

PECVD polymerised coatings on thermo-sensitive plastic support

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Abstract. With this paper we describe several alternative approaches aimed at polymer-on-polymer coatings, produced by Plasma Enhanced Chemical Vapour Deposition (PECVD) technique. In our case three types of input compounds were applied for varied “cold plasma” PECVD deposition of nano-thick functional layers: namely hexamethyldisiloxane (HMDSO), pentane and toluene onto plastic substrates. The output characterisations through SEM imaging, ATR-FTIR, EDX, AFM and contact angle measurements, proved the methods’ feasibility and properties of the plasma-polymerised coatings.

1. Introduction

During the last three decades applications of Chemical Vapour Deposition (CVD) and Plasma Enhanced Chemical Vapour Deposition (PECVD) technologies show constant growth in various fields of scientific research, followed by technology and medicine [1-3]. In particular PECVD is an outstanding alternative for depositing a range of thin films at lower temperatures than those applied in CVD reactors; this often without settling for a lesser coating quality. The application of “cold plasma” PECVD equipment provides an excellent opportunity to etch, modify and coat thermally sensitive substrates, including porous and nanostructured plastics. In the same time plasma-assisted polymerisation renders possible an utilisation of “non-conventional” organic monomers for highly branched and cross-linked thermoset films having pronounced resistance towards solvents and strong adhesion to the substrate. The creation of composite materials, or layers, provides the researchers with an ability to combine the desirable properties of each of the materials involved in the layered composite. The versatility of plasma polymer depositions in aspects of production of insoluble and infusible films, electrically conductive polymers, controllably crosslinked networks and their potential to reduce environmental, health, and safety issues associated with solvents are well described [4].

Plasma-enhanced CVD depositions onto porous and soft plastic materials are of particular interest not only due to wide area of polymer applications in medicine, separation science and industry. They also attract attention because of the “coating challenge” related to the thermally sensitive and susceptible to stress damage flexible substrates. Deposition of SiO_x thin films on polyethyleneterephthalate (PET) as a barrier anti-oxygen coating for packaging industry was researched by [5]; precursor combination of oxygen-diluted hexamethyldisiloxane (HMDSO) was used with



varied concentration in MW and RF plasmas. Along with plasma-deposition of HMDSO onto Si wafers, substrates of polylactic acid films were used by [6]. In [7] a common mechanism of plasma polymerization of aromatic compounds is proposed, with conclusions based on PECVD of benzaldehyde, benzyl alcohol, styrene, and benzyl chloride. [8-9] studied the plasma polymerization of toluene, on inorganic copper and silicon substrates though. Hydrogenated carbon films deposited by PECVD of methane are described in [10]. PECVD of hexane aliphatic hydrocarbon onto PET was researched by [11], in parallel with HMDSO-based coatings.

With present work we demonstrate a practical application of PECVD method, aimed at “cold plasma” depositions on sheets of porous thermo-sensitive polymers and their characterisation. The scopes of this paper are especially the surface coatings and their properties. Substrates here will be denoted as S1÷S3 due to related ongoing work; their properties will be topic of following distinct article.

2. Experimental part

2.1. Materials

All reagents used were of analytical grade quality: hexamethyldisiloxane (Merck-Schuchardt, Germany), pentane (Fluka AG, Buchs, Switzerland), toluene (Valerus Ltd, Bulgaria). Distilled water (GFL Typ 2004, Burgwedel, Germany) was used throughout this work where necessary.

2.2. PECVD coatings

Coatings were deposited using RF plasma chamber of type B 30.2, VEB Hochvakuum Dresden, Germany).

Polymer samples were placed horizontally onto an intermediate fluoropolymer plate, between the two working electrodes layered with aluminium foil (figure 1). The vapour pressure of the used precursors was high enough to ensure introduction without carrier gas. The depositions occurred within 85-100 Pa working pressure, with RF powers of several watts depending of the plasma stability. The thicknesses of the coatings were simultaneously compared by those derived with quartz resonator frequency changes [12], and visually, trough SEM images of corresponding cross sections.

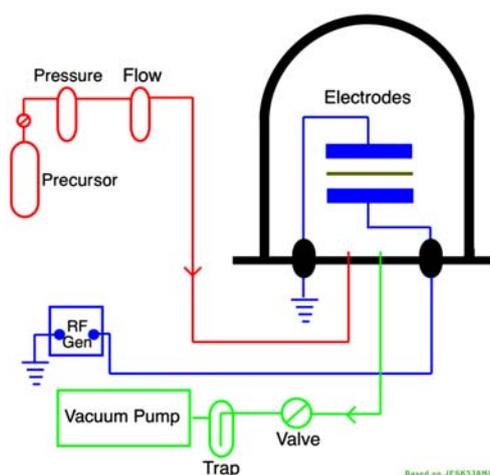


Figure 1. PECVD setup.

2.3. Instruments

Following instrumentation was used throughout the work:

SEM. For higher resolution images, LEO Gemini 1525 FEGSEM (Karl Zeiss), with an accelerating voltage of 5 kV, was used. Prior to analysis for both SEM analysis (here and EDX), samples were

sputter coated (Q150T S turbo-pumped sputter coater, Quorum Technologies Ltd., Ashford, UK) with 10 nm chromium under an Ar atmosphere (0.02 mbar).

Infrared spectra. The FTIR analysis was performed using a Spectrum 100 FT-IR Spectrometer fitted with Universal ATR Accessory. The scanning range was 600-4000 cm^{-1} and the resolution was 1 cm^{-1} . “Net” absorption spectra of the differences between the plasma-covered and initial plain polymers were collected and analysed, because of the picture of pure related changes.

EDX. Especially for the Si-containing films, corresponding SEM-EDX elemental analysis was performed using a JEOL JSM 6010 LA. For EDX mapping an accelerating voltage of 20 kV was used.

Contact angle measurements were performed with an Easy-Drop Instrument (Krüss) at room temperature. 2 microlitres of DI water was deposited on the surface, and analysed via the sessile drop method. A minimum of 6 samples from different spots were obtained for each film.

AFM. The analyses were performed on a Multimode 8 (Bruker, USA) AFM equipped with E-type pizzo scanner. Samples were attached to a magnetic sample disc using carbon adhesive tabs. Scans were conducted using a silicon tip on nitride lever (MSNL-10, Bruker). The cantilever resonance frequency is in the range 90-160 kHz, with a nominal spring constant of 0.6 N/m. Nanoscope analysis 1.5 was used to process the obtained images.

3. Results and Discussion

Films having different surface properties and degree of hydrophobicity were developed with the course of our work. Depending on the different durations of each procedure not only the thicknesses vary, but also varied surface morphology was observed.

3.1. Polysiloxane plasma-deposition

An application of pure HMDSO vapour, unlike the SiO_x films from HMDSO/oxygen mixtures [13], outputs siloxane polymer having distinctive organic nature. As visible on figure 2, siloxane coatings together with the pentane-based ones display intrinsic hydrophobic nature.

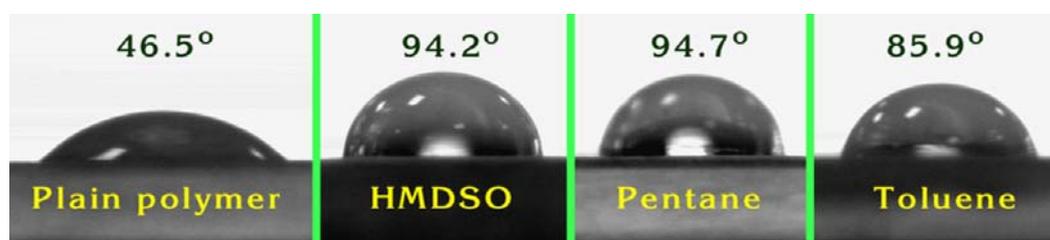


Figure 2. Contact angles for plain substrate S1 and the plasma-deposited films type H (20 min), P (5 min) and T (20 min deposition). Corresponding standard deviations are (from left): 7.8°; 3.7°; 3.4°; 5.0°.

PECVD deposited siloxanes show dense well defined surface layers onto the initial polymers. After 20 minutes long deposition in average 110-120 nm thick film develops (figure 3); with parallel quartz resonator proof measurement of 110 nm. Some surface peculiarities show up throughout the procedure though. Depending on the coating time, the surface morphology of the primary layers is characteristic with granular surface nanostructures of varying sizes and quantities, randomly distributed throughout the surface of the siloxane deposit. Figure 3b clearly presents such topography after 20 minutes deposition time: with particles being on the surface, fallen off their nests during the SEM preparations, and some partially immersed into the layer. After total of 40 minutes PECVD treatment however the final layer displays smoother look, with less but rounded granular structures. Besides of these heterostructures, AFM reveals rather smooth siloxane surface: with unevenness of the plain S1 substrate within 0-15.1 nm (area 1x1 μ), coated for 20 min specimens vary within 0-12 nm (1x1 μ), 0-18.2 nm (2x2 μ ; 0.6 N/m cantilever) and 0-17.6 nm (2x2 μ ; 4.0 N/m cantilever).

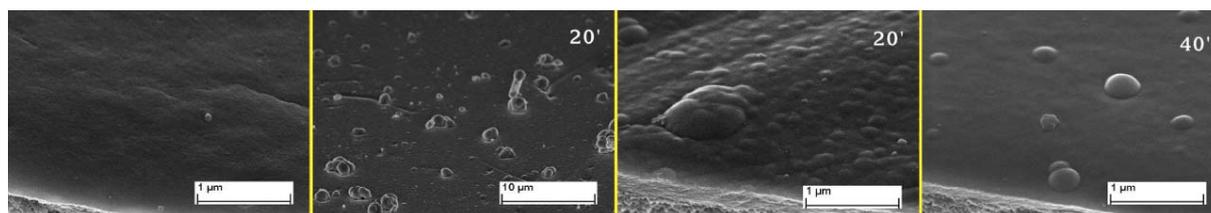


Figure 3. Plain polymer substrate S1 (left), and plasma coated (HMDSO 20 and 40 min; right). Magnification 5.00 and 50.00k.

Previous researches connect the topographic nature of the siloxane plasma films with the type of the precursor: HMDSO/O₂ mixture (rough) and HMDSO (even) [13-14]. Our results partially verify this conclusion; averaged EDX of 20 and 40 minutes-long deposited coatings reveals an increase of Si and O content with the time (Table 1). However, SEM-EDX mapping testifies about enhanced further presence of these two elements at the places of granular structures; according to this a mixed-mode mechanism of the depositions could be proposed here. Most probably, the nanogranules of interest (rather inorganic SiO_x/SiOCH-type) firstly develop into the working volume of PECVD instrument, and subsequently fall onto the organic siloxane film, becoming further partially dissolved and immersed. It is still to be researched where the oxygen arises in the deposition process; with possible sources: adsorbed onto the porous substrate, or through specific plasma decomposition.

Table 1. EDX content of the siloxane coated vs. plain surface

Element	Material								
	Plain S1			HMDSO 20'			HMDSO 40'		
	Mass %	At %	SD	Mass %	At %	SD	Mass %	At %	SD
C	89.2	91.67	0.01	79.64	84.24	0.01	59.61	67.54	0.01
O	10.8	8.33	0.03	19.15	15.21	0.04	35.23	29.96	0.04
Si	-	-	-	1.21	0.55	0.01	5.16	2.5	0.01

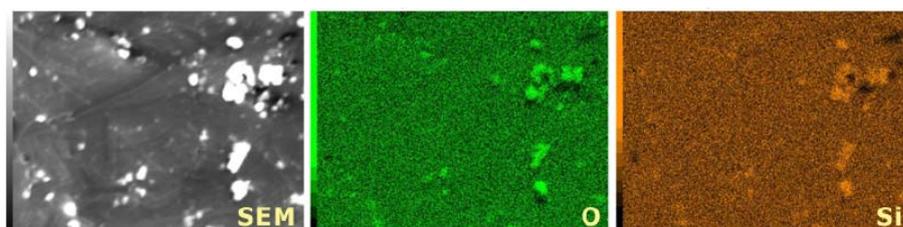


Figure 4. EDX-mapping of Si and O content for the surface of 40' siloxane coating.

In order to investigate the composition of the surface plasma polymers, Fourier transform infrared spectroscopy was applied. Several typical for the siloxanes adsorptions are distinctively pronounced here (Figure 5): Si-O-Si asymmetric stretching vibration mode around 1035 cm⁻¹ and bending vibration around 800 cm⁻¹; strong peaks of methyl groups (Si-(CH₃)₃ rocking vibration) at about 845 cm⁻¹ and symmetric bending at 1265 cm⁻¹; surface Si-OH groups situated around 3300 cm⁻¹ for some of the coatings [13, 15-16].

The characteristic absorption bands between 2847 and 2960 correspond to the asymmetric and symmetric stretching CH_x vibration (all sp³-hybridized CH₃ and CH₂). All in all, we observe the pique at around 1687-1735 cm⁻¹ to appear and rise simultaneously with the -OH vibration at around 3300 cm⁻¹, so we associate this quite strong for some coatings feature with bending mode δ_(OH) of surface hydroxyl groups. The intensity of Si-related absorptions generally increases with the enhancement of Si content of the coatings, which is not necessarily connected with the higher thickness of the layer, but also with the degree of "inorganication" and the presence of SiO_x/SiOCH-inclusions.

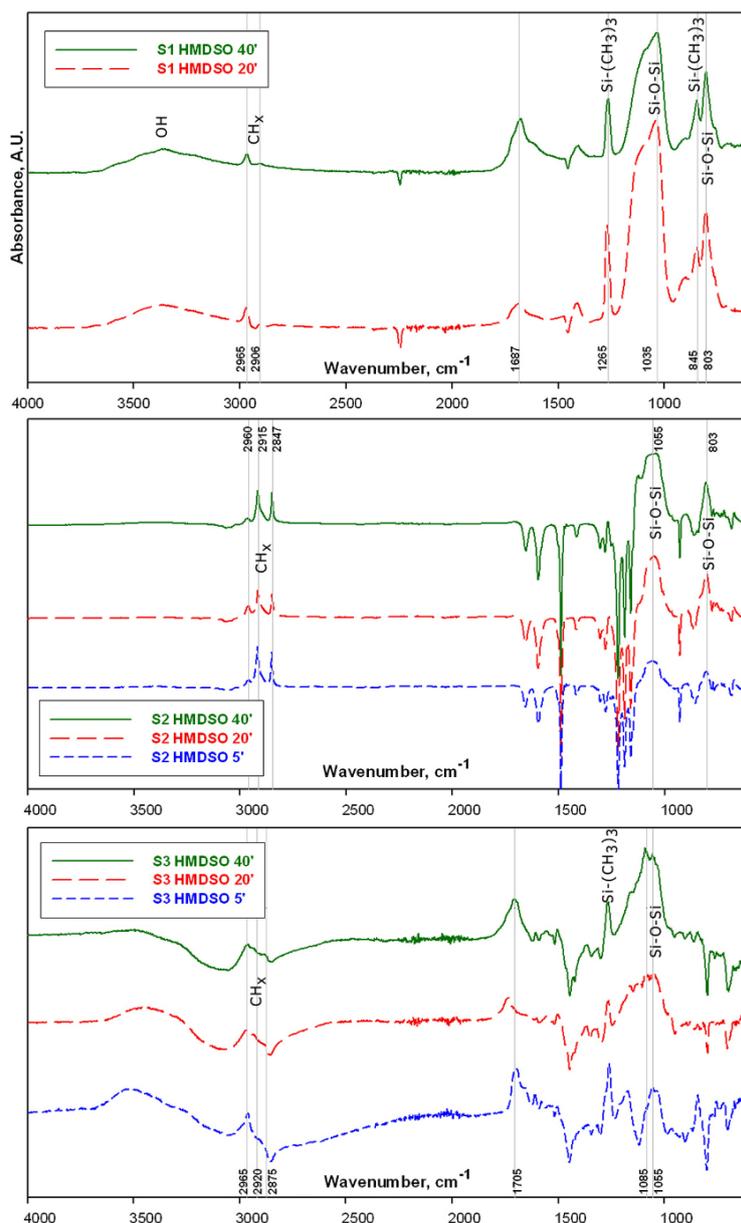


Figure 5. ATR-FTIR “net” spectra of siloxane coatings on substrates S1÷S3.

3.2. Pentane and Toluene plasma depositions

Aliphatic and aromatic hydrocarbons were also applied as plasma polymer-forming precursors, under conditions that we used for siloxane coatings. Figure 6 clearly displays the most prominent change following the plasma deposition of these types: namely enhancement of the peaks related to hydrocarbon groups, and especially the CH_x stretches around $2800\text{--}3000\text{ cm}^{-1}$. These alterations are pronounced after short 5 min long PECVD treatment; longer coating times make them far stronger (Figure 6-upper). Looking at the pentane coating’s FTIR spectra for substrate S1 (Figure 6-lower, top), we see it as a sole indicator of the surface change.

A comparison between the spectra of pentane and toluene coatings on S2 substrate reveals strong similarity (Figure 6-lower). Most likely this can be evidence for decomposition of aromatic hydrocarbons in PECVD plasma conditions, where the deposition of plain hydrocarbon chains and fragments occurred by the “pentane mechanism”. Similar conclusions have been also drawn by other authors [7-8].

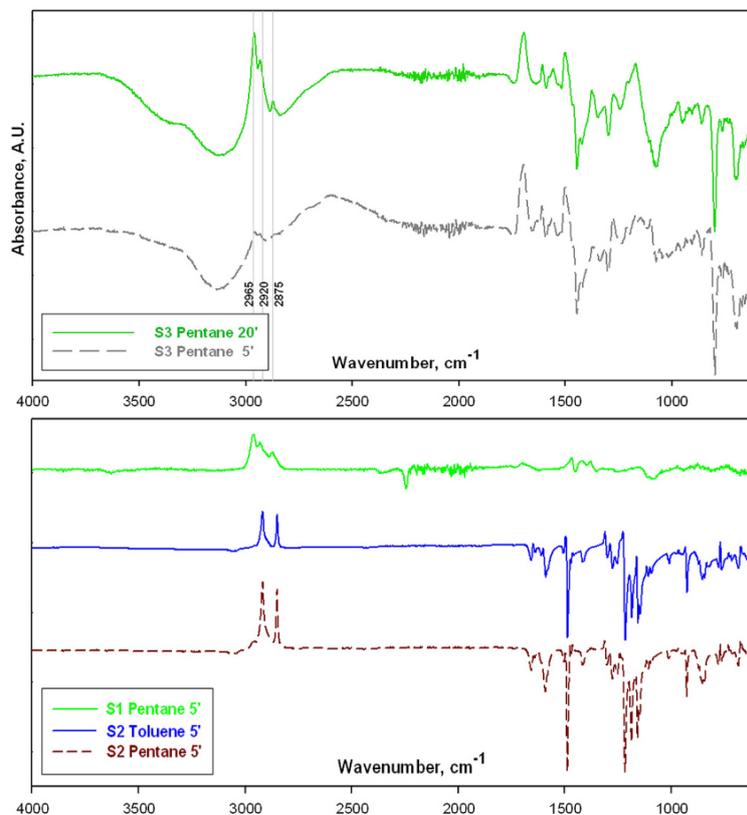


Figure 6. ATR-FTIR “net” spectra of pentane and toluene coatings on substrates S1–S3.

Corresponding SEM images for pentane coatings show homogenous surface with no inclusions, although having more “rugged” appearance (Figure 7). Toluene-derived layers, similar to the pentane ones, demonstrate looser structure unlike the siloxanes, and sharp well defined interface can not be observed at the cross sections.

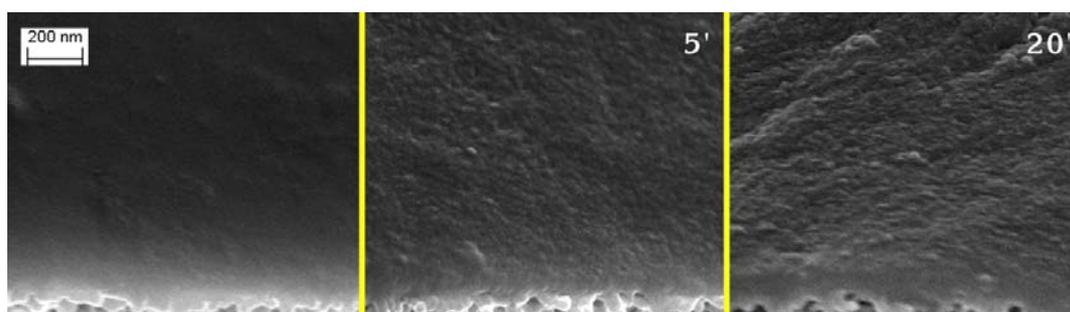


Figure 7. Plain polymer substrate S2 (left), and plasma coated (Pentane 5 and 20 min; right). The thicknesses of the coatings are 12 and 85 nm (quartz resonator). Magnification 100.00k.

4. Conclusions

With this work we studied the deposition and properties of three types of PECVD polymerised films, under different duration conditions. Low-temperature plasma processes rendered possible the application of three porous thermo-sensitive substrates. Surface coatings of siloxane type are dense and well differentiable on SEM microscopy images; they exhibit dual-mode mechanism of the deposition combined with possible hetero-inclusions within the layers. In addition, siloxane FTIR

characterisations are substrate-dependent, which must be taken into account when analyzing. On the contrary, films derived by aliphatic hydrocarbons are rather loose, but uniform polymer deposits, as found also by [10] for methane. Although having some specifics, toluene-based films show close proximity with the pentane-derived ones.

Acknowledgements

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