Characterization of a plasma polymer coating from an organophosphorus silane deposited at atmospheric pressure for fire-retardant purposes

Julien Bardon[a,*], Kadir Apaydin[a], Abdelghani Laachachi[a], Maude Jimenez[b], Thierry Fouquet[a], Florian Hilt[a,c], Serge Bourbigot[b], David Ruch[a]

[a] Luxembourg Institute of Science and Technology (LIST), Avenue des Hauts-Fourneaux 5, L4362 Esch-sur-Alzette, Luxembourg
[b] UMET-ISP, UMR 8207, ENSCL, Université Lille Nord de France, BP 90108, 59652 Villeneuve d'Ascq Cedex, France
[c] Université de Toulouse, UPS, INPT, LAPLACE – Laboratoire Plasma et Conversion d'Energie, 118 route de Narbonne, Toulouse Cedex 9 31062 France

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ABSTRACT

Protective coatings from diethylphosphatoethyltriethoxysilane (DEPETS) have been deposited on different polymer substrates in a plasma discharge operated at atmospheric pressure. Plasma polymer chemistry and structure were characterized by means of Fourier transform infrared spectroscopy (FTIR), laser desorption ionization-mass spectrometry (LDI-MS), nuclear magnetic resonance (NMR) and scanning electron microscopy (SEM). A chemical structure of the plasma polymer has been proposed based on the coating molecular characterization. Coatings were deposited on polycarbonate (PC) and polyamide 6 (PA6) substrates. The flame retardant properties of coated substrate samples were assessed using cone calorimetry and compared to those of bare substrates. A significant increase in the time to ignition (TTI), up to +143%, was recorded after coating deposition due to the formation of a high-performance barrier layer at the surface of both polymer substrates.

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1. Introduction

Polymers are intrinsically flammable materials, and therefore they need to be protected against fire. Commercially available polymers are generally flame retarded by incorporating fillers in the polymer bulk. However, high loading of flame retardant (FR) fillers, sometimes up to 60% weight, is necessary to achieve a significant improvement of fire resistance. This high loading of fillers is usually detrimental to (i) processability, (ii) mechanical properties, (iii) aging of polymer materials, and hence increases the cost of the final product. Recently, new approaches based on surface treatments to flame retard polymers or textile fibers have been reported. These can be sol–gel treatments [1–5], layer-by-layer (LbL) coatings [6–17] or plasma coatings [18–24].

Plasma processing is a versatile treatment for the modification or coating of surfaces. When operated at atmospheric pressure in a dielectric barrier discharge configuration, it is relatively easily implemented at industrial scale for in-line treatment since no vacuum chambers are needed [25]. Furthermore, it is particularly

suitable for the treatment of temperature sensitive materials such as polymers as cold plasmas are generated. Finally, plasma treatment does not involve solvents, and therefore is considered to be promising because it is environmentally friendly [26].

Different chemistries are considered when flame retardancy of polymer materials is targeted. Till the year 2000, the main flame-retardant chemicals were organohalogen compounds since they are very effective and relatively inexpensive. However, some halogen FR chemicals are forbidden due to toxicity issues, which can explain why industries are reluctant to further investigate halogen base solutions to flame retard polymers. This has generated an increased research effort for the development of phosphorus-based FR as an alternative solution. More recently, some effort has been dedicated to the development of silicon-based compounds as potentially effective FR agents [2,3]. DEPETS is a functional silane molecule and contains both silicon and phosphorus. The addition of DEPETS and tetraorthosilicate (TEOS) to an epoxy polymer *via* sol–gel reaction to improve flame retardancy of the hybrid epoxy has been reported [27,28]. A sol–gel coating based on DEPETS and deposited on cotton fabrics improves the thermal resistance of treated cotton [29]. A significant increase in the mass residue after flammability tests was attributed to the promotion of a char formation from this DEPETS based coating.

Deposition of phosphorus containing coatings by plasma processing has therefore been explored as a new method for protecting polymers against fire. Such coatings have been reported, however fire retardancy is seldom mentioned [23,24,30–33]. The deposition of a plasma polymer coating at atmospheric pressure from an organophosphorus precursor, triethylphosphate, has been described [33]. The ability to tune the thickness and composition of the plasma polymer by choosing suitable parameters is an important step toward the deposition of organophosphorus coatings with flame retardant properties. The ability for plasma coatings based on organophosphorus chemistry to fire retard polymeric materials has sometimes been reported [24,34–40]. For instance, it has been demonstrated that an organophosphorus coating for flame retardancy can be obtained by a four-step process called plasma-induced graft-polymerization (PIGP). For fire retardancy of poly(acrylonitrile) (PAN) fabrics [35], an organophosphate precursor containing an acrylate or methacrylate group leads to a coating covering the fabric after the PIGP process. The limiting oxygen index (LOI) of the textile is significantly increased by coating, from 18.5% up to 26.5% LOI, i.e., the textile is effectively flame retarded.

Coating deposition from silane precursors such as aminopropyltriethoxysilane (APTES) [41,42], aminopropyltrimethoxysilane (APTMS) [43,44], vinyltriethoxysilane [45], TEOS [46] or other functional silane molecules [47] has been reported. When deposited for barrier purposes, the coatings based on silanes showed a chemical structure with a strong cross-linking [45,47]. Therefore, plasma coatings based on DEPETS were expected to provide phosphorus groups into a strongly cross-linked organosilicon plasma polymer.

A plasma coating based on DEPETS has been investigated in this study. An insight of its chemical structure was provided by different characterization methods. Its flame retardancy effect was evaluated when this coating was deposited on PC and PA6 polymer substrates.

To the authors' knowledge, this work is the first showing the possibility to deposit coatings based on DEPETS by means of a plasma process. Furthermore, it is also the first study showing that coatings improving flame retardant properties of bulk polymer substrates can be obtained by a one-step plasma deposition at atmospheric pressure of an organophosphorus precursor, which has not been the case in previous works [34–40] since PIGP is a multi-step process.

2. Experimental

2.1. Materials

The precursor used for plasma coatings was diethylphosphatoethyltriethoxysilane (DEPETS) purchased from ABCR Company. It was used as received in the plasma deposition experiments.

Polyamide 6 (PA6) and polycarbonate (PC) plates with a thickness of 0.5 mm were purchased from Goodfellow (Cambridge, England). These substrates were used for cone calorimetry test. Two sides polished silicon wafers, purchased from Siltronix (France), were used for characterization purpose.

2.2. Plasma coatings deposition

Plasma polymer coatings based on DEPETS were deposited in a semi-dynamic DBD reactor in open atmosphere already described elsewhere [48]. The precursor was atomized with an atomization pressure of 2 bar (nitrogen), corresponding to an aerosol flow of 0.11 g/min. It was injected into the N_2 carrier gas before entering the plasma zone through a slit between the two top high voltage electrodes. Gap distance and N_2 gas flow were set to 2 mm and 20 L/min, respectively. Substrates were positioned in holes in the bottom electrode so that their external surface was at the same level as the rest of the bottom electrode. During the deposition experiment, the top electrode block moved to and fro over the sample at a constant speed (4 m/min) and the coating thickness was controlled by the experiment duration.

Plasma was generated by a chopped alternative current signal. On-time, i.e., time when high voltage was on, was set to 5 ms and was followed by a 5 ms off-time, giving a duty cycle (DC) value of 50%. Peak-to-peak voltage and frequency during on-time were 30 kV and 6 kHz, respectively. Power during on-time is 1 kW and corresponds to a power density close to 1.6 W/cm^2.

2.3. Plasma coatings characterization

2.3.1. Scanning electron microscopy

Plasma coatings cross-sections were obtained by cutting the coated polycarbonate sample with a razor blade before being observed by scanning electron microscopy (SEM). SEM analyses were carried out on a Quanta 200 FEG apparatus supplied by FEI, equipped with a X Genesis XM 4i energy-dispersive X-ray spectroscopy (EDS) supplied by EDAX. This microscope is a variable pressure SEM apparatus which enables direct observation of insulating samples without additional coating. Water vapor was introduced into the analysis chamber to set the pressure and to avoid charging effect. SEM pictures were obtained at 200 Pa with an electron beam voltage of 10 kV.

2.3.2. Fourier transform infrared spectroscopy (FT-IR)

The chemical structure of coatings was investigated using FT-IR spectroscopy in transmission mode with a Bruker Optics Tensor 27 spectrometer. Coatings were deposited onto double sided polished wafers. Spectrum measured on a bare wafer was recorded as a background signal.

2.3.3. Laser desorption ionization-time of flight mass spectrometry (LDI-TOF MS)

Mass spectrometry analyses were performed directly onto the plasma-polymers deposited onto silicon wafers. Samples were attached to an indium-tin oxide (ITO) coated glass slide using double sided adhesive carbon tape. The so-fabricated set was then carefully mounted on a MTP Slide Adapter II target (Bruker Daltonics, Leipzig, Germany) so that the top of the sample did perfectly reach the surface of the target, thus avoiding any calibration errors. The quality of this assembly was finally checked by multiplying the polylactic acid (PLA) calibration spots, deposited at each corner of the sample and expected to provide highly reproducible signals (i.e., no m/z shifts). LDI-TOF mass spectra were recorded using a Bruker Autoflex III mass spectrometer (Bruker Daltonics) equipped with a frequency-tripled Nd-YAG laser (λ = 355 nm) operating at a pulse rate of 50 Hz. Ions were accelerated by a 21 kV voltage in the positive mode, and a 19 kV voltage in the negative mode with pulsed ion extraction (based on the mass range of the polymer distribution, around 10 ns here). The analyzer was operated in reflectron mode and ions were detected using a microchannel plate detector. External calibration was performed using poly(lactic acid) Mn = 600 g.mol^{-1} (SALDI-like deposits using carbon nanofibers to detect the deprotonated oligomers of PLA). FlexControl software version 3.0 (Bruker Daltonics) was used for instrument control and data acquisition, and FlexAnalysis software version 3.0 (Bruker Daltonics) for data processing.

2.3.4. Nuclear magnetic resonance (NMR)

Solid state NMR was performed for three different nuclei: ^{13}C, ^{29}Si and ^{31}P.

^{31}P NMR measurements were performed using a Bruker Avance II 400 spectrometer (static field 9.4 T) operating at a Larmor