

Spectral investigations of the processes observed at polydimethylsiloxane polymer-substrate interface during its polymerization process in negative and positive corona discharges

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In this paper we demonstrate that negative and positive corona discharge in air at atmospheric pressure is a convenient physical method for generation of germanium oxides in polydimethylsiloxane based polymers layers during the polymerization processes. The dependence of content distribution of the different germanium oxides in the polymers layers with the electrodes polarity was investigated by infrared (IR) and Glow Discharge Optical Emission (GD-OES) spectroscopies. The results of the spectroscopic measurements show that in positive corona discharges, the germanium oxide diffuses in the polymers while in negative corona discharges, the germanium oxide layer formed at the polymer-substrate interface has a limited diffusion due to the formation of Si-O-Ge bonds.

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1. Introduction

Polymer layers of polysiloxane deposited on various substrates have proved their importance for corrosion resistance. In these siloxane binders layers the Si-O bond is already oxidized and so atmospheric oxygen and most oxidizing chemicals do not affect the coatings. These layers are thus acting as an effective barrier preventing the contact of water based corrosive media with the underlying metallic surface. Moreover, the silicon-oxygen backbone of this type of polymers endows the layer with a variety of intriguing properties. For example, the bonding strength of the silicon-oxygen network gives the siloxane based polymers a remarkable thermal stability and as the Si-OH groups can perform strong bonds with the substrate surfaces this kind of layers are being used as an adhesion promoter providing a link between metallic/semiconductor surfaces and organic coatings [1, 2].

In this paper we report a physical method for the generation of polymer layers on germanium substrate starting from liquid precursors of polydimethylsiloxane, which at the same time allows the formation of germanium oxides at the polymer-substrate interface and their it diffusion in the bulk polymer layer. This physical method consists of a corona discharge at atmospheric pressure with a wire to plane electrode configuration. The distribution of the germanium oxides in the polymer layers obtained both in negative and positive corona discharges has been investigated by infrared (IR) and Glow Discharge Optical Emission (GD-OES) Spectroscopies.

2. Experimental set-up

The experimental set-up was described in [3]. It consists in a wire-to plane corona discharge electrode configuration.

The tungsten wire electrode of 40 mm length was placed in air at atmospheric pressure perpendicular to the center of a germanium disk electrode of 20 mm diameter. The interelectrode gap was 10 mm. In order to avoid any fluctuation of ambient air in the interelectrode gap, the electrodes were introduced in a glass cage. A DC high voltage of 9 kV was applied through a resistor $R = 5 \text{ M}\Omega$.

The temporal evolution of the current discharge in both negative and positive corona discharges was visualized on a Tektronics TDS 1012B oscilloscope. The discharge current in a Trichel pulsed regime of the negative corona discharge, measured across a resistor $r = 1 \text{ k}\Omega$ (the Trichel pulses being accompanied by a DC permanent current), is about $70 \text{ }\mu\text{A}$.

When a high DC negative voltage is applied to the sharp electrode, the surrounding air becomes ionized creating charged particles that form a cloud drifting along the field lines. Due to both the geometric configuration and the local presence of these clouds, the electric field between the electrodes is strongly non-uniform and varies with time as successive clouds drift from one electrode to the other, which explain the pulsating nature of the current.

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) with the given electrical and geometrical conditions.

By introducing a liquid precursor (0.1 μl) of polydimethylsiloxane with hydroxyl end groups (provided by Sigma Aldrich company) in the corona discharge on the plane electrode, the negative and positive ions injection on the free surface of the liquid induces electrohydrodynamic instabilities associated to the high electric fields [4].

The convection currents generated in the bulk liquid assure the transport of the charged particles to the plane electrode and after 2 hours of corona charge injection, stable polymer layers are obtained.

3. Results and discussions

The role of negative and positive corona charges injection on the polymerization and on the oxide formation processes was evidenced by recording the IR spectra of the polymeric layers with a Perkin Elmer IR spectrometer operating in reflection configuration at 30° reflection angle.

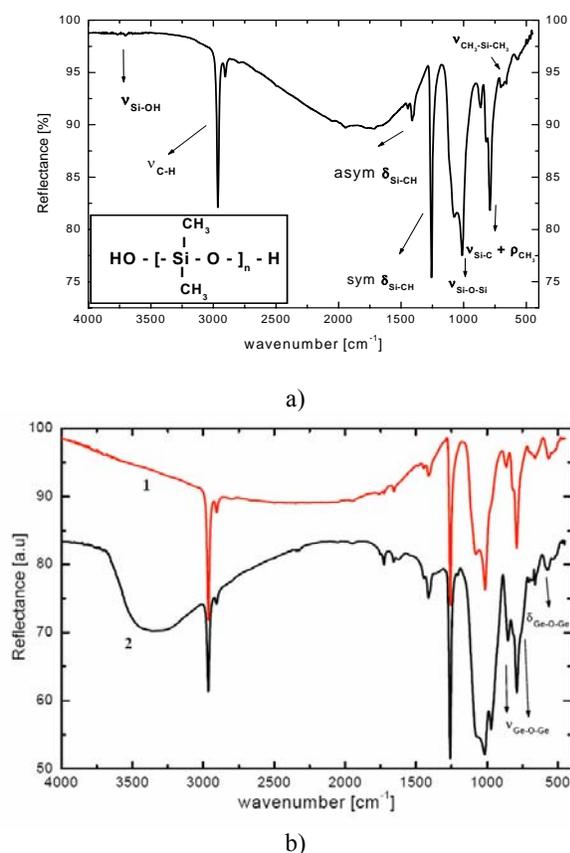


Fig. 1. IR spectra of: a) polydimethylsiloxane hydroxy terminated liquid; b) polymer layer generated in negative corona discharge after 2 hours of charge injection (line 2); polymer layer generated in positive corona discharge after 2 hours of charge injection (line 1) for a 30° reflection angle.

The IR spectrum of the polydimethylsiloxane hydroxy terminated liquid precursor and its chemical structure are presented in Fig. 1a and the IR reflection spectra of the polydimethylsiloxane polymer layer generated in negative (black) and positive (red) corona discharge respectively are shown in Fig. 1b.

Unlike the liquid precursor IR spectrum, in the IR polymer layer spectrum obtained in negative corona discharge one can observe absorption bands in the range $3700\text{--}3200$, 1630 and 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 bands characteristic of the Ge-O-Ge bonds are more intense in the transmission IR spectra.

The presence of such bonds in the polymer layers may be explained by the injection of negative ions like O^{2-} , O^{3-} , O^{4-} , CO^{2-} , CO^{3-} [8] and water vapor from atmosphere [9] produced in the negative corona discharge on the free surface of the liquid precursor which acts as a virtual electrode [4]. Furthermore, we also estimate that in the polymerization process of the polydimethylsiloxane the end groups are involved following the reaction:



Thus, water present in the polymers from the atmosphere and from the polymerization process of polydimethylsiloxane can be decomposed under the influence of the corona electric fields and associated charges injection generating OH radicals in the liquid bulk.

As a result, the negative ions produced in the negative corona discharges and the OH radicals present in the material bulk can oxidize the substrate surface and generate germanium oxides by a process similar to anodization, Fig. 2b [10].

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

In the IR spectra of the polymer obtained in positive corona discharge there are no OH or Si-OH vibrational bands. Thus, the positive ions O_2^+ , N_2^+ and associated electric fields produced in positive corona discharge favours the polymerization process of the polydimethylsiloxane precursors. Oxide formation is indicated by the Ge-O-Ge vibrational band observed at 570 cm^{-1} .

Thus, the IR spectral investigations show that the germanium oxides present in the polymer layers generated both in positive and negative corona discharges do not affect the polymerization process.

In order to investigate the distribution of the germanium oxides within the polymer layers we performed elemental depth profile compositional analysis using a glow discharge optical emission spectrometer GD Profiler 2 from Horiba Jobin Yvon [11].

This technique relies on the sputtering of the material by an Ar RF plasma and the optical characterization of the

plasma giving the spectrum of the sputtered species excited by inelastic collisions.

The emitted light is constantly monitored providing the sample composition as a function of depth. The experimental conditions used for the samples analysis are: 20 W Rf power and 600 Pa pressure.

In order to increase the electric coupling efficiency between RF plasma and the samples, a 100 nm copper layer has been deposited on the polymer layer following a recommendation from Belenguer & al [12]. The depth profile analysis of the polymeric layers generated in negative and positive corona discharges on germanium substrate are presented in Fig 2a and 2b respectively.

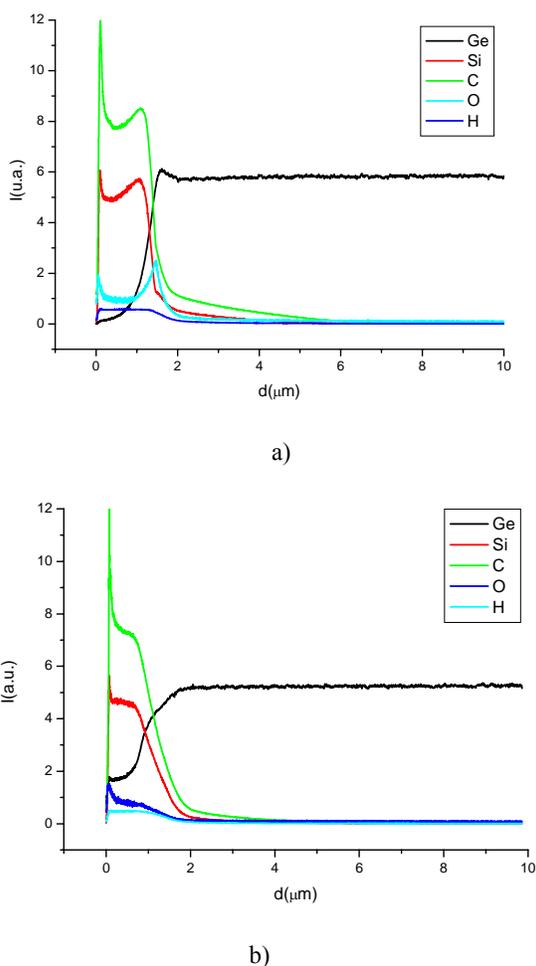


Fig.2. Depth profile of the polymeric layers generated on a germanium substrate: a) negative corona discharges; b) positive corona discharges.

In our analysis we took the silicon profile as marker for the polymer layer depth. As it can be seen, the Si, C, O, H depth profiles are similar for both negative and positive corona discharges unlike the Ge depth profiles which indicate a different germanium content distribution in the polymer layers generated by the two types of discharges.

In Fig.2a, at the polymer - Ge interface, one 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. The change of sputtering rates characteristic of the GD-OES analysis of different type of layers cannot simply explain this phenomena. These indicate a dominant polymer bonds accumulation at the polymer - Ge interface and a germanium oxide formation due to negative oxygen ions, OH radicals which attain the plane electrode and associated electric fields obtained in negative corona discharges by a process similar to anodization.

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.

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

4. Conclusions

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

The mechanism of polydimethylsiloxane polymerization process and germanium oxides formation in the polymer layers was investigated by IR and GD-OES spectroscopies for both negative and positive corona charge injections.

Unlike polymers generated in positive corona discharges which contain germanium oxides, the germanium atoms from the polymers obtained 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 polydimethylsiloxane based polymers layers generated by the physical method presented in this paper is also beneficial as a supplementary blocking element against corrosion factors on metallic and semiconductor substrates.

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