Evidence of aluminum oxides formation at polymer/Al substrate interface in atmospheric pressure discharges

A. Groza[1(*)], A.Surmeian[1], C.Diplasu[1], C.Luculescu[1], A.Tempez[2], M.Ganciu[1]

[1]*National Institute for Laser, Plasma and Radiation Physics, 077125 Bucharest-Magurele, Romania*
[2]*Horiba Jobin Yvon, 91665 Longjumeau, France*
(*) andreea@infim.ro

In this paper the processes occurring at polymer/substrate interface during the polymerization of polydimethylsiloxane in atmospheric pressure corona discharges as a function of the liquid precursor end groups are investigated. The formation of aluminosilicates type compounds at polymer/substrate interface and its linkage to the polymers chains by Si-O-Al bonds are evidenced by energy dispersive X - ray spectroscopy (EDS), plasma profiling time of flight mass spectrometry (PP-TOFMS) and infrared (IR) spectral analysis.

Layers of polysiloxane deposited on different substrates have proved their utility as corrosion protective layers towards heat, ozone and chemicals. For an improved adherence of polymeric layers to substrate materials, the substrate surfaces are usually anodized, especially the aluminum ones.

Depending on substrate material and on end groups of polydimethylsiloxane liquid precursors, during their polymerization time duration in corona discharges, anodized oxide layers can be generated at polymer/substrate interface which can increase the adherence of the polymers to the substrates. The method of generating this kinds of polymers on different substrates was presented in [1].

The EDS spectrum of polydimethylsiloxane and atomic percentages contained in the layers generated in corona discharges on aluminum substrates from different end groups liquids precursors are presented in Fig. 1. The measurements were performed at low voltage (5 kV) in order to avoid the substantial presence of metal atoms in the spectrum. Although, due to the diffusion of the aluminum oxides formed at polymer/substrate interface in the layer bulk, the C, O and Si atoms lines intensity distribution in the spectrum Fig. 1a is different from that observed in Fig. 1b. In Fig.1c it is presented a scanning electron microscopy (SEM) image of the aluminum anodized layer from the polymer/substrate interface.

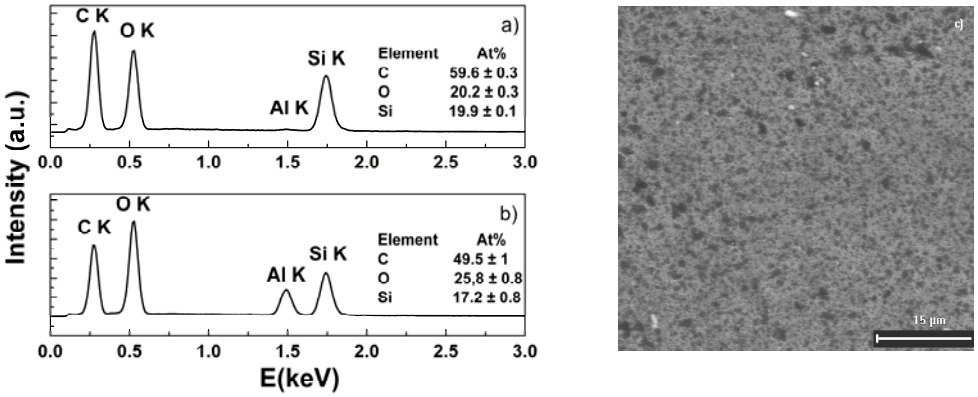

Fig. 1: EDS spectrum of polymers deposited on Al substrates starting from a) vinyl terminated; b) hydroxyl terminated; polydimethylsiloxane precursors; c) SEM image of an anodized aluminum layer.

By PP-TOFMS we investigated the types of aluminum oxides formed at the polymer/substrate interface for 2 different polymerization times in corona discharges. In PP-TOFMS technique, species sputtered from the investigated sample are ionised in an Ar RF plasma and directed to a mass spectrometer. The experimental conditions used for the analysis of the polymers deposed on Al substrates in PP-TOFMS are: 670 Pa pressure and 30 W Rf power working in pulsed mode. The pulse duration is 1 ms and the period 4 ms. Mass spectra are recorded on the entire pulse duration and also in the afterglow plasma. Signals of investigated ions exhibit a considerable intensity enhancement when the rf pulse is turned off.

Fig.2 shows the mass spectrum recorded in the afterglow of the pulsed RF plasma. It can be identified the formation of Al_2O_3 compounds. Because in the pulsed RF plasma a lot of chemical bonds are

broken, especially those with hydrogen, we will have a lot of byproducts. Thus, due to H addition, these aluminum oxides based compounds are observed in the mass spectrum as $Al_2O_3H^+$ (m/z 102.9), $Al_2O_3H_2^+$ (m/z 103.9), $Al_2O_3H_3^+$ (m/z 104.9), $Al_2O_3H_4^+$ (m/z 105.9), $Al_2O_3H_5^+$ (m/z 106.9), $Al_2O_3H_6^+$ (m/z 107.9), $Al_2O_3H_7^+$ (m/z 108.9). The fragments like $Al_2Si_2O^+$ (125,9 m/z), $Al_2Si_2OH^+$ (m/z 126.9), $Al_2Si_2O_2^+$ (m/z 141.9) possible indicate the formation of aluminosilicates type compounds $(Al_2Si_2O_5(OH)_4$ at polymer/substrate interface. These signals appear in the recorded mass spectrum only on the duration of the aluminum temporal profile.

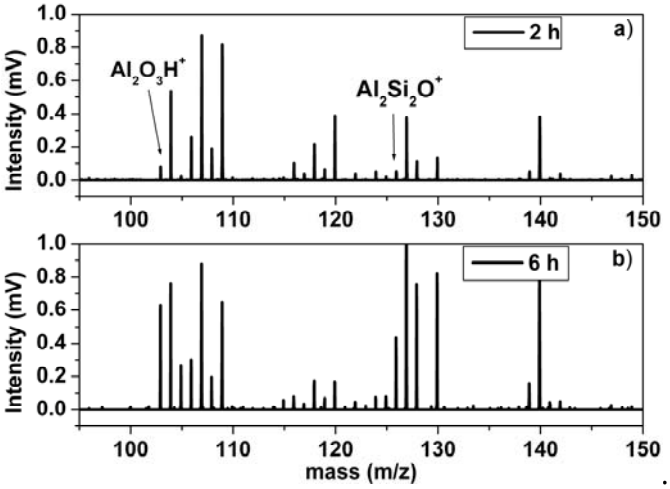

Fig. 2: Mass spectrum of compounds obtained at polymer/substrate interface for a) 2h; b) 6h polymerization time duration of polydimethylsiloxane liquid precursors with hydroxyl terminated end groups in corona discharges.

The IR reflection spectrum, Fig.3a, of a polymer layer obtained in corona discharges after 2 hours of negative ions deposition [1] on the free surface of a liquid precursor placed on an Al substrate, reveals the main IR vibrational bands characteristic to polydimetylsiloxane and some possible new bands formation. Using the SPETRUM software of the FT-IR SP100 Perkin Elmer spectrometer we calculated the coresponding absorption spectrum and from its second order derivative, Fig.3b, we identified two new IR bands at around 900 cm^{-1} and 642 cm^{-1}. These bands are assigned to the formation of Al-O and Si-O-Al bonds, respectively [2].

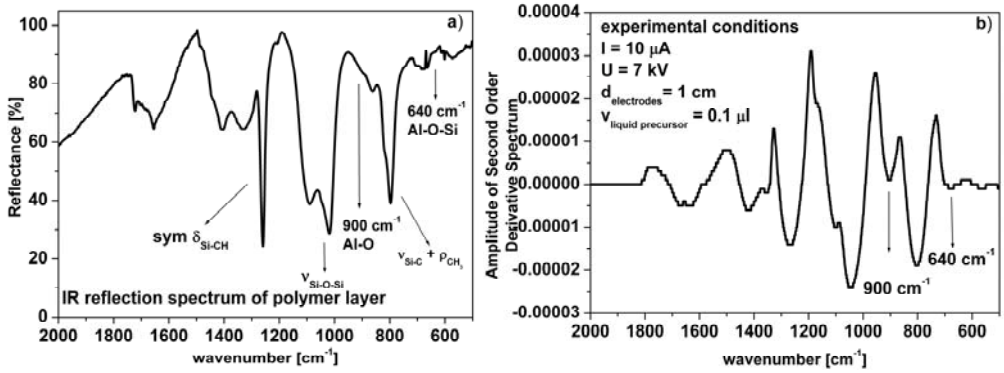

Fig. 3: a) IR reflection spectrum of polymer layer; b) Second order derivative of the IR spectrum of a polymer layer deposited on Al substrate from a hydroxyl terminated polydimethylsiloxane liquid precursor.

The experimental results obtained in this paper by three different methods demonstrate the anodized aluminum layers formation at polymer/substrate interface during the polymerization time duration in corona discharges of polydimethylsiloxane liquids precursors with hydroxyl terminated end groups.

References

[1] A.Groza, A.Surmeian, C.Diplasu, M.Ganciu, P.Chapon, I.I.Popescu, *Journal of Optoelectronic and Advanced Materials*,12, 11, (2010), 2311-2314;

[2] Sigurdur Jakobsson, *Spectroscopic Techniques* ***56(6)****, (*2002), 797-9.