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Novel flame retardant flexible polyurethane foam: plasma induced graft-polymerization of phosphonates

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ABSTRACT

Flame retardancy of flexible polyurethane foams has become an issue due to very severe regulations. To overcome the challenge of incorporating flame retardant (FR) additives during foaming process without altering the foam properties, a plasma surface treatment was used for the first time in this research field: a cold plasma induced graft-polymerization of phosphonate containing precursors (diethylvinylphosphonate-DEVP) with or without a crosslinking agent (1,4 butanedioldiacrylate) was applied on open cell flexible polyurethane foams (PUF). The flame retardant properties of these foams, before and after further rinsing, were evaluated using horizontal UL-94 test for 10s and 60s. One of the tested systems (DEVP + crosslinker), even after sonication, completely stops the melt dripping of the foams when exposed to the flame of the butane torch and charring occurs. This efficient surface treatment was characterized before and after burning by Scanning Electron Microscopy (SEM), Electron Probe Microanalysis (EPMA), ^{31}P solid state NMR and X-Ray Photoelectron Spectroscopy (XPS). Its FR mechanism of action was then further investigated using microscale combustion calorimetry (MCC), Thermogravimetric analyses coupled with Infrared Fourier Transform spectroscopy (TGA-FTIR), pyrolysis gas-chromatography coupled with mass spectrometry (GC-MS pyrolysis) and ^{31}P solid state NMR. The results obtained show that it is necessary (i) to use the crosslinking agent, as DEVP mainly reacts with this crosslinker and (ii) to activate the PU foam before graft-polymerization to promote further reaction with the crosslinker. The characterizations also proved that before sonication, non-reacted DEVP precursors mainly act in the gas phase, preventing ignition, whereas after sonication the covalently grafted phosphorus containing species mainly act in the condensed phase to form phosphonic acid which will promote charring and thus will limit dripping and flame spread.

Introduction

Flexible polyurethane foams (PUF) are primarily used in furniture and automotive industry. These foams burn rapidly, producing large amount of heat and smoke. For example, flexible PUF in furniture and bedding is capable of setting a room to flashover in 5-10 min once ignited[1]. As a result, these last years, a great attention has been paid in some countries to improve flame-retardant (FR) properties of flexible PUF due to strict standards being established both in home furniture safety and in traffic safety regulation.

Flexible PUF flammability is usually minimized by incorporating during processing flame retardant additives, acting as flame retardants either on the basis of condensed-phase or gas-phase mechanisms. However, the most common FRs (e.g., brominated or chlorinated small molecules) for flexible PUF have been proven to be harmful both to human health and the environment [2, 3], resulting in worldwide bans on the use of some of these compounds [4-6].

These concerns have resulted in numerous studies addressing the issue of foam flammability with new FRs (phosphorus, silicon,…) in an attempt to achieve both minimal environmental impact and reduced foam flammability [7-10].

Incorporating flame retardant additives in the bulk during FPUF processing is however a challenge, as both the foaming process and the mechanical behavior of the foam can be altered by these fillers [11, 12]. For that reason, another approach consisting in applying a surface treatment to concentrate the FR effect where it is crucially needed, i.e. on the surface of the material, appears as promising since it eliminates the issues related to the incorporation of FR. However, only few examples of this approach exist in the literature. In particular, recent major advances were published by Grunlan et al.[13] and Laufer et al. [14] on the development of layer-by-layer assembled carbon nanofiber-filled coatings and of sulfur based layer by layer assemblies to efficiently flame retard flexible PUF. Following this work, recent papers were published using this multilayer concept or a one pot coating concept [15-17]. Other techniques, such as cold plasma, however exist to graft-polymerize functional precursors on various substrates such as textiles to bring some flame retardant properties to the materials. This technique was for example successfully applied to flame retard cotton, using plasma induced graft polymerization (PIGP) of acrylate phosphates [18-20], but the concept has never been applied to foams. Some papers also report the interesting use of phosphonate based compounds [21] to flame retard flexible PUF in the bulk [9, 10]. For example, Wang et al. recently incorporated dimethyl methylphosphonate in a flexible PUF during foam processing [22].

According to these different studies, our idea consists in graft-polymerizing by cold plasma a precursor containing both a vinyl function to favor the graft-polymerization onto the foam and a phosphonate function to provide a durable flame retardant action. The objective is indeed to keep this flame retardant effect even if the coated foam is washed. Liepins et al. [23, 24] and Sato et al. [25] reported that dimethylvinylphosphonate (DMVP) and diethylvinylphosphonate (DEVP) exhibit fire retardant properties of interest. We chose in this paper to investigate the plasma graft-polymerization of diethylvinyphosphonate (DEVP) on open cell flexible polyurethane foams.

In the papers reporting the grafting of precursors such as acrylate phosphates on cotton fabrics, it is however mentioned that a crosslinking agent (e.g. ethyleneglycoldiacrylate or EGDA) is usually added to the precursor in order to obtain a good grafting rate after soxhlet washing [19, 26]. A photoinitiator or plasma activation are also reported to increase the grafting rate.

In this paper, the influence of (i) the pre-activation of the foams, (ii) the use of a crosslinker and (iii) the plasma treatment conditions on the FR properties of the foams before and after sonication will thus be investigated. The flame retardant properties of the functional foams will first be evaluated by horizontal flame spread test and are presented in the first part of this paper. The characterizations by Scanning Electron Microscopy (SEM), Electron Probe Microanalysis (EPMA), X-Ray Photoelectron Spectroscopy (XPS) and ^{31}P solid state NMR of the most efficient FR foams are then presented and the possible plasma grafting mechanism of DEVP is presented. In the last part of the paper, the flame retardant mechanisms of action of the plasma polymer are investigated using Microscale Combustion Calorimetry (MCC), Thermogravimetric analyses coupled with infrared spectroscopy (TGA-FTIR), pyrolysis gas-chromatography coupled with mass spectrometry (py-GC/MS) and ^{31}P solid state NMR.

Experimental

Materials

Samples (15 cm x 5 cm x 1.5 cm) were cut from open-cell flexible molded Polyurethane (PU) foams provided by Saira Seats, France and cleaned in an ethanol-water ultrasonic bath for one hour before use. They were then dried for 12 hours in a heating chamber at 60°C.

The Saira Seats foams are composed of more than 98 wt.-% polyurethane and less than 2 wt.-% Bis(chloromethylène bis(bis(2-chloroethyl)Phosphate (Amgard V6, CAS n° 38051-10-4). They are obtained by (i) polymerization of a polyol on an isocyanate and (ii) release of carbon dioxide resulting from the polycondensation of an isocyanate on a water molecule. Both reactions occur simultaneously, and the components are added in stoichiometric amounts, in order to guarantee total polymerization and neutrality of each reactive function (hydroxyle, amine, isocyanate) and the obtention of an inert polymer, without any free monomer.

Surface modification

The scheme summarizing the experimental strategy is detailed in **Figure 1**.

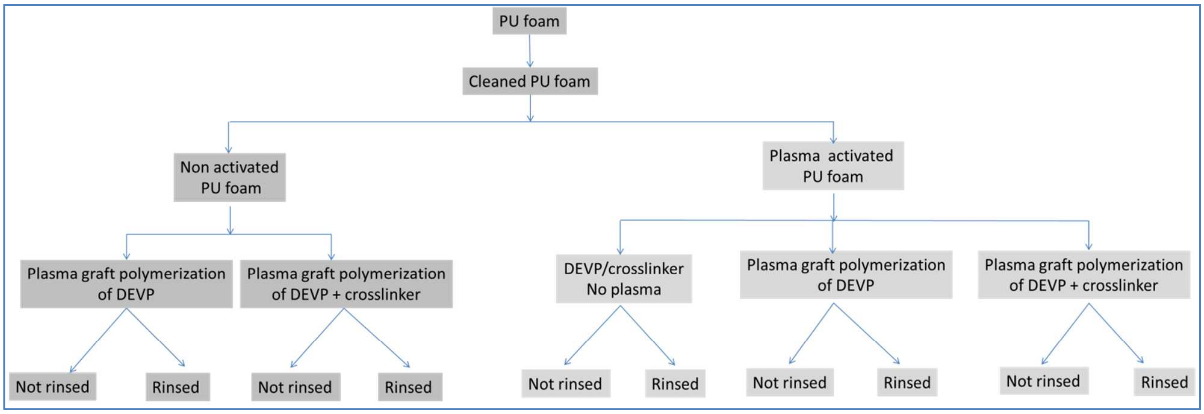

Figure 1. Scheme summarizing the experimental strategy

Half of the clean and dried PUF samples panel was activated by low pressure plasma (Europlasma apparatus CD1200-400 COMBI MC, Radio Frequency generator Dressler, 13.56 MHz) with a pure argon flow (100W, 180s, 15 sccm). Both non activated and activated samples were then immersed for one minute in methanol containing 300g/L Diethyl Vinyl Phosphonate (DEVP) (provided by Sigma Aldrich) (**Figure 2a**), containing or not a crosslinker: 20 wt.-% of 1-4 butanediol diacrylate (provided by Sigma Aldrich) (**Figure 2b**). The samples were then padded one time using a roll-padder (KMS Colortech Service Co., Ltd) at 0.2 MPa.

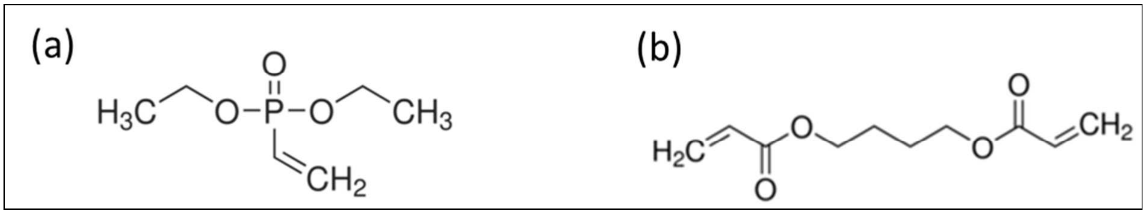

Figure 2. (a) Diethyl Vinyl Phosphonate (DEVP) and (b) 1,4 Butanediol diacrylate (crosslinker)

They were then again submitted to pure argon low pressure cold plasma (100W, 1200s, 50 sccm) to graft-polymerize the DEVP onto and possibly inside the foam. In order to look at the grafting durability, some samples were finally sonicated for one hour in an ethanol-water bath and dried at ambient temperature whereas some others were not rinsed after plasma treatment.

One sample activated by plasma, immersed in the solution containing DEVP and the crosslinker but simply dried in an oven without plasma post-treatment was taken as reference.

All samples were weighed before activation and after DEVP plasma induced graft polymerization (without and with sonication) in order to evaluate the weight gain.

Surface characterizations

The morphologies of the virgin foam and of the most efficient DEVP-coated foam after rinsing were observed using a **Scanning Electron Microscope** Hitachi S4700 at an accelerating voltage of 6 kV and a current of 10 µA. Images were taken at X30, X500 and X2000 magnifications.

To analyse the chemical composition of samples, **Electron Probe Microscopy Analyses** (EPMA) were carried out on a CAMECA SX100. The samples were mainly analysed in cross-sections: they were embedded into an epoxy resin, polished (up to 1/4 µm) and carbon coated by means of a Bal-Tec SCD005 sputter coater. Back scattered electron (BSE) images of the cross sections were obtained at 15 kV, 15 nA. On BSE pictures, the darkest parts correspond to the “lightest” elements. Low and high magnification images were taken in various parts of the samples in order to have a representative picture. Phosphorus X-ray mappings were carried out at 15 kV and 40 nA.

Residues after burning were analysed by ^{31}P **solid-state NMR** measurements using a Bruker Avance II 400 spectrometer. Bruker probe heads equipped with 4mm MAS (Magic Angle Spinning) assembly were used. The experiments were carried out at 162 MHz using these parameters: number of scans was 16, recycling delay was 120s, pulse length was 2.5µs and spinning rate was 10 KHz. H_3PO_4 in aqueous solution (85%) was used as reference.

XPS analyses were performed on an Axis ultra DLD (Kratos analytical) using a monochromatic Al KR X-ray source (hm = 1486.6 eV). The emission voltage and the current of this source were set to 15 kV and 10 mA, respectively. The pressure in the analyzing chamber was maintained at 10^7 Pa or lower during analysis, and the size of the analyzed area was 300 x 700 µm^2, with a depth of 10 nm.

Survey (0–1300 eV) spectra were recorded at pass energies of 160 eV with a step of 1 eV, and high-resolution (C1s) spectra were recorded at pass energies of 40 eV with a step of 0.1 eV.

Data treatment and peak-fitting procedures were performed using Casa XPS software. Obtained spectra were rescaled by shift of C1s C–C at 285 eV. The C1s peaks were decomposed using Gaussian–Lorentzian peak shapes and the full-width at half maximum (fwhm) of each line shape was maintained below 1.3 eV.

Fire testing:

The samples were horizontally mounted in a support (**Figure 3**) and the smallest side of the rectangle was exposed to a Bunsen burner flame for 10s. In some cases, a second sample was exposed in the same conditions to the flame for 60s. During both tests, (i) the dripping and the potential cotton ignition, (ii) the time of combustion after removing the flame, (iii) the char length and (iv) the self-extinguishment of the sample when the flame is removed were assessed.

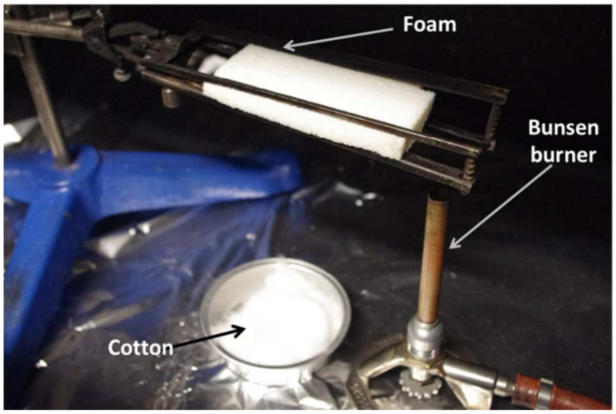

Figure 3. Experimental horizontal flame spread test

Videos of the tests were recorded, and pictures of the samples were taken before and after the test.

Thermal analyses

TG analyses were performed on a Q-5000 TA instruments apparatus. The thermograms were recorded in the 40 - 800°C temperature range with a heating rate of 10°C/min under nitrogen flow, Air Liquide grade (100 mL/min). For each experiment, samples of 10 mg material were positioned on a gold sheet in alumina open pans.

Gases released during the degradation of the virgin foam and of the coated foams were analysed using a **TGA apparatus (TGA Q5000, TA Instrument) connected to a Fourier transformed infrared (FTIR) spectrometer** (ThermoScientific) Nicolet iS10. The IR spectra were recorded between

400 cm^{-1} to 4000 cm^{-1} (spectra recorded every 5s). For each experiment, samples of 10 mg material were positioned on a gold sheet in alumina open pans. All the analyses were carried out in nitrogen flow, Air Liquide grade (100 mL/min). **Combustion flow calorimeter** (PCFC) (Fire Testing Technology, UK) was used to determine on a milligram scale the flammability characteristics of PUFs, following ASTM D7309. PCFC is a useful instrument to determine the fuel content of the decomposing volatile products and can also offer valuable insight into the action mechanism of the FRs. Each sample (approximately 7 mg) was exposed to a heating rate of 1°C/sec from 150 to 750 °C in the pyrolysis zone. Through MCC, the peak of heat release rate (pHRR) was measured in W/g. All experiments were repeated in triplicate. **Pyrolysis-GC/MS** provides an extremely sensitive tool to determine the nature of gases evolved during the thermal decomposition of a material. The Pyrolysis-GC/MS measuring system was provided by Shimadzu. A micro-furnace pyrolyzer (Frontier Lab PY-2020iD), a gas chromatograph equipped with a capillary column and a quadrupole mass spectrometer equipped with an Electron-Impact (EI) ionization source (Shimadzu GC/MS QP2010 SE) are directly connected in series. About 0.2 mg of the samples is added in a stainless steel sample cup. The latter is first placed at the upper position of the pyrolyzer, and then introduced into the center of the furnace (inside a quartz tube vial) under a helium gas flow. In the pyrolyzer furnace, the temperature was initially set at 35°C and then raised to a defined temperature with a selected heating rate (generally 5°C/min). The temperature of the interface between the pyrolyzer and the GC injection port and the injection port were respectively set at 320°C and 280°C. A fused silica capillary column (30 m x 0.25 mm x 0.25 µm film thickness) was used and the linear velocity of helium as a carrier gas was 40 cm/s. The GC column temperature was maintained at 35°C during the whole temperature ramp of samples in the pyrolyzer and then programmed up to 300°C at the rate of 5°C/min, followed by an isotherm of at least 10 min at 300°C. The studied PU foam and DEVP-coated PU foam (rinsed or not) were submitted to a ramp of 10°C/min from 35 to 800°C in inert atmosphere (He) in the pyrolyzer, while volatile compounds were observed, and then the heavier compounds were desorbed. Electron-Impact spectra were recorded at 85eV with a mass scan rate of 2 scan/s. Pyrograms and mass spectra were treated using a GC/MS post-run analysis program (Shimadzu). The NIST and FSearch mass spectral databases were used for the identification of products. MSFragmenter tool, from ACDlabs, was used to help identifying synthesis molecules (not belonging to databases).

Results

A screening of the samples described in **Figure 1** was carried out: the samples were weighed after plasma treatment, before and after sonication, and were then tested to the 10s horizontal UL94 test. The results in terms of weight uptake and fire retardant properties are summarized in the **Figure 4**.

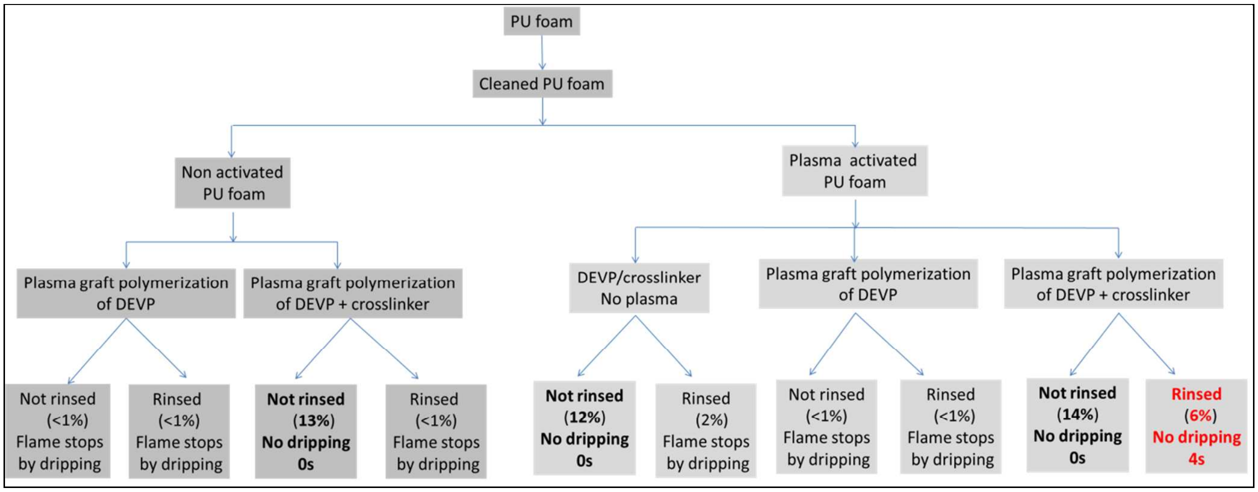

Figure 4. Scheme of experiments and results in terms of uptake and dripping

Most of the samples show an uptake percentage less than 1% after sonication. Only four samples lead to higher weight gain: three non-rinsed samples (14, 13 and 12% weight gain) and only one sonicated sample, i.e. the rinsed pre-activated plasma graft-polymerized foam using the solution containing both DEVP and the crosslinker, which shows a weight gain of 6%. This is the only sample that shows a significant weight gain after rinsing.

The FR performances of the samples were also evaluated using the horizontal UL 94 test for 10s. The results in terms of dripping, which is a critical parameter, are summarized in **Figure 4** for all samples. Virgin PU foam ignites very rapidly and the molten PU drips and ignites the cotton placed in an aluminum pan under the foam. Since the dripping is very intense, the sample self-extinguishes. If the flame is applied on the foam a second time, the same phenomenon occurs. An example of burnt sample is shown in **Figure 5**.

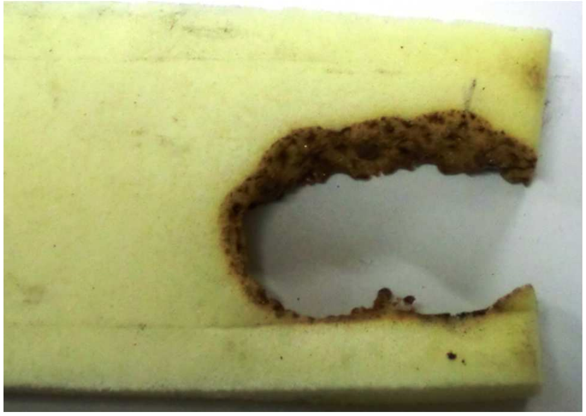

Figure 5. Burnt virgin PU foam

All coated samples exhibit dripping except the four foams with a weight uptake percentage above 6%. Dripping leads to self-extinguishment of the flame but in all cases the cotton placed beneath the foam ignites.

On the contrary, the foams with weight gains of 13%, 12%, 14% and 6% do not drip. Moreover, when the flame is removed from these samples after 10s, flame stops quite instantaneously (0s for the samples with weight uptakes of 13, 12 and 14% and 4s for the washed sample with weight uptake of 6%).

According to the weight gain results, it seems that both pre-activation, plasma post-treatment and the use of the crosslinking agent are necessary to anchor the coating on the foam whereas in other cases only impregnation is obtained. Indeed, it is possible to assume that when the coating is not durable to washing, the polymer or monomers are present at the surface of the foam but without chemical bonding with the polyurethane foam, which explains the drop of weight gain after rinsing.

There is also a clear relationship between the uptake rate and fire test results. It is noteworthy that only 2% weight uptake is not sufficient enough to prevent dripping whereas 6% is, even after sonication.

In order to understand if the DEVP is covalently grafted on the PUF having a weight uptake of 6% after sonication and what is the FR mechanism of DEVP on the PUF before and after sonication, two characteristic samples were chosen for further investigation: the activated plasma graft-polymerized samples using the solution containing both DEVP and the crosslinking agent, before sonication (14% uptake) and after sonication (6% uptake). It has to be underlined that the visual aspect of these two foams is not altered by the plasma and rinsing treatments.

As a consequence, in the following parts of this paper, only these two samples will be considered and will be referenced as “coated PU foam” and “coated PU foam after rinsing”.

It was previously assumed that when using plasma induced graft polymerization of DEVP in presence of a crosslinker, chemical bonding between the foam and the coating occurs since this coating is stable to sonication. It is thus of interest to first understand the DEVP potential grafting mechanism. In order to do that, characterizations were carried out using (i) SEM analyses to evaluate the quality of the grafting and the aspect of the foam cells after grafting and rinsing, (ii) solid state ^{31}P NMR to analyze the phosphorus species graft-polymerized on the activated PUF samples and (iii) XPS analyses in order to evaluate the influence of the activation and of the grafting on the chemistry of the samples.

Figure 6 presents the SEM pictures of the virgin PU foam at three magnifications. The pictures show typical open-cell foam structure. It is observed that the walls of the foam are pretty smooth and that there is no gradient within the foam.

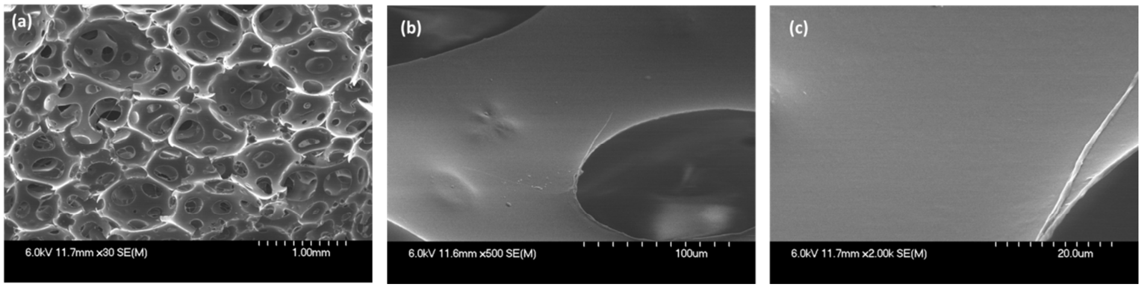

Figure 6. SEM pictures of the virgin foam at x30 (a), x 500 (b) and x 2000 (c)

The coated and sonicated foam was then analyzed and the pictures are presented in **Figure 7**.

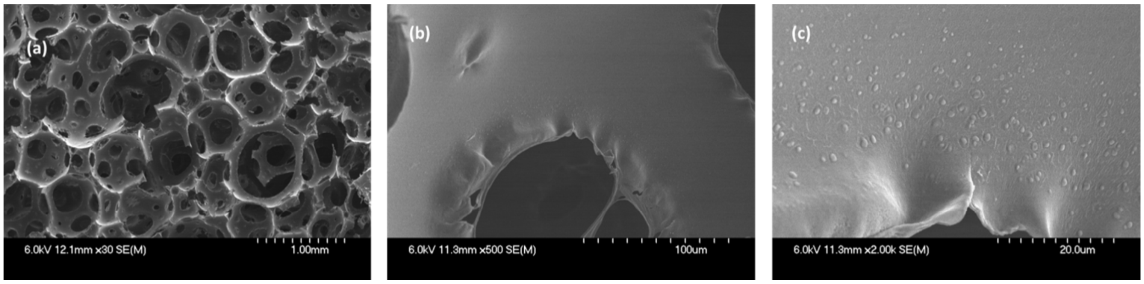

Figure 7. SEM pictures of the PU coated foam after rinsing at x30 (a), x 500 (b) and x 2000 (c)

At magnification x30, the open-cell structure is similar to that observed for the virgin foam structure. However, at higher magnifications, a thin homogeneous coating is observed on and around the PU cells. To confirm this homogeneous coating, phosphorus X-Ray mapping of a cross-section of the foam was carried out using EPMA and is presented in **Figure 8**. To facilitate the cross-section preparation, cells were filled in with an epoxy resin. On the Back Scattering Electron (BSE) picture presented in **Figure 8(a)**, the light grey parts correspond to the coated PU structure whereas dark grey parts correspond to the embedding epoxy resin.

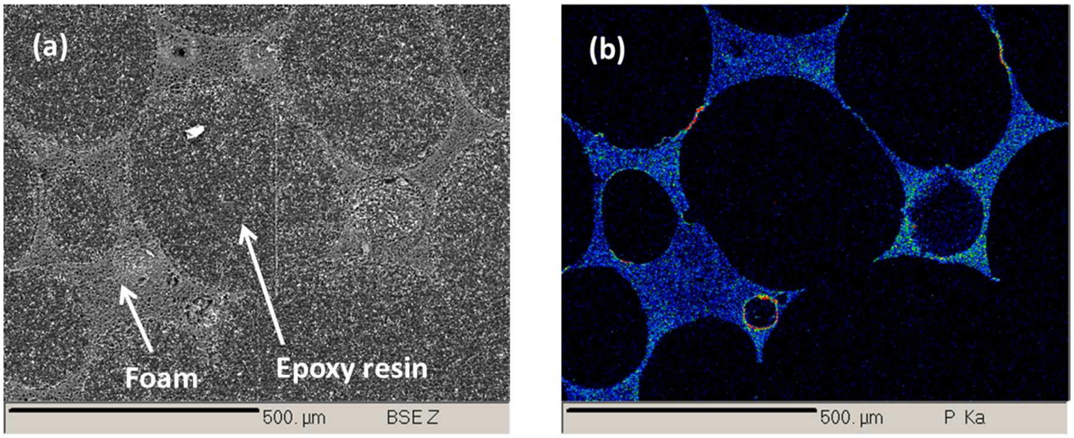

Figure 8. EPMA BSE image (a) and P X-Ray mapping (b) of the DEVP-coated and rinsed PU foam

On **Figure 8(b)** it is clearly visible that the phosphorus containing coating is homogeneously spread everywhere in and on the whole polyurethane foam structure after sonication. It so confirms our previous assumption that the foam is homogeneously coated and that the coating is homogeneous on the whole foam, both inside and on the surface of the PU foam. It also corroborates the hypothesis that the graft-polymerized precursor is strongly anchored to the polyurethane foam.

In order to try to identify the species present at the foam surface, ^{31}P solid state NMR was carried out on both non rinsed and rinsed coated PU foams.

The spectra obtained for the coated PU foams before and after rinsing are presented in **Figure 9**.

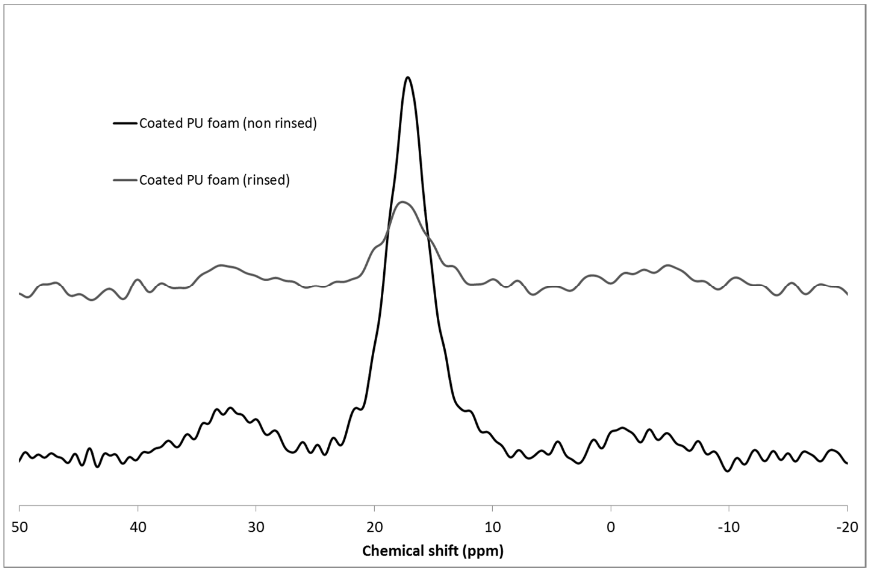

Figure 9. ^{31}P MAS NMR of the non-rinsed and rinsed PU foams

When DEVP is plasma graft-polymerized on the PU foam, an intense and broad peak at 17 ppm is observed, corresponding to phosphonate units [27]. The smaller and large peaks around 33 ppm and -2 ppm can be attributed to phosphonate derivatives [28] resulting from the plasma gas action (chain scission, recombination, etc.). The peak at 17 ppm characteristic of phosphonates still exists after rinsing, with lower intensity as well as the two other peaks. It demonstrates that the phosphorus containing species still remain on the PU foam after rinsing.

Cold plasma is a very efficient process to graft-polymerize monomers containing vinyl groups by reaction between hydrophilic functions present at the surface of a sample with the vinyl group of a monomer through covalent bonding. These hydrophilic functions can be introduced through an activation treatment as it was previously shown in various works [19], [29], [30]. Such activation will create hydroxide, peroxide and hydroperoxide groups on the surface of the sample. This is in good agreement with the results obtained in this work: when no activation was done before coating, the DEVP coated foam did not show any FR properties after rinsing.

A simplified PU foam activation mechanism is shown in **Figure 10**.

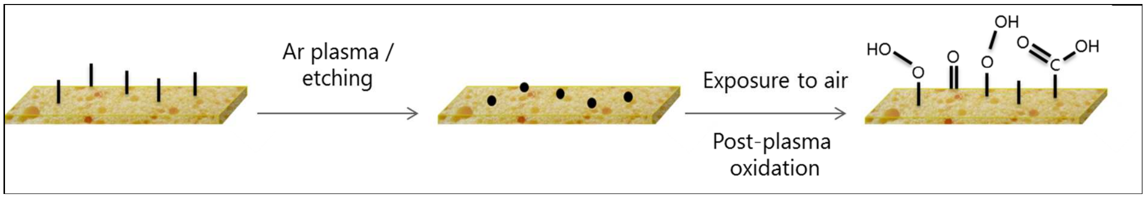

Figure 10. Simplified mechanism of PU foam activation (sample surface)

Moreover, it was shown that when no crosslinker is added, the weight gain is very low and consequently no FR effect is observed (**Figure 4**). It could then reasonably be assumed that the crosslinker reacts with the hydroperoxide functions of the activated PU and that this crosslinker grafting favors further immobilization of the DEVP precursor in the plasma by radical reaction [31]. To try to go further in the mechanism of formation of the deposit, XPS analyses were carried out on two representative samples: virgin PUF and coated PUF after rinsing.

The atomic percentages obtained for both samples are summarized in **Table 1.**

Table 1. Quantification by XPS of various elements at the surface of the foams

	C1s (%)	**O1s (%)**	**N1s (%)**	**P2p(%)**	**O1s/C1s(%)**	**P2p/C1s(%)**
Neat PUF	75,3	22,2	2,5	0,0	29,5	0,0
Coated PUF (after rinsing)	72,0	26,8	0,1	1,1	37,2	1,5

Looking at the phosphorus percentage, it is clear that some phosphorus is still present on the PUF surface after rinsing. It confirms the results obtained by EPMA (Figure 8). Considering the nitrogen content, the polyurethane surface is not detected anymore since a negligible amount of nitrogen is observed. It must be reminded that with the XPS technique, only the extreme surface (10 nm depth) is analyzed. Thus, when a new layer is present on the foam, the underlying layer cannot be detected.

The decompositions of C1s peaks obtained for both materials were then carried out. The percentage of each bond was calculated and results are shown in **Table 2**.

Table 2. Quantification of bonds for C1s peaks of the virgin PU foam and of the coated and rinsed PU foam

Virgin PU foam **C1s**

bonds	eV	%
C=C	283,6	35,35
C-C	285	53,73
C-O/C-N	285,7	6,75
O=C(-N)-O	287,6	4,17

Coated and rinsed PU **C1s**

bonds	eV	%
C-C	285	47,84
C-O/C-N	286,2	29,28
O-C-O	287	11,66
C-P	288,8	11,22

On the coated and rinsed PU foam, no C=C bonds are detected. The absence of C=C bonds confirms again that the PU surface is not detected by XPS analysis and it can thus be assumed that (i) all non-reacted precursor has been removed from foam surface and that (ii) only reacted crosslinker is present. Moreover, a large amount of C-P (11%) bonds are identified, confirming the presence at the surface of the DEVP derivatives previously observed by ^{31}P NMR.

Considering NMR and XPS results, the following mechanism of action can be suggested: the crosslinker could covalently bind the PUF, and then the vinyl group of DEVP could react with the radical formed on the crosslinker (**Figure 11)**.

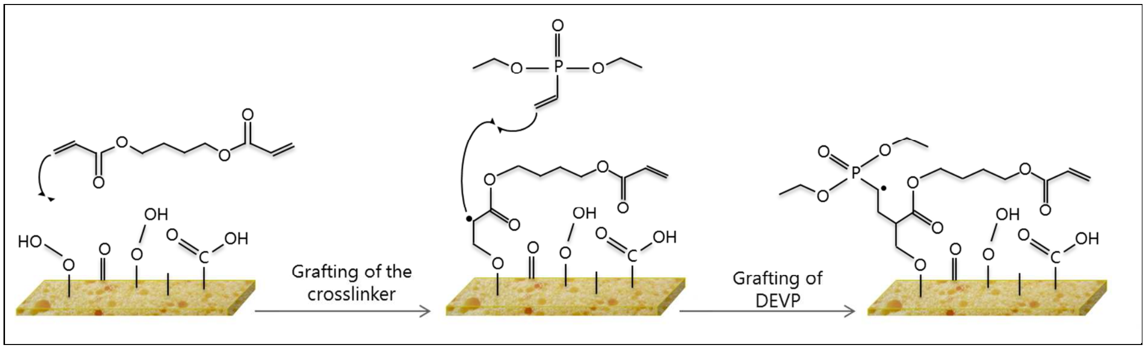

Figure 11. Mechanism of DEVP grafting on activated PU foam

However, this figure gives only a hint of the principle mechanisms, and the last figure does not completely correspond to the coating obtained at the end of the process, as the C=C bonds react in the plasma, and the residual radicals tend to react with oxygen from air after the process.

It is possible that some phosphonates also directly graft onto the PUF, but as no FR effect is observed when no crosslinker is added, the configuration presented in **Figure 11** is more likely.

As observed in the previous parts, the presence of only 6% weight uptake is sufficient to obtain a clear fire retardant effect. The next step of this study thus consists in understanding the flame retardant mode of action of DEVP based coating on both sonicated and non-sonicated coated PU foams.

First, on both non sonicated and sonicated samples, fire performances were evaluated using the UL94 horizontal burning test, applying a flame for 10s but also for 60s.

The results are summarized in the **Table 3**.

Table 3. Behavior of the samples exposed to horizontal flame spread test

	PU foam		**DEVP-coated foam- no rinsing**		**DEVP-coated foam - rinsed**	
Time to exposure to flame	10 s	60 s	10 s	60 s	10 s	60 s
Dripping	Yes Cotton ignition	Yes Cotton ignition	no	no	no	no
Time of combustion after removing of the flame	1s (dripping)	1s (dripping)	0s	0s	4s (on a 5 mm² zone)	5s (on a 5 mm² zone)
Charring length while PU foam in contact with the flame	NC	NC	5 mm	1,5 cm	2 cm	2 cm
Self - extinguishment when flame out	Yes (due to dripping)	Yes (due to dripping)	NC	NC	Yes	Yes

Pictures of the coated samples after 10s and 60s exposure to the flame are presented in **Figure 12**.

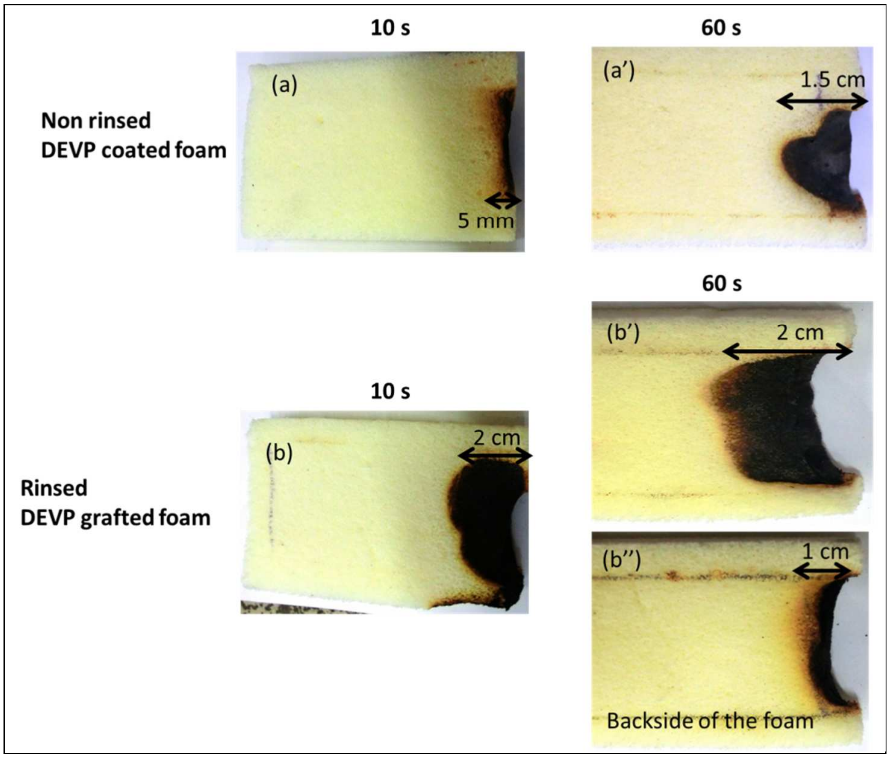

Figure 12. Numerical pictures of the samples obtained after 10s and 60s exposure to horizontal burning test of the non-washed coated foam (a and a') and of the washed coated foam (b, b' and b'').

The non-sonicated coated PUF does not ignite or drip when put in contact with the Bunsen burner, only the part in contact with the flame becomes black on a 5 mm wide zone when the sample is exposed for 10s to the flame and on a 1.5 cm wide zone when it is exposed to the flame for 60s. In both cases, when the flame is removed, no flame or ignited part is visible and charring phenomenon stops immediately.

The sonicated coated PUF ignites, and flame spreads on about 2 cm whatever the time of exposure (10s or 60s). When the char is formed the flame remains on the charred part and does not spread on the rest of the foam. When the burner is removed, small flames remain on tiny zones (about 5 mm²) of the charred part, which self-extinguish very rapidly and no additional charring is observed.

In order to understand the fire retardant mechanism of action, thermal decompositions of virgin PUF and coated PUF (before and after sonication) were first studied by TGA. TG and DTG curves as well as corresponding data of virgin and coated PUF (before and after sonication) are presented respectively in **Figure 13(a)**, **Figure 13(b)** and **Table 4.**

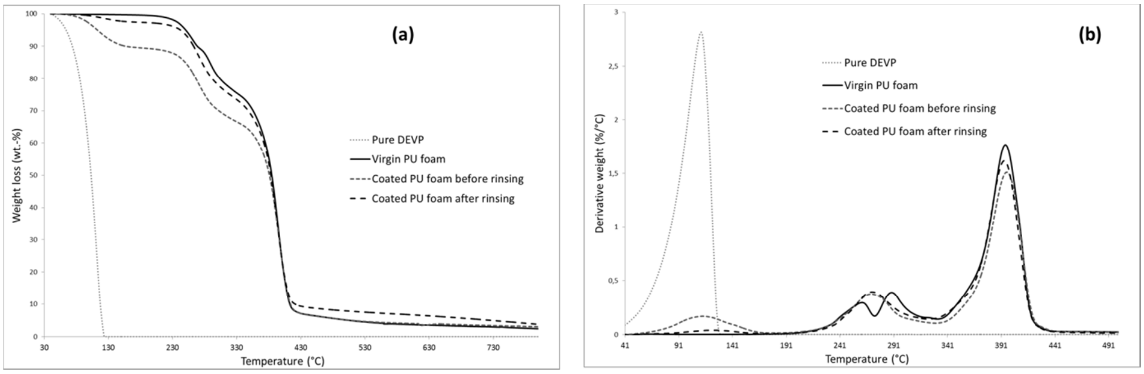

Figure 13. (a) TGA curves and (b) DTG curves of pure PUF, pure DEVP, non-rinsed DEVP coated foam and rinsed DEVP coated foam

Table 4. TGA data of pure PUF, pure DEVP, non-rinsed DEVP coated foam and rinsed DEVP coated foam *(* $T_{5\%}$: 5% weight loss temperature and ** T_{max}: maximum weight loss temperature)*

Sample	T5%* (°C)	Tmax** 1 (°C)	Tmax 2 (°C)	Tmax 3 (°C)	Tmax 4 (°C)	Char Residue 600°C (wt.-%)	Char Residue 800°C (wt.-%)
DEVP	**64**	**111**				**0**	**0**
Neat PU foam	**246**		**259**	**290**	**394**	**3,8**	**2,4**
Coated PUF(no sonication)	**113**	**113**	**270**	**311**	**398**	**4**	**3**
Coated PU foam(sonication)	**242**	**118**	**270**	**311**	**394**	**7**	**3,8**

The thermal decomposition of virgin PUF and the formation of its various decomposition products are well described in the literature[32, 33]. The first stage of decomposition leads to depolymerization reactions which are characteristic of urethane and substituted urea bond cleavage, to form isocyanate, polyol, primary or secondary amine. Surprisingly it is observed that both treated foams start to degrade at lower temperature as compared to that of virgin PUF. This might also be attributed to the catalytic effect of phosphonic acid derivatives formed during the thermal decomposition of phosphonates, thus accelerating the depolymerization of the urethane moiety [34, 35]. The following stages of decomposition are mainly due to subsequent degradation of the remaining polyol chains and dimerization and trimerization of isocyanates [36, 37].

TG data of the coated PUF before sonication indicate a degradation step in the range of 100-200°C compared to the virgin PUF and thus a higher weight loss (see T5% in **Table 4**). This could be attributed to the presence of non-coated DEVP, which is completely degraded at 123°C. The rinsed coated PUF also shows a higher weight loss in the range of 100-200°C, but much lower than for the non-rinsed foam.

The different foams were then evaluated by microscale combustion calorimetry (MCC) [38] (Figure 14). The data are summarized in **Table 5**.

In MCC technique, the gases released during the pyrolysis are evacuated into an oven at 900°C containing a 80/20 N_2/O_2 mixture. In these conditions, a total combustion of these gases takes place. The MCC calculates the heat release rate by measuring the consumption of oxygen.

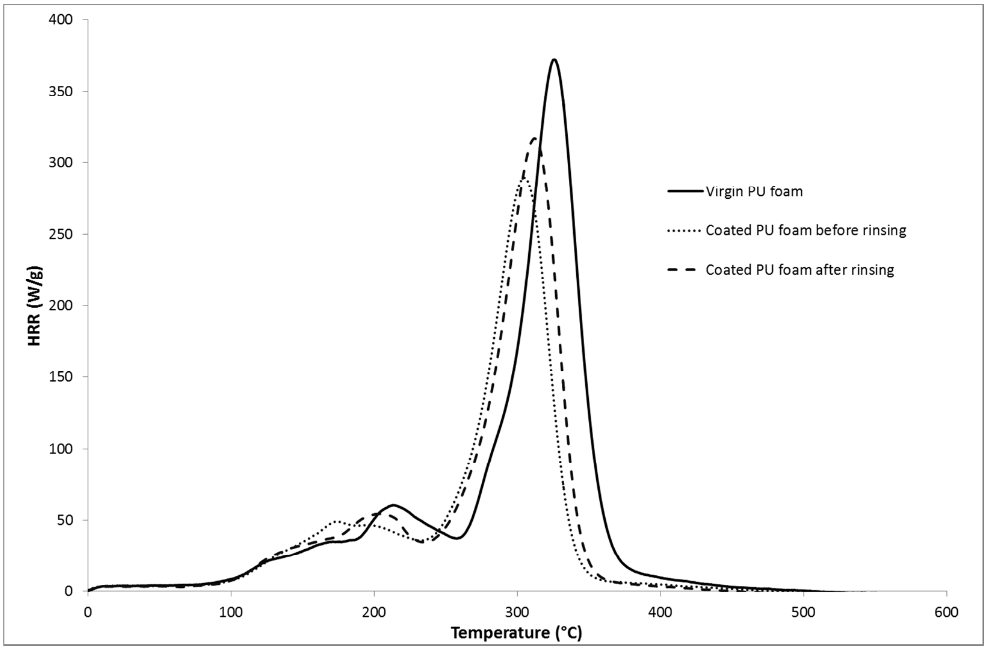

Figure 14. Microcalorimeter results on virgin foam and non-rinsed and rinsed DEVP coated foams

Table 5. Microcalorimeter characteristic data

	pHRR (W/g)
Virgin PU	375 ± 5
Coated PU foam before rinsing	289 ± 6
Coated PU foam after rinsing	312 ± 3

The virgin PU foam exhibits a maximum pHRR of 375 W/g and a corresponding decomposition temperature of 325°C. The combustion of flexible polyurethane foams is known to be a two main steps process. The first step corresponds to the melting and degradation of the foam into a tar and the second step to the combustion of the tar previously produced [33, 39]. These two degradation steps lead to two distinct peaks of rate of heat release.

The graft-polymerized sample before rinsing shows a decrease of pHRR of about 23% and a shift to lower temperatures in comparison with the reference PU foam, which is explained by the fact that phosphonate containing flame retardants catalyze the char formation by their decomposition in phosphonic acid [40-42]. The sample after sonication presents a decrease of pHRR of about 17%, which is slightly lower than the sample before sonication, but which can be also related to the difference in term of weight uptake (14% before sonication against 6% after sonication).

These microcalorimeter results can be explained by two hypotheses: (i) the phosphonate based coatings partly flame retard the foam by a gas phase mechanism or (ii) the FR mechanism is a condensed phase mechanism with only a small amount of gases released. To confirm one of these hypotheses, MCC curves were overlapped with TGA curves. For the three formulations, the second combustion step observed by MCC around 300°C corresponds to the third main degradation step observed by TGA (Figure 13). Looking at this third step, no particular difference in term of weight loss between the three samples is observed, whereas a decrease of HRR is observed at the same temperature using MCC. If the FR mechanism was only a condensed phase mechanism, the degradation rate would have been different between the samples. This proves that this decrease of HRR is at least partly driven by a gas phase mechanism.

Taking into account these results and the results obtained in the previous section, one hypothesis is thus that the non-grafted DEVP present on non-sonicated coated PUF may get vaporized earlier for possible flame-poisoning or gas phase actions at low temperature (100-150°C), while the grafted DEVP might act mainly in the condensed phase at higher temperature.

To distinguish both condensed or gas phase action phenomena and understand the FR mechanism of action of DEVP, further analyses were carried out.

The char obtained after flame spread test of the rinsed DEVP-coated sample was analyzed by phosphorus X-Ray mapping in cross-section using EPMA. Again, the char was embedded in an epoxy resin to facilitate the cross-section preparation (**Figure 15**).

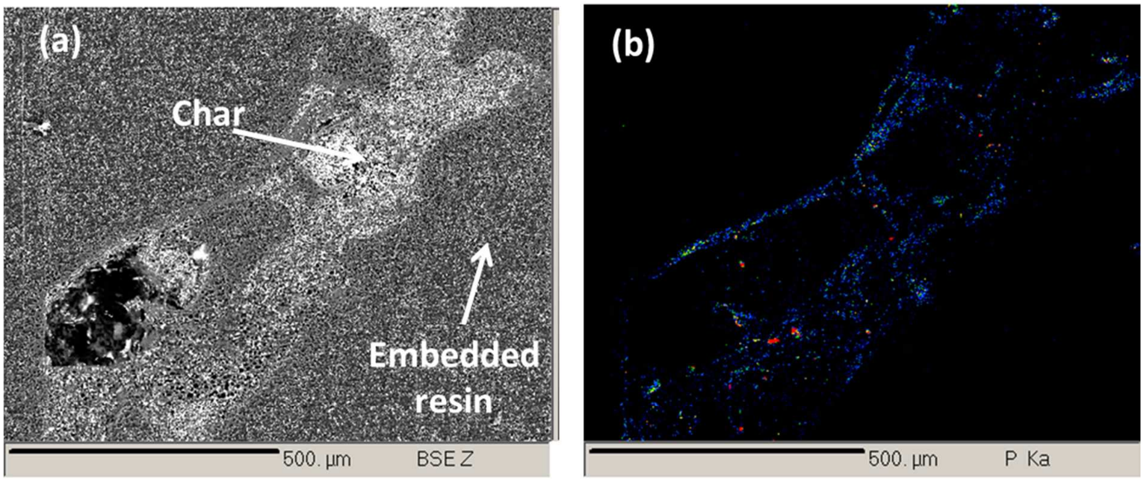

Figure 15. EPMA BSE image (a) and P X-Ray mapping (b) of the char of the sonicated coated PUF

Phosphorus is still present after burning and is homogeneously dispatched in the char. In order to identify the phosphorus species, a ^{31}P solid state NMR was then carried out on the char residue (**Figure 16**).

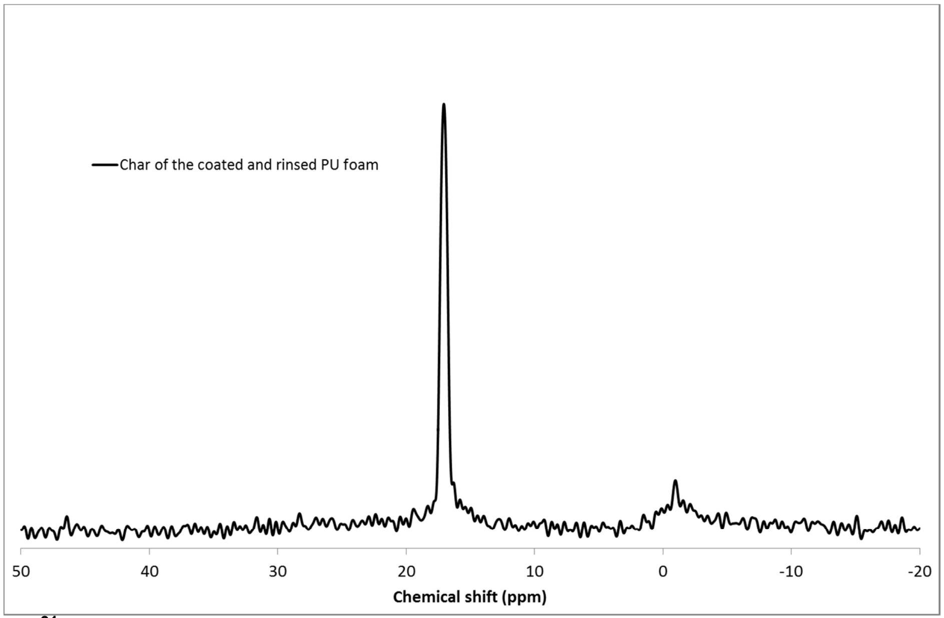

Figure 16. ^{31}**P MAS NMR of the char residue of the rinsed coated foam**

One very thin peak is observed at 17ppm, same chemical shift as the one observed before burning, characteristic of phosphonates (cf. **Figure 9**). However, based on literature review, this chemical shift also corresponds to well crystallized phosphonic acid derivatives [43, 44]. The attribution of this peak to phosphonic acid is in accordance with the literature, thermal decomposition of phosphonates leading to the formation of phosphonic acid [45]. The other small peak at -1ppm corresponds to orthophosphates, which is also in accordance with the mechanism of degradation of phosphonates.

As phosphorus species, and in particular phosphonic acid, are still present in the char after burning, it is possible to conclude that, after sonication the phosphorus grafted species act, at least partly, as FR in the condensed phase.

The gaseous degradation products were first investigated during thermal degradation by FTIR analyses (TGA-FTIR). The virgin PU foam decomposes between 200 and 450°C when heated and produces numerous compounds containing for example C=O and NCO functions due to depolymerization and chain scissions. Some of the gases released during degradation of virgin PU foam, such as CO_2 (2200 à 2400 cm^{-1}), CO (2100 à 2200 cm^{-1}), or other compounds including NCO (2275 cm^{-1}), RC=O (1720 à 1740 cm^{-1}) or aliphatic groups' bands (2700-3200 cm^{-1}) can be identified on FTIR spectra of neat PU foam and coated PU foams before and after rinsing (not presented in the paper) [46-48]. However, as already mentioned according to TGA data, the products released by the grafted DEVP appear at lower temperatures than those of the virgin PUF.

The **Figure 17** presents a comparison of the FTIR spectra of pure DEVP collected at T=20°C with the one of the gases collected at T=135°C during the TGA-FTIR analyses. Spectra of the degradation gases of DEVP-coated PUF before and after rinsing at T=135°C are also compared. The peaks obtained for DEVP at 20°C and DEVP at 135°C are relatively similar. The same peaks are retrieved in the case of the PU coated foams before rinsing. It thus confirms our previous assumption: the first step of degradation corresponds to the release of non-grafted and non-polymerized DEVP. The absorbance is however much lower and the peaks are hardly detected when the foam has been rinsed, confirming that most of the residual non-grafted DEVP has been removed during rinsing.

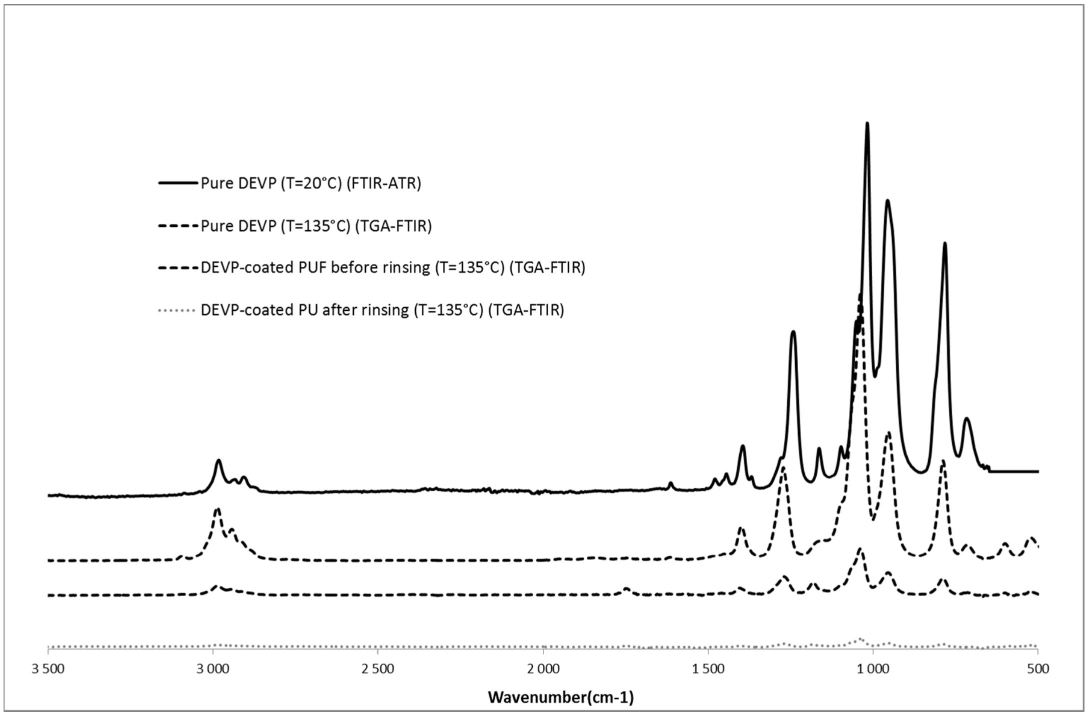

Figure 17. Comparison between FTIR-ATR of pure DEVP at 20°C and FTIR (obtained by TGA-FTIR) of DEVP and DEVP-coated PUF before and after rinsing at T=135°C.

The majority of non-grafted DEVP is thus vaporized at low temperature (100-150°C) for flame-poisoning or gas phase action [37]. This is in accordance with the behavior of the non-rinsed PUF during flame spread test: the sample does not ignite, which is characteristic of a gas phase mechanism.

This gas phase mode of action of non-grafted DEVP is confirmed by Liang et al. who show by mass spectrometry analyses [37] and more recently by vacuum ultraviolet ionization [49] that in the case of allyl-substituted phosphonates the formation of the important PO° fragment during the foam degradation is favored. These radicals play an important role in the flame inhibition cycle in which the H° and OH° radicals (formed from the decomposition of the substrate) are readily scavenged. This reduces the fuel (H° and OH° radicals) available to propagate the flame, and further results in the decrease of heat production.

At higher temperatures, no differences in the FTIR spectra (results not presented) between neat PU foam and non-rinsed and rinsed coated PU foams are observed.

It seems that no phosphorus containing species other than those from DEVP precursor are identified in the FTIR spectrum of the rinsed PU foam. Thus it is likely that the remaining amount of phosphorus containing species is retained in the residue, exhibiting subsequently mainly condensed phase activity. To confirm this, pyrolysis-GC/MS was carried out on the same samples. The chromatograms are presented on **Figure 18**.

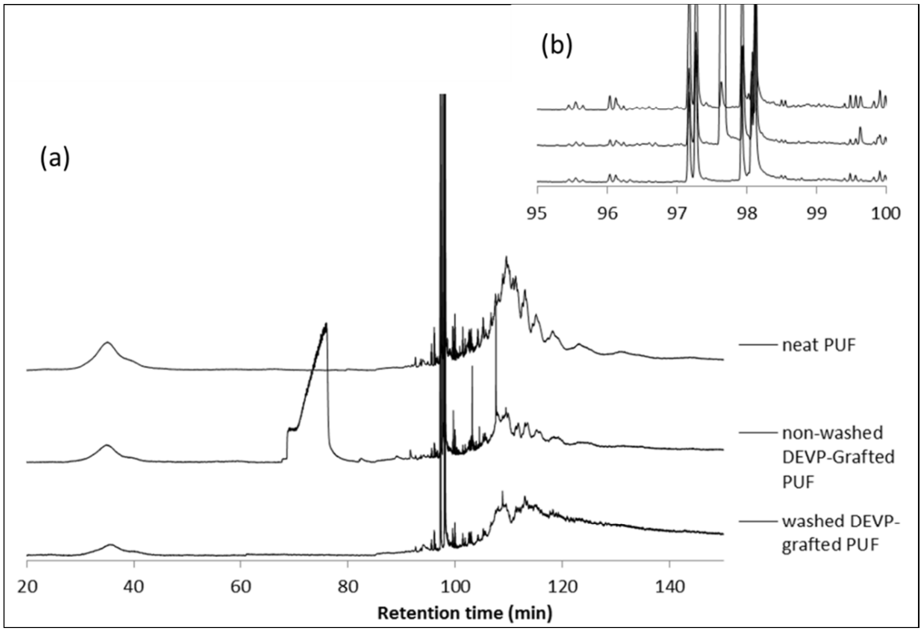

Figure 18. a) py-GC/MS of PU foam and DEVP-Coated PU foam (rinsed or not), b) zoom on the 95-100 min region

In the chromatogram of neat PU foam, three parts are identified. The broad band between 30 and 42 min corresponds to small aliphatic fragments probably produced by the decomposition of the polyol. The fine peaks bewteen 97 and 99 min correspond to the isocyanate units obtained by a depolymerization processes. Over 100 min, a broad band containing some undefined structures would correspond to various PU fragments (mixture of aromatic structures and aliphatic structures).

The chromatogram of non-rinsed DEVP-coated PU foam reveals the same bands as for neat PU foam except one between 70 and 80 min corresponding to free DEVP, and one at 97.6 min characteristic of the crosslinker (**Figure 18b**). Small peaks around 105 and 110 min also correspond to structures derived from the crosslinker.

Finally, the chromatogram of rinsed DEVP-coated PU foam evidences the absence of DEVP as the characteristic band previously observed disappears. The band from 100 to 130 min is slightly different from that of neat PU foam. The band is thinner and more resolved and the earlier retention time suggests a possible shift to shorter mass elements and thus a change in the degradation pathway of PU foam. Py-GC/MS analysis allowed showing the degradation of rinsed DEVP-coated PU foam may be slightly modified, and all the volatile DEVP has been removed, which means that if any phosphorus was observed, the compound would be grafted at the surface.

As phosphonic acid is depicted by ^{31}P solid state NMR in the char of the rinsed coated PU foam (**Figure 16**), this proves that the grafted phosphorus containing species mainly play a FR role in the condensed phase.

Discussion

The analyses of the condensed and gas phase of the non-sonicated and sonicated coated PU foams show two different FR modes of action, represented in the Figure 19.

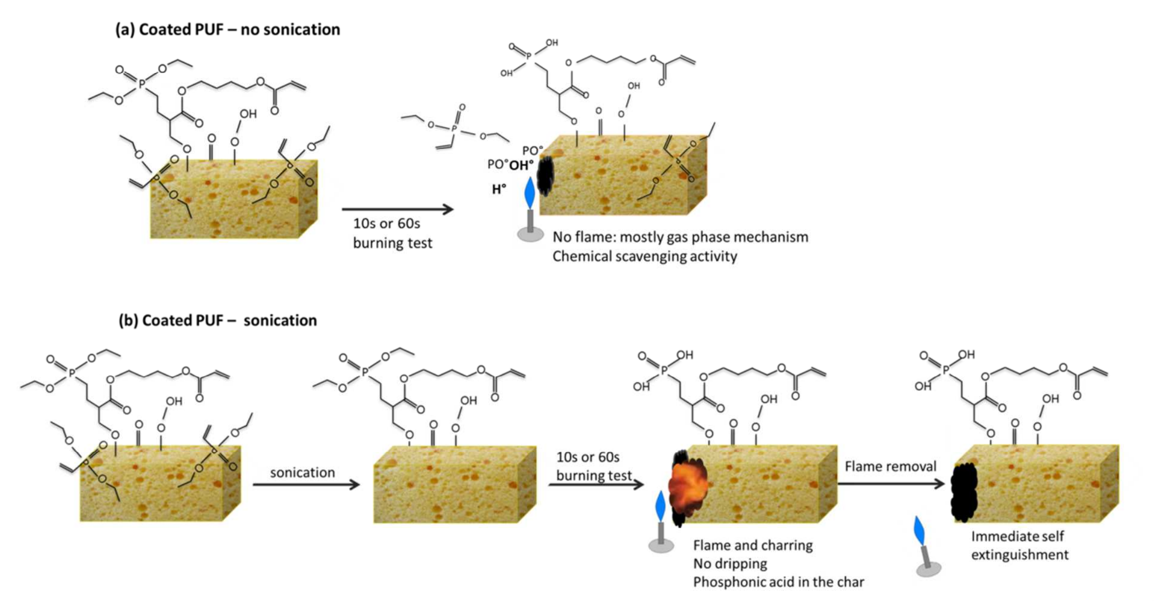

Figure 19. Simplified FR mechanism of action for non-sonicated (a) and sonicated (b) PU foams.

When the foam is plasma treated and tested to UL94 horizontal test without any sonication (**Figure 19a**), its surface is covered with (i) non grafted DEVP and (ii) grafted DEVP, with a total weight gain of about 14%. Under the action of the flame, non-grafted DEVP is vaporized at low temperature (100-150°C), as it was proven by TGA-FTIR and py-GC/MS. The PO° radicals formed play an important role in the flame inhibition cycle in which the H° and OH° radicals (formed from the decomposition of the substrate) are readily scavenged. This explains why during the 10s or 60s burning test no flame is produced.

The FR mechanism is different after sonication (**Figure 19b**). Indeed, after sonication, only grafted DEVP (as it was proven by XPS) is present at the PUF surface, and the total weight gain is 6%. When the sonicated sample is submitted to the horizontal burning test, a flame appears, but charring occurs very rapidly, without any dripping. Analyses of the char show the presence of phosphonic acid (degradation product of phosphonates) and an homogeneous repartition of phosphorus in the char. In that case, the most probable FR mechanism of action is a condensed phase mechanism: the presence of phosphorus promotes the char formation, which protects the underlying PU foam from burning. When the flame is removed, the flame thus self-extinguishes.

Conclusion

Flexible open-cell polyurethane foams were coated, using cold plasma induced graft polymerization treatments, with DEVP precursors. These PUF were then sonicated and their weight uptake and behavior to UL-94 horizontal test were investigated. The results obtained show that in order to obtain a sufficient weight gain after sonication it is necessary (i) to use a crosslinker, as DEVP mainly reacts with this crosslinker and (ii) to activate the PU foam before graft-polymerization to promote further reaction with the crosslinker. One coating system reaches 14% grafting rate before sonication and 6% after sonication. Both these coatings prevent foam dripping during horizontal burning test and promote charring and self-extinguishment after flame removal.

Microscopic analyses after sonication show that the coating is homogeneously spread everywhere in and on the whole polyurethane foam structure. Considering solid state NMR and XPS results, the following mechanism of action can be suggested: the crosslinker reacts with the PUF, and simultaneously the phosphorus containing species (i.e. mainly phosphonates) covalently react with the crosslinker, which explains the good resistance to sonication.

The condensed and gas phase analyses proved that before rinsing, non-reacted DEVP precursors mainly act in the gas phase, preventing ignition, whereas after rinsing the covalently grafted phosphorus containing species mainly act in the condensed phase to form phosphonic acid which will promote charring and thus will limit dripping and flame spread.

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Notes

The authors declare no competing financial interest

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Graphical Abstract