



## Deposition of thick polymer or inorganic layers with flame-retardant properties by combination of plasma and spray processes

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### ARTICLE INFO

#### Article history:

Received 28 September 2012  
Accepted in revised form 17 April 2013  
Available online 23 April 2013

#### Keywords:

Plasma polymerization  
Hexamethyldisiloxane plasma polymer  
Polystyrene  
Polyethylene  
Flame retardancy

### ABSTRACT

Mixtures of hexamethyldisiloxane (HMDSO) and oxygen have been used for deposition of SiO<sub>2</sub>-like layers by plasma polymerization under low-pressure conditions onto polyethylene and polystyrene used as basecoat. Water glass was cast onto these 0.5 μm plasma thick siloxane-like layers with a thickness of 5 to 40 μm. The adhesion of these bilayer systems and their flame resistance were tested.

The effect of different plasma parameters such as monomer/gas ratio, pressure and power input into the discharge on the deposition rate and the composition of the formed layers was studied. Characterization and chemical composition of the formed films were performed using infrared, X-ray photoelectron and solid state nuclear magnetic resonance spectroscopy.

Peel strengths of composites were measured and the locus of peel front propagation was detected. Thermal properties of composites were analyzed by thermo-gravimetric analysis. Finally, the fire-retardant properties of thick coated polymers were determined by exposure to flames and the behavior of coatings on the polymers during flaming was observed visually.

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### 1. Introduction

Functional groups are absent at the surface of polyolefins and polystyrene. However, the presence of such groups is indispensable for any interaction to coatings. Therefore, polymer surface modification is needed for introduction of functional groups, which are capable to interact with those of the coating. Two modification techniques are principally used, the introduction of functional groups onto the polymer surface [1] or the deposition of well adherent coatings using methods such as plasma polymerization [2], spray or electrospray coating [3], dipping, laminating etc.

One of the most important applications of gas discharge plasmas is the surface activation and functionalization of polymers by covalently bonding of plasma gas species onto the polymer molecules. Thus, the plasma treatment allows adjusting the surface characteristics of polymers without significant effect on the bulk properties. The polymer surface can be modified non-specifically using the exposure to noble gas plasmas for generating crosslinks and post-plasma oxidation such as the CASING process (crosslinking by activated species of inert gases) [4]. Thereby, such noble gas plasma particularly produces a high concentration of radicals in near-surface layers. Thus, the polymer surface can be functionalized by plasma induced grafting onto these radicals, which is a combination of plasma activation and

radical chemistry [5–7]. Using chemically reactive plasma gases such as O<sub>2</sub>, N<sub>2</sub>, NH<sub>3</sub> and Br<sub>2</sub> atoms or molecular fragments are introduced into the polymer surface as new functional group [8]. The choice of the plasma gas allows the rough tuning of the elemental composition of formed functional groups. The same is true for depositing plasma polymers from monomers bearing functional groups. These groups in the monomer determine the functionality of the plasma polymer coating [9]. In this way, the plasma treatment can change a variety of surface characteristics for example chemical, adhesive, tribological, electrical, optical and mechanical ones.

Polymers were often needed for lightweight constructions such as used in transportation, automotive and aerospace constructions. Two of the most important problems for application of polymers in these fields are their poor adhesion ability and their flammability. Different strategies were developed to improve these properties [10,11].

Fire-retardancy by intumescent coatings needs layer thicker than 10 μm. Such thick layers are not easy to produce using the technique of low-pressure plasma polymerization. Usually, maximal 1 μm thick layers can be easily prepared in passable time [12]. Moreover, such thick plasma polymer layers have often much internal stress or they shrink. Additionally, the differences in thermal expansion coefficients between polymer and inorganic coating produce also stress along the interface. Then, the coating shows cracks and crazes or the mechanical stress is focused on the interface between substrate and plasma polymer coating. Therefore, delamination occurs spontaneously or under heat exposure, which is contra-productive for application as intumescent layer [13,14]. On the other hand, thin plasma polymer

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layers show generally excellent adherence on polyethylene and polystyrene [15]. Therefore, such thin plasma polymer layers were used as adhesion-promoting base layers, which were covered by much thicker layers using known classic deposition techniques. Such simple classic processes are spraying and dipping. Then, a combination layer (two-layer system) is prepared with the need of high adhesion to the substrate and between the two layers. Proper adhesion of the layer system is necessary to fulfill a hermetical closing-off to avoid the entrance of air and the direct attack of flame to uncovered regions of the polymer.

To check the weakest point in adhesion of such combination layer the peel test was applied and the peeled surfaces were inspected. It was expected that the peel front propagates along the interfaces (interface failure) between substrate and plasma polymer or between plasma polymer and inorganic coating. The other possibility is a cohesive failure within the substrate or plasma polymer or inorganic coating. Such adhesive or cohesive failures are easily identified by XPS (X-ray photoelectron spectroscopy) analysis. It shows either two different spectra characteristic for interface failure or two identical spectra for cohesive failure.

Polyethylene (PE) and poly(styrene) (PS) are thermoplastic polymers characterized by low price but poor adhesivity caused by absence of adhesion-promoting functional groups. Foamed polystyrene is known under the trade names Styrofoam, Styropor etc. (expanded polystyrene) containing 2–3 mm large pores along baked foam balls. Depending on the production process a distinction is made between the normal white and coarse EPS (expanded polystyrene foam) and fine-pored XPS (extruded polystyrene foam). PS foams are good thermal insulators and therefore they are often used as a building thermal insulation material, for example in structural insulated panel building systems. They are also useful for non-weight-bearing architectural structures. The construction industry is the largest purchaser of EPS. They made up 60% of the global EPS sales. The plasma polymer deposition modifies the polystyrene surface and partially its pores.

Porous insulating polymer materials have often a high fire risk because of their high specific surface and additionally most of the polymers are flammable. According to DIN 4102-1 a distinction can be made between non-flammable materials of class A and flammable materials of class B. PS foams are usually classified as B1 material. During building fires the high temperatures let melt and drip the insulating materials. Because of this fact the fire spread easily. Due to the enormous fire load of foamed PS it comes to devastating fires with catastrophic consequences. An additional protection layer on the surface or processed with additional fire retardants in the polymer bulk can prevent the spreading of the fire or at least retarding of the fire.

In this work PS and also PE were coated with thick fire-retardant layers using the combination of plasma and traditional technologies. Here, the plasma polymer deposition has the purpose to act as adhesion-promoting basecoat (primer) for thick siloxane-like layers with fire-retardancy. Such thick topcoats are deposited by spraying and dipping-casting techniques to achieve easily and rapidly a sufficient and effective fire-retardant coverage as mentioned before. However, to achieve this fire retardancy without fail the primary interest is focused onto sufficient adhesion of such two-layer deposits to the PS or PE substrates and to the adhesion between the plasma polymer and the conventional layer. The before mentioned internal stress and the different thermal expansion coefficients of PS, plasma polymer and sprayed coatings cause material shrinking or bending and, therefore, the formation of cracks in the coating or self-peeling of material. In case of poor adhesion the locus of failure at peeling offers the possibility to improve the adhesion by optimization of layer deposition and its anchoring.

First principle of fire-retardancy is to shield the flammable polymer from heat or fire by a non-flammable and oxygen barrier layer which is achieved by coating with thick flame-retardant inorganic

layers. Future prospects of this work are preparation of intumescent layers blowing up and developing sticking gases such as nitrogen, ammonia or water and produce thermal isolation. Another principle is char formation, which is also sticking flames using substances like pentaerythritol. Polyphosphates such as ammonium phosphates support also flame retardancy. Hexabromocyclododecane (HBCD) is the most used bromine-containing flame-retardant additive for expanded polystyrene foams; however, it is suspicious to cause cancer. Thus, different layer systems with flame shielding properties are in the focus.

Here, the following layer system was produced:

- a) Depositions of layers made in the low-pressure plasma consisting of hexamethyldisiloxane (HMDS) and a surplus of oxygen, thus forming SiO<sub>2</sub>-like layers [16]:



- b) Overlaying the SiO<sub>2</sub>-deposit with thick layers of Na-silicate (water-glass) to thicken the siloxane-like layers.

## 2. Experimental

### 2.1. Materials

Polyethylene foils of a thickness of 0.1 mm (Goodfellow) and polystyrene of 0.4 mm (obtained from Petri dishes) were used as substrates. Before coating they were washed in an ultrasonic bath with diethyl ether (PE) and ethanol (PS) for 15 min to remove residual slip agents, light stabilizers, antioxidants etc. as much as possible. Hexamethyldisiloxane (HMDSO, 99.9%) was obtained from Merck-Schuchardt.

### 2.2. Plasma polymerization

The plasma polymerization was carried in a stainless steel reactor [9] (Ilmvac, Germany, volume of 50 dm<sup>3</sup>). The reactor was equipped with a radio-frequency (rf) generator (13.56 MHz, Dressler Caesar 13) working in the continuous-wave mode, an automatic matching unit and a flat powered rf electrode (5 × 35 cm). A plate with the dimensions of 25 × 10 cm served as ground electrode. It was mounted at a distance of 2.5 cm with respect to the powered (hot) electrode. The effective area of the ground electrode is 1.5 to 2 times larger than the rf powered electrode. The substrate is placed on the ground electrode. The liquid monomer was dosed by mass flow controller for liquids (liquid-flow®, Bronkhorst). The liquid flows were adjusted to 5 g/h. The liquid monomers were introduced by a heatable gas/vapor distributor consisting of perforated metallic tubes. The pressure was adjusted by varying the speed of the turbomolecular pump and by regulation of the automatic butterfly valve (V.A.T.). A quartz microbalance was used for monitoring the deposition rate. As the densities of ultra thin layers are difficult to measure, a density of 1.0 g/cm<sup>3</sup> was taken to calculate the film thickness of poly(allyl alcohol) and the density of 2.0 g/cm<sup>3</sup> was used for SiO<sub>2</sub>-like layers (HMDSO + O<sub>2</sub>) adapted from the known density polydimethylsiloxane (PDMS). This means that the absolute values of the thickness can have some error, but this potential error is the same for all the discussed films. Moreover, one can argue that the density of the deposited layers can depend on the plasma conditions like the pressure and wattage. This might be the case but the expected differences in the density values are small and negligible as compared to other effects. All the HMDSO deposited layers are additionally exposed to oxygen plasma for 1 min in order to remove any residual carbon from its surface.

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