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GD-OES AND GD-MS INVESTIGATIONS OF THE PROCESSES INVOLVED IN THE POLYMERIZATION OF POLYDIMETYLSILOXANE IN CORONA DISCHARGES

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In acest articol raportam un nou mechanism de generare a oxizilor in polidimetil siloxan atat la interfata substratului cu polimerul, cat si in volumul acestuia, in timpul procesului de polimerizare prin descarcare Corona in configuratia electrozilor vârf-plan.

In this paper we report a new mechanism of oxides generation in the polydimetylsiloxane at the substrate-polymer interface and in the bulk, during the polymerization processes in a point to plane corona discharge electrode configuration.

1. Introduction

It is well known that the polysiloxane polymer layers can improve the corrosion resistance of the metallic substrates. The atmospheric oxygen and most oxidizing chemicals do not affect coatings based on siloxane binders, these layers acting as an effective barrier against the contact of water based corrosive media. [1, 2].

In this paper, we report a physical method, consisting in a corona discharge produced in air at atmospheric pressure in a point to plane electrode configuration, for oxides generation at the polymer substrate interface and its diffusion in the polymer layer bulk during the polymerization process of the polydimetylsiloxane. The substrate material oxides distributed in polymer layers

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can increase the adherence of the polymers to the substrate and its corrosion resistance. These processes have been investigated by infrared (IR) spectroscopy, Glow Discharge Optical Emission Spectroscopy (GD-OES).and Glow Discharge Mass Spectrometry (GD-MS)

2. Experimental conditions

The experimental set-up presented in detail in [3] consists in a point-to plane corona discharge electrode configuration. A DC high voltage of 7 kV was applied through a R = 5 MΩ resistor between the electrodes placed at 10 mm distance.

The discharge current in a Trichel pulsed regime of the negative corona discharge, measured across a resistor r = 1 kΩ (the Trichel pulses being accompanied by a DC permanent current), is about 70 μA. Unlike the negative corona discharge, the current of the positive corona discharge consists only in a DC component having the same value as that of the permanent current of the negative corona discharge (20 μA) in the given electrical and geometrical conditions.

The injection on the free surface of the liquid precursor (0.1 μl of polydimetilesiloxane with hydroxyl end groups) of the negative and positive ions generated in corona discharge in air at atmospheric pressure induces electrohydrodynamic instabilities associated to high electric fields [4]. The convective currents generated in the liquid bulk provide the charged particles transport to the plane electrode and after 2 hours of corona charge injection polymer layers are obtained.

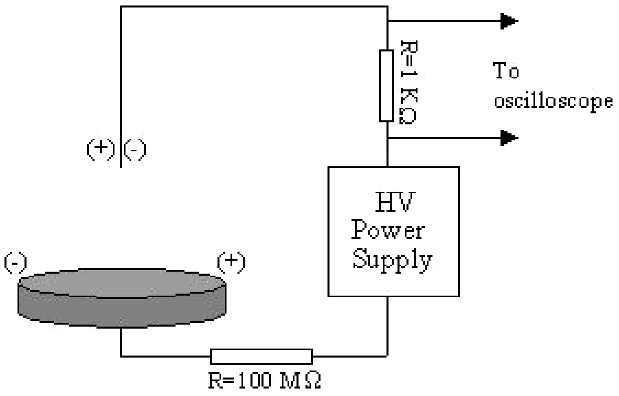


Fig. 1: Experimental set-up.

2.1 Results and discussions

The polymerization processes obtained in corona discharges was emphasized recording the IR spectra of the polymeric layers with an IR Perkin Elmer spectrometer in a reflection configuration at 30^0 reflection angle.

The IR spectrum of the polydymetylsiloxane hydroxy terminated liquid precursor and its chemical structure are presented in Fig. 2a. In the IR spectra of the polymers obtained in negative respectively positive (Fig.2b) corona discharges on titanium substrates it can be observed some additional absorption bands at 3300 cm^{-1} and 1660 cm^{-1} which characterize the O-H groups [5]. In addition, the polymers obtained on germanium substrates presents IR bands at 970 cm^{-1} which characterize the OH and Si–OH groups [5], bands at 860 cm^{-1}, 750 cm^{-1} and 570 cm^{-1} which are assigned to stretching and bending of Ge-O-Ge bonds [6], and band at 660 cm^{-1}, which evidence the Si-O-Ge bonds formation [7].

The presence of hydroxyl groups in the polymer layers could be explained by the injection of the negative ions like O^{-2}, O^{-3}, O^{-4}, CO^{-2}, CO^{-3} [6] respectively the positive ions O_2^+, N_2^+ produced in air in corona discharges and water vapor from atmosphere [7], on the free surface of the liquid precursor which acts as a virtual electrode [4].

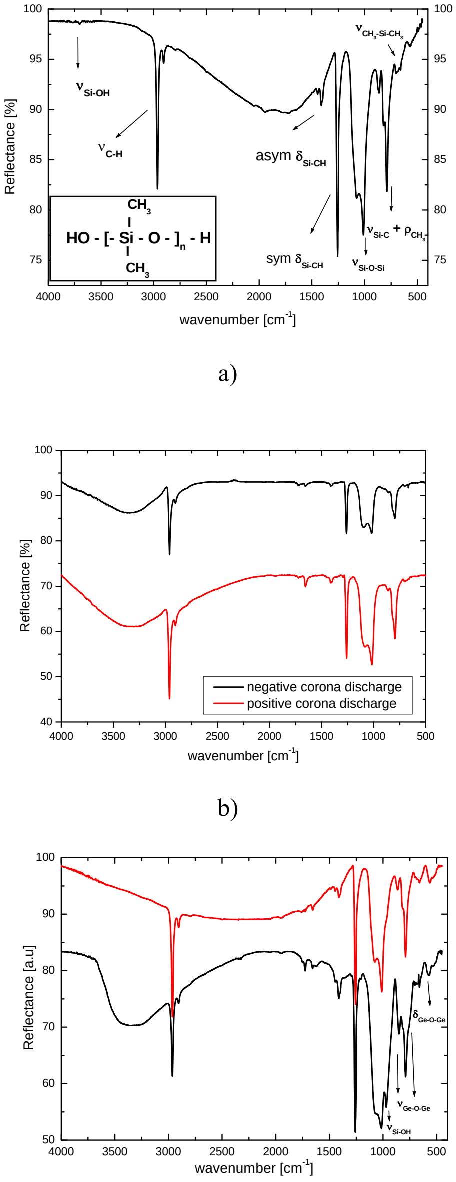
The end groups of the polydimetylsiloxane are involved in the polymerization process following the reaction:

$$\text{-Si-O-H + -Si-O-H = Si-O-Si + } H_2O.$$

Thus, the water present in the polymers from atmosphere and from polymerization process of polydimetylsiloxane can be decomposed under the influence of corona electric fields and associated charges injection generating OH radicals in the liquid bulk. So, the ions produced in negative corona discharges and OH radicals present in the material bulk can oxidize the substrate surface and generate the oxides by a process similar to anodization, [8]. A similar process can also be obtained in positive corona discharges.

The Si-OH groups present in the polymer layers obtained on germanium substrates after 2 hours of negative corona charge injection can perform strong bonds to the surface and favour the Si-O-Ge bond formation.

The oxides content distribution in the polymer layers deposed on different substrates of Ge, Ti and Al was investigated by elemental depth profile analysis using a glow discharge optical emission spectrometry technique (GD-OES) [9].



a)

b)

c)

Fig.2: IR spectra of: a) polydimetylsiloxane hydroxy terminated liquid precursor; b) polymer layer generated in negative corona discharge after 2 hours of charge injection (black line); polymer layer generated in positive corona discharge after 2 hours of charge injection (red line) on titanium substrate; c) polymer layer generated in negative corona discharge after 2 hours of charge injection (black line); polymer layer generated in positive corona discharge after 2 hours of charge injection (red line) on germanium substrate.

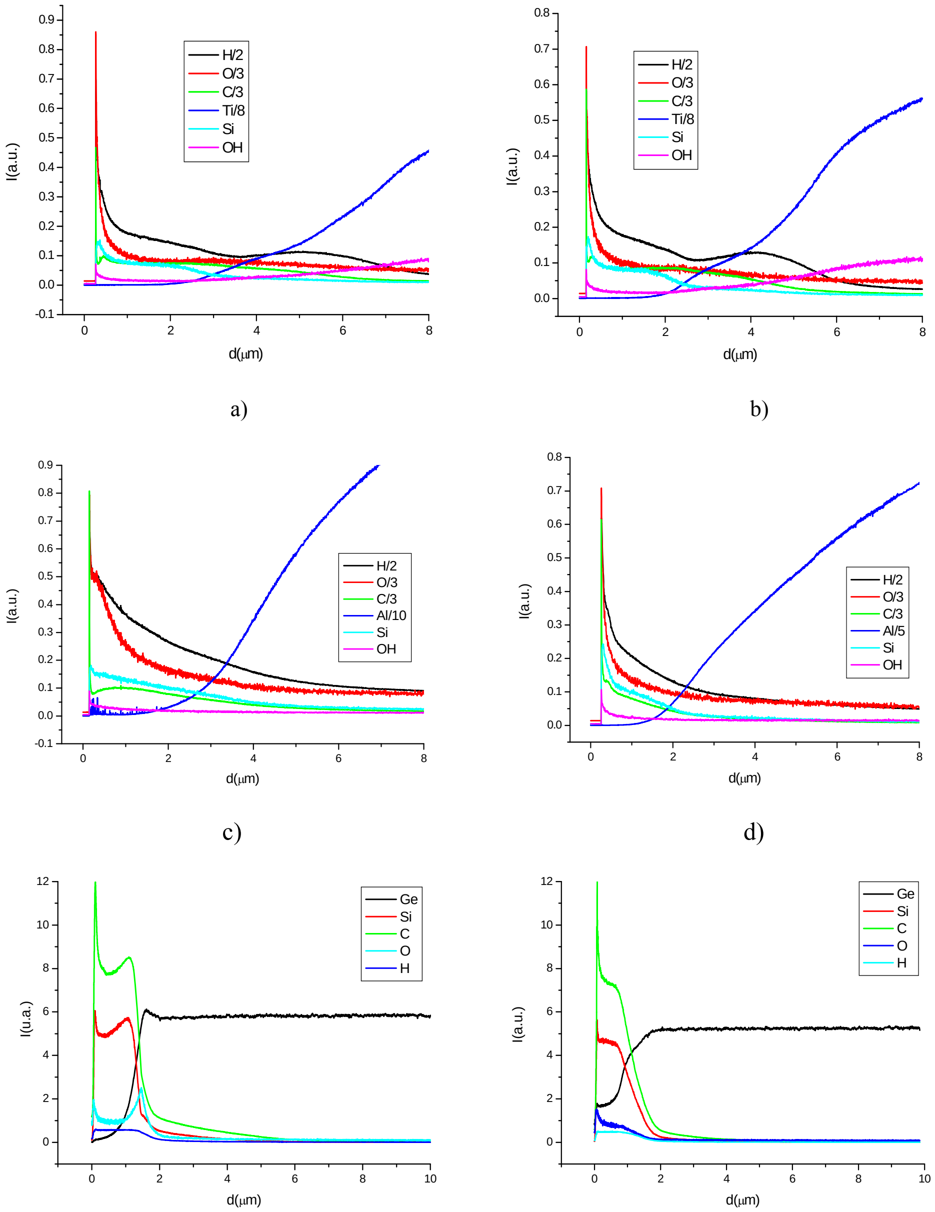
The depth profile analysis of the polymeric layers generated in negative and positive corona discharges on Ti, Ge and Al substrates are presented in Fig 3. The silicon profile is used as marker for the polymer layer depth. As it can be seen, the Si, C, O, H, Ti and Al depth profiles indicate a relative uniform distribution of these elements in polymer layers. The Ti and Al depth profiles indicate the metal diffusion in the polymer layers in both positive and negative corona discharges, Fig. 3a-d.

At the polymer - Ti interface Fig.3a, can be observed a hump on the O depth profile curve. This indicates a bigger amount of titanium oxide formation at the polymer- titanium interface in negative corona discharges than in positive corona discharges.

The polymers layers deposed on germanium substrates present a different distribution of Si, C and Ge contents in their bulk. In Fig. 3e, f at the polymer - Ge interface, can be observed a hump on Si, C, Ge and also a peak on the O depth profile curve. There are no humps on the H depth profile. So, the polymers generated in negative corona discharges have dominant polymer bonds accumulation at the polymer – Ge interface. The germanium depth profile shows that the generated germanium oxide layer efficiently acts as a barrier layer for the germanium oxide diffusion in the polymer bulk.

On the opposite, the germanium oxides generated in positive corona discharge diffuse in the polymer layer. There is no dominant bonds formation at Ge - polymer interface.

The composition of the polymers layers was also investigated by glow discharge mass spectrometry technique (GD-MS). This method consist in the sputtering of the sample in a radio frequency discharge coupled with a time of flight mass spectrometer. The molecular fragments of the polymers was obtained for a RF power of 20 W and $p = 6.4\ 10^{-1}$ mbar. In the mass spectra presented below can be observed polymer fragments like CH_3, $SiCH_3$, SiH, SiOH and some products produced during the discharge.

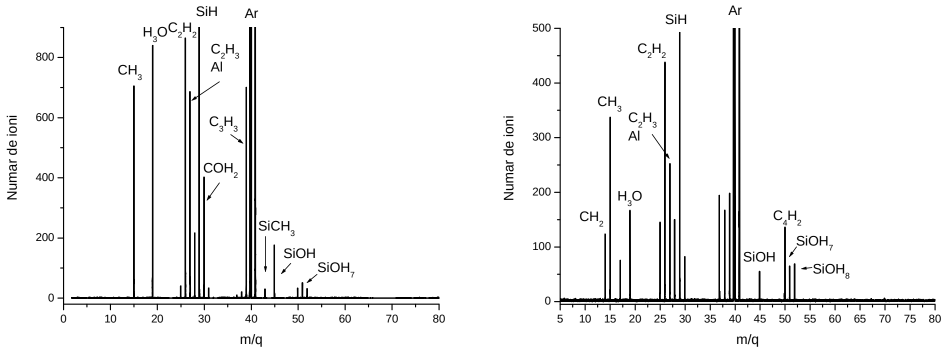


a) b)

c) d)

e) f)

Fig..3: Depth profile of the polymeric layers generated on a: titanium substrates: in a) negative and b) positive corona discharges; aluminium substrates in c) negative and d) positive corona discharges germanium substrates in e) negative and f) positive corona discharges.



a) b)

Fig. 4: Mass spectra of the polymers obtained in a) negative and b) positive corona discharges

3. Conclusions

In this paper, we presented a convenient physical method for the generation of substrate oxides in polydimethylsiloxane based polymer layers during it polymerization process in negative and positive corona discharges in air at atmospheric pressure.

Unlike polymers generated on metallic substrates in corona discharges those obtained on germanium substrates in negative corona discharges are chemically linked to the polymer network by Si-O-Ge bonds. Thus, the germanium oxide diffusion in polymers is blocked by the germanium oxide layer formed at the polymer-substrate interface

The substrate oxides content in the polydimetylsiloxane based polymers layers can act as a supplementary blocking element against corrosion factors of substrates.

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