

On-line SiO_x Coating of Extruded Polystyrene Sheets Utilizing Atmospheric Pressure Plasma Treatment

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Abstract: Coating of polystyrene sheets with SiO_x layer was performed by employing an atmospheric pressure plasma device. Mixtures of hexamethyldisiloxane with different compositions of carrier gas based on synthetic air, oxygen, and/or nitrogen were utilized for coating deposition. The chemical composition and morphology of the deposited layers were characterized by free surface energy evaluation, energy-dispersive X-ray spectroscopy, atomic force microscopy, and UV-vis spectrophotometry.

Key-Words: Sheet Extrusion, Polystyrene, Coating Deposition, Hexamethyldisiloxane, Atmospheric Pressure Plasma, Surface Treatment

1 Introduction

Application of plasma treatments for product surface modification through chemical functionalization and etching plays an important role not only in science but also in advanced industrial processing. Plasma treatment is used in a great variety of applications, including semiconductor fabrication, treatment of metals, papers, textiles or polymers. In general, these treatments are desirable when the need of surface cleaning and functionalizing, for the purposes of improved adhesion, chemical compatibility with other materials, printing, etc, is arisen. Up to now most of the surface modifications utilized in industrial scales processes are limited to short-time surface activation via atmospheric plasma treatments. For example corona treatment, while many cases of longer-range alteration of surface properties are carried out under low-pressure conditions. Since the preparation of persisting coating is more complicated to achieve using techniques operating at atmospheric pressures, modified surface properties preservation for long time yields several limitations for industrial efficiency of surface modification of large-scale objects or continuous processes [1].

The latest atmospheric plasma devices work at low temperature (up to 200 °C) for coating purposes have not been fully industrialized. It even offers several potential environmental and economical advantages. The main complication for industrial

expansion is connected with the difficulties of sustaining a spatially homogenous and efficient glow discharge under ambient conditions [3]. To achieve homogenous plasma at atmospheric pressure is necessary to increase voltage for gas breakdown in comparison with vacuum pressure working plasma apparatus. The employment of noble gases as plasma medium is usually also required, especially for plasma polymerization [1]. The achievement of the cold homogenous plasma without arcing phenomenon is still not guaranteed even if all these conditions are fulfilled. To overcome this fact several schemes have been proposed, such as the use of pointed electrodes in corona discharges by *Goldman and Sigmond* [4], insulating inserts in dielectric barrier discharges discovered by *Elliason and Kogelschatz* [5] etc.

Consequently, plasma enhanced chemical vapor deposition (PECVD) has been used for several number of applications. Unlike conventional chemical vapor deposition (CVD) is activated by heating, PECVD is exclusively activated by electric energy. The energy is used for initiating electric-chemical reactions, resulting in the creation of active ions and radicals, which participate in plasma deposition layer process. Temperature conditions assure non-devastation of polymer substrate is the main presumption of this coating via PECVD [6]. Organosilicon precursors are very often chosen for plasma deposition, since they are generally safe, easy to handle and are chemically stable. Hexamethyldisiloxane (HMDSO) is the most

utilized one as the precursor (*Sawada et al* [7], *Foest et al* [8], or *Starostine et al* [9]). It is a liquid at room conditions, commercially available, ideally volatile at a particular state and moreover relatively cheap [1]. HMDSO plasma polymerized coatings are nowadays applied as barrier layers [10], anticorrosive treatments for various surfaces [11], anti-scratch layers, hard coatings on soft materials e.g. PMMA or polycarbonate [12] etc.

The development and characterization of SiO_x coating based on PECVD concept on a surface of extruded polymer substrate employing atmospheric pressure plasma apparatus was the main task of the presented work as well as verification of its further application in industry scale.

2 Experimental

Surface plasma modifications were performed utilizing on-line apparatus equipped with a source of atmospheric corona plasma with the rectangular wire/plate electrode of 500 mm length and 1.5 mm width orifice. A plasma assembly attached to a high voltage source with low frequency generator was used for a discharge production. Used electrode case connected to a gas mixture from a side provides downstream flow of gas along the whole electrode. Thus it distributes the mixture containing the chosen precursor (HMDSO) uniformly. A discharge gap between polymer substrate and the orifice was controlled via adjustable mounting and was kept 2 cm during the experiments.

The thin SiO_x coating was deposited on the 25 cm width transparent sheets made of general purpose polystyrene (PS) with thickness of 1.5 mm. The coating was deposited through homogenous stream of HMDSO vapors mixed within synthetic air, nitrogen or oxygen in presence of corona plasma, which is described in Table 1. HMDSO at the flow rate of 0.55 smlm and at 30 °C was applied through the carrier gas utilizing glass bubbler. Total amount of the flowing gas mixture including precursor was kept 42 slm for nitrogen, 55 slm for oxygen and 40 slm for synthetic air. Speed of conveyor used for constant movement of PS sheet was set to 0.5 $\text{m}\cdot\text{min}^{-1}$ during the depositions except at the speed of 0.1 $\text{m}\cdot\text{min}^{-1}$ utilized for the last tested sample (marked 8 in the text below). All treatments were performed at corona dosage 2609 $\text{W}\cdot\text{min}\cdot\text{m}^{-2}$, where it is given by the ratio of generator power to fold of conveyor speed and treatment width. All samples were treated once except Sample 7, which was passed under plasma source three times.

The measuring of free surface energy and contact angle was performed as indirect method of surface

treatment evaluation. While surface energy was evaluated immediately after the plasma treatment via testing inks (provided by company Ahlbrandt System GMBH, Germany) in range from 29 to 60 $\text{mJ}\cdot\text{m}^{-2}$, the second evaluation of surface energy was carried out fifty days after the treatment in order to evaluate the stability of modifications by the help of See System Standard contact angle measuring device (Advex Instruments', Czech Republic). Lifshitz-van der Waals/acid-base model was employed for evaluation of free surface energy. Free surface energy was evaluated from contact angle of five drops of three different liquids (distilled water, glycerol, and ethylene glycol) dripped on each sample.

Topography of the plasma treated and non-treated PS sheets were characterized by atomic force microscopy (AFM). AFM images were taken in semi-contact mode with 0.5 Hz frequency (NTEGRA-Prima, NT-MDT Europe BV, The Netherlands). Sensor NSG 10 (NT-MDT Europe BV) was utilized for scanning of the examined area which was focused at 50 μm x 50 μm . Energy-dispersive X-ray spectroscopy (EDX) have been used in order to evaluate chemical composition of un/modified surfaces (Tescan, VEGA-3 LMU VPSEM, Czech Republic). Beam energy of 30 kV was utilized for all the measurements in order to obtain the excitation of all the elements.

Wear-resistance of the un/treated PS sheets was determined by utilizing a homemade abrasive testing device used for evaluation of surface stability characterization of synthetic leather. A sample of a rectangular shape (25 cm x 4 cm) was horizontally clamped with treated side upward. Subsequently a counterpart of square shape non-woven fabric (1.5 cm x 1.5 cm) weight-bearing with 1 kg load (0.044 MPa). Cycle movement of the testing site (length of 5.5 cm) after the counterpart apposing was turned on and repeated for 250 times. A testing procedure was carried out according to the standard CSN 64 7031. Evaluation of coating efficiency to reduce wear-resistance tested sheets was determined via visible light absorbance measurements carried out on UV-VIS spectrophotometer (HELIOS Gamma UV6, Thermo Fisher Scientific, Inc., USA) at 500 and 600 nm.

3 Results and Discussion

3.1 Free surface energy

The results of free surface energy measurements immediately, and fifty days after the treatment can be found in Table 1.

Table 1 Surface energy of plasma un/modified samples where γ_0 stands for the surface energy of samples evaluated after a treatment and γ_1 for an evaluation 50 days after a treatment

| Sample | No. of cycles | Carrier gas [-] | Conveyor speed [m.min ⁻¹] | γ_0 [mJ.m ⁻²] | γ_1 [mJ.m ⁻²] |
|--------|---------------|-----------------|---------------------------------------|----------------------------------|----------------------------------|
| UN | - | - | 0.5 | 35 | 37.72 |
| 0 | 1 | Air | 0.5 | 56 | 38.90 |
| 5 | 1 | N ₂ | 0.5 | >29 | 21.38 |
| 6 | 1 | O ₂ | 0.5 | >29 | 37.98 |
| 7 | 3 | O ₂ | 0.5 | >29 | 28.36 |
| 8 | 1 | O ₂ | 0.1 | >29 | 25.46 |

As can be seen from the table surface energy value of 56 was reached for Sample 0 immediately after the modification. This finding is in contrast to the results determined for samples treated in the presence of precursor (HMDSO) when the drop of surface energy under the measurable range (below 29 mJ.m⁻²) was observed regardless the number of treatment cycles, conveyor speed or type of carrier gas used.

Furthermore, it could be noted that long term stability of surface treatment had been successfully achieved for Samples 5, 7, and 8 (even fifty days after a modification the hydrophobicity was not changed significantly), while it was not ensured for Samples 0 and 6. Such behavior can be assigned to newly generated elements of a long term permanency nature e.g. mono-layer deposition.

On the other hand the inconsistency of treatment stability observed for Sample 0 is not surprising according to the well-known fact that plasma surface activation has limited durability. Many oxygen plasma treated polymers evolve upon the exposure of air increased wettability (higher surface energy), which is however followed by surface energy decline in time, even goes down to the value of the untreated polymer [12]. Regarding Sample 6, it can be concluded that surface treatment at chosen conditions do not provide enough stable modification.

3.2 EDX

With regard to the hydrophilic behavior of plasma modified samples, tested samples were analyzed employing energy-dispersive X-ray spectroscopy (EDX). Results of chemical composition characterization of un/treated surfaces carried out in this way is graphically presented in Fig. 1 while numbered in Table 2.

Table 2 Chemical composition of plasma modified samples acquired from EDX investigation

| Sample | Chemical composition [at. %] | | |
|--------|------------------------------|-------|------|
| | C | O | Si |
| UN | 94.80 | 5.20 | 0 |
| 0 | 96.19 | 3.81 | 0 |
| 5 | 95.39 | 4.61 | 0 |
| 6 | 95.07 | 4.93 | 0 |
| 7 | 90.93 | 7.99 | 1.08 |
| 8 | 86.03 | 11.32 | 2.65 |

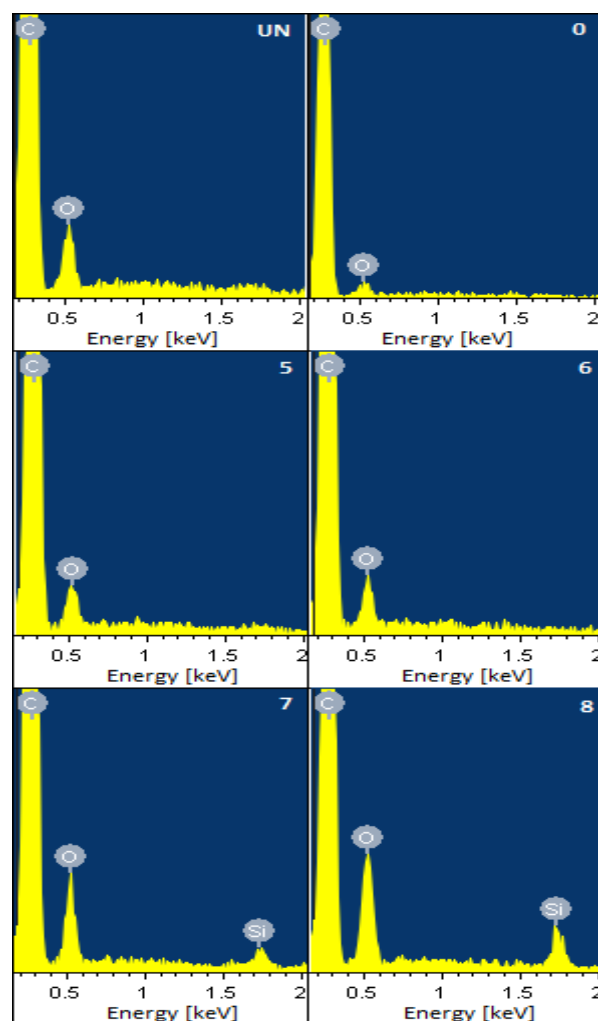


Fig. 1 EDX spectrum of all plasma treated samples

It is clear from the results that the presumption of Samples UN, 0 and 6 do not contain any other elements than carbon and oxygen, which was raised in accordance with previous findings, was correct. Moreover, the presence of silicon in the surface layer was confirmed for Samples 7 and 8, while it was not proved for Sample 5. The persistence of stable hydrophobicity could be related to the utilization of nitrogen plasma source and its influence on final surface energy. Nitrogen plasma ability for the long term modification of surface

properties has been presented many times and is connected with the generation of carboxyl and carbonate linkages on modified surfaces [13]. The chemical composition results of Sample 7 and 8 support an assumption that these samples contain newly created entities incorporated on their surfaces. Despite the relative small amount of chemical findings that had been proved the presence of silicone was clear and it warranted further analysis.

3.3 AFM

AFM scanning was utilized as a tool for samples' surface topography characterization. AFM images with a resolution 50 per 50 μm shown in Fig. 2 depict the surface appearance of Samples UN, 6, 7, and 8 as selected representatives having surface untreated, and treated with HMDSO precursor under various operation conditions of plasma treatment. As seen from the scan fields of Samples UN and 6, there are no visible fragments presented apart from micro-scratches and small dust particles (white spots). Contrary to this observation, a successful modification was induced on Samples 7 and 8. It is exhibited by lighter areas corresponding to significant surface topography changes. Obviously specific relief presenting small circular spots incorporated into the surface predominantly in one line which is interrelated probably with a direction given by sample movement on conveyor (yellow arrow in the pictures) and stands for the presence of SiO_x deposited layer. Described patterns are most likely produced by the heterogeneous nature of corona plasma where filamentary discharge occurs [3].

3.4 Wear resistance

Measuring of light absorbance characteristic was performed consequently to the wearing procedure which was applied to all the tested samples according to standard CSN 64 7031 (as described in experimental part). Determined absorbance values are given in Table 3. From presented data expressed by the lowest values of transmission it is evident that Sample 0 (treated by oxygen plasma in absence of the precursor) has the most sensitive surface to the wearing impact. This phenomenon could be caused by the creation of free radicals and new functional groups due to oxygen plasma treatment [12].

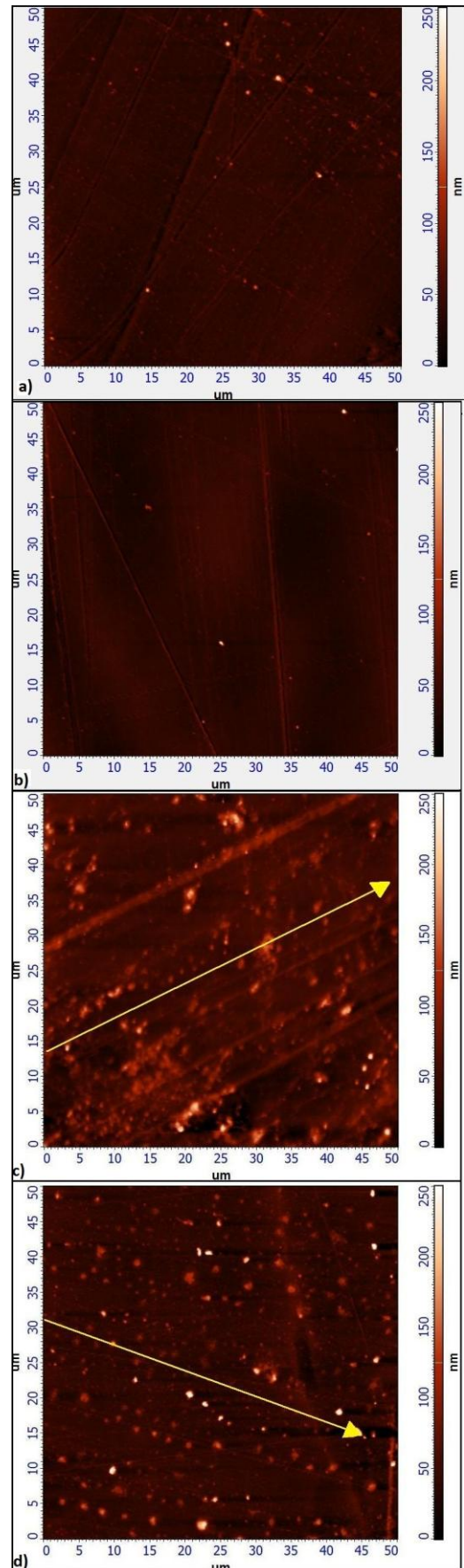


Fig. 2 AFM scans where every single one represents samples: a) UN, b) 6, c) 7, d) 8

Table 3. Light absorbance of plasma surface treated samples after wear resistance testing in wavelength spectra at 500 to 600

| Sample | Absorbance | |
|-----------------|------------|-------|
| | [-] | |
| UN | 0.016 | 0.005 |
| 0 | 0.022 | 0.018 |
| 5 | 0.011 | 0.007 |
| 6 | 0.006 | 0.003 |
| 7 | 0.007 | 0.006 |
| 8 | 0.010 | 0.008 |
| Wavelength [nm] | 500 | 600 |

On the other hand, the most durable samples are Samples 7, and surprisingly also Sample 6 where no SiO_x traces have been detected. The influence of oxygen plasma in combination with HMDSO has probably a different impact on a sample's surfaces than pure oxygen plasma in which no deposition was evident. It should be noted that the increase of wear resistance in comparison to UN Sample, indirectly evaluated through a light transmission, was improved for Samples 6, 7 and 8. It was found to be more or less unchanged for Sample 5, which was even worse for Sample 0.

4 Conclusion

The plasma enhanced chemical vapor deposition via atmospheric pressure plasma treatment was performed on extruded polystyrene sheets. Selected experimental conditions including the changes in carrying gas composition, time and energy of surface treatment were applied in order to prepare required coating layer of SiO_x nature. The investigation of prepared samples proved that a proper deposition of SiO_x layer on PS substrates in the mixture of HMDSO could be achieved at appropriate processing mode. Even EDX analysis revealed that the approximate oxygen-to-silicon ratio of such coating could reach the values up to 7.4. AFM images indicated that the filamentary discharge nature of the corona plasma source is the reason for rather discrete form of the coating layer. Increased wear resistivity to rubbing with non-woven wear-plate was however verified via light absorbance experiments for coated samples compared with the untreated ones.

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