounds from being released.

It is expected that the direct copolymerization of two precursors in vapor phase allows the deposition of a coating with such a complex structure and composition. For instance, depositions of copolymerized plasma polymers were reported at atmospheric pressure, which avoids the use of pumping systems [148]. Such direct copolymerization was already carried out by using a Dielectric Barrier Discharge (DBD) plasma process at atmospheric pressure [149, 150]. In this previous study, one silane precursor was used to get an adherent and dense coating, and one COOH-containing precursor was used to control the amount of COOH group in-and at the surface of the silane coating.

In the FRCoatings project coordinated by CRP H. Tudor in Luxembourg, coatings containing phosphorus and nitrogen compounds are targeted. When nitrogen rich compounds are considered, a silazane (HMDS) [151, 152] or silane 3-aminopropyltrimethoxysilane (APTMS) [153] precursor can allow to deposit a dense and adherent coating rich in NH_2. A triethylphosphate (TEP) precursor which contains phosphorus can be used to control the quantity of phosphorus incorporated in the coating. Performing fire-retardant properties will be obtained by working on a multilayer structure (**Figure 71**), each layer providing different kind of FR compounds:

i) Triethylphosphate, for instance, as an acid source able to release phosphoric acid in the temperature decomposition range of polymer in order to promote charring.

ii) A nitrogen rich coating targeted as a swelling agent source. This coating will have to release an inert gas during the decomposition of polymer.

iii) Furthermore, incorporation of nanoparticles into the top layers could provide an additional fire-retardant effect [98, 154, 155] [156], in particular if such metal oxide particles are functionalized by means of phosphorus-containing molecules.

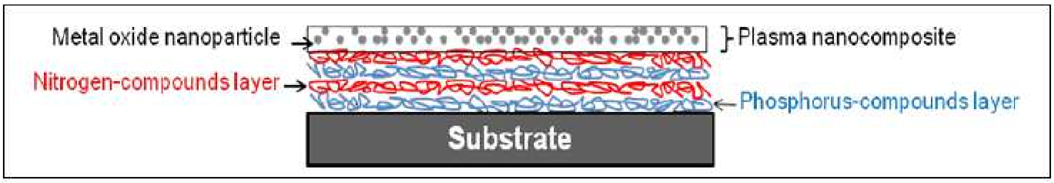


Figure 71 : Schematic of model multilayer of flame retardant nanocomposite coating

Since most of organic polymers thermally decompose in the range of 300-400°C, fireproofing action of the intumescent coating has to take place in this range. Nevertheless, both acid source and swelling agent can be adjusted depending on the decomposition temperature of the polymer substrate. The presence of these different elements should lead to the formation of a carbon rich foam layer (char) at the surface during the combustion in order to heat insulate, reduce further oxygen access, reduce fuel transport into the flame and prevent dripping.

These functional coatings are deposited by means of the Vapor Polymerization Deposition assisted by a Dielectric Barrier Discharge (VPD-AP-DBD) (**Figure 72**).

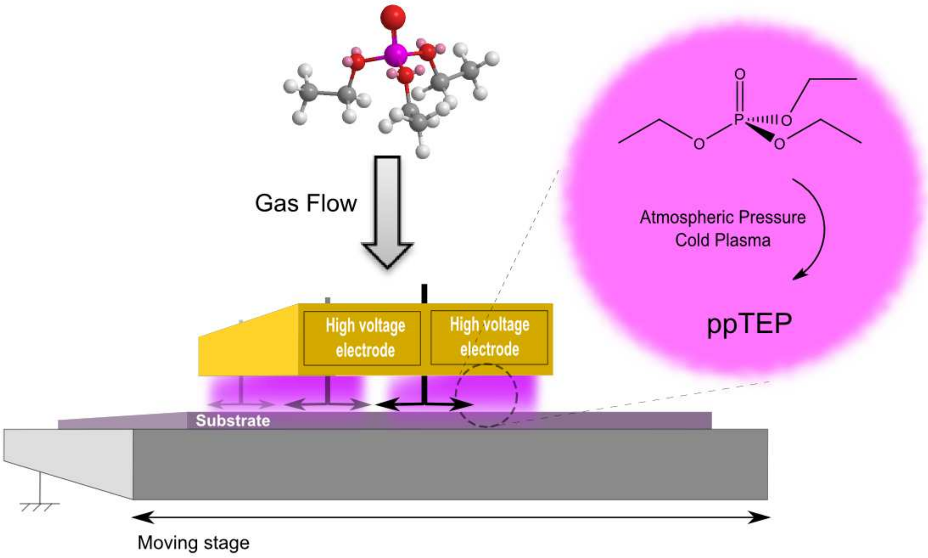


Figure 72 : Example of VPD-AP-DBD process applied to a phosphorus containing monomer (apparatus in CRP Lippmann, Luxembourg)

Among Atmospheric-Pressure plasma processes, Vapor Polymerization Deposition assisted by a Dielectric Barrier Discharge (VPD-AP-DBD) is a versatile and promising technology, which allows the deposition of a wide variety of organic monomers. It combines the advantages to generate low-temperature plasmas and to operate at atmospheric pressure. It does not require any vacuum system in comparison with low-pressure plasmas and no heating systems like in classical CVD. No large amount of unwanted by-products or waste are produced during the process and inexpensive plasma gases such as nitrogen or air can be used. Plasma is initiated using a Corona generator with processing parameters leading to a filamentary discharge, which can however allow the deposition of homogeneous films by tuning the plasma parameters.

The next section presents some preliminary results obtained by the PhD F.Hilt (not supervised by our group) and tested to fire by the PhD student K.Apaydin (2011-2014) I co-supervise with S.Bourbigot and A.Laachachi (CRP Luxembourg).

- **Preliminary results**

Various phosphorus containing precursors (TEP, Dimethyl vinylphosphonate (DMVP), Diethylphosphatoethyltriethoxysilane (DEPS), etc.) were coated onto polycarbonate thin films (0.4 mm) using the previously described VPD-AP-DBD process.

In this manuscript, I will only present some interesting preliminary results in terms of fire retardancy recently obtained with the DMVP precursor (**Figure 73**).

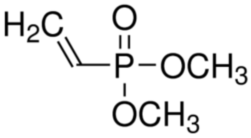


Figure 73 : Developed formula of DMVP

The deposits were applied using a pulsed nitrogen VPD-AP-DBD process on PC thin films (0.4 mm). For an easier characterization, the coating was first deposited on silicium wafers and a cross section was analyzed by SEM (**Figure 74**).

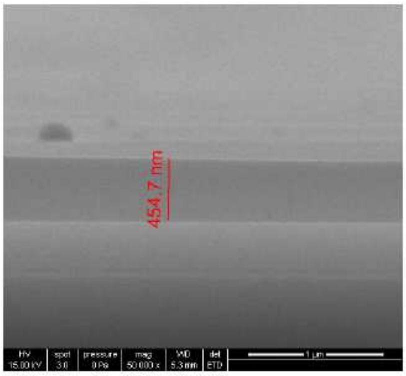


Figure 74 : SEM (SE) cross section characterization of a DMVP-based plasma coating

The deposit thickness is around 500nm. The deposit was then applied on a large substrate, removed and analyzed by ^{31}P MAS solid state NMR (**Figure 75**).

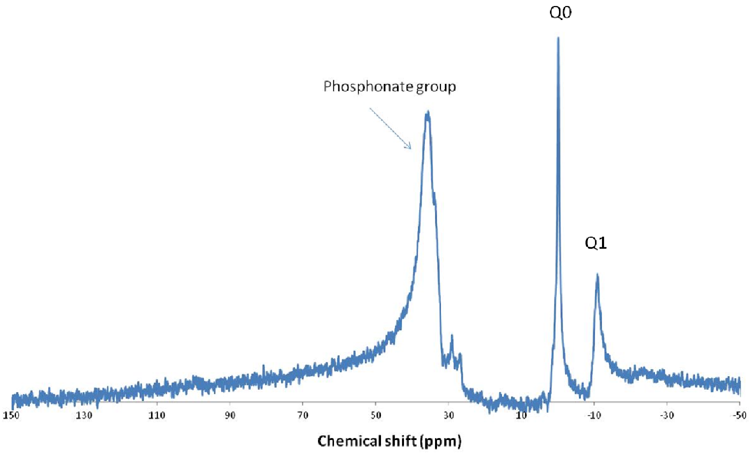


Figure 75. ^{31}P MAS NMR spectrum of DMVP-based coating

Q_0 species (orthophosphates or phosphoric acid), Q_1 species (pyrophosphate species) were identified. The peak around 40 ppm corresponds to the phosphonate groups of some remaining monomer. It can be concluded from this ^{31}P NMR that the polymerization degree of the DMVP-based coating is quite low, as an important amount of monomers is retrieved, and no Q_2 species (polyphosphates), characteristic of a well-polymerized network are detected. However we don't know yet if it is more interesting to have a well-polymerized network to enhance the fire retardant properties of the coating. This will be studied in the incoming year.

Some polycarbonate thin films covered with the DMVP-based coatings (samples noted 1-a, 1-b and 1-c) were then tested by cone calorimetry under a 50 kW/m² heat flux, with a distance cone-sample of 30 mm.

Visual observations of the samples show that they swell under heating, thus protecting the underlying PC before ignition. (**Figure 76**)

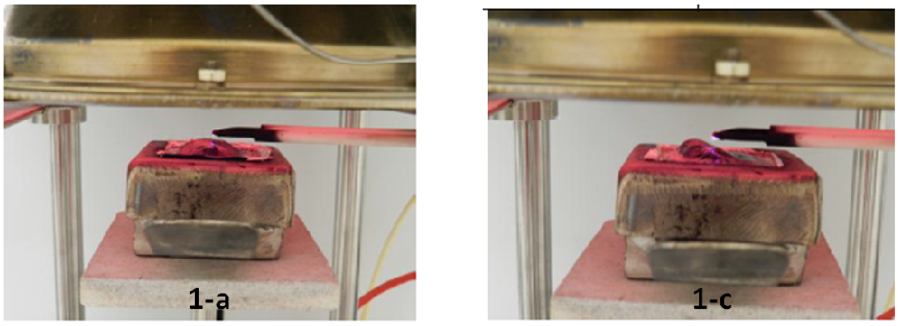


Figure 76 : Pictures under cone calorimeter of coated PC samples

Moreover, looking at the PHRR and the TTI, it is observed in the **Table 14** that when a sufficient coating amount (coating mass) is deposited on the samples (e.g. samples 1-a and 1-c), the ignition time increases (from 38s for pure PC to max. 77s for 1-c sample). The PHRR also decreases from 316 kW/m² to min. 243 kW/m² for both samples 1-a and 1-c.

Table 14 : Cone calorimeter results (TTI, PHRR) for PC plates (1-a to 1-c) coated with DMVP based deposits

Sample	Composition	Coating mass (g)	TTI (s)	PHRR (kW/m²)
PC	PC	-	38 ± 2	310 ± 16
1-a	PC-DMVP	0.0050	55	243
1-b	PC-DMVP	0.0016	54	309
1-c	PC-DMVP	0.0051	77	243

When the coating is however in low amount (e.g. 1-b sample), the PHRR is not improved even if the TTI increases somehow.

After burning, the analysis of the remaining char by ^{31}P NMR (not shown here) only reveals the presence of orthophosphates (Q_0 species), but no signal characteristic of phosphocarbonaceous species (P-O-C bonds) appears.

These preliminary results show that a 500 nm thick phosphorus containing thin coating obtained by atmospheric plasma leads to a slight improvement of the fire protection (decrease of PHRR and increase of TTI) of the underlying substrate, i.e. PC in this case. However the results are not very repeatable yet and some efforts have to be dedicated to the plasma process to obtain homogeneous and reproducible coatings so that a mechanism of action of this coating on the polycarbonate can be established.

In this chapter, various ways to fire retard textiles and polymer films by in-development surface treatment processes were described. The LbL deposition of the systems (PAH-MMT) and (PAH-PSP) will be further developed in the incoming years and applied on both synthetic textiles and polymer films; the mechanisms of action of these thin coatings in terms of fire retardancy will also be investigated. This is an efficient and rapid methodology, however a possible issue could be the upscaling of this surface treatment to very large panels.

The PIGP process leads to promising results in terms of fire retardancy. Even if it is a multistep wet process, we are still using it to fire retard open-cells foam core composite materials, as it allows grafting functional monomers on and inside the whole foam.

The R-LP-PECVD treatment is efficient on both textiles and polymer plates, however issues associated to this process make it not easy to conduct on large panels and at industrial scale. This is why the development of atmospheric plasmas is preferred and is currently in development in our team. The preliminary results presented earlier in this manuscript using the VPD-AP-DBD process were obtained in Luxembourg. However, the laboratory will be equipped from March 2013 of a similar process (ULD, Acxys technologies), and experiments on that subject can thus be carried out in our team as well.

Remark: The competences I acquired on the technologies developed in this chapter, and particularly on the low pressure cold plasma technologies, allowed me then to enlarge my research activities to other topics than fire retardancy. The use of RF low pressure cold plasma process was first developed to modify biomaterials surfaces: for example, anticoagulant and antibacterial molecules were successfully immobilized on polypropylene and polyester nonwovens through a PIGP process. With a colleague from UMET (S. Degoutin), we meantime obtained the funding of a young researcher project on the functionalization of polypropylene by biomolecules [16]. During this project, I was in charge of the PIGP technique development, and my colleagues from UMET (B.Martel, S.Degoutin) and Lille2 University (N.Blanchemain, F.Chai) were respectively responsible for the biomolecule immobilization and the biological tests [15, 16].

The same process is also currently used and improved to develop functional textiles modified by biomolecules allowing the chelation of heavy metals trapped in marine and fluvial sediments (PhD M. Vandenbossche) [19, 20, 23]

The last three chapters of this manuscript detailed the two main topics I have been developing these last years, that could be entitled “thick and thin film functional coatings”, mainly applied for fire retardant purposes. However, this functional property has to be kept for certain duration in certain conditions. The durability issue is as a consequence of highest importance. During my research work on coatings for fire retardant purpose or for some other purposes (biocompatibility, heavy metals remediation, etc.), I could observe, whatever the couple substrate/coating, the great importance of the phenomena at the material surface (aging, fouling) or at the interface (adhesion, delamination…) which appear when the sample is stored, when it is submitted to external constraints (UV, temperature, moisture…) or when it is in contact with a liquid (water, salt water, blood …). These phenomena have to be taken into account when a coating - whatever the coating process- is developed or when an intrinsic functional property of a material needs to be kept. In the next Chapter, I will evidence some phenomena that can lead to the loss of the functional properties of a material or of a coating. I am currently in charge of further developing this topic on the functional durability of materials and coatings in the group.

Chapter 4- Functional durability

This topic was first developed through a personal research work, and also supported by the PhD of G.Alogaili (2011-2014). Two papers have been recently published on this topic [26, 27], one is currently being revised [28] and two papers have been submitted for publication [18, 25].

Coatings lose their functional properties when submitted to different constraints such as chemical (UV, chemical products, water…) or physical (mechanical strain, scratches…) attacks. In a first place, the mechanisms involved in the various possible aging processes have to be identified, in order to then provide some potential solutions to limit this phenomenon. In the first part of this section, particular attention will be paid to the aging of intumescent coatings applied on steel or on polymers: in this field, the literature is very poor, and great enhancements can be made.

Another topic, not linked with fire retardancy, but clearly related to functional durability concerns fouling: fouling is generally defined as the unwanted formation of thermally insulating materials or deposits from process fluids onto surfaces. As the surface is then covered with contaminants, it usually loses its functional properties. It is then of primary importance to understand the mechanisms of fouling deposition at the surface to then try to find solutions to prevent it. I had the opportunity to discover dairy fouling through a partnership with INRA and Arcelor Mittal, and I will develop and extend this collaboration in the incoming years. The preliminary interesting results obtained will be thus presented in the second section of this chapter, even if they are not related to the fire retardant topic.

IV-1 Aging of intumescent coatings

Long-term chemical and physical stabilities are necessary conditions for obtaining durable functional coatings. Degradation occurs as the result of environment-dependent chemical or physical attacks, often caused by a combination of degradation agents, and may involve several chemical and physical mechanisms [157, 158]. It is generally accepted that the coating efficiency is dependent on the functional properties durability, the adhesion properties of coating/substrate interface and the degree of environment aggressiveness [159].

Chemical aging caused by UV radiation, temperature and moisture has been the subject of numerous investigations, and its general mechanism is relatively well known [159-167]. Photo-oxidation induced by UV radiation can produce, among other effects, oxidation of double bonds, polymer segment scission and cross-linking, while high temperature and moisture produce thermal degradation and hydrolysis. Since all these processes change the coating composition, they act against its chemical stability. As a result, the coating toughness decreases and the hygrothermal stresses increase [168-170], negatively affecting the coating adhesion and cohesion. The direct practical results are the detachment and/or cracking of the coating that in turn cause the degradation of metallic, mineral and organic substrates via corrosion, disintegration and putrefaction, respectively.

Physical aging is also an important phenomenon affecting the physical stability of polymeric materials and thus of organic coatings. It is now accepted that this phenomenon has an impact on the formulation, application and on the service life behavior of organic coatings in many fields, such as those designated for aerospace and automotive applications. Contrary to the great number of studies dedicated to physical aging of polymeric plastic materials, more than 800 publications in the last 20 years [171], the physical aging of organic coatings, despite of its importance, has not produced a similar interest. There are several likely reasons why physical aging was so little investigated by organic coating industry. The main reason is probably due to the number and complexity of processes occurring during coating service lifetime and degradation, such as photo-oxidation, loss of solvents, leaching and cross-linking, that tend to mask the effects induced by physical aging. Some papers [168-170, 172, 173] and a review [174] published by Perera et al. show that while on the molecular scale the physical aging phenomenon is not yet completely understood and certain aspects of its origin are still subject to controversy, its effect on polymeric material, in general, and on organic coatings, in particular, is undisputable. Some of its effects, such as the increase in rigidity and relaxation time, and the decrease in ductility and fracture resistance, alone or in combination with other factors (e.g. stresses arising in the film) contribute to coating failure. These changes are determined by the environmental conditions, represented e.g. by the difference in temperature between the real glass transition temperature—affected by the relative humidity—and the aging temperature and the coating composition, (e.g. structure and cross-link density of the binder, pigmentation, etc.).

The literature dedicated to the aging of specific functional coatings such as fire retardant coatings is very poor. Examples in literature mostly report the influence of various aging conditions on the fire protective behavior of some polymer blends. For example, Almeras et al. [175] simulated accelerated weathering on an intumescent flame-retarded ammonium polyphosphate (APP)/polyamide-6 (PA-6)/polypropylene (PP) blend under a Xenon lamp exposure, with rain and temperature cycling. The chemical modifications of the blends after aging were investigated by solid state ^{31}P nuclear magnetic resonance (NMR) and scanning electron microscopy (SEM). It was shown that APP is degraded into ortho-, pyrophosphate and short chain polyphosphates. These modifications lead to the loss of the

ammonium contents which could explain the decrease of fire performance and mechanical properties. No papers are however devoted to the aging of intumescent coatings applied on polymers, as the concept has only been recently developed by our group (cf. Chapter 2).
For applications on buildings made of steel, solar radiation (particularly UV radiation), temperature, water, moisture, corrosive middles such as seawater are the main factors inducing degradation that can reduce its fire-resistance effectiveness. A screening test on the fire resistance of passive fire protection coatings after long-term weathering (15 years) has been recently carried out [176, 177] on different commercial intumescent coatings. These ones were then tested in industrial furnaces. The results were discussed in relation to alterations in physical form, corrosion of the substrate and changes in fire resistance. The results have shown that the intumescent materials are susceptible to weathering and should be protected by an adequate and compatible topcoat system. More recently, Wang et al. [178, 179] studied the effect of accelerated aging in hydrothermal conditions on the fire barrier properties of two different intumescent coatings (without topcoat) applied on steel. They characterized the coatings after aging by XPS, FTIR and also compared their thermal conductivity after aging to explain the loss of fire protective properties.

As durability is a crucial property from our point of view in the development of functional intumescent coatings, we thus recently decided in the group to dedicate a topic to the aging study of intumescent coatings. We started this topic by investigating the aging of two intumescent coatings applied on different substrates: steel and polymer. First of all, the weathering of a thick epoxy based intumescent coating applied on steel has been studied in drastic weathering conditions [26] and will be presented in the first part of this section. This coating is, due to a confidential issue, different from the one used in the Chapter 1 and its name will not be given for the same reasons as well. Then, in the second part of this section, preliminary results obtained on the aging of the waterborne intumescent coating (used in Chapter 2) exposed to UV-filtered light exposure and applied on polymers (PP and PC) will be briefly presented.

IV-1.1 Aging of intumescent coating designed to protect steel structures

In this section the effect of water immersion on the fire protective behavior of an intumescent thick epoxy based coating applied on steel is investigated, and the influence of the ionic strength (salt added in water) is investigated as well. This coating contains in particular APP, TiO_2 and melamine. The influences of accelerated sunlight and moisture exposures also have been studied, but as no differences are visible after 3 months of accelerated aging, these investigations will not be described in this manuscript (see [26] for more information).

Coated steel samples were immersed in water or salt-water thermostated at 20°C without stirring. The coatings submitted to aging treatments (coating immersed one month in distilled water at 20°C and coating immersed one month in salted water at 20°C) were first of all tested using the small furnace test presented in Chapter 1 in **Figure 28** and compared to a virgin steel plate exposed in the same conditions and to the reference coated plate without any aging treatments. **Figure 77** shows the obtained temperature versus time curves. 400°C was chosen as the failure temperature.

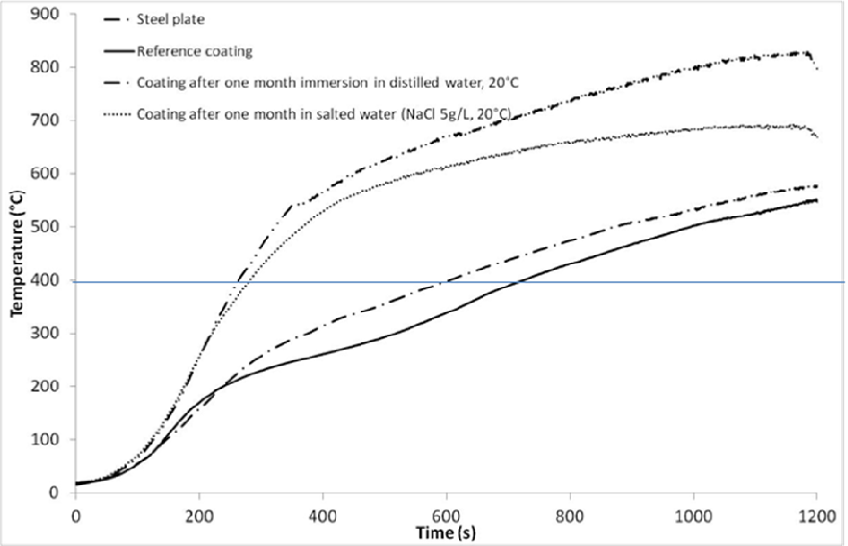


Figure 77. Temperature versus time curve for the coated plates (without aging and after aging in distilled water and aging in salted water) during furnace test compared to the virgin steel plate.

A difference appears between the reference coating curve and the curve of the coating immersed in distilled water. The failure temperature (400°C) is reached after 600 s for the coating immersed in distilled water against 730 s for the reference coating, which means that part of the efficiency of the protective coating is lost. Looking at the curve of the coating immersed one month in salted water, the failure temperature is reached after only 285 s, compared to 730 s for the reference coating. The fire protective effect of the coating is dramatically decreased when the sample is immersed in presence of salt.

Figure 78 shows the pictures of the chars obtained after furnace test for the reference coating and for the coatings submitted to aging tests, the duration of the test being similar in the three cases.

Figure 78. Pictures of the char after furnace tests (a) reference plate (b) plate after 1 month immersion in distilled water (c) plate after 1 month immersion in salted water

The char of the coating immersed one month in salted water is completely different from the others: there is still a white hard residue on top of the plate, well adhesive to the plate, however no more swelling is observed: the intumescence phenomenon does not occur anymore. It clearly explains why the performance is poor.

To try to understand the influence of salted water, the reference coating and the coating after 1 month immersion in salted water were compared before burning (the characterization of the coating after 1 month exposure in distilled water will not be presented in this section, see [26] for more details).

IV.1.1.a Characterizations before furnace test

SEM (BSE) images of the cross-section and X-Ray mappings (in P, Ti, Na and Cl) of the reference coating and of the coating after 1 month immersion in salted water are respectively presented in **Figure 79** and **Figure 80**.

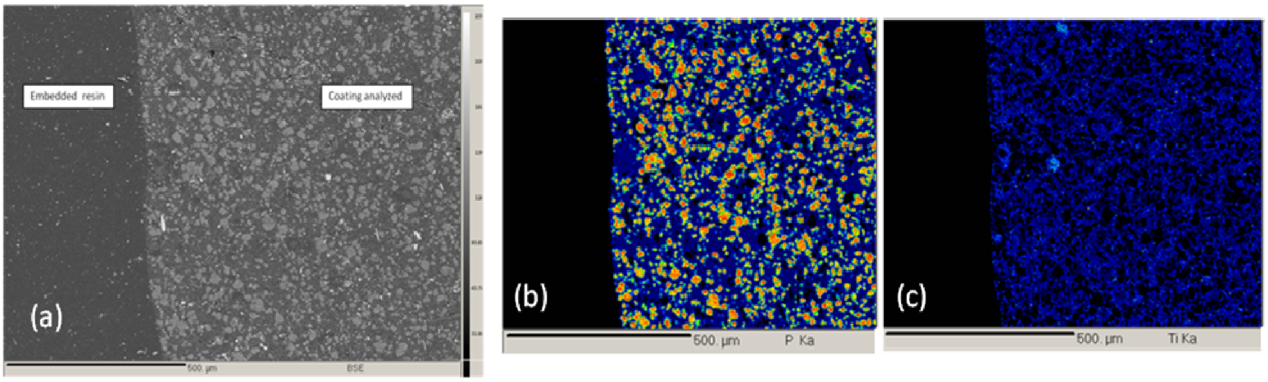


Figure 79. BSE pictures of cross-section (a) and EPMA X-Ray mappings in P (b) and Ti (c) of the reference coating

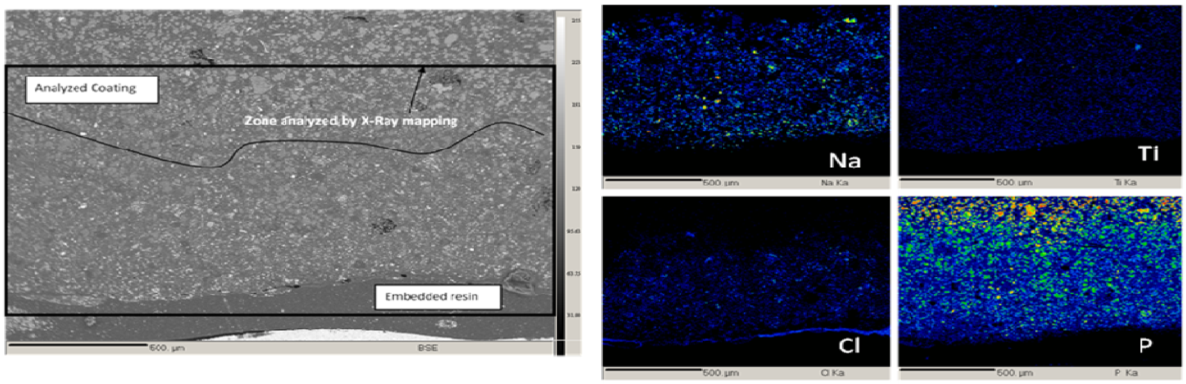


Figure 80. BSE cross-section picture (a) and EPMA X-Ray mappings in Na, Ti, Cl and P of the coating immersed one month in salted water

In the case of the reference coating, the fillers are well dispersed, the coating is homogeneous and compact and X-Ray mapping results show that phosphorus, i.e. APP, and titanium, i.e. TiO_2 are homogeneously dispersed into the whole matrix.

When the coating is put in salted water for one month, the analyzed coating is not homogeneous anymore, two parts are noticeable; one part with big-size particles on the upper side of the picture, the other part containing smaller particles. X-Ray mappings show that sodium and chloride have penetrated deeply inside the epoxy matrix, the sodium migrating more rapidly (migration on a thickness of about 800µm) than the chloride (migration on a thickness of about 500µm). Cl^- ions are however highly concentrated on the extreme surface of the coating, whereas sodium is not present anymore in the extreme surface of the coating. Looking at the phosphorus, only a low amount of phosphorus is detectable on the zone where sodium appears. When no sodium is visible, the APP particles are retrieved (this is visible on the upper side of the X-Ray mapping in phosphorus with red-orange colors). It means that the presence of these ions in water completely modifies the system. Hypothesis is that water, Na^+ and Cl^- ions migrate into the coating, leading to the dissolution/detachment of APP particles and maybe of melamine as well. Complementary X-Ray mappings (not presented here) also show that some melamine particles have left the surface. The pores left are perfectly surrounded with chloride in high amount and some of them are filled in with sodium (in lower amount). Chlorides, combined with some water erosion mechanical effect, might accelerate the melamine detachment. The pores left by the disappearing of melamine will then allow the salted water to penetrate deeper into the matrix.

To try to investigate further the chemical modifications of the system, the coatings were analyzed in terms of chemical composition using solid state ^{31}P NMR and XRD.

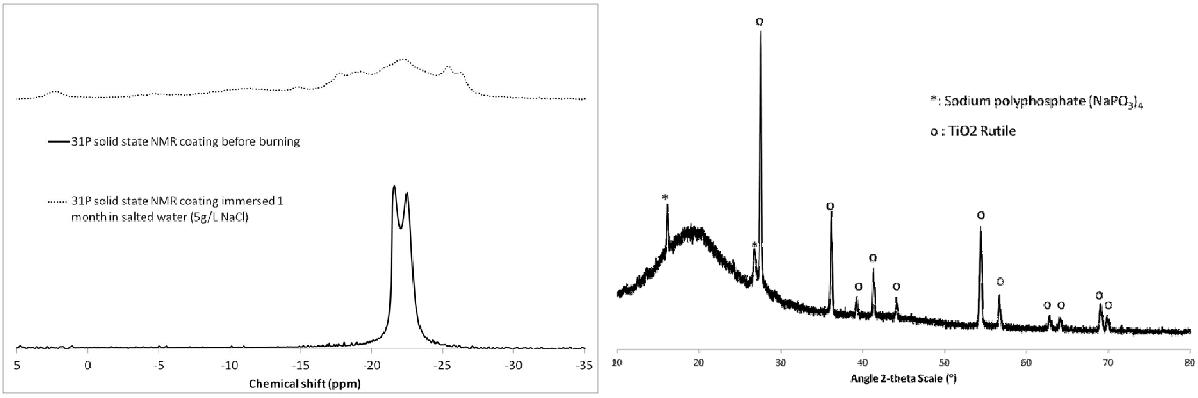


Figure 81. ^{31}P solid state NMR of the reference coating and of the coating put one month in salted water; XRD of the coating put in salted water.

The two peaks of the reference coating obtained at -21 and -23 ppm are typical of a well crystallized structure with Q_2 phosphorus units [2] contained in polyphosphate chains.

The spectrum of the coating immersed for one month in salted water is completely different. A small peak characteristic of orthophosphates appears at 3 ppm, probably corresponding to sodium orthophosphates. Moreover, instead of the two peaks characteristic of the crystalline phase of APP, a large massif of low-resolution peaks is observed between -15 and -30 ppm. This massif is assigned to low crystallized sodium polyphosphates [180]. This hypothesis is confirmed by XRD analyses. On the diffractogram, TiO_2 Rutile is retrieved, and two other peaks at 17° and 27° appear, which are assigned to sodium polyphosphate. It is thus confirmed that the ammonium polyphosphate turns into sodium polyphosphate. It is also interesting to look at the water solubility of the sodium polyphosphate formed: APP has a solubility in water of 5 g/L, whereas sodium polyphosphate has a solubility in water of about 140 g/L. This difference of solubility explains the disappearing of phosphorus in the whole zone where sodium migrates. When the ammonium polyphosphate turns into sodium polyphosphate, this latter is then easily dissolved into the water. The pores created through this loss of phosphate particles allow deeper penetration into the matrix of the salted water.

Gathering all results (**Figure 82**) (including TGA-FTIR results not shown here) allows to conclude that two phenomena contribute to the absence of intumescence development: first of all, the ammonium ions of the APP, which are necessary for the release of ammonia during heating and thus the swelling of the char, are replaced by sodium cations and released into the water on different forms ($NH_4^+Cl^-$, NH_3).

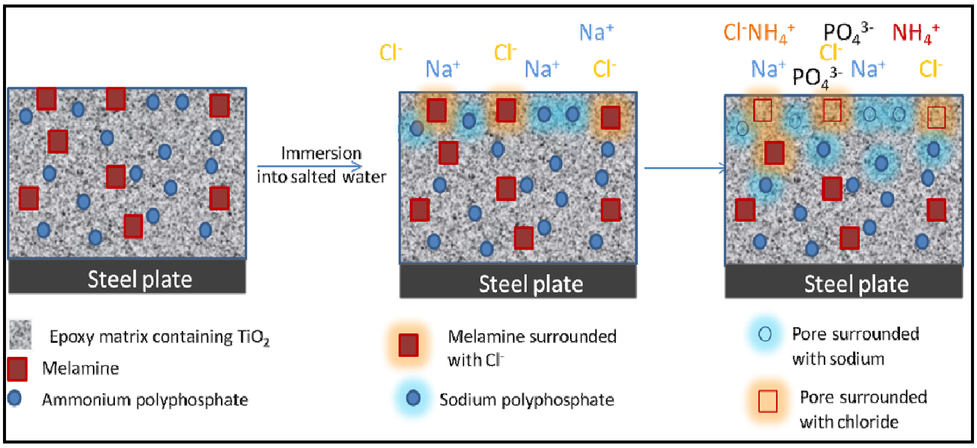


Figure 82. Summarizing scheme of the aging of the coating in salted water at different aging times.

Secondly, the sodium polyphosphates formed have high water solubility and are dissolved more rapidly in the water. The dissolution process might be accelerated by the presence of chlorides [181]. As a consequence, the phosphorus content, and thus the acid source amount necessary to the intumescence development, is decreased and hence the fire resistant properties of the coating as well.

IV.1.1.b Characterizations after burning

The different chars were then analyzed after furnace tests, using ^{31}P solid state NMR and XRD. The spectra obtained are presented in **Figure 83**.

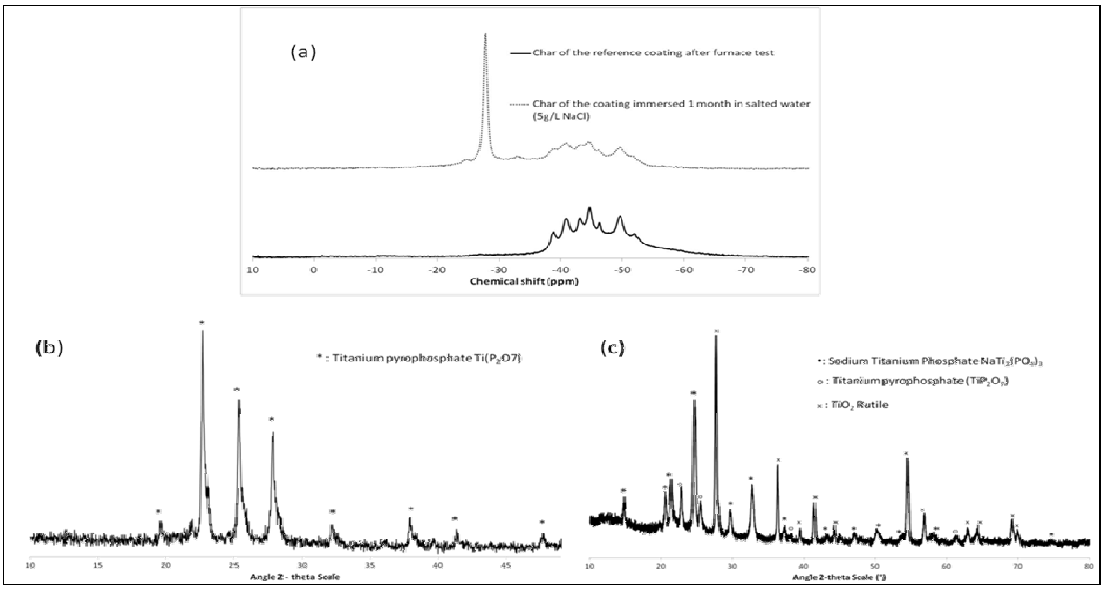


Figure 83. ^{31}P NMR spectra of chars (a), XRD spectra of reference coating char (b) and of immersed coating char (c).

The ^{31}P NMR of the reference coating char shows a massif of well-defined peaks between -38 and -53 ppm which can be attributed to a crystallized structure corresponding to titanium pyrophosphate[182]. The XRD analysis confirms the presence of Titanium Pyrophosphate TiP_2O_7. No remaining titanium dioxide is visible, meaning that the whole titanium reacted with phosphorus. Looking now at the ^{31}P NMR spectrum of the coating immersed in salted water, the char also contains titanium pyrophosphates (TiP_2O_7), corresponding to the massif of peaks between -40 and -60 ppm. However, an additional and well defined peak appears at -28 ppm, corresponding to a crystallized specie, which could be an oxide containing both P, Ti and Na. These kinds of oxides are known under the name of NASICON [183]. The XRD spectrum confirms this hypothesis, as it is possible to distinguish the characteristic peaks of TiO_2 (Rutile form) and some peaks characteristic of a NASICON, the Sodium Titanium Phosphate ($NaTi_2(PO_4)_3$). The formation of the $NaTi_2(PO_4)_3$ can be explained by the reaction between the sodium polyphosphates and the titanium dioxide during burning. The presence of TiO_2 in the char can be explained by the lower amount of phosphorus remaining in the coating after aging: the titanium is now in excess compared to phosphorus.

In this study, it was thus demonstrated that when a thick epoxy based intumescent coating is put in contact with salted water for one month, the conditions to develop an intumescent system are not present anymore, and obviously no char is formed during burning, only a residue – still stuck to the steel plate - containing mainly TiO_2, TiP_2O_7 and a Nasicon: $NaTi_2(PO_4)_3$ was observed. This study points out the risks for steel structures exposed to contact with seawater of a complete loss of their properties after a few months or years if no additional protection is provided to the coating. It is thus necessary to find some ways (topcoat, sensitive fillers encapsulation, hydrophobic thin film...) to avoid the migration of water and NaCl and thus to avoid a too rapid dissolution.

We are currently carrying the same test protocol in presence of a topcoat to look both at the influence of the topcoat on the fire resistant properties and on the water and salted water resistance.

As mentioned previously, in the frame of the development of the application of intumescent coatings on polymers, we also decided to study the durability of the fire retardant properties of the waterborne intumescent coating used in chapter 2, submitted in this case to UV-filtered light exposure [184]. Hydrothermal tests were not tempted, as the coating is sensitive to water.

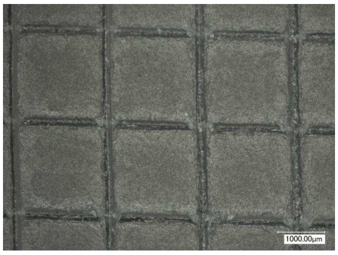
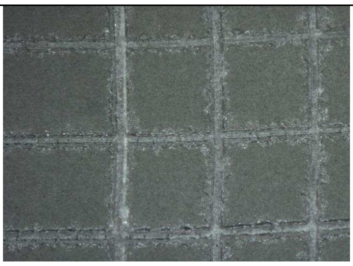
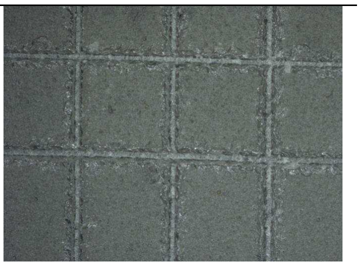
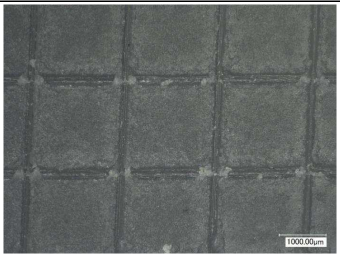
IV-1.2 Aging of a waterborne intumescent coating applied on polymers

Material coated with 64µm of the water-based intumescent coating for PC and 158µm for PP (thicknesses optimized in the work previously presented in Chapter 2) were chosen for this part of the study. The aging conditions were fixed in order to simulate the aging inside a building (with an UV-filter) for 200 and 400 hours. After these treatments, the fire retardant properties of the coated samples were evaluated with MLC and UL 94. Additionally an adhesion test was made, to see the influence of the aging on the adhesion between the paint and the substrate. A film of pure intumescent varnish was also exposed to the same aging conditions to study the stability of the varnish regarding UV-filtered light (FTIR, TGA).

IV.1.2.a Adhesion assessment

Adhesion is a key parameter when dealing with flame retardancy of material using intumescent coatings [7],[75]. The adhesion of the coating was thus evaluated on PC and PP before and after aging using the "Tape" test. Pictures of the materials as well as classification obtained according to ASTM D 3359-02 are reported in Table 15.

Table 15. Adhesion properties of intumescent varnish on PC and PP versus aging time

Material	**Virgin material**	**200h exposure time**	**400h exposure time**
PC	 5B	 3B	 3B
PP	 4B	 2B	 1B

Concerning the untreated material, the adhesion of the varnish on PC achieves the best classification (5B) demonstrating a good adhesion between the coating and the substrate. After 200 hours of UV-filtered light exposure, the picture of the coated PC plate shows a clear difference with the virgin sample. The adhesion decreases after aging and the specimen is classified 3B. After 400 hours of UV-filtered light treatment, the adhesion does not change significantly compared to the sample treated for 200 hours treatment (the sample is still classified 3B). Thus, those results demonstrate that the adhesion of the varnish decreases after UV-filtered light exposure. Similar results have been obtained in the case of PP. Indeed, the adhesion test of virgin coated PP shows a slightly worse adhesion compared to PC since the sample is classified 4B. The adhesion of the PP sample after 200 hours is affected by the UV-filtered light treatment and the sample only reaches 2B rating. This aging of the adhesion is even more pronounced after 400h since in that case, very low adhesion of the varnish is obtained and the material is classified 1B.

IV.1.2.b Effects on fire protection

UL94 rating of coated PP and PC after 200h and 400h exposure under UV-filtered light was then determined. It was shown that PP-based materials are affected by the aging (V1 after 400h) while PC-based materials do not (V0 rating is kept).

HRR curves of coated PC and PP before and after 200h exposure at UV-filtered light are reported in **Figure 84**. These curves demonstrate that for both PC and PP, the FR properties of materials are affected by the aging treatment.

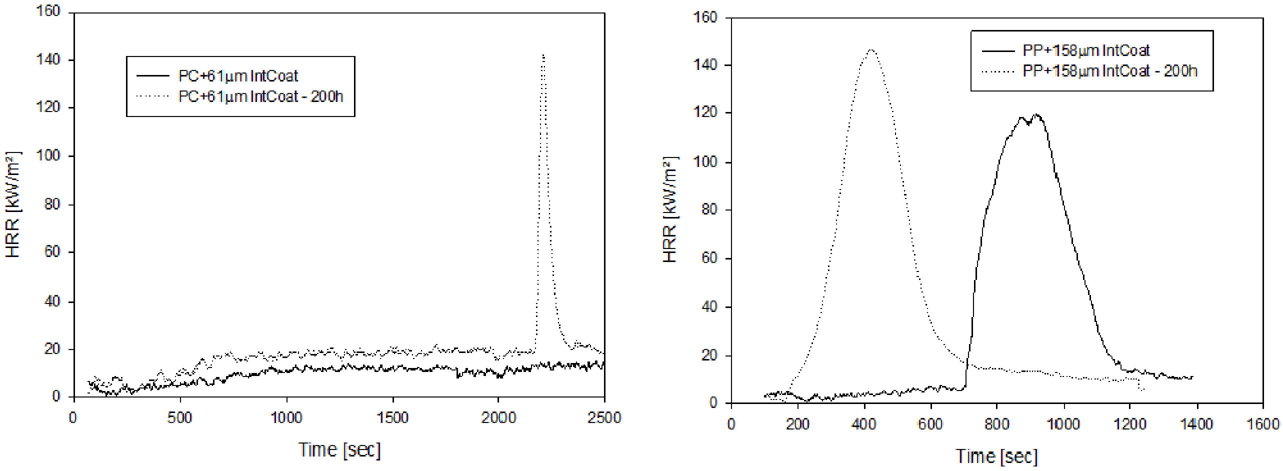


Figure 84. HRR versus time for coated PC (left) and PP (right) before and after 200h exposure at UV-filtered light (IntCoat : Intumescent Coating)

In the case of PC, whereas no ignition was observed for the coated plate before aging, ignition of the material occurs for the aged material at around 2200s (more than 30min), which might be explained by the loss of adhesion (4B to 3B) leading to a local detachment of the coating layer inducing a sudden fuel liberation. So, even if the FR properties of coated PC are very good, it demonstrates that the UV-filtered light aging can affect the properties at longer time.

In the case of PP, similar results are observed. Indeed, the TTI decreases from 705s for non-aged material to 164s for aged material, this again being explained by the lower adhesion of the coating on the PP plate (2B). The value of the PHRR is, however, only slightly affected by the aging treatment. It was thus evidenced that the adhesion is affected by the UV-filtered light exposure and that it results in a decrease of the FR performance of the materials.

In order to evaluate if the decrease in the FR properties should also be attributed to a chemical modification of the intumescent varnish, its aging was studied analyzing the FTIR spectra of both the non-aged and aged coatings (not shown here). It was observed that the spectra for non-aged and aged-coating are very similar. However, after UV-filtered light exposure, three peaks appear at 1976, 2027 and 2158 cm^{-1}. These three peaks could be attributed to stretching vibrations of triple bonds (C≡C, C≡N) and/or of cumulated double bonds (X=Y=Z). However, since we do not have any precise information on the composition of the varnish, it is not possible to further explain the formation of such species. Thermogravimetric analyses (not shown here) also did not show any particular difference.

Dealing with intumescent coatings, it is generally proposed, as evidenced in the previous section of this chapter, that the hydrophilic components of the intumescent coatings migrate to the surface of the coating and are dissolved in the environmental media (water, air..) leading to a decrease of the FR performance of the coatings. This should not be the case in this study since the aged material exhibits similar expansion than the non-aged material, which suggests that the intumescent process occurs in a similar way. Moreover, according to the FTIR and TGA analyses carried out in this study, it appears that, in our aging conditions (UV-filtered light radiation), the chemistry of the coating is only slightly affected by the aging treatment. Thus, physical aging, and particularly a loss of adhesion between the coating and the plate, was suspected and its influence on the loss of FR performance of the coating was evidenced.

It must in fact not be forgotten that a flame treatment was previously carried out on the polymer surface to enhance the adhesion of the coating. Pre-treatments such as flame treatments lead most of the time to the creation of weak bonds between the substrate and the coating, maybe thus preventing a durable adhesion. This is why complementary experiments have to be carried out, using more durable activation techniques such as RF cold plasma treatments or atmospheric

plasma treatments; one sample will also be protected during 3 months from light exposure and the results will be compared with the UV-filtered light exposed samples.

Moreover, the detailed formula of the waterborne intumescent used in this study (Pyroplast HW100) is unknown. It means that all the results obtained in terms of mechanisms of action (fire retardancy, aging) can only consist in assumptions. This is why we just started to collaborate with an intumescent coatings manufacturer in order to test its coatings on polymeric substrates, to carry out aging tests on them and to analyze the effect of topcoats on the durability of the functional properties. As the main ingredients providing fire retardancy will be known in that case, the mechanisms established will be more precise and accurate.

As mentioned in the introduction of this chapter, other aging phenomena exist, such as for example fouling. Because of fouling, the materials or coatings are hidden, and functional durability is thus lost. Different kinds of fouling exist. A common one is membrane fouling: this is a process where solute or particles deposit onto an artificial membrane surface or into membrane pores in a way that degrades the membrane's performance. It is a major obstacle to the widespread use of this membrane technology. Membrane fouling can cause severe flux decline and affect the quality of the water produced (e.g. in ultrafiltration or reverse osmosis processes). Severe fouling may require intense chemical cleaning or membrane replacement. A second kind of fouling is the biological fouling, also called biofouling or marine fouling, which is the accumulation of microorganisms, plants, algae or animals on wetted surfaces. Biofouling is divided into microfouling — biofilm formation and bacterial adhesion — and macrofouling — attachment of larger organisms.

Finally, a third category of fouling can be identified, which appears on heat exchangers surfaces in contact with hot fluids. It is commonly called "scaling" or "precipitation fouling". This involves crystallization of solid salts, oxides and hydroxides from solutions. These are most often water solutions, but non-aqueous precipitation fouling is also known. Precipitation fouling is a very common problem in boilers and heat exchangers operating with hard water and often results in limescale.

In the following section, I will mainly discuss the mechanisms of action of dairy fouling on steel plates, which is a combination between precipitation fouling and protein fouling, and which remains a current unsolved issue in food-processing industries. As mentioned earlier, I had the opportunity to discover this issue through a partnership with INRA and Arcelor Mittal [27, 28] and I will develop further this collaboration in the incoming years.

IV-2 Dairy fouling mechanisms

Fouling in food-processing industries leads to the functional decline of thermal and hydrodynamic equipment performances, decreased product quality and lack of sterility as well as decrease of the surface hygiene [185]. These two last points particularly induce a severe sanitary risk by favoring the development of pathogenic agents. Food contamination creates an enormous social and economic burden on communities and their health systems. These serious consequences, as well as the environmental concerns, force the food-processing industries to take drastic and expensive cleaning measures [186]: in petrochemical industries, pipe cleaning is carried out once a year whereas in food-processing industries it has to be done at least once a day. These frequent cleanings of food-contact surfaces result in a pronounced economic impact since i) costs of chemical and energy required for cleaning are fairly high ii) time consuming is important iii) cleaning generates excess effluent.

Milk is a complex biological fluid composed of several components including whey proteins, calcium and lipids. Under 100°C, thermal treatments in heat exchangers induce fouling of the stainless steel surfaces, which proceeds essentially from the denaturation of whey proteins. Among them, β-lactoglobulin (BLG), accounting for half of the whey proteins [187, 188], is predominant in fouling ability of milk derivatives. These last twenty years, many research teams have tried to understand the mechanisms leading to dairy fouling of plate heat exchangers. The chemical composition of fouled layers has been characterized in various process conditions, and the main role of temperature was evidenced [189]. Indeed, two main chemical compositions of dairy fouling can be distinguished. Type A fouling is found under 100°C: it forms a rough and white deposit, composed of 50-60% proteins, half of which being BLG, as well as 30-35% minerals (essentially calcium and phosphate), and about 5% lipids [190]. Temperatures over 100°C lead to the formation of type B fouling, which is a grey and brittle deposit containing 70% minerals, 15-20% proteins, and around 5% lipids [191, 192]. The present study was carried out using conditions leading to type A fouling, like in industrial heat treatments of pasteurization or sterilization, where BLG is known to play the major role [190].

The mechanisms leading to fouling are nowadays intensively investigated. According to literature, the fouling phenomenon can be separated in two phases. The first step, namely the induction period [193, 194], corresponds *presumably* to the adsorption of a whey protein monolayer onto hot surfaces [195, 196], during which almost no change of heat transfer coefficient or pressure drop happens. The induction period is *assumed to* correspond to a nucleation phase which will gather the conditions for the attachment of subsequent whey protein layers [190, 196]. The successive layers *would be* bound together by means of proteic thiol groups and calcium [197], the latter acting like bridges between protein layers and thus limiting deposit erosion [198, 199]. In fact, mineral salts are usually present in milk, thus interacting with proteins both in the solution and on the substrate surface during fouling. Among the mineral salt, the interaction between Ca and BLG in the fouling solution has been the most studied. It has been recognized that calcium ions affect substantially the interactions between protein molecules [200] and have a strong impact on the BLG denaturation/aggregation mechanism [201-204]. However, these mechanisms describing *calcium ion - protein* interactions are still poorly understood at a molecular level. At the present time, there has been little published information which show how the calcium ions interfere with the substrate [205] and/or how the calcium allows making bridges and provide cohesion between elements of the material.

The aim of this work was thus to set a characterization procedure to generate a type A fouling, and to investigate particularly the role of calcium in the fouling growth, at the first instants of the fouling phase (when no fouling can be visually observed) and after longer fouling times.

To investigate the adhesion of foulant components on a 316L stainless steel surface, various analytical techniques were used: SEM, EPMA, Time-of-Flight Secondary Ion Mass Spectroscopy (ToF-SIMS) and Atomic Force Microscopy (AFM). Different fouling solutions and time of processing runs (two hours and 1 minute) were used to attempt to understand dynamic of fouling and the effects of material using a multiscale approach.

IV-2.1 Characterizations after long time fouling

The steel samples were submitted in a pilot heat exchanger (700L of solution) in INRA, during two hours, to two dairy solutions. The first solution (solution 1) contains only whey proteins dissolved in TH0 water. Calcium content was determined using an atomic absorption spectrophotometer and this analysis shows that the solution 1 contains 30 ppm calcium, issued from the reconstituted proteins: calcium was trapped when the proteins were dehydrated.

The second solution (solution 2) contains whey protein dissolved in water containing 90 ppm calcium. Again, absorption analysis shows a total calcium content of 120 ppm, the difference being again due to the calcium issued from the whey proteins. The samples obtained after two hours contact with both solutions are completely different (**Figure 85**).

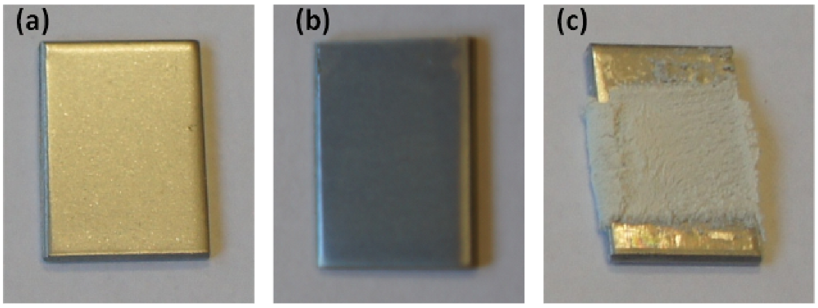


Figure 85. Comparison of the pictures of the samples before fouling (a) and after two hours fouling in solution 1 (b) and solution 2 (c).

After two hours fouling in the solution 1, the plate shows homogeneous blue reflects which are characteristic of a thin fouling layer; when the solution 2 is used, the fouling layer is completely different: it is very thick, white, and it seems very rough. Both fouling layers were then investigated using different techniques in order to look at their morphology and composition.

- <u>**Characterizations after two hours in solution 2**</u>

When the solution 2 is used, the fouling layer is very thick, white and seems very rough. A SEM analysis was carried out on the surface of the fouling layer (not shown here).This SEM image confirms the important roughness of the fouling layer, in which some voids and heterogeneities are also visible. Moreover, a complementary SEM picture was taken on the steel surface after having removed using a cutter the main part of the fouling layer (**Figure 86**).

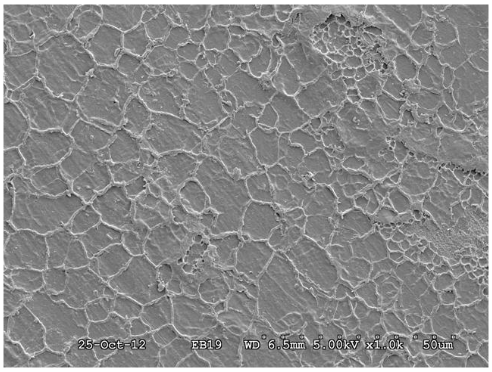


Figure 86. SEM(SE) analysis of the steel surface when the main fouling layer has been removed

This picture is very interesting as it proves that the fouling layer covers not only the plate surface but also fills in the inside of the grain boundaries. It means that the fouling is well anchored to the steel plate through the grain boundaries, which can explain the fact that it is then very difficult to remove the fouling during the cleaning procedures. The aim was then to investigate the chemical composition and morphology of the fouling layer, and EPMA was chosen as analyzing tool.

In order to look at the repartition of the calcium (Ca) and of the elements characteristic of the protein (S) and of the steel plate (Cr, Fe), X-Ray mappings of these elements on a fouling cross-section were carried out (**Figure 87**).

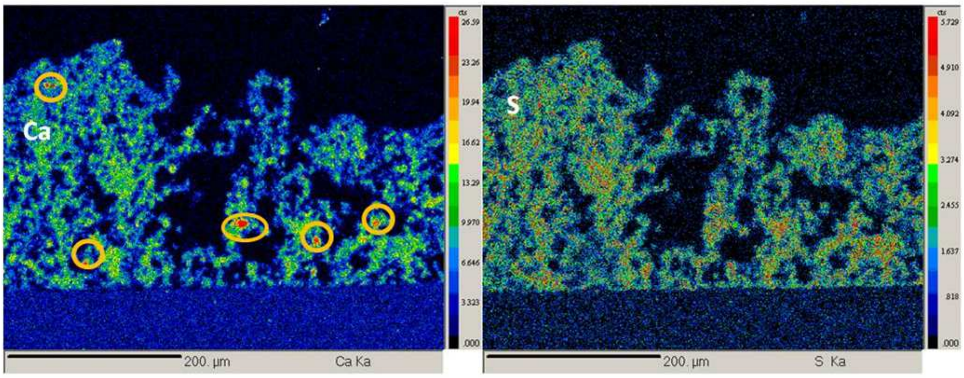


Figure 87. Ca and S X-Ray mappings of the cross section of the fouling layer

Looking at the Ca and S mappings (Cr and Fe not presented), it can be stated that the layer has developed following an arborescence growth. What is interesting is that both Ca and S are detected at the same places in the fouling layer. The protein is quite homogeneously dispatched. This is not really the case for calcium: some well visible big calcium aggregates (orange circles) are visible inside the layer.

➢ <u>Characterizations after two hours in solution 1</u>

When the solution 1 is used, the fouling layer is quasi-invisible to the naked eye, on the contrary to the previous deposit. The main difference with the virgin stainless steel consists in a difference of surface color: the plate shows homogeneous blue reflects which are characteristic of the thin fouling layer.

The fouling layer is too thin to hide the grain boundaries with the optical microscope resolution. It was also not possible to carry out a cross-section analysis using EPMA: the electron interaction volume is 1µm^3 and the layer is too thin to be detected. SEM analyses carried out on the surface of the fouling layer (not presented here) show that the grain boundaries are filled in with the fouling layer, consisting in small clusters, also covering the surface.

As a very thin fouling layer is obtained, it was however possible to carry out an AFM analysis on a 2µm*2µm surface to better investigate the deposit morphology and roughness (**Figure 88**).

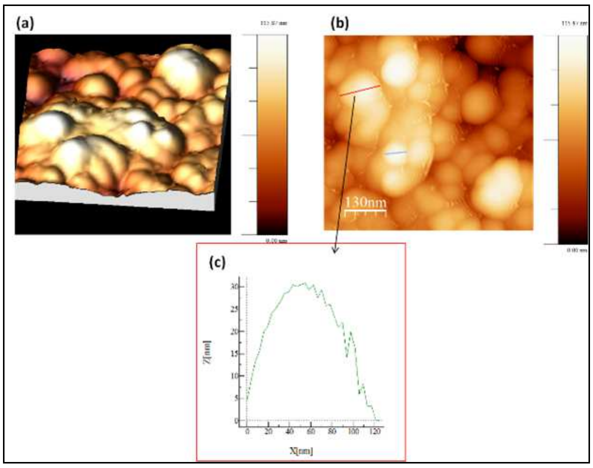


Figure 88. AFM pictures taken on the plane part of the 2µm*2µm surface: 3D picture (a), picture obtained using phase imaging (b) and particle profile (c).

The fouling layer is quite homogeneous, and the deposit covers the steel surface as well the steel fissures. It is composed of regular clusters covered with small particles.

The surface layer has a RMS roughness of 32 nm. The fouling layer is composed of a juxtaposition of clusters of different sizes varying from 100 nm inside the layer to 60 nm in extreme surface. The whey protein contains mainly β-Lactoglobulin (BLG). On heating BLG first dissociates into monomers which then partially-unfold before associating into clusters of around 60nm in diameter [206, 207].

The size of the clusters observed corresponds quite well to the unfolded protein. We can then assume that the proteins in unfolded states deposit on the steel surface during fouling and finally form a homogeneous thin fouling layer.

The different analyses of the fouling layers obtained after 2 hours fouling in the two different solutions show complete different behaviors. When whey proteins are dissolved in solution 1, the layer obtained is thin, homogeneous, with low roughness. On the contrary, when solution 2 is used, the layer is very thick (more than 200 µm), white, very rough, not homogeneous and shows a growth in arborescence.

The aim of the study was also to determine if the protein is the first to deposit on the surface or if a competition between calcium and protein occurs during fouling. To minimize the thickness of the fouling, it was decided to analyze samples after a fouling duration of only 1 minute in both fouling solutions. After 1 minute the fouling layers are quasi invisible to naked eyes. However they can be detected by AFM and ToF-SIMS.

IV-2.2 Characterizations after short time fouling

- **Characterizations after 1 minute in solution 1**

First of all, the fouling layer obtained after 1 minute using the solution 1 was investigated using AFM at different surface scales. The AFM images obtained for a 500nm*500nm surface are presented in **Figure 89**. The fouling layer obtained after 1 minute is well detected. It is homogeneous and seems to fit the roughness defects.

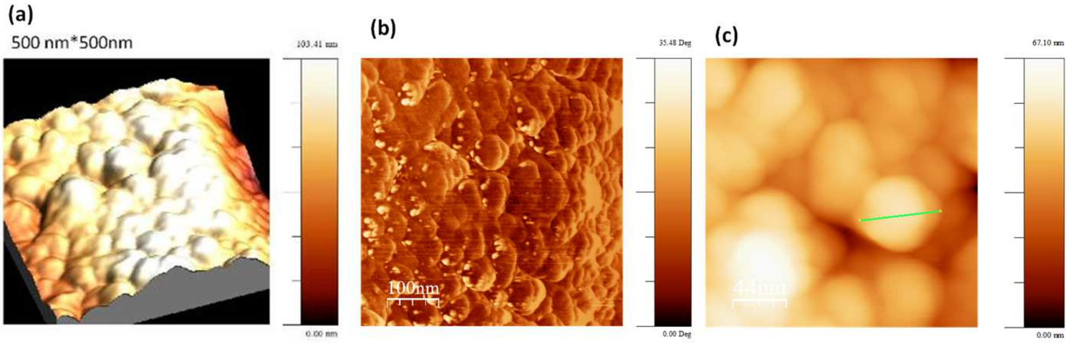


Figure 89. AFM images of the fouling layer obtained after 1 min in the solution 1 on a 500nm*500nm surface (a) 3D representation, (b) picture obtained using phase imaging (c) zoom on some particles.

The 3D picture taken on the 500 nm*500 nm surface (**Figure 89a**) shows a regular structure, with clusters (**Figure 89b**), probably issued from whey proteins, with sizes comprised between 40 and 60 nm (**Figure 89c**). The sizes of the particles obtained after 1 min fouling and on the extreme surface after 2 hours fouling are well correlated, which confirms the fact that the unfolded protein rapidly deposits on the steel surface.

ToF-SIMS was then carried out on the same sample on a 100 * 100 µm² surface. First of all erosion depth profiles from the surface layer to the steel plate were carried out (not shown here), obtained in positive polarity analyses. The main ions detected were $CNCs_2^+$ and Ca^+. The 3D reconstructed pictures obtained for Ca^+ and $CNCs_2^+$ ions from the burst alignment analysis are presented in **Figure 90**.

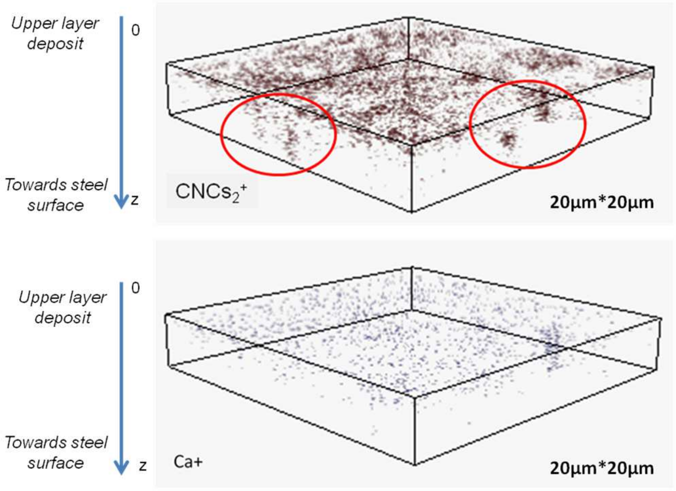


Figure 90. 3D ToF-SIMS reconstructed pictures of the fouling layer after 1 minute fouling in solution1

It is clear on those pictures that the protein is deposited quite homogeneously in significant amount on the surface, as well as inside the steel defects (red circles). The calcium that is detected comes from the dissolved protein. In this case, the trapped calcium does not seem to play a role on the fouling layer roughness, as a very homogeneous surface is observed by AFM.

The fouling layer obtained after 1 minute fouling when solution 2 is used has then been studied using the same techniques.

- **Characterizations after 1 minute in solution 2**

First of all the fouling layer obtained after 1 minute in the solution 2 was investigated using AFM at different surface scales. Looking at the **Figure 91**, the surface is covered with a homogeneous smooth layer. However, grapes of quite round particles appear on the surface, increasing the roughness.

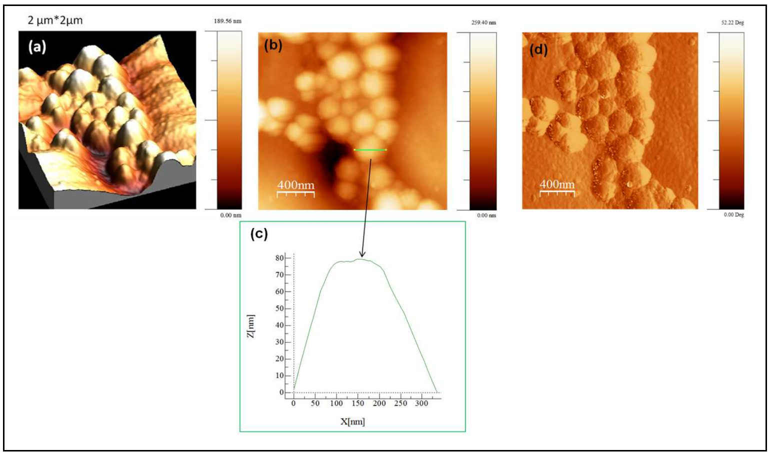


Figure 91. AFM images of the fouling layer obtained after 1 min in the solution 2 on a 2µm*2µm surface : 3D representation (a), imaging mode (b), particle profile (c) picture obtained using phase imaging (d).

Figure 91a shows that particules are numerous in the vicinity of steel surface defects. The sizes of particles (**Figure 91b**) were measured by profiles, and their sizes are comprised between 150 nm to 350 nm (**Figure 91c**). These particles are much bigger than the protein deposits (60 nm size after 1 min fouling), and looking at the previous EPMA results we assume that they are mineral aggregates of calcium-containing particles (this will be later discussed).

On the phase picture (**Figure 91d**), it seems that the particles show a certain surface roughness or that they are covered by a thin rough layer. This is why 500nm*500nm pictures were taken, both on the smooth part and on part containing particles with a further zoom on one particle. Looking at the picture of the particles on the 500nm*500nm surface (not presented here), these ones seem to be re-covered by a layer having the morphology of the protein deposit. When the size of one grain covering the particle is measured, the same protein cluster size (60 nm) is obtained. The hypothesis is that some particles constituted of calcium are deposed in the surface steel defects and that the protein recovers these particles.

However, looking at all these images, it is not possible to determine whether the calcium is firstly deposited on the steel plate and then covered by the protein, or whether the protein layer first appears and then the calcium particles deposit in the surface defects and then a subsequent layer of protein coats the calcium particles.

To address these questions, additional ToF-SIMS analyses were carried out on this layer to try to precise the chronology of apparition of the elements constituting this layer.

The 3D reconstructed pictures obtained for Ca^+ and $CNCs_2^+$ ions from the burst alignment analysis are presented in **Figure 92**.

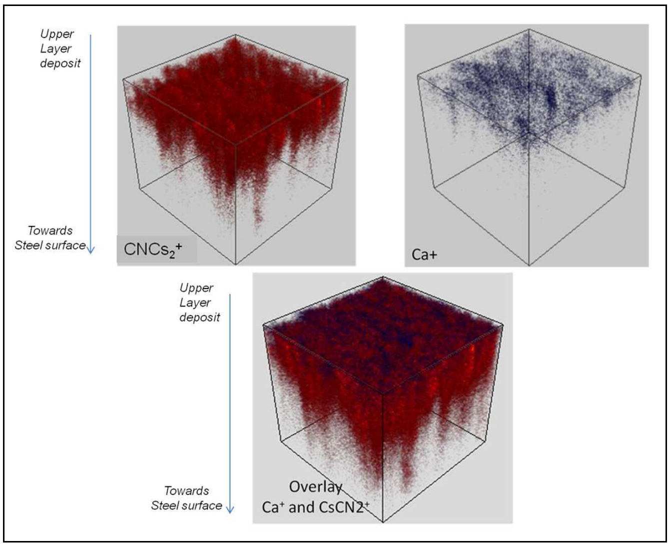


Figure 92. 3D ToF-SIMS reconstructed pictures of the fouling layer after 1 minute fouling in solution 2.

These images confirm the previous observations: it is clear that the protein (in red colour) is homogeneously present on the surface, as well as in the steel defects and inside the grain boundaries. The calcium (blue colour) is however mainly present at the surface of the fouling layer and also detected inside the grain boundaries but it can be noticed that it is mainly concentrated in the upper side of the grain boundary. It can also be observed that on the major part of the extreme surface calcium is re-covered by the protein, which is well correlated with the previous AFM observations.

IV-2.3 Mechanisms involved

The dynamic growth phenomenon of the fouling layers obtained in the case of a predominantly organic dairy fouling has never been visualized by such experimental approach in literature. This study, combining different surface analysis techniques, such as AFM, EPMA and ToF-SIMS, allows identifying very clearly the protein-based layer and the calcium-containing particles.

A schematic representation of the fouling growth mechanism in presence of whey protein dissolved in TH0 water is presented in **Figure 93**.

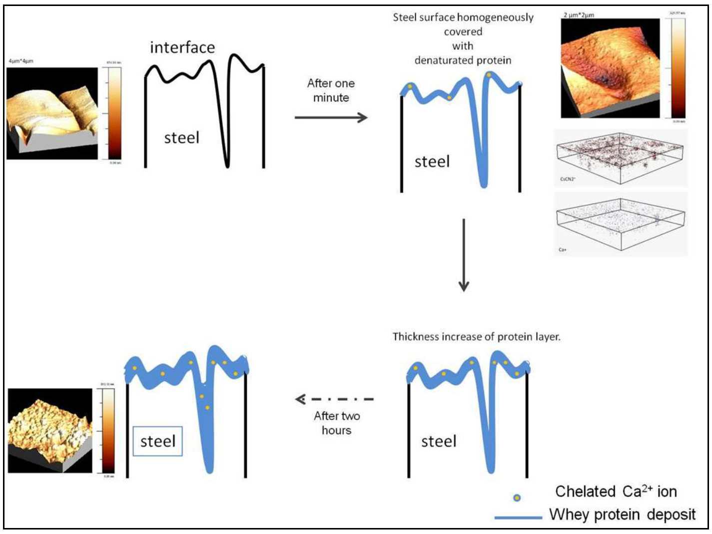


Figure 93. Schematic representation of the fouling growth mechanism in presence of whey protein dissolved in TH0 water

AFM after 1 minute fouling shows a deposit covering homogeneously the steel surface. The morphology of the deposit is similar after 1 minute and after 2 hours. It consists in the juxtaposition of small size (60 nm) clusters, coming from unfolded protein [206]. The 3D ToF-SIMS reconstruction pictures confirm that the protein homogeneously covers the steel surface and that it is also present inside grain boundaries. “Residual” calcium present in the whey protein is also detected by ToF-SIMS. It seems well dispersed in the protein layer and it does not affect the fouling layer roughness. It must be under its ionic form and chelated inside the protein layer. After 2 hours of fouling, the whole surface is covered and the grain boundaries are partly or completely filled in with the protein fouling layer.

The growth mechanism in presence of whey protein dissolved in the 90 ppm calcium containing water is different from the previous one. A schematic representation of this mechanism is shown in **Figure 94**.

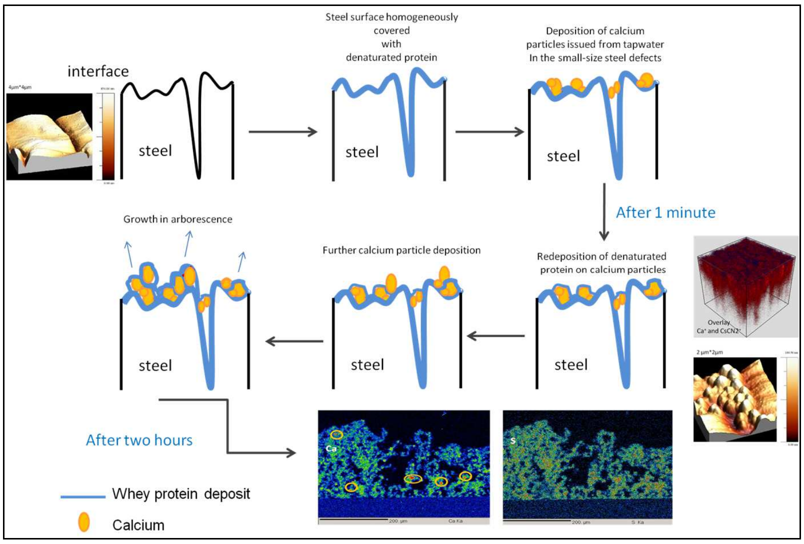


Figure 94. Schematic representation of the fouling growth mechanism in presence of whey protein dissolved in a 90 ppm calcium containing water.

SEM analyses after 2 hours fouling show a thick fouling layer, dispatched both on the surface and inside the grain boundaries. EPMA and SEM also allow detecting an important amount of calcium in the fouling layer. This observation is correlated with AFM observations after 1 minute fouling: on the protein layer (same morphology as when only whey proteins are present), grapes of big round particles are observed, corresponding to calcium-containing particles. These particles of important dimensions (150-300 nm) compared to the protein clusters are mainly dispatched in the steel surface valleys and are then covered again by protein. AFM and 3D reconstructed ToF-SIMS pictures show that calcium particles are also present in the grain boundaries, but not in the whole depth: they are mainly concentrated in the upper side of the grain boundary, being possibly trapped inside the protein layer before going further inside. The protein layer would be thus the first one being deposited during fouling. The presence of calcium containing particles in the fouling layer would increase the total roughness of the sample. This roughness increase favours further deposition/trapping of other calcium particles, thus creating preferential fouling pathways. This explains perfectly the arborescence structure observed by EPMA after two hours fouling and the fact that the layer obtained at the end is not very dense.

Some questions however remain, such as the composition of the calcium containing particles. An XPS study (not shown here) revealed that these particles are made of $CaCO_3$. A detailed literature investigation [208-214] allowed us to conclude that we were in presence of amorphous calcium carbonate (ACC) nuclei: the whey protein used contains amine groups as well as carboxylic acid and thiol groups, and according to the literature, the proteins can thus stabilize the amorphous calcium carbonate nuclei, preventing their further crystallisation in calcite/vaterite/aragonite. The fouling solution then contains both the unfolded proteins and the $CaCO_3$ nuclei stabilized by the protein, as well as protein aggregates. The ACC particles deposit preferentially inside steel roughnesses: once they are trapped in the surface defects and in contact with the protein layer, they cannot easily be dragged away by the water flow and remain on the protein layer. The part of the fouling due to the presence of mineral salts would be then favoured by mechanical factors (surface roughness) and chemical interactions (the ACC are dredged by the protein to the surface by ionic interactions).

The **Figure 95** summarizes all these hypotheses of fouling mechanism during the first minutes of experiment in our experimental conditions.

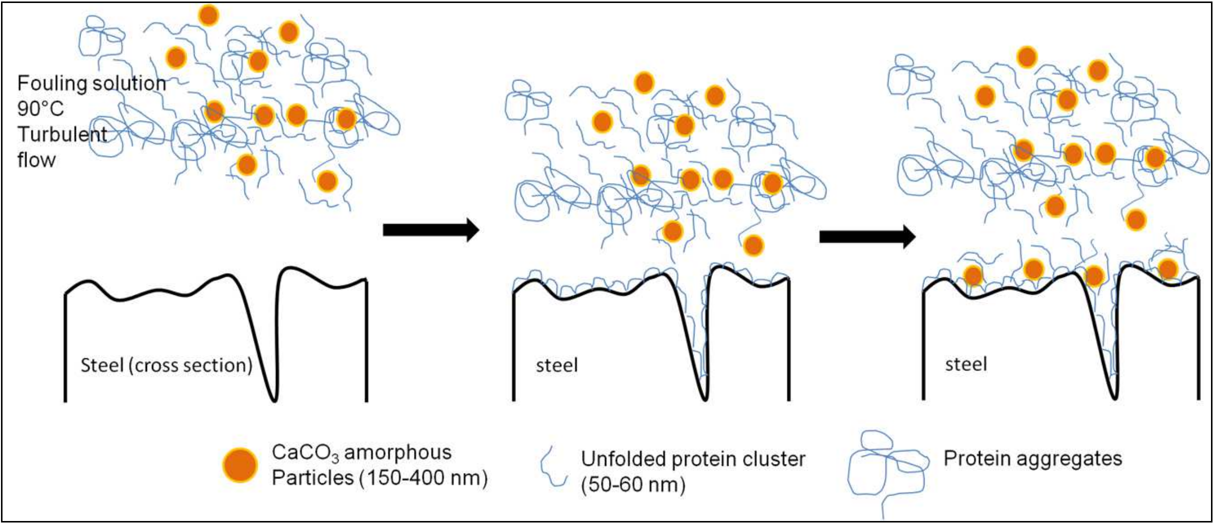


Figure 95. Deposition mechanism of the first fouling layers when solution 2 is used.

As the ACC particles are immediately covered by the protein, there is no time to initiate the crystallization of vaterite or calcite, and this explains why at the end of the fouling experiments only ACC is found in the fouling layer (XRD pattern not shown).

Through this study we managed to evidence a dairy fouling growth mechanism from the nano to the micro-scale in standard fouling conditions. We also pointed out the influence of the unfolded

proteins on the calcium carbonate deposition. It is the first time in literature that these nano-thick fouling layers are investigated and it constitutes a great advance in the anti-fouling field, as it allows understanding the influence of the material microstructure on the fouling deposition, and not only the influence of the material macrostructure, usually evaluated by surface energy and large-size roughness measurements.

Next steps will consist in modifying the substrate chemistry, the substrate roughness and the fouling solution composition to identify using the same characterization methodology the main factors influencing the fouling deposition.

Through these various studies based on the adhesion, aging and fouling issues, I thus evidenced the importance of the durability aspects of the functional properties of some materials or coatings when exposed to various constraints (light, immersion, temperature...). This topic also allowed me to develop my knowledges and experience in surface analysis: I had the opportunity to study the surface of materials from the nano-scale (through ToF-SIMS, XPS, AFM analyses) to the micro-scale (SEM, EPMA). I also could input in the lab some protocols and methodologies to study the mechanisms of aging of various materials at different scales.

General Conclusion and Outlooks

Through this manuscript, I have detailed the main different topics I have been involved in since my PhD. My PhD thesis, concerning the study of intumescent coatings applied on steel, allowed developing in the group the "Similitude, degradation and modeling" topic by the input of multiscale methodologies and of tests at a reduced scale correlated with large industrial tests. I still carry on participating to this topic developement through the input of other small scale tests, such as the "mini Steiner tunnel test" and the "small scale furnace test" for applications on composites or metals.

When I got a position in the group as assistant professor, I however mainly focused on the development of the topic entitled "Functional coating engineering". The aim was to develop various surface treatments – including intumescent coatings – to flame retard in particular polymers and textiles. I managed to start this topic first by internal studies (on PP, PC) and I then supported its developement through various academic and industrial projects. We have extended our concept to the fire protection of foam-core composites and we are currently developing this topic on the fire protection of skin structures of composites as well.

I meantime used or implemented other techniques in the laboratory allowing the deposition of thin functional coatings on various substrates. I mainly used low pressure RF cold plasma treatment and PECVD to reach these objectives. I also extended these last years the use of low pressure cold plasma techniques to other topics than fire retardancy: biomaterials, heavy metals remediation, glass treatments through various local, national and international collaborations and I will carry on some of these collaborations in the incoming years.

I am currently developing the RF low pressure technique to fire retard open-cells thermoplastic foams: fire retarding these foams in the bulk is an issue due to their manufacturing process, and surface treatment is a potential efficient solution to overcome this issue. The literature being extremely poor on the fire retardancy of foams by surface treatments, it opens the door to numerous developments.

Recently, through a collaboration with the CRP H.Tudor in Luxembourg, surface treatments carried out at atmospheric pressure (DBD plasma and LbL deposition) were also proven to be effective to fire retard polymer and textile substrates. Moreover, as it was also recently proven by Edwards et al. that the low pressure PIGP process can be successfully transferred to an atmospheric process [215] to flame retard cotton fabrics, I am thus convinced that atmospheric plasma can be of great benefit to develop the "Functional engineering coatings" topic in the group and that it can be used for various applications as well (e.g. biomaterials development etc.). This is why the group recently decided to invest in two types of atmospheric plasma allowing to clean/functionalize/modify various substrates. I also started a collaboration with the plasma manufacturer (AcXys Technologies, Grenoble, France) to implement novel functions on our machines depending on the topics we are working on. I will be in charge in the incoming years to develop intensively these technologies in the laboratory mainly for fire retardant purpose.

The functional coatings developed, whatever their nature and purpose, are applied on various substrates and are thus submitted to different durability constraints. They have to adhere on surfaces, they have to resist to factors affecting their chemistry or their mechanical resistance and they have to remain active even when put in contact with different kinds of fluids. I am convinced that a coating or material development has to be associated with this functional durability topic. I have observed many times and in various applications the influence of these phenomena on the efficiency of coatings and I am currently in charge of this topic in the group.

Since two years, I have started to study the aging of intumescent coatings for fire resistance (on steel) or fire retardancy (on polymers) applications. First results are promising and show that these coatings or their adhesion to the substrate they protect are not durable when submitted to some constraints. As literature is very poor in this field, I will further develop this topic in the group, and more particularly the study of the mechanisms leading to the loss of functional properties: we will look at the chemical or physical aging mechanisms induced by UV-light exposure and humidity or immersion on a coating composition and adhesion on various substrates (metal, polymer, composite, textile…). The second point I will investigate in the frame of this "Functional durability" topic is the study of potential solutions against aging. In fact, we aim at studying not only the influence of aging on the functional properties of a coating but also the possible solutions that could be implemented to limit this phenomenon. As E.D. Weil reported it in a recent state of the art review on the fire protective and flame retardant coatings [216], various possible solutions could be considered, such as the encapsulation of sensitive fire retardant additives, the use of top-coats, the development of self-priming formulations, the use of multi-layers fire retardant coatings, the synthesis of less sensitive fire retardant additives… We are for example currently investigating the role of various top coats applied on intumescent coatings, to look at their possible influence on the fire protective effect of the coating and on their influence on aging protection. Meantime, we also work on enhanced pre-treatment processes to favor adhesion of water-based coatings on polymer substrates. In particular, atmospheric plasmas are considered and their influence on the activation and functionalization of the polymer substrates will be carefully investigated. Finally, as I aim at developing intensively the atmospheric plasma technologies in the group, I intend to associate the development of the functional coatings obtained to a study of the durability of their properties.

To enlarge my research activities and to apply to other topics the competences developed in fire retardancy, I have extended this part of the “functional durability” topic to the study of aging phenomena appearing at the extreme surfaces and/or at the interfaces. One example concerns the study of nano-thick fouling layers on stainless steel surfaces. We recently obtained very promising results and to support this topic development and to complement our internal work I submitted as coordinator in January 2013 an ANR young researcher project entitled “INTERFOUL” (Multiscale fundamental understanding of dairy fouling adhesion and growth mechanisms at an interface: towards elaboration of antifouling surfaces) in partnership with INRA, with the regional platform of analyses of Lille University (PRAS) and with the “Institut de Recherche Interdisciplinaire” (IRI) which is currently being reviewed.

Annex 1: Teaching activities and responsibilities

➢ Teaching activities

- **Courses / Tutorials in the first and second year promotions** of apprenticeship training students in IUTA, Chemistry department.

  First year (44h) : Fluid Dynamics
  Characteristic curves of a pump
  Membrane separation processes
  Heat transfers

  Second year (44h) : Unit operations in chemical engineering
  (Distillation, liquid-liquid extraction)
  Reactors

- **Tutorials** in chemical engineering, IUTA, Chemistry department, students in classical training.

  First year (36h) : Fluids mechanics
  Characteristic curves of a pump
  Heat transfers

- **Practical works (PW)** for first year students in IUTA, Chemistry department, classical training.

  9 PW (36h) : Pressure loss
  Characteristic curves of a pump
  Characteristic curves of a circuit
  Pitot Tube / Reynolds number
  Viscosity measurements of low-viscous liquids
  Viscosity measurements of high-viscous liquids
  Water flow in a tank
  Ultrafiltration
  Reverse osmosis

- **Practical works for second year students in IUT A**, Chemistry department, classical training

  7 PW (56h) : Methanol-water liquid-vapor equilibrium
  Discontinuous distillation
  Continuous distillation
  Liquid-liquid extraction
  Absorption in a pack column (water/air)
  Thermal heat exchanger
  Azeotropic distillation-decantation

- **Teacher** in the professional license « Chemical and Pharmaceutical industries » IUT A

  18 h: CV redaction, bibliographic search engines, literature monitoring

- **Practical works for students in professional licence** (Chemical and Pharmaceutical Industries), IUTA, Chemistry department.

  2 PW (16h) : Low pressure cold plasma surface treatment
  Flame-treatment of polymers and glasses

- **Supervision and animation of a theme day meeting**, master of Biomaterials, Lille 2 University

  8 h: applications of low pressure cold plasmas in biomaterials
  (Theory, practical work, conferences)

- **Responsibilities in Lille University**

2013	Responsible for the demand of habilitation of a professional bachelor's degree entitled « Innovative processes and materials », IUT A, Lille University (opening September 2014)
2011-now	Facilitator of the CNU 62 section of Lille University assistant professors.
2010-now	Responsible for the teaching coordination of chemical engineering courses for the apprenticeship training (first and second years) in IUT A de Lille, chemistry department.
2009-now	First-aid rescue worker certificate (SST)
2008-2011	Co-supervisor of the bachelor's degree (Chemical and Pharmaceutical Industries), option PTSFRF (Surface Treatment Processes and Formulation of Functional Coatings)
2008-now	Pedagogical supervisor of the process engineering hall in IUT A, chemical department. Responsible for extensive renovation and for maintenance of this building (100 k€ investments since 2008). Responsible for teaching coordination and training of teachers from other departments who have to teach in the process engineering hall.

Annex 2: List of contracts and projects

- **2011-2014: 3 years project funded by FNR Luxembourg**, in partnership with CRP H. Tudor and G. Lippmann, LAPLACE (Toulouse) and the "Institut de Chimie de Clermont Ferrand". "FRCoatings: New nanocomposite coatings for fire retardant applications".
  2 PhD students (M. Kadir Apaydin and M. Florian Hilt) hired in that frame.
  ***1 paper* [24]**
  Scientific co-direction of a PhD student (Kadir Apaydin) - solid-state NMR expertise – Quarterly meetings

- **2011-2014: 3 years FUI contract** - **DEPOLTEX project** in partnership with IDRA environnement, Nordlys, Baudelet, Affitex, Dylco, Mines de Douai, IFTH, ENSAIT.
  "Eco-conception and development of depolluting geotextiles to treat marine and fluvial sediments".
  1 PhD student (Mme Marianne Vandenbossche) hired in that frame.
  ***1 paper*[20], *1 paper submitted* [19] and *1 review in revision* [23]**
  Scientific cold plasma expertise – Quarterly meetings

- **2011-2014: 3 years FUI project - ATMOSVERRE project** in partnership with ARC International, Saverglass and AcXys technologies labeled by competitivity cluster MAUD.
  "Development of atmospheric cold plasma for glass industry".
  1 Post-doctoral student (M. Nicolas Renaut) hired in that frame.
  Confidential project (***no paper, no patent***)
  Scientific co-direction of a Post-Doctoral student - Monthly meetings

- **2011-2014: 3 years CIFRE contract** with **ARC International**
  "Deposition of metallic oxide coatings by atmospheric plasma".
  1 PhD student (M. Hassan HAMZE) hired in that frame.
  Confidential project (***1 paper submitted* [17]**)
  Scientific co-direction of a PhD student - Quarterly meetings

- **2009-2014: 4 years FUI project - DRAWSPEEDGLASS Project** in partnership with **Saverglass** labeled by competitivity cluster MAUD.
  "Development of organic coloring on glass at high speed".
  1 PhD student (Mlle Clémence Vallet) and 2 Post-doctoral students (Mlle Mathilde Ferrand and Mme Marion Collinet) hired in that frame.
  Confidential project ***(1 paper submitted* [18]*).***
  Scientific co-direction of the two Post-doctoral students - Quarterly meetings

- **2009-2011**: **Co-responsible with S.Degoutin of a 2 years young researcher project (CPER)** thanks to a Fédération Chevreul financial support.
  "Biocompatibilization and immobilization of biomolecules on polypropylene nonwovens".
  2 master students (Thibaut Pinalie and Jonathan Moris) hired in that frame.
  1 paper* [16] , *1 paper in preparation
  Project management – scientific development
  Proposal of a young researcher ANR project in 2013 (coordinator S.Degoutin) on that subject, currently reviewed.

- **2009-2011**: **18 months ARCir contract** (Action de Recherche Coordonnée d'Initiative Régionale) in partnership with **INRA** (Institut National de Recherche Agronomique) and **ARCELORMittal**. “Bacterial and dairy fouling - Consequences in terms of surface hygiene”.
  Responsible for axe 2: “Influence of the flow rate conditions and of the interface physico-chemistry and properties on adhesion/cohesion of dairy fouling on heat exchanger surfaces”.
  1 master student (M. Hassan Hamze) **hired in that frame**.
  ***1 paper* [27] , *1 paper submitted* [28]**
  Proposal of a young researcher ANR project in 2013 on that subject, currently reviewed.

- **2008-2011**: Participation in **3-years TEXTHERM FCE project in partnership with** Dylco, Amkey Management, Duflot, Jehier, Kermel, Alstom Transport, Polyacrylate SL, IFTH, CREPIM and ENSCL.
  “Innovative light thermal screens based on textile structures for automotive, rolling stock and airplanes”.
  ***1 paper* [14]**
  Cold plasma expertise and experiments in the « surface treatment » task.

- **2008**: 6 months contracts with **CLAYRTON'S** and **AGC Glass** (Belgium).
  Scientific co-direction of bachelor trainees – Monthly meetings – redaction of reports

- **2006-2010**: **4 years FCE project – DECOUVERRE project -** with **Arc International**.
  “Organic decoration on glass”.
  1 PhD student (Mlle Mathilde Ferrand) hired in that frame (2006-2009) and same student hired as post-doctoral position in 2009-2010.
  Confidential project (***no paper, no patent***)
  Scientific co-direction of the post-doc student – Quarterly meetings

- **2007-2010**: **3 years CIFRE contract with Rhodia**.
  “Improvement of fire retardancy of polyamide 6,6”.
  A PhD student (Mlle Hélène Gallou) hired in that frame.
  Confidential project (*2 patents* [10, 13]*, 1 paper* [12], *1 paper submitted* [11])
  Scientific co-direction of a PhD student – Quarterly meetings

- **2006-2008: FANsBAMed project** in partnership with the “Groupe de recherche sur les Biomatériaux” of Lille 2 university and CERLA.
  "Functionalization, Activation and Nanostructuration of Biomaterials Surfaces for Medical Applications".
  1 post-doc student (M.Ousmane Lam) hired in that frame.
  ***1 paper* [15]**
  Scientific co-direction of a Post-Doctoral student

- **2003-2006**: **3 years contract with Akzo Nobel (UK)**.
  “Study of the mechanisms of fire resistance of intumescent coatings – Application to epoxy resins”.
  Confidential project (***5 papers* [1-5]**)
  PhD student - Quarterly meetings and annual reports

Annex 3: List of students (PhD, Post-Doc, master) co-supervized

➢ Co-supervision of PhD students

2011-2014: APAYDIN Kadir (New nanocomposite coatings for fire retardant applications)
Funding: Luxembourg FNR
PhD supervisor: Pr. Serge BOURBIGOT
Supervision rate: 50%
Publications: [24]

2011-2014: ALOGAILI Ghassan (Development of superhydrophobic coatings on stainless steel by atmospheric plasma treatment to limit dairy fouling – fundamental interactions between surface and fouling)
Funding: Scholarship from Irak.
PhD supervisor: Pr. Michel TRAISNEL
Supervision rate: 50%
Publications: [27, 28]

2011-2014: HAMZE Hassan (Deposition of metallic oxide coatings by atmospheric plasma)
Funding: CIFRE ARC International
PhD supervisor: Michel TRAISNEL
Supervision rate: 50%
Publications: [17]

2008-2012: KACEM Imen (Modification of biological properties of polyester by physical pre-treatments and by acrylic acid grafting) – defended 15/03/2012.
Funding: Tunisian scholarship
PhD supervisor: Pr. Bernard MARTEL – Pr. Sadok ROUDESLI (Tunisie)
Supervision rate: 30%
Publications: [15, 16]

2007-2011: ZOBRIST Cédric (Elaboration and transformation of titanium-based biomaterials with therapeutic agents controlled-release properties) – defended 02/12/2011.
Funding: CNRS-Region
PhD supervisor: Pr. Patrice WOISEL
Supervision rate: 40%
Publications: [21, 22]

2007-2010: GALLOU Hélène (Improvement of fire retardancy of polyamide 6,6) – defended 01/04/2010.
Funding: CIFRE Rhodia
PhD supervisor: Pr. Charafeddine JAMA
Supervision rate: 50%
Patents: [10, 13]
Publications: [11, 12]

➢ Co-supervision of post-doctoral students

2012-2013: COLLINET Marion (Development of a hot-melt ink for silkscreen printing)
Funding: DRAWSPEEDGLASS FUI project
Co-supervision: M.Traisnel, U.Maschke

2011-2013: RENAUT Nicolas (Deposition of oxide metallic coatings by atmospheric plasma)
Funding: ATMOSVERRE FUI project
Co-supervision: M.Traisnel

2010: FERRAND Mathilde (Development of a UV-curable resin for glass)
Funding: DRAWSPEEDGLASS FUI project
Co-supervision: M.Traisnel, U.Maschke

2009: FERRAND Mathilde (Optimization of an organic coating for glass)
Funding: DECOUVERRE FCE project
Co-supervision: M.Traisnel

2007: LAM Ousmane (Titanium functionalization by cold plasma treatment)
Funding: FANSBAMed project
Co-supervision: M.Traisnel

➢ Co-supervision of master students

2013: TOMSON Alban
Development of a small scale fire test to predict the behavior of composites in a fire
Co-Supervision: F. Samyn (50%)

2013: LESAFFRE Nicolas
Study of intumescence mechanisms and weathering of intumescent formulations applied on polymers
Supervision: 100%

2013: MORIS Jonathan
Surface modifications of biomaterials by atmospheric cold plasma
Co-Supervision: S.Degoutin (50%)

2012: PINALIE Thibaut
Immobilization of bioactive molecules on polypropylene nonwoven textiles
Co-Supervision: S.Degoutin (50%)

2012: MACHADO Lorena
Study of the weathering of an epoxy based intumescent coating
Supervision: 100%

2011: HAMZAOUI Asmae
Developement of sol-gel superhydrophobic coatings for stainless steel
Co-Supervision: S.Bellayer (50%)

2011: FUERST Carolin
Development and optimization of intumescent coatings for plastics
Supervision rate: 100%

2010: HAMZE Hassan
Development of anti-fouling coatings for stainless steel surfaces
Co-Supervision: G.Delaplace (INRA) (50%)

2010: COQUELLE Matthieu
Optimization of acrylic acid grafting on PET textiles
Co-supervision: N.Blanchemain (Lille2 Univ.) (50%)

2009: AIT HAMMOU R'Kia
Acrylic acid grafting on cold plasma pre-treated PET
Co-supervision: N.Blanchemain (Lille2 Univ.) (50%)

2008: LEGIER Olivier
Characterization of PET pre-treated by cold plasma
Co-supervision: N.Blanchemain (Lille2 Univ.) (50%)

Annex 4: List of papers and communications

- **Peer-reviewed papers in international journals**

1. **C.Vallet, M.Collinet, M. Jimenez, U.Maschke, M. Traisnel,** Effects of surface treatments on adhesive bonding properties of urethane-acrylate coatings on tin oxide model substrates, ***submitted in International Journal of adhesion and adhesives***, **march 2013**.

2. **S. Bourbigot, P. Bachelet, F. Samyn, M. Jimenez, S. Duquesne**, Intumescence as method for providing fire resistance to structural composites: application to PET foam sandwich structured composite, ***submitted in Composite Interface,*** **feb. 2013, under revision**.

3. **H.Hamze, M.Jimenez, D. Deresmes, A. Beaurain, N. Nuns, M. Traisnel,** Influence of processing gases on the properties of atmospheric cold plasma SiOx coatings, ***submitted in Thin Solid Films,*** **feb. 2013.**

4. **S.Duquesne, M.Jimenez, S.Bourbigot,** Aging of the flame retardant properties of Polycarbonate and Polypropylene protected by an intumescent coating***, accepted in Journal of Applied Polymer Science*****.**

5. **M.Vandenbossche, M.Casetta, M.Jimenez, S. Bellayer, M.Traisnel,** Cysteine-grafted Nonwoven Geotextile: A New and Efficient Material for Heavy Metals Sorption, ***submitted in Journal of Environmental Management,*** **feb. 2013.**

6. **M.Jimenez, N. Nuns, S. Bellayer, D.Desresmes G. Alogaili, G.Ronse, M.Collinet G. Delaplace, M.Traisnel**, Fundamental comprehension of the interfacial behavior of dairy fouling at a stainless steel surface, **submitted in *Journal of Colloid and Interface Science*, accepted.**

7. **M.Jimenez, S.Duquesne, S. Bourbigot,** Enhanced fire retardant properties of glass-fibre reinforced Polyamide 6,6 by combining bulk and surface treatments: toward a better understanding of the synergistic interactions between aluminium phosphinate and an intumescent coating, ***submitted in Polymer Degradation and Stability, accepted*****.**

8. **M.Vandenbossche, M.Jimenez, M.Casetta, M.Traisnel,** Biomolecules for the Trapping of Heavy Metals in the Environment: A Review, ***submitted in Critical Reviews in Environmental Science and Technology, under revision***.

9. **M.Jimenez, S.Bellayer, B.Revel, S.Duquesne, S.Bourbigot**, Weathering of an epoxy based fire protective intumescent coating in different environments, ***Industrial and Engineering Chemistry Research, 2013,*** 52(2), 729-743.

10. **K. Apaydin, A. Laachachi, V. Ball, M. Jimenez, S. Bourbigot, V. Toniazzo, D. Ruch** Polyallylamine-Montmorillonite as Super Flame Retardant Coating Assemblies by Layer-by-Layer Deposition on Polyamide, ***Polymer degradation and Stability***, **2013,** 98(2), 627-634.

11. **M. Vandenbossche, M. Jimenez, M. Casetta, S. Bellayer, A. Beaurain, S. Bourbigot, M. Traisnel,** Chitosan-grafted nonwoven geotextile for heavy metal sorption in sediments, ***Reactive and Functional Polymers***, **2013,** 73, 53-59.

12. **S.Bourbigot, P.Bachelet, M.Jimenez, S. Duquesne**, Intumescent coating providing fire resistance to materials. ***European Coatings Journal*, 2012, Vol. p.28-33**.

13. **M.Jimenez, H.Gallou,S.Duquesne, C.Jama, S.bourbigot, X.Couillens, F.Speroni** "New routes to flame retard PA6,6 for electrical applications", ***Journal of Fire Science***, **2012,** 30(6), 535-551**.**

14. **M.Jimenez, H.Hamze, A.Allion, G.Ronse, G. Delaplace, M.Traisnel**, Antifouling stainless steel Surface: competition between roughness and surface energy, ***Materials Science Forum,* 2012**, ***Vol. 706-709*, p.2523-2528**

15. **M. Jimenez, S. Duquesne, S. Bourbigot,** Fire protection of polypropylene and polycarbonate by intumescent coatings**. *Polymers for Advanced Technology*, 2012, 23(1), p.130-135.**

16. **S. Degoutin, M.Jimenez, M. Casetta, S. Bellayer, F. Chai, N. Blanchemain, C. Neut' B. Martel, M. Traisnel**, Optimization of cold plasma induced graft copolymerization of acrylic acid onto polypropylene (PP) nonwoven textiles for anticoagulant and antimicrobial application, ***Biomedical Material*, 2012, *Vol. 7(3), p.035001***.

17. **N. Blanchemain, M.R. Aguilar, M. Jimenez, F. Chai, E. Jean-Baptiste, A. El-Achari, B. Martel, H.F. Hildebrand, J. San Roman**, Selective Biological response of Human Pulmonary Microvascular Endothelial Cells (HPMEC) and Human Pulmonary Artery Smooth Muscle Cells (HPASMC) on Cold plasma modified polyester vascular prostheses, ***Biomedical Material,* 2012*, Vol.6, p.065003***,

18. **C. Zobrist, J. Sobocinski, J. Lyskawa, D. Fournier, V.Miri, M. Traisnel, M.Jimenez, P. Woisel,** Functionalization of titanium surfaces with polymer brushes prepared from a biomimetic RAFT agent, **2011**, ***Macromolecules***, ***Vol.44(15), p.5883-5892***.

19. **M. Jimenez, S. Duquesne, S. Bourbigot,** Keeping cool in the mass-Waterborne intumescent coatings can prevent thermoplastics from burning**. *European Coatings Journal*, 2010, *p.26-31*.**

20. **M.A. Watson, J. Lyskawa, C. Zobrist, D. Fournier, M. Jimenez, M. Traisnel, L. Gengembre, P. Woisel,** A "clickable" titanium surface platform**, *Langmuir,* 2010, *26, p.15920-15924*.**

21. **M. Jimenez, S. Bellayer, S. Duquesne, S. Bourbigot,** Improvement of heat resistance of high performance fibers using a cold plasma polymerization process. ***Surface and coatings Technology*, 2010, *205, p.745-758***

22. **M.Jimenez, S. Duquesne, S. Bourbigot,** Kinetic analysis of the thermal degradation of an epoxy based intumescent coating. ***Polymer Degradation and Stability,* 2009*, 94(3), p.404-409.***

23. **S. Duquesne, M. Jimenez, S. Bourbigot,** Fire retardancy and fire protection of Materials using Intumescent Coatings – A versatile solution? ***Royal Society of Chemistry book: Fire retardancy of Polymers - new strategies and mechanisms,* Eds: R. Hull, B. Kandola*, 2008, Chap.16: p.240-252.***

24. **M.Jimenez, S. Duquesne, S. Bourbigot,** Multiscale experimental approach for developing high-performance intumescent coatings. ***Industrial and Engineering Chemistry Research,* 2006*, 45, p. 4500-4508***

25. **M.Jimenez, S. Duquesne, S. Bourbigot,** Characterisation of the performance of an intumescent fire protective coating. ***Surface and Coatings Technology,* 2006*, 201 (3-4), p.979-987*.**

26. **M.Jimenez, S. Duquesne, S. Bourbigot,** Intumescent fire protective coating: toward a better understanding of their mechanism of action. ***Thermochemica Acta,* 2006*, 449, p.16-26*.**

27. **M.Jimenez, S. Duquesne, S. Bourbigot,** High throughput fire testing for intumescent coatings. ***Industrial and Engineering Chemistry Research,* 2006*, 45(22), p.7475-7481.***

- **Patents**

1. **H. Gallou, M. Jimenez, C. Jama, R. Delobel**, Polyamide based fireproof article including a coating formed by plasma treatment, WO/ 2012/084955, **2012**, ***Brevet*** déposé par la société Rhodia.

2. **H. Gallou, M. Jimenez, S. Duquesne, C. Jama, R. Delobel S. Bourbigot,X. Couillens,** Fireproof polyamide molded articles having an intumescent coating **, 2011,** WO/2011/045426,KR 2012066656, EP 2488574, CN 102656217, ***Brevet*** déposé par la société Rhodia.

- **Technical articles**

1. **M.Jimenez, C. Reti, M. Casetta, S. Duquesne, S. Bourbigot**, "Nuove Techniche di lavorazione dei rivestimenti ritardanti di Fiamma, **Part II** ", ***Pitture e Vernici-European Coatings*, Vol.4, 2011, p.7-12.**

2. **M.Jimenez, C. Reti, M. Casetta, S. Duquesne, S. Bourbigot**, "Nuove Techniche di lavorazione dei rivestimenti ritardanti di Fiamma, **Part I** ", ***Pitture e Vernici-European Coatings*, Vol.3, 2011, p.25-29.**

3. **M.Jimenez, C. Reti, M. Casetta, S. Duquesne, S. Bourbigot**, "Nuove Techniche di lavorazione dei rivestimenti ritardanti di Fiamma", **Part II*, Via Mare by Sea*, Vol.11, 2011, p.23-30.**

4. **M.Jimenez, C. Reti, M. Casetta, S. Duquesne, S. Bourbigot**, "Nuove Techniche di lavorazione dei rivestimenti ritardanti di Fiamma, **Part I**, ***Via Mare by Sea*, Vol.2, 2011.**

5. **M. Jimenez, N. Blanchemain, M. Traisnel,** Le plasma froid : une nouvelle technologie au service du biomédical**, *mensuel « Tout Prévoir », n°412,* june 2010, *p.37-38.***

6. **S. Bellayer, M.Jimenez, F. Chai, M. Traisnel,** Analyse par microsonde électronique d'implants et prothèses explantés**, *mensuel « Tout Prévoir »*, *n°412*, june 2010, *p.24-25*.**

- **Oral communications (peer-reviewed proceedings)**
  (*Remark: the first name indicated is the speaker*)

1. **M. Jimenez, S. Bellayer, S. Duquesne, S. Bourbigot,** Weathering of intumescent coatings, ***24rd Annual Recent Advances in Flame Retardancy of Polymeric Materials (BCC research Flame conference), USA, 10 pages, may 2013.***

2. **M. Vandenbossche, M. Jimenez, M. Casetta, M. Traisnel,** grafting of cysteine on geotextiles to trap heavy metals from polluted solutions**, *INTERSOL 2013, Lyon, 7 pages, march 2013*.**

3. **S. Degoutin, M.Jimenez, M.Casetta, S.Bellayer, F.Chai, N. Blanchemain, C. Neut, B. Martel,** Nonwoven polypropylene textiles with anticoagulant and antimicrobial properties**, *CIRAT-5, Monastir, Tunisie, p. 72-75, January 2013.***

4. **M. Vandenbossche, M. Jimenez, M. Casetta, S. Bellayer, S. Bourbigot, M. Traisnel,** Heavy metal sorption on PP nonwoven geotextiles grafted with biomolecules**, *CIRAT-5, Monastir, Tunisie, p. 311-314, January 2013***

5. **M.Vandenbossche, M.Jimenez, M.Casetta, S.Bellayer, S.Bourbigot, M.Traisnel** Sorption of heavy metals on a chitosan-grafted-polypropylene nonwoven geotextile***, ICHMET 2012, Rome, Italie, september 2012, 5 pages***.

6. **S.Bourbigot, M. Jimenez, S. Duquesne,** Coatings for providing low flammability to polymeric materials: an overview, ***2nd International Symposiumon on Flame - Retardant Materials and Technologies (ISFRMT), Chengdu, Chine, september 2012, 4 pages.***

7. **S.Bourbigot, P.Bachelet, F.Samyn, M.Jimenez, S.Duquesne**, Intumescence as method for providing fire resistance to composites, ***15th.european conference on composite materials, june 2012, Venise, Italie, 7 pages.***

8. **M.Jimenez, S.Duquesne, S. Bourbigot,** Protective Coatings for reaction and resistance to fire of materials, ***COSI 2012, june 2012, Hollande.p.87-91***

9. **S.Bourbigot, M.Jimenez, S. Duquesne**, New trends in flame retardancy of engineering plastics, ***23rd Annual Recent Advances in Flame Retardancy of Polymeric Materials (BCC research Flame conference), may 2012, USA, 10 pages***.

10. **S.Bourbigot, P. Bachelet, M. Jimenez, S. Duquesne,** Intumescent coating providing fire resistance to materials***, European Coating2012-Fire retardancy-Berlin, march 2012, p.28-33.***

11. **M.Jimenez, H.Hamze, A. Allion, G. Ronse, G. Delaplace, M. Traisnel,** Antifouling stainless steel surface: Competition between roughness and surface energy**, *THERMEC 2011,august 2011, Québec, p.2523-2529***

12. **S.Bourbigot, B. Gardelle, M. Jimenez, V. Rerat, S. Duquesne**, Silicone-based coatings for reaction and resistance to fire of polymeric materials, ***22th BCC Conference - Recent Advances in Flame Retardancy of Polymeric Materials, Stamford, États-Unis, May 2011***

13. **I. Kacem, R. Ait Hammou, N. Blanchemain, M. Jimenez, F. Chai, M. Majdoub, M. Traisnel, H. F. Hildebrand, B. Martel**, Functionalization of PET fabric via cold plasma for biomedical applications, ***Proceedings of International Conference of Applied Research in Textile, CIRAT-4, Monastir, december 2010*, 4 pages.**

14. **S. Bourbigot, G. Fontaine, M. Jimenez, S. Duquesne,** Intumescence: a concept for designing novel flame retarded and flame resistant materials***, 2010' International Symposium on Flame - Retardant Materials and Technologies (ISFRMT),Chengdu, Chine, september 2010, 4 pages***

15. **M. Jimenez, S. Duquesne, S. Bourbigot, C. Reti, M.Casetta,** Novel approaches for processing flame retardant coatings***, Proceedings of European coatings 2010-Fire retardancy- Berlin, june 2010, p.69-85.***

16. **M. Traisnel, M. Jimenez, I. Kacem, N. Blanchemain, F. Chai, M.R. Aguilar, B. Martel, J. San Roman, H.F. Hildebrand –** Immobilization of therapeutic molecules onto polyester vascular prostheses via cold plasma treatments***, Congrès SFGP 2009, Marseille, october 2009, 7 pages*.**

17. **F. Chai, N. Blanchemain, M.R. Aguilar, M. Jimenez, I. Kacem, E. Jean-Baptiste, B. Martel, J. San Roman, H.F. Hildebrand** - Cell Selectivity and Antithrombolytic Effect of Polyester Vascular Prosthetic Material Grafted with Acrylic Acid. ***BIOmaterialien 10-S1:58,* 2009.**

18. **M. Jimenez, S. Duquesne, S. Bourbigot,** Increasing intumescence efficiency by a systematic approach. ***Proceedings BCC 2005, 16th symposium on flame retardant systems, p104-119, Stamford, Connecticut, USA, may 2005.***

- Oral communications (no proceedings)
  (Remark: the first name indicated is the speaker)

1. **S.Duquesne, M.Jimenez, S. Bourbigot,** Fire retardancy of polymers using intumescent coatings***, European conference on smart and functional coatings, Torino (Italie), september 2013.***

2. **S. Degoutin, M.Jimenez, T. Pinalie, F.Chai, N. Blanchemain, C. Neut, B. Martel, M. Traisnel,** Nonwoven polypropylene textile with multiple bioactivity***, ESB 25th European Conference on Biomaterials, Madrid, september 2013.***

3. **K. Apaydin, A. Laachachi, V. Ball, M. Jimenez, S. Bourbigot, V. Toniazzo and D. Ruch**, Polyallylamine-Montmorillonite as Super Flame Retardant Coating Assemblies by Layer-by Layer Deposition on Polyamide, ***Interflam 2013, Egham, UK, June 2013.***

4. **M.Jimenez, F.Hilt, D.Duday, N.Gherardi, S.Bourbigot,** The use of plasma technology for the functionalization of non-woven textiles, **Seminar on Atmospheric Plasma pre-treatment for continuous processing,** organized by Mikrocentrum in cooperation with VITO, Belgium, ***May 2013***.

5. **M. Vandenbossche, M. Jimenez, M. Casetta, S. Bellayer, M. Traisnel,** Greffage de chitosane sur des géotextiles pour fixer le cuivre présent dans les sédiments pollués***, Journée des doctorants UGéPE, Roubaix, may 2012.***

6. **S. Bourbigot, G. Fontaine, M.Jimenez, S. Duquesne**, Reaction to fire of polymers: how to apply the concept of intumescence? ***Polymers for Advanced Technologies 2011, Lodz, Pologne, october 2011.***

7. **M. Jimenez, S. Degoutin, N. Blanchemain, F. Chai, B. Martel, M. Traisnel,** Functionalization of PP fabric via in situ cold plasma polymerization for biomedical applications, ***THERMEC 2011, Québec, august 2011.***

8. **M. Jimenez, N. Blanchemain, M. R. Aguilar, F. Chai, E. Jean Baptiste, B. Martel, H. F. Hildebrand, S. Haulon, J. San Roman,** Immobilization of Simvastatin Onto Polyester Vascular Prostheses Via Cold Plasma Treatment, ***THERMEC 2009, Berlin, august 2009.***

9. **F. Chai, N. Blanchemain, M.R. Aguilar, M. Jimenez, I. Kacem, E. Jean-Baptiste, B. Martel, J. San Roman, H.F.Hildebrand,** Cell selectivity and anthitrombolytic effect of polyester vascular prosthetic material grafted with acrylic acid, ***International Conference on Materials for Advanced Technologies ICMAT'2009, Symposium A: "Advanced Biomaterials and Regenerative Medicine" Singapore, july 2009.***

10. **H. Gallou, M. Jimenez, C. Jama, S. Duquesne, S. Bourbigot, R. Delobel, F. Spéroni, X. Coulliens and J. Mitchell,** Fire retardant performances of polyamide 6,6 coated by organosilicon thin films using cold plasma process***, CIP 09, Marseille, june 2009.***

11. **E. Jean-Baptiste, I. Kacem, N. Blanchemain, M. Jimenez, F. Chai, B. Martel, H.F. Hildebrand, S.Haulon,** Improved biologic properties of polyethylene terephtalate vascular prostheses grafted with acrylic acid***, 6th European Symposium of Vascular Biomaterials, Strasbourg (France), 13-15 may 2009.***

12. **I. Kacem, E. Jean-Baptiste, M. Jimenez, N. Blanchemain, F. Chai, B. Martel, S. Roudesli, H.F. Hildebrand, M. Traisnel** - Greffage de l'acide acrylique sur polyester pour l'immobilisation de molécules bioactives, ***3ème édition du 15ème colloque National de la Recherche dans les IUT (CNRIUT), Lille (France), may*** **2009.**

13. **I.Kacem, N.Blanchemain, S.Willai, M.Jimenez, F.Chai, M.R.Aguilar, E.Jean-Baptiste, J.San Roman, B.Martel, H.F.Hildebrand,** Plasma froid: généralités, greffage et activation biologique, ***Journée Scientifique Symposium Fédération Biomatériaux FANSBAMed, Lille, February 2009.***

14. **N.Blanchemain, M.R. Aguilar, M.Jimenez,F. Chai,E.Jean-Baptiste, S. Willai, B. Martel, H.F. Hildebrand, S. Haulon, J. San Roman,** Immobilization of simvastatin onto vascular prostheses via cold plasma treatment, ***LIAC, Reims, october 2008.***

15. **M.Ferrand, M.Jimenez, C. Jama, U. Maschke, M. Traisnel,** Optimization of epoxy resin reticulation, ***JEPO, Nancy, september 2008***

16. **M. Jimenez, S. Bourbigot, Séminaire TA Instruments,** Etude de la stabilité thermique de et de la thermocinétique de polymères contenant des charges***, ENSCL, june 2008*****.**

17. **M.Jimenez, S. Duquesne, S. Bourbigot,** Epoxy resin based intumescent coating as fire resistant protection for steel. ***IX ICFPAM, Cracovie, Pologne, july 2007.***

18. **M.Jimenez, F.Chai, N.Blanchemain, B. Martel, C. Jama, M. Traisnel, H.F. Hildebrand,** Optimization of RF cold plasma treatment to biocompatibilize and functionalize polyester. ***Séminaire fonctionnalisation de biomatériaux, CSIC, Madrid, november 2007.***

19. **N. Blanchemain, M. Jimenez, F. Chai, B. Martel, H.F. Hildebrand,** Simvastatin or saponified simvastatin fixation onto non-woven PET treated by cold plasma and grafted with acrylic acid. ***Séminaire fonctionnalisation de biomatériaux, CSIC, Madrid, novembre 2007*.**

20. **M. Ferrand, M. Jimenez, C. Jama, U. Maschke, M. Traisnel,** Optimization of epoxy resin reticulation, ***A greener Chemistry for industry, USTL, october 2007.***

21. **S. Duquesne, M. Jimenez, S. Bourbigot,** A Holistic approach of the fire protection using intumescent paints, ***11th European meeting on Fire Retardant Polymers, FRPM07, Bolton, UK, july 2007.***

22. **M.Jimenez, S. Duquesne, S. Bourbigot,** Comsol multiphysics et transferts de chaleur : quelques applications, de l'acier aux PCMs, ***Workshop COMSOL Multiphysics, ENSC Lille, march 2006.***

23. **M.Jimenez, S. Duquesne, S. Bourbigot,** Les peintures intumescentes à base résine époxyde, ***Forum Polymères organisé par la Fédération Gay Lussac, ENSC Clermont Ferrand, december 2005.***

24. **F.Boschin, M.Jimenez, R. Meziane, E. Delcourt-Debruyne, M. Morcellet, HF. Hildebrand, B.Martel,** Libération continue et prolongée de Chlorhexidine par des membranes de Régénération Tissulaire Guidée : Apport des Cyclodextrines. ***Congrès de la Société Française de Parodontologie et d'Implantologie Orale, Aix en Provence, June 2004.*** 1er Prix Communications recherche

25. **M. Jimenez, S. Duquesne, S. Bourbigot,** Use of rheology to characterize an intumescent coating. ***« Journées nord-européennes des jeunes chercheurs », Villeneuve d'Ascq, march 2004.***

26. **F.Boschin, M.Jimenez, R. Meziane, E. Delcourt-Debruyne, M. Morcellet, HF. Hildebrand, B.Martel,** Systèmes à libération contrôlée en Parodontologie: Apport des Cyclodextrines**.** ***« Journées nord-européennes des jeunes chercheurs », Villeneuve d'Ascq, march 2004.***

27. **F.Boschin, M.Jimenez, R. Meziane, E. Delcourt-Debruyne, M. Morcellet, HF. Hildebrand, B.Martel** Fonctionnalisation de membranes utilisées pour la régénération tissulaire guidée ***« 7ème Journées du club français des Cyclodextrines », Villeneuve d'Ascq, January 2004.***

- **Posters (peer-reviewed proceedings)**

1. **S.Duquesne, M.Jimenez, S.Bourbigot**, Flame retardancy of polypropylene with an intumescent coating**, *2nd International Symposiumon on Flame - Retardant Materials and Technologies (ISFRMT), Chengdu, Chine, september2012, 4 pages.***

2. **S. Degoutin, M. Jimenez, N. Blanchemain, F. Chai, B. Martel, M. Traisnel**, optimization of the functionalization of non-woven PP surfaces by cold plasma for the immobilization of biomolecules (heparin), ***SFGP2011, Lille, november 2011, 6 pages*.**

3. **H. Hamze, M.Jimenez, G.Ronse, G.Delaplace, M.Traisnel, A. Allion,** Mise en évidence de la compétition entre les effets de la rugosité et de l'énergie de surface dans les phénomènes d'encrassement de conduites en acier inoxydable, ***SFGP2011, Lille, november 2011, 8 pages*.**

4. **M. Jimenez, S. Duquesne, S. Bourbigot,** Dépôt chimique en phase vapeur assisté par plasma-application aux revêtements de barrière thermique**, *Proceedings « Congrès Français de Thermique » 2010, p. 401-407, Le Touquet, may 2010.***

5. **S. Bourbigot, S. Duquesne, F. Samyn, M. Jimenez,** L'intumescence: un concept de barrière thermique contre le feu**, *Proceedings « Congrès Français de Thermique » 2010, p. 407-413, Le Touquet, may 2010.***

6. **S.Bourbigot, M.Jimenez, S. Duquesne,** Modeling heat barrier efficiency of flame retarded materials**, *Proceedings « Comsol multiphysics conference 2006 », p.59-65, Paris, november 2006.***

7. **M.Jimenez, S.Duquesne, S. Bourbigot,** Modeling of heat transfer on a steel plate, first approach in presence of intumescent coating. ***Proceedings « Comsol multiphysics conference 2005», p.87-93, Paris, november 2005.***

8. **M.Jimenez, S.Duquesne, S Bourbigot,** La rhéologie, outil de caractérisation et d'optimisation de formulations intumescentes.***Proceedings « 39ème colloque annuel du Groupe Français de Rhéologie », p.257-261, Mulhouse, october 2004.***

◆ Posters (no proceedings)

1. **H. Van Den Berghe, J. Lyskawa, C. Zobrist, W. Laure, J. Sobocinski, S. Degoutin, N. Tabary, M. Jimenez, F.Chai, N. Blanchemain, F.H. Hildebrand, B. Martel and P. Woisel**, Multidrug eluting stents based on poly-β-cyclodextrin and chitosan layer by layer assembly, ***EUROCD2011***, ***Asti***, ***October 2011***.

2. **S.Degoutin, M.Jimenez, N. Blanchemain, M. Casetta, C. Neut, B. Martel, M. Traisnel,** Optimization of the functionalization of non-woven Polypropylene surface by cold plasma for the immobilization of biomolecules**, *24^{th}. European Conference on Biomaterials*, *Dublin, September 2011*.**

3. **C. Zobrist, P. Woisel, J. Lyskawa, M. Jimenez, F. Hildebrand, M. Traisnel**, Functionalization of Titanium Alloys By Well-Defined Biocompatible Polymers, ***THERMEC 2009, Berlin, august 2009.***

4. **I. Kacem, E. Jean-Baptiste, N. Blanchemain, M. Jimenez, M.R. Aguilar, F. Chai, B. Martel, J. San Roman, H.F. Hildebrand, M. Morcellet**, Immobilization of a therapeutic molecule onto polyester vascular prostheses via cold plasma treatment, ***2nd Asian Biomaterials Congress, Singapore, June 2009.***

5. **F. Chai, N. Blanchemain, M.R. Aguilar, M. Jimenez, I. Kacem, E. Jean-Baptiste, B. Martel, J. San Roman, H.F. Hildebrand**, Cell Selectivity and Antithrombolytic Effect of Polyester

Vascular Prosthetic Material Grafted with Acrylic Acid, ***3rd International Symposium: Interface Biology of Implants, Rostock (RFA), May 13-15, 2009.***

6. **S. Bellayer, M. Jimenez, M. Traisnel, H.F. Hildebrand,** Analyse d'implants dentaires par microsonde électronique***, Journée Microsonde, Lille, june 2008.***

7. **M.Jimenez, A.Vannier, S. Duquesne, C. Jama, A. Mazzah, S.Bourbigot, M. Traisnel, R. Delobel,** Cold plasma induced polymerization technology to develop fire retardant textiles**.** ***« Colloque International sur les Procédés Plasma », CIP 2007, Toulouse, june 2007.***

8. **M. Jimenez, S. Duquesne, S. Bourbigot, B. Revel** ^{11}B and ^{31}P solid state NMR study of the thermal degradation of boric acid/ ammonium polyphosphate mixture. ***« Congrès AMPERE/EENC», Lille, september 2004.***

9. **F.Boschin, M.Jimenez, R. Meziane, E. Delcourt-Debruyne, M. Morcellet, HF. Hildebrand, B.Martel** Interest of Cyclodextrins in periodontal Guided Tissue Regeneration: Release of Chlorhexidine by PVDF-membranes. ***12th. International Cyclodextrin Symposium, Montpellier, may 2004***

10. **F.Boschin, M.Jimenez, E. Delcourt-Debruyne, B.Martel, HF. Hildebrand, M. Morcellet** Libération de chlorhexidine par des membranes de PVDF : apport des cyclodextrines. ***« Journées Nord Européennes des Jeunes Chercheurs », Villeneuve d'Ascq, march 2004.***

11. **F.Boschin, M.Jimenez, E. Delcourt-Debruyne, B.Martel, HF. Hildebrand, M. Morcellet** Libération de chlorhexidine par des membranes de PVDF : apport des cyclodextrines. ***« 7ème Journées du club français des Cyclodextrines », Villeneuve d'Ascq, January 2004.***

Annex 5 : Scientific Outreach

- **Co-organization of events**

2008 : **Co-organizer of an EPMA (Electron probe Micro-Analyzer) symposium at ENSCL** with S.Bellayer (organization, speaker selection, installation)

2005 : **Supervisor of the organization of the Young researchers Sigma-Aldrich congress** (SAJEC2005) from 17 to 19 October 2005 in Lezennes (F). Coordination of the team (M.Sauthier, F.Samyn, J.Keldenich), selection of speakers and posters. 80 attendees.

- **Scientific expertise**

2012-now : Editorial Board member of the « Journal of textiles », Hindawi publisher

2009-now : External member in the recruitment board of CNRS and local research engineers (3 participations)

2008-now : **Reviewer for the following journals (total of around 15 reviews/year)**
Journal of Engineered Fibers and Fabrics
Composite Interfaces
Journal of Applied Polymer Science
Surface and Coatings Technology
Industrial and Engineering Chemistry Research
Progress in organic coatings
Royal Interface Society
Cellular Polymers

2004-2006 : President of the young researchers section in Nord - Pas de Calais - Picardie of the “Société Française de Chimie”. Responsible for a congress organization in 2005.

2003-2011 : **5 invited conferences (first author and speaker)**

M.Jimenez, F.Hilt, D.Duday, N.Gherardi, S.Bourbigot, The use of plasma technology for the functionalization of non-woven textiles, **Seminar on Atmospheric Plasma pre-treatment for continuous processing,** organized by Mikrocentrum in cooperation with VITO, Belgium, ***May 2013**. **(fees paid by the seminar organizers)***

M.Jimenez, H.Hamze, A. Allion, G. Ronse, G. Delaplace, M. Traisnel, Antifouling stainless steel surface: Competition between roughness and surface energy**, *THERMEC 2011, Québec, august 2011. (invitation letter)***

M. Jimenez, S. Duquesne, S. Bourbigot, C. Reti, M.Casetta, Novel approaches for processing flame retardant coatings**, *European coatings 2010-Fire retardancy- Berlin, june 2010. (entrance fees payed by the congress organizers)***

M. Jimenez, N. Blanchemain, M. R. Aguilar, F. Chai, E. Jean Baptiste, B. Martel, H. F. Hildebrand, S. Haulon, J. San Roman, Immobilization of Simvastatin Onto Polyester

Vascular Prostheses Via Cold Plasma Treatment, ***THERMEC 2009**, **Berlin, august 2009 (invitation letter)***

M. Jimenez, S. Bourbigot, Séminaire TA Instruments, Etude de la stabilité thermique et de la thermocinétique de polymères contenant des charges**, *ENSCL, june 2008***

Networking

2012-now: Member of A3TS (Association of thermal treatments and surface treatments)

2012-now: Member of ECIS (European Colloid and Interface Society) and of IACIS (International Association of Colloid and Interface Scientists)

2007-now: Member of the « Société Française de Génie des Procédés » (SFGP) and of the « Union du Génie des Procédés et de l'énergétique du Nord Pas de Calais » (UGéPé).

2006-now: Member of the french cold plasma network

2006-now: Member of the « Fédération Biomatériaux du Nord-Pas de Calais ».

References

[1] Jimenez M, Duquesne S, Bourbigot S. Characterization of the performance of an intumescent fire protective coating. Surface and Coatings Technology. 2006;201:979-87.
[2] Jimenez M, Duquesne S, Bourbigot S. Intumescent fire protective coating: Toward a better understanding of their mechanism of action. Thermochimica Acta. 2006;449:16-26.
[3] Jimenez M, Duquesne S, Bourbigot S. Multiscale experimental approach for developing high-performance intumescent coatings. Industrial and Engineering Chemistry Research. 2006;45:4500-8.
[4] Jimenez M, Duquesne S, Bourbigot S. High-throughput fire testing for intumescent coatings. Industrial and Engineering Chemistry Research. 2006;45:7475-81.
[5] Jimenez M, Duquesne S, Bourbigot S. Kinetic analysis of the thermal degradation of an epoxy-based intumescent coating. Polymer Degradation and Stability. 2009;94:404-9.
[6] Bourbigot S, Bachelet P, Jimenez M, Duquesne S. How to keep cooler under fire. European Coatings Journal. 2012:28-33.
[7] Jimenez M, Duquesne S, Bourbigot S. Fire protection of polypropylene and polycarbonate by intumescent coatings. Polymers for Advanced Technologies. 2012;23:130-5.
[8] Jimenez M, Duquesne S, Bourbigot S. Keeping cool in the mass. European Coatings Journal. 2010:26-31.
[9] Bourbigot S, Bachelet P, Samyn F, Jimenez M, Duquesne S. Intumescence as method for providing fire resistance to structural composites: application to PET foam sandwich structured composite. submitted in Composite Interface. 2013.
[10] Gallou H, Jimenez M, Duquesne S, Jama C, Delobel R, Bourbigot S, et al. Fireproof polyamide molded articles having an intumescent coating. Patented by Rhodia, WO/2011/045426 2011.
[11] Jimenez M, Duquesne S, Bourbigot S. Enhanced fire retardant properties of glass-fibre reinforced Polyamide 6,6 by combining bulk and surface treatments: toward a better understanding of the synergistic interactions between aluminium phosphinate and an intumescent coating. accepted in Polymer Degradation and Stability. 2013.
[12] Jimenez M, Gallou H, Duquesne S, Jama C, Bourbigot S, Couillens X, et al. New routes to flame retard polyamide 6,6 for electrical applications. Journal of Fire Sciences. 2012;30:535-51.
[13] Gallou H, Jimenez M, Jama C, Delobel R. Polyamide based fireproof article including a coating formed by plasma treatment. Patented by Rhodia, WO/ 2012/084955. 2012.
[14] Jimenez M, Bellayer S, Duquesne S, Bourbigot S. Improvement of heat resistance of high performance fibers using a cold plasma polymerization process. Surface and Coatings Technology. 2010;205:745-58.
[15] Blanchemain N, Aguilar MR, Jimenez M, Chai F, Jean-Baptiste E, El-Achari A, et al. Selective Biological response of Human Pulmonary Microvascular Endothelial Cells (HPMEC) and Human Pulmonary Artery Smooth Muscle Cells (HPASMC) on Cold plasma modified polyester vascular prostheses. Biomedical Materials (Bristol, United Kingdom). 2011;Accepted.
[16] Degoutin S, Jimenez M, Casetta M, Bellayer S, Chai F, Blanchemain N, et al. Anticoagulant and antimicrobial finishing of non-woven polypropylene textiles. Biomedical Materials. 2012;7.
[17] Hamze H, Jimenez M, Deresmes D, Beaurain A, Nuns N, Traisnel M. Influence of processing gases on the properties of atmospheric cold plasma SiOx coatings. submitted in Thin Solid Films. 2013.
[18] Vallet C, Collinet M, Jimenez M, Maschke U, Traisnel M. Effects of surface treatments on adhesive bonding properties of urethane-acrylate coating on tin oxide model substrates. submitted in International Journal of adhesion and adhesives. 2013.
[19] Vandenbossche M, Casetta M, Jimenez M, Bellayer S, M.Traisnel. Cysteine-grafted Nonwoven Geotextile: A New and Efficient Material for Heavy Metals Sorption. submitted in Journal of Environmental management 2013.

[20] Vandenbossche M, Jimenez M, Casetta M, Bellayer S, Beaurain A, Bourbigot S, et al. Chitosan-grafted nonwoven geotextile for heavy metals sorption in sediments. Reactive and Functional Polymers. 2013;73:53-9.

[21] Watson MA, Lyskawa J, Zobrist C, Fournier D, Jimenez M, Traisnel M, et al. A "clickable" titanium surface platform. Langmuir. 2010;26:15920-4.

[22] Zobrist C, Sobocinski J, Lyskawa J, Fournier D, Miri V, Traisnel M, et al. Functionalization of titanium surfaces with polymer brushes prepared from a biomimetic RAFT agent. Macromolecules. 2011;44:5883-92.

[23] Vandenbossche M, Jimenez M, Casetta M, Traisnel M. Biomolecules for the Trapping of Heavy Metals in the Environment: A Review. Critical Reviews in Environmental Science and Technology, in revision. 2013.

[24] Apaydin K, Laachachi A, Ball V, Jimenez M, Bourbigot S, Toniazzo V, et al. Polyallylamine-montmorillonite as super flame retardant coating assemblies by layer-by layer deposition on polyamide. Polymer Degradation and Stability. 2013;98:627-34.

[25] Duquesne S, Jimenez M, Bourbigot S. Ageing of the Flame Retardant properties of Polycarbonate and Polypropylene protected by an Intumescent Coating Journal of Coatings Technology and Research 2013;submitted.

[26] Jimenez M, Bellayer S, Revel B, Duquesne S, Bourbigot S. Comprehensive study of the influence of different aging scenarios on the fire protective behavior of an epoxy based intumescent coating. Industrial and Engineering Chemistry Research. 2013;52:729-43.

[27] Jimenez M, Hamze H, Allion A, Ronse G, Delaplace G, M.Traisnel. Antifouling stainless steel surface: Competition between roughness and surface energy. Materials Science Forum. 2012;706-709:2523-8

[28] Jimenez M, Nuns N, Bellayer S, Desresmes D, Alogaili G, Ronse G, et al. Fundamental comprehension of the interfacial behaviour of dairy fouling at a stainless steel surface. submitted in Journal of Colloid and Interface Sciences. 2013.

[29] Duquesne S, Jimenez M, Bourbigot S. Fire Retardancy and Fire Protection of Materials Using Intumescent Coatings - A Versatile Solution? Fire Retardancy of Polymers: New Strategies and Mechanisms (FRPM '07), 11th, Bolton, UK, 4-6 July. 2009:240-52.

[30] Gay Lussac LJ. Note sur la propriété qu'ont les matières salines de rendre les tissus incombustibles. Annales de Chimie et de Physique. 1821;18:211-8.

[31] Tramm H, Clar C, Kühnel P, Schuff W. Fireproofing of wood. In: Office USP, editor. United States Patent Office. USA: Ruhrchemie Aktiengesellschaft; 1938. p. 1-2.

[32] Vandersall HJ. Intumescent coating systems, their development and chemistry. Journal of Fire and Flammability. 1971;2:97-140.

[33] Bourbigot S, Le Bras M, Duquesne S, Rochery M. Recent Advances for Intumescent Polymers. Macromolecular Materials and Engineering. 2004;289:499-511.

[34] Bugajny M, Le Bras M, Bourbigot S. New approach to the dynamic properties of an intumescent material. Fire and Materials. 1999;23:49-51.

[35] Camino G, Costa L. Martinasso, G. Intumescent fire retardant systems. Polym Degrad Stab. 1989;23.

[36] Bourbigot S, Bras ML, Delobel R. Carbonization mechanisms resulting from intumescence association with the ammonium polyphosphate-pentaerythritol fire retardant system. Carbon. 1993;31:1219-30.

[37] Delobel R, Le Bras M, Ouassou N, Alistiqsa F. Thermal behaviour of ammonium polyphosphate-pentaerythritol and ammonium pyrophosphate-pentaerythritol intumescent additives in polypropylene formulations. J Fire Sci. 1990;8.

[38] Cullis CF, Hirschler MM. The Combustion of Organic Polymers, Clarendon Press. 1981.

[39] Chen L, Wang YZ. A review on flame retardant technology in China. Part I: Development of flame retardants. Polymers for Advanced Technologies. 2010;21:1-26.

[40] Arthur T, Quill K. Proceedings of Flame Retardant'92. 1992:223.
[41] Horrocks AR. Developments in flame retardants for heat and fire resistant textiles - The role of char formation and intumescence. Polymer Degradation and Stability. 1996;54:143-54.
[42] Drevelle C, Duquesne S, Le Bras M, Lefebvre J, Delobel R, Castrovinci A, et al. Influence of ammonium polyphosphate on the mechanism of thermal degradation of an acrylic binder resin. Journal of Applied Polymer Science. 2004;94:717-29.
[43] Lewin M. Physical and chemical mechanisms of flame retarding of polymers. Fire Retardancy of Polymers: The Use of Intumescence. 1998:3-32.
[44] Bourbigot S, Flambard X, Revel B. Characterisation of poly(p-phenylenebenzobisoxazole) fibres by solid state NMR. European Polymer Journal. 2002;38:1645-51.
[45] Bourbigot S, Le Bras M, Delobel R, Decressain R, Amoureux JP. Synergistic effect of zeolite in an intumescence process: Study of the carbonaceous structures using solid-state NMR. Journal of the Chemical Society - Faraday Transactions. 1996;92:149-58.
[46] Bourbigot S, Vanderhart DL, Gilman JW, Awad WH, Davis RD, Morgan AB, et al. Investigation of nanodispersion in polystyrene-montmorillonite nanocomposites by solid-state NMR. Journal of Polymer Science, Part B: Polymer Physics. 2003;41:3188-213.
[47] Bourbigot S, Vanderhart DL, Gilman JW, Bellayer S, Stretz H, Paul DR. Solid state NMR characterization and flammability of styrene-acrylonitrile copolymer montmorillonite nanocomposite. Polymer. 2004;45:7627-38.
[48] Gilman JW, Bourbigot S, Shields JR, Nyden M, Kashiwagi T, Davis RD, et al. High throughput methods for polymer nanocomposites research: Extrusion, NMR characterization and flammability property screening. Journal of Materials Science. 2003;38:4451-60.
[49] Pécoul N, Bourbigot S, Revel B. 13C, 25Mg and 11B solid-state NMR study of a fire retarded ethylene-vinyl acetate copolymer. Macromolecular Symposia. 1997;119:309-15.
[50] Jimenez M, Duquesne S, Bourbigot S. Increasing intumescence efficiency by a systematic approach. Proceedings of the Conference on Recente Advances in Flame Retardancy of Polymeric Materials. 2005;16:104-18.
[51] Duquesne S, Magnet S, Jama C, Delobel R. Thermoplastic resins for thin film intumescent coatings - Towards a better understanding of their effect on intumescence efficiency. Polymer Degradation and Stability. 2005;88:63-9.
[52] Bugajny M, Bourbigot S, Le Bras M, Delobel R. The origin and nature of flame retardance in ethylene-vinyl acetate copolymers containing hostaflam AP 750. Polymer International. 1999;48:264-70.
[53] Anna P, Marosi G, Csontos I, Bourbigot S, Le Bras M, Delobel R. Influence of modified rheology on the efficiency of intumescent flame retardant systems. Polymer Degradation and Stability. 2001;74:423-6.
[54] Camino G, Luda MP. Mechanistic study on intumescence. Fire Retardancy of Polymers: The Use of Intumescence. 1998:48-63.
[55] Bourbigot S, Le Bras M, Gengembre L, Delobel R. XPS study of an intumescent coating application to the ammonium polyphosphate/pentaerythritol fire-retardant system. Applied Surface Science. 1994;81:299-307.
[56] Marosi G, Anna P, Balogh I, Bertalan G, Tohl A, Maatoug MA. Thermoanalytical study of nucleating effects in polypropylene composites: III. Intumescent flame retardant containing polypropylene. Journal of Thermal Analysis. 1997;48:717-26.
[57] Marosi G, Csontos I, Ravadits I, Tohl A, Anna P, Sommer F, et al. Thermal and surface analytical study of flame retarded polyolefins. I. Interaction of additives and structure formation. Journal of Thermal Analysis and Calorimetry. 1999;56:1071-80.
[58] Berlin AA, Khalturinskii NA, Reshetnikov IS, Yablokova MY. Some aspects of mechanical stability of intumescent chars. Fire Retardancy of Polymers: The Use of Intumescence. 1998:104-12.

[59] Reshetnikov IS, Yablokova MY, Potapova EV, Khalturinskij NA, Chernyh VY, Mashlyakovskii LN. Mechanical stability of intumescent chars. Journal of Applied Polymer Science. 1998;67:1827-30.
[60] Duquesne S, Delobel R, Le Bras M, Camino G. A comparative study of the mechanism of action of ammonium polyphosphate and expandable graphite in polyurethane. Polymer Degradation and Stability. 2002;77:333-44.
[61] Narayanan TSNS. Surface pretreatment by phosphate conversion coatings - A review. Reviews on Advanced Materials Science. 2005;9:130-77.
[62] Bourbigot S. Intumescence: an older concept for future applications. . Proceedings of FRPM, Alessandria, Italy. 2011.
[63] Lewin M., in: Le Bras M., Camino G., Bourbigot S., Delobel R. (Eds.), Fire Retardancy of Polymers – The Use of Intumescence, The Royal Society of Chemistry, Cambridge, UK, 1998; p.3-32.
[64] Khanna YP, Pearce EM. Flame Retardant Polymeric Materials. 1978;2:10.
[65] Lyon RE. Solid state thermochemistry of flaming combustion. Fire Retardancy of Polymeric Materials. 2000:391-447.
[66] Nelson G.L. in: Nelson G.L. (Ed.), Proceedings of the American Chemical Society Symposium, Fire and Polymers II, American Chemical Society, Washington, DC, 1995; p.1e24.
[67] Bourbigot S, Le Bras M, Delobel R. Fire degradation of an intumescent flame retardant polypropylene using the cone calorimeter. J Fire Sci. 1995;13:3-22.
[68] Montaudo G, Scamporrino E, Vitalini D. Intumescent flame retardants for polymers. II The polypropylene-ammonium polyphosphate- polyurea system. Journal of polymer science Part A-1, Polymer chemistry. 1983;21:3361-71.
[69] Lv P, Wang Z, Hu K, Fan W. Flammability and thermal degradation of flame retarded polypropylene composites containing melamine phosphate and pentaerythritol derivatives. Polymer Degradation and Stability. 2005;90:523-34.
[70] Lu SY, Hamerton I. Recent developments in the chemistry of halogen-free flame retardant polymers. Progress in Polymer Science (Oxford). 2002;27:1661-712.
[71] Duquesne S, Magnet S, Jama C, Delobel R. Intumescent paints: Fire protective coatings for metallic substrates. Surface and Coatings Technology. 2004;180-181:302-7.
[72] Gu Jw, Zhang Gc, Dong Sl, Zhang Qy, Kong J. Study on preparation and fire-retardant mechanism analysis of intumescent flame-retardant coatings. Surface and Coatings Technology. 2007;201:7835-41.
[73] Horrocks AR, Davies PJ, Kandola BK, Alderson A. The potential for volatile phosphorus-containing flame retardants in textile back-coatings. Journal of Fire Sciences. 2007;25:523-40.
[74] Magniez C, Dubois A, Vouters M, Delobel R, Poutch F. J Industr Text. 2003;32:255-66.
[75] Duquesne S, Renaut N, Bardollet P, Jama C, Traisnel M, Delobel R. In Fire and Polymers V, ACS Symposium Series 1013, Wilkie, CA, Morgan, AB and Nelson, GL, Eds ACS. 2009;Chap. 12:200-12.
[76] Wolf RA. How to determine optimal treatment levels for plastic films. Flexo. 2009;34:34-6.
[77] DiGiacomo J. Top Conf Path Innov. 2008;1:19.
[78] Goodarzi V, Monemian SA, Angaji MT, Motahari S. Improvement of thermal and fire properties of polypropylene. Journal of Applied Polymer Science. 2008;110:2971-9.
[79] Chen D, Zheng Q, Liu F, Xu K, Chen M. Flame-retardant polypropylene composites based on magnesium hydroxide modified by phosphorous-containing polymers. Journal of Thermoplastic Composite Materials. 2010;23:175-92.
[80] Ishikawa T, Maki I, Koshizuka T, Takeda K. Thermal degradation and flame retardancy of polycarbonate as a flame retardant polymer. Zairyo/Journal of the Society of Materials Science, Japan. 2004;53:1301-8.
[81] Ishikawa T, Maki I, Koshizuka T, Ohkawa T, Takeda K. Effect of perfluoroalkane sulfonic acid on the flame retardancy of polycarbonate. Journal of Macromolecular Science - Pure and Applied Chemistry. 2004;41 A:523-35.

[82] Wang J, Xin Z. Flame retardancy, thermal, rheological, and mechanical properties of polycarbonate/polysilsesquioxane system. Journal of Applied Polymer Science. 2010;115:330-7.
[83] Tuominen M, Lahti J, Lavonen J, Penttinen T, Räsänen JP, Kuusipalo J. The influence of flame, corona and atmospheric plasma treatments on surface properties and digital print quality of extrusion coated paper. Journal of Adhesion Science and Technology. 2010;24:471-92.
[84] Lyon RL, Filipczak R, Walters RN, Crowley S, Stoliarov SI. FAA Report, DOT/FAA/AR-07/2. 2007.
[85] Braun U, Schartel B. Flame retardancy mechanisms of aluminium phosphinate in combination with melamine cyanurate in glass-fibre-reinforced poly(1,4-butylene terephthalate). Macromolecular Materials and Engineering. 2008;293:206-17.
[86] Gallo E, Braun U, Schartel B, Russo P, Acierno D. Halogen-free flame retarded poly(butylene terephthalate) (PBT) using metal oxides/PBT nanocomposites in combination with aluminium phosphinate. Polymer Degradation and Stability. 2009;94:1245-53.
[87] Gallo E, Schartel B, Braun U, Russo P, Acierno D. Fire retardant synergisms between nanometric Fe 2O 3 and aluminum phosphinate in poly(butylene terephthalate). Polymers for Advanced Technologies. 2011;22:2382-91.
[88] Yi J, Liu Y, Cai X. The synergistic effect of adjuvant on the intumescent flame-retardant ABS with a novel charring agent. Journal of Thermal Analysis and Calorimetry. 2012:1-9.
[89] Braun U, Schartel B, Fichera MA, Jäger C. Flame retardancy mechanisms of aluminium phosphinate in combination with melamine polyphosphate and zinc borate in glass-fibre reinforced polyamide 6,6. Polymer Degradation and Stability. 2007;92:1528-45.
[90] Samyn F, Bourbigot S. Thermal decomposition of flame retarded formulations PA6/aluminum phosphinate/melamine polyphosphate/organomodified clay: Interactions between the constituents? Polymer Degradation and Stability. 2012;97:2217-30.
[91] Lippmaa E, Samoson A, Mägi M. High-resolution 27Al NMR of aluminosilicates. Journal of the American Chemical Society. 1986;108:1730-5.
[92] McCrary-Dennis MC, Okoli OI. A review of multiscale composite manufacturing and challenges. Journal of Reinforced Plastics and Composites. 2012;31:1687-711.
[93] Babrauskas V, Lucas D, Eisenberg D, Singla V, Dedeo M, Blum A. Flame retardants in building insulation: A case for re-evaluating building codes. Building Research and Information. 2012;40:738-55.
[94] Quintiere J. Some factors influencing fire spread over room linings and in the ASTM E84 tunnel test. Fire and Materials. 1985;9:65-74.
[95] Balabanovich AI, Levchik GF, Levchik SV, Schnabel W. Fire retardance in polyamide-6. The effects of red phosphorus and radiation-induced cross-links. Fire and Materials. 2001;25:179-84.
[96] Jana T, Roy BC, Maiti S. Biodegradable film: 7. Modification of the biodegradable film for fire retardancy. Polymer Degradation and Stability. 2000;69:79-82.
[97] Carosio F, Di Blasio A, Alongi J, Malucelli G. Layer by layer nanoarchitectures for the surface protection of polycarbonate. European Polymer Journal. 2013;49:397-404.
[98] Laachachi A, Ball V, Apaydin K, Toniazzo V, Ruch D. Diffusion of Polyphosphates into (Poly(allylamine)-montmorillonite) Multilayer Films: Flame Retardant-Intumescent Films with Improved Oxygen Barrier. Langmuir. 2011;27:13879-87.
[99] Quédé A, Jama C, Supiot P, Le Bras M, Delobel R, Dessaux O, et al. Elaboration of fire retardant coatings on polyamide-6 using a cold plasma polymerization process. Surface and Coatings Technology. 2002;151-152:424-8.
[100] Quédé A, Mutel B, Supiot P, Jama C, Dessaux O, Delobel R. Characterization of organosilicon films synthesized by N2-PACVD. Application to fire retardant properties of coated polymers. Surface and Coatings Technology. 2004;180-181:265-70.
[101] Horrocks AR. Flame retardant challenges for textiles and fibres: New chemistry versus innovatory solutions. Polymer Degradation and Stability. 2011;96:377-92.
[102] Iler RK. Journal colloid interface sci. 1966;21:569.

[103] Decher G, Hong JD. Makromol Chem Macromol Symp. 1991;46:231.
[104] M. DVM, P. OD, J. SS, M. LY. Introduction to nanocoatings produced by layer-by-layer (LbL) self-assembly. Advanced Drug Delivery Reviews. 2011;63:701-15.
[105] Saurer EM, Flessner RM, Sullivan SP, Prausnitz MR, Lynn DM. Layer-by-Layer Assembly of DNA- and Protein-Containing Films on Microneedles for Drug Delivery to the Skin. Biomacromolecules. 2010;11:3136-43.
[106] Hiller J. MJDea. Nat Mater. 2002;1:59-63.
[107] Shimomura H, Gemici Z, Cohen RE, Rubner MF. Layer-by-Layer-Assembled High-Performance Broadband Antireflection Coatings. ACS Applied Materials & Interfaces. 2010;2:813-20.
[108] Schmidt DJ, Pridgen EM, Hammond PT, Love JC. Layer-by-Layer Assembly of a pH-Responsive and Electrochromic Thin Film. Journal of Chemical Education. 2010;87:208-11.
[109] Montazami R, Jain V, Heflin JR. High contrast asymmetric solid state electrochromic devices based on layer-by-layer deposition of polyaniline and poly(aniline sulfonic acid). Electrochimica Acta. 2010;56:990-4.
[110] Sheng K, Bai H, Sun Y, Li C, Shi G. Layer-by-layer assembly of graphene/polyaniline multilayer films and their application for electrochromic devices. Polymer. 2011;52:5567-72.
[111] Jang W-S, Rawson I, Grunlan JC. Layer-by-layer assembly of thin film oxygen barrier. Thin Solid Films. 2008;516:4819-25.
[112] Priolo MA, Gamboa D, Grunlan JC. Transparent Clay−Polymer Nano Brick Wall Assemblies with Tailorable Oxygen Barrier. ACS Applied Materials & Interfaces. 2009;2:312-20.
[113] Priolo MA, Gamboa D, Holder KM, Grunlan JC. Super Gas Barrier of Transparent Polymer−Clay Multilayer Ultrathin Films. Nano Letters. 2010;10:4970-4.
[114] Priolo MA, Holder KM, Gamboa D, Grunlan JC. Influence of Clay Concentration on the Gas Barrier of Clay–Polymer Nanobrick Wall Thin Film Assemblies. Langmuir. 2011;27:12106-14.
[115] Yang Y-H, Haile M, Park YT, Malek FA, Grunlan JC. Super Gas Barrier of All-Polymer Multilayer Thin Films. Macromolecules. 2011;44:1450-9.
[116] Svagan AJ, Åkesson A, Cárdenas M, Bulut S, Knudsen JC, Risbo J, et al. Transparent Films Based on PLA and Montmorillonite with Tunable Oxygen Barrier Properties. Biomacromolecules. 2012;13:397-405.
[117] Laufer G, Kirkland C, Cain AA, Grunlan JC. Clay–Chitosan Nanobrick Walls: Completely Renewable Gas Barrier and Flame-Retardant Nanocoatings. ACS Applied Materials & Interfaces. 2012;4:1643-9.
[118] Li Y-C, Schulz J, Grunlan JC. Polyelectrolyte/Nanosilicate Thin-Film Assemblies: Influence of pH on Growth, Mechanical Behavior, and Flammability. ACS Applied Materials & Interfaces. 2009;1:2338-47.
[119] Li Y-C, Schulz J, Mannen S, Delhom C, Condon B, Chang S, et al. Flame Retardant Behavior of Polyelectrolyte−Clay Thin Film Assemblies on Cotton Fabric. ACS Nano. 2010;4:3325-37.
[120] Li Y-C, Mannen S, Schulz J, Grunlan JC. Growth and fire protection behavior of POSS-based multilayer thin films. Journal of Materials Chemistry. 2011;21:3060-9.
[121] Laufer G, Carosio F, Martinez R, Camino G, Grunlan JC. Growth and fire resistance of colloidal silica-polyelectrolyte thin film assemblies. Journal of Colloid and Interface Science. 2011;356:69-77.
[122] Carosio F, Laufer G, Alongi J, Camino G, Grunlan JC. Layer-by-layer assembly of silica-based flame retardant thin film on PET fabric. Polymer Degradation and Stability. 2011;96:745-50.
[123] Carosio F, Alongi J, Malucelli G. [small alpha]-Zirconium phosphate-based nanoarchitectures on polyester fabrics through layer-by-layer assembly. Journal of Materials Chemistry. 2011;21:10370-6.
[124] Kim YS, Davis R, Cain AA, Grunlan JC. Development of layer-by-layer assembled carbon nanofiber-filled coatings to reduce polyurethane foam flammability. Polymer. 2011;52:2847-55.
[125] Li Y-C, Mannen S, Morgan AB, Chang S, Yang Y-H, Condon B, et al. Intumescent All-Polymer Multilayer Nanocoating Capable of Extinguishing Flame on Fabric. Advanced Materials. 2011;23:3926-31.

[126] Carosio F, Alongi J, Malucelli G. Layer by Layer ammonium polyphosphate-based coatings for flame retardancy of polyester–cotton blends. Carbohydrate Polymers.
[127] Alongi J, Carosio F, Malucelli G. Layer by layer complex architectures based on ammonium polyphosphate, chitosan and silica on polyester-cotton blends: flammability and combustion behaviour. Cellulose. 2012;19:1041-50.
[128] Alongi J, Carosio F, Malucelli G. Influence of ammonium polyphosphate-/poly(acrylic acid)-based layer by layer architectures on the char formation in cotton, polyester and their blends. Polymer Degradation and Stability. 2012;97:1644-53.
[129] Laufer G, Kirkland C, Morgan AB, Grunlan JC. Intumescent Multilayer Nanocoating, Made with Renewable Polyelectrolytes, for Flame-Retardant Cotton. Biomacromolecules. 2012;13:2843-8.
[130] Shi L. Investigation of surface modification and reaction kinetics of PET in RF CF4-CH4 plasmas. Journal of Polymer Engineering. 1999;19:445-55.
[131] Shi L. Characterization of the flame retardancy of EVA copolymer by plasma grafting of acrylic acid. European Polymer Journal. 2000;36:2611-5.
[132] Shi LS. Approach to the flame retardation and smoke suppression of ethylene-vinyl acetate copolymer by plasma grafting of acrylamide. Reactive and Functional Polymers. 2000;45:85-93.
[133] Tsafack MJ, Levalois-Grützmacher J. Plasma-induced graft-polymerization of flame retardant monomers onto PAN fabrics. Surface and Coatings Technology. 2006;200:3503-10.
[134] Tsafack MJ, Levalois-Grützmacher J. Flame retardancy of cotton textiles by plasma-induced graft-polymerization (PIGP). Surface and Coatings Technology. 2006;201:2599-610.
[135] Tsafack MJ, Hochart F, Levalois-Grützmacher J. Polymerization and surface modification by low pressure plasma technique. EPJ Applied Physics. 2004;26:215-9.
[136] Pearce EM, Weil ED, Barinov VY. Fire and Polymers. ACS Symposium series. 2001;797:37.
[137] Bourbigot S, Duquesne S, Vannier A, Delobel R. Nonwoven as heat barrier: Modeling of the efficiency of carbtex fibers. Journal of Applied Polymer Science. 2008;108:3245-55.
[138] Morent R, De Geyter N, Verschuren J, De Clerck K, Kiekens P, Leys C. Non-thermal plasma treatment of textiles. Surface and Coatings Technology. 2008;202:3427-49.
[139] Luo S, Van Ooij WJ. Surface modification of textile fibers for improvement of adhesion to polymeric matrices: A review. Journal of Adhesion Science and Technology. 2002;16:1715-35.
[140] Jama C, Delobel R. Springer Series in Material Science. 2007;97:109.
[141] Li ZF, Netravali AN. Surface modification of UHSPE fibers through allylamine plasma deposition. II. Effect on fiber and fiber/epoxy interface. Journal of Applied Polymer Science. 1992;44:333-46.
[142] Aragi LM. Low temperature deposition of a thin film protective coating on fibers improves their durability. Materials Technology. 1995;10:192-4.
[143] Kilic B, Aksit AC, Mutlu M. Surface modification and characterization of cotton and polyamide fabrics by plasma polymerization of hexamethyldisilane and hexamethyldisiloxane. International Journal of Clothing Science and Technology. 2009;21:137-45.
[144] Wu Q, Gleason KK. Plasma-Enhanced CVD of Organosilicate Glass (OSG) Films Deposited from Octamethyltrisiloxane, Bis(trimethylsiloxy)methylsilane, and 1,1,3,3-Tetramethyldisiloxane. Plasmas and Polymers. 2003;8:31-41.
[145] Schartel B, Kühn G, Mix R, Friedrich J. Surface controlled fire retardancy of polymers using plasma polymerisation. Macromolecular Materials and Engineering. 2002;287:579-82.
[146] Horrocks AR, Nazaré S, Masood R, Kandola B, Price D. Surface modification of fabrics for improved flash-fire resistance using atmospheric pressure plasma in the presence of a functionalized clay and polysiloxane. Polymers for Advanced Technologies. 2011;22:22-9.
[147] Horrocks AR, Kandola BK, Nazaré S, Price D. Flash fire retardant fabric. UK Patent application 09000696. 2009.
[148] Thomas M, von Hausen M, Klages CP, Baumhof P. Generation of stable coatings with carboxylic groups by copolymerization of MAA and VTMS using DBD at atmospheric pressure. Plasma Processes and Polymers. 2007;4:S475-S81.

[149] Hody H, Choquet P, Moreno M, Pireaux JJ. Optimization of an atmospheric pressure plasma copolymerization process with a view to nanopowder functionalization. Plasma Processes and Polymers. 2009;6:S883-S7.
[150] Hody H, Choquet P, Moreno-Couranjou M, Maurau R, Pireaux JJ. Optimization of Carboxyl surface functionalization by MA-VTMS copolymerization using atmospheric pressure plasma DBD: Influence of the Carrier Gas. Plasma Processes and Polymers. 2010;7:403-10.
[151] Boscher ND, Choquet P, Duday D, Verdier S. Influence of cyclic organosilicon precursors on the corrosion of aluminium coated sheet by atmospheric pressure dielectric barrier discharge. Surface and Coatings Technology. 2011;205:5350-7.
[152] Maurau R, Boscher ND, Guillot J, Choquet P. Nitrogen introduction in pp-HMDSO thin films deposited by atmospheric pressure dielectric barrier discharge: An XPS study. Plasma Processes and Polymers. 2012;9:316-23.
[153] Borges JN, Belmonte T, Guillot J, Duday D, Moreno-Couranjou M, Choquet P, et al. Functionalization of copper surfaces by plasma treatments to improve adhesion of epoxy resins. Plasma Processes and Polymers. 2009;6:S490-S5.
[154] Laachachi A, Cochez M, Leroy E, Ferriol M, Lopez-Cuesta JM. Fire retardant systems in poly(methyl methacrylate): Interactions between metal oxide nanoparticles and phosphinates. Polymer Degradation and Stability. 2007;92:61-9.
[155] Laachachi A, Ferriol M, Cochez M, Lopez Cuesta JM, Ruch D. A comparison of the role of boehmite (AlOOH) and alumina (Al 2O 3) in the thermal stability and flammability of poly(methyl methacrylate). Polymer Degradation and Stability. 2009;94:1373-8.
[156] Del Frari D, Bour J, Bardon J, Buchheit O, Arnoult C, Ruch D. Hybrid layers deposited by an atmospheric pressure plasma process for corrosion protection of galvanized steel. Journal of Nanoscience and Nanotechnology. 2010;10:2611-9.
[157] White JJR, Turnbull A. Surface Degradation of Polymeric Materials. J Mater Sci. 1994;29.
[158] Williams JG. FRACTURE MECHANICS OF POLYMERS. Fract Mech of Polym. 1984.
[159] Hu J, Li X, Gao J, Zhao Q. UV aging characterization of epoxy varnish coated steel upon exposure to artificial weathering environment. Materials and Design. 2009;30:1542-7.
[160] Bussière PO, Rivaton A, Thérias S, Gardette JL. Multiscale investigation of the poly(N-vinylcarbazole) photoageing mechanism. Journal of Physical Chemistry B. 2012;116:803-12.
[161] Collin S, Bussière PO, Thérias S, Lambert JM, Perdereau J, Gardette JL. Physicochemical and mechanical impacts of photo-ageing on bisphenol a polycarbonate. Polymer Degradation and Stability. 2012;97:2284-93.
[162] Larché JF, Bussière PO, Thérias S, Gardette JL. Photooxidation of polymers: Relating material properties to chemical changes. Polymer Degradation and Stability. 2012;97:25-34.
[163] Larché JF, Bussière PO, Wong-Wah-Chung P, Gardette JL. Chemical structure evolution of acrylic-melamine thermoset upon photo-ageing. European Polymer Journal. 2012;48:172-82.
[164] Martin JW. Quantitative characterization of spectral ultraviolet radiation-induced photodegradation in coating systems exposed in the laboratory and the field. Progress in Organic Coatings. 1993;23:49-70.
[165] Martin JW, Saunders SC, Floyd FL, Wineburg JP. Methodologies for predicting the service lives of coating systems. Federation Series on Coatings Technology. 1996.
[166] Bauer DR. Predicting in-service weatherability of automotive coatings: A new approach. Journal of Coatings Technology. 1997;69:85-96.
[167] Bauer DR, Mielewski DF, Gerlock JL. Photooxidation kinetics in crosslinked polymer coatings. Polymer Degradation and Stability. 1992;38:57-67.
[168] Perera DY. Stress phenomena in organic coatings. Paint and Coating Testing Manual. 1995;17:585-99.
[169] Perera DY. Stress induced in organic coatings by weathering. Proceedings of the 24th FATIPEC Congress. 1998;A:149.

[170] Perera DY, Oosterbroek M. Hygrothermal stress evolution during weathering in organic coatings. Journal of Coatings Technology. 1994;66:83-8.
[171] Robertson CG, Wilkes GL. Physical aging behavior of miscible blends of poly(methyl methacrylate) and poly(styrene-co-acrylonitrile). Polymer. 2001;42:1581-9.
[172] Perera DY. Effect of thermal and hygroscopic history on physical ageing of organic coatings. Progress in Organic Coatings. 2002;44:55-62.
[173] Perera DY. Role of stress on durability of organic coatings. Plastics and Coatings: Durability-Stabilization Testing. 2001:115.
[174] Perera DY. Physical ageing of organic coatings. Progress in Organic Coatings. 2003;47:61-76.
[175] Almeras X, Le Bras M, Hornsby P, Bourbigot S, Marosi G, Anna P, et al. Artificial Weathering and Recycling Effect on Intumescent Polypropylene-based Blends. Journal of Fire Sciences. 2004;22:143-61.
[176] Roberts TA, Shirvill LC, Waterton K, Buckland I. Fire resistance of passive fire protection coatings after long-term weathering. Process Safety and Environmental Protection. 2010;88:1-19.
[177] Wade R. A review of the robustness of epoxy passive fire protection (PFP) to offshore environments. Houston, TX2011.
[178] Wang LL, Wang YC, Li GQ. Experimental study of hydrothermal aging effects on insulative properties of intumescent coating for steel elements. Fire Safety Journal. 2013;55:168-81.
[179] Wang LL, Wang YC, Yuan JF, Li GQ. Thermal conductivity of intumescent coating char after accelerated aging. Fire and Materials. 2012.
[180] Glonek T, Costello AJR, Myers TC, Van Wazer JR. Phosphorus-31 nuclear magnetic resonance studies on condensed phosphates.1,2 III. Polyphosphate spectra. Journal of Physical Chemistry. 1975;79:1214-8.
[181] Wang Z, Han E, Liu F, Ke W. Fire and corrosion resistances of intumescent nano-coating containing nano-SiO 2 in salt spray condition. Journal of Materials Science and Technology. 2010;26:75-81.
[182] Lin M, Li B, Li Q, Li S, Zhang S. Synergistic effect of metal oxides on the flame retardancy and thermal degradation of novel intumescent flame-retardant thermoplastic polyurethanes. Journal of Applied Polymer Science. 2011;121:1951-60.
[183] Xu RG, Z.; Xu, Y.;. NASICON, Progress in zeolite science: a Chinese perspective. Pub: World Scientific Publishing Co. 1995;Chap. 5:79.
[184] Duquesne S, Jimenez M, Bourbigot S. Ageing of the flame retardant properties of Polycarbonate and Polypropylene protected by an intumescent coating. Submitted in Journal of Applied Polymer Science. 2013.
[185] Midelet G, Kobilinsky A, Carpentier B. Construction and analysis of fractional multifactorial designs to study attachment strength and transfer of Listeria monocytogenes from pure or mixed biofilms after contact with a solid model food. Applied and Environmental Microbiology. 2006;72:2313-21.
[186] Ozden HO, Puri VM. Computational analysis of fouling by low energy surfaces. Journal of Food Engineering. 2010;99:250-6.
[187] Sava N, Van Der Plancken I, Claeys W, Hendrickx M. The kinetics of heat-induced structural changes of β-lactoglobulin. Journal of Dairy Science. 2005;88:1646-53.
[188] Schmitt C, Bovay C, Rouvet M, Shojaei-Rami S, Kolodziejczyk E. Whey protein soluble aggregates from heating with NaCl: Physicochemical, interfacial, and foaming properties. Langmuir. 2007;23:4155-66.
[189] Burton H. Deposits of whole milk in treatment plants : a review and discussion. Journal of Dairy Research. 1968;35:317-30.
[190] Belmar-Beiny MT, Gotham SM, Paterson WR, Fryer PJ, Pritchard AM. The effect of Reynolds number and fluid temperature in whey protein fouling. Journal of Food Engineering. 1993;19:119-39.

[191] Fryer PJ, Christian GK, Liu W. How hygiene happens: Physics and chemistry of cleaning. International Journal of Dairy Technology. 2006;59:76-84.
[192] Prakash S. DH, Grandison A., Lewis M. . Role of ionic calcium in fouling of heat treated milk. Fouling, cleaning & desinfection in food processing. Cambridge, UK2006.
[193] Benning R, Petermeier H, Delgado A, Hinrichs J, Kulozik U, Becker T. Process design for improved fouling behaviour in dairy heat exchangers using a hybrid modelling approach. Food and Bioproducts Processing: Transactions of the Institution of of Chemical Engineers, Part C. 2003;81:266-74.
[194] Changani SD, Belmar-Beiny MT, Fryer PJ. Engineering and chemical factors associated with fouling and cleaning in milk processing. Experimental Thermal and Fluid Science. 1997;14:392-406.
[195] Kim JC, Lund DB. Milk protein/stainless steel interaction relevant to the initial stage of fouling in thermal processing. Journal of Food Process Engineering. 1998;21:369-86.
[196] Santos O, Nylander T, Schillén K, Paulsson M, Trägårdh C. Effect of surface and bulk solution properties on the adsorption of whey protein onto steel surfaces at high temperature. Journal of Food Engineering. 2006;73:174-89.
[197] Rosmaninho R, Melo LF. Protein-calcium phosphate interactions in fouling of modified stainless-steel surfaces by simulated milk. International Dairy Journal 2008;18:72-80.
[198] Blanpain-Avet P, Hédoux A, Guinet Y, Paccou L, Petit J, Six T, et al. Analysis by Raman spectroscopy of the conformational structure of whey proteins constituting fouling deposits during the processing in a heat exchanger Journal of Food Engineering. 2012;110:86-94.
[199] Simmons MJH, Jayaraman P, Fryer PJ. The effect of temperature and shear rate upon the aggregation of whey protein and its implications for milk fouling. Journal of Food Engineering. 2007;79:517-28.
[200] Schmidt RH, Illingworth BL, Deng JC, Cornell JA. Multiple regression and response surface analysis of the effects of calcium chloride and cysteine on heat-induced whey protein gelation. Journal of Agricultural and Food Chemistry. 1979;27:529-32.
[201] Sherwin CP, Foegeding EA. The effects of CaCl2 on aggregation of whey proteins. Milchwissenschaft. 1997;52:93-6.
[202] O'Kennedy BT, Mounsey JS. The dominating effect of ionic strength on the heat-induced denaturation and aggregation of β-lactoglobulin in simulated milk ultrafiltrate. International Dairy Journal. 2009;19:123-8.
[203] Petit J, Herbig AL, Moreau A, Delaplace G. Influence of calcium on β-lactoglobulin denaturation kinetics: Implications in unfolding and aggregation mechanisms. Journal of Dairy Science. 2011;94:5794-810.
[204] Jeyarajah S, Allen JC. Calcium binding and salt-induced structural changes of native and preheated β-lactoglobulin. Journal of Agricultural and Food Chemistry. 1994;42:80-5.
[205] Simons JWFA, Kosters HA, Visschers RW, De Jongh HHJ. Role of calcium as trigger in thermal β-lactoglobulin aggregation. Archives of Biochemistry and Biophysics. 2002;406:143-52.
[206] Carrotta R, Bauer R, Waninge R, Rischel C. Conformational characterization of oligomeric intermediates and aggregates in β-lactoglobulin heat aggregation. Protein Science. 2001;10:1312-8.
[207] Relkin P. Thermal Unfolding of β-Lactoglobulin, α-Lactalbumin, and Bovine Serum Albumin. A Thermodynamic Approach. Critical Reviews in Food Science and Nutrition. 1996;36:565-601.
[208] Tester CC, Brock RE, Wu CH, Krejci MR, Weigand S, Joester D. In vitro synthesis and stabilization of amorphous calcium carbonate (ACC) nanoparticles within liposomes. CrystEngComm. 2011;13:3975-8.
[209] Rodriguez-Blanco JD, Shaw S, Benning LG. The kinetics and mechanisms of amorphous calcium carbonate (ACC) crystallization to calcite, via vaterite. Nanoscale. 2011;3:265-71.
[210] Addadi L, Raz S, Weiner S. Taking advantage of disorder: Amorphous calcium carbonate and its roles in biomineralization. Advanced Materials. 2003;15:959-70.

[211] Loste E, Wilson RM, Seshadri R, Meldrum FC. The role of magnesium in stabilising amorphous calcium carbonate and controlling calcite morphologies. Journal of Crystal Growth. 2003;254:206-18.
[212] Ajikumar PK, Ling GW, Subramanyam G, Lakshminarayanan R, Valiyaveettil S. Synthesis and characterization of monodispersed spheres of amorphous calcium carbonate and calcite spherules. Crystal Growth and Design. 2005;5:1129-34.
[213] Kontrec J, Kralj D, Brečević L, Falini G. Influence of some polysaccharides on the production of calcium carbonate filler particles. Journal of Crystal Growth. 2008;310:4554-60.
[214] Meiron OE, Bar-David E, Aflalo ED, Shechter A, Stepensky D, Berman A, et al. Solubility and bioavailability of stabilized amorphous calcium carbonate. Journal of Bone and Mineral Research. 2011;26:364-72.
[215] Edwards B, El-Shafei A, Hauser P, Malshe P. Towards flame retardant cotton fabrics by atmospheric pressure plasma-induced graft polymerization: Synthesis and application of novel phosphoramidate monomers. Surface and Coatings Technology. 2012;209:73-9.
[216] Weil ED. Fire-protective and flame-retardant coatings - A state-of-the-art review. Journal of Fire Sciences. 2011;29:259-96.