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Tribological behavior of plasma-polymerized aminopropyltriethoxysilane films deposited on thermoplastic elastomers substrates

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ABSTRACT

Thermoplastic elastomers (TPE) are multifunctional polymeric materials that are characterized by moderate cost, excellent mechanical properties (high elasticity, good flexibility, hardness, etc.), high tensile strength, oxidation and wettability. With an objective of reducing the superficial friction coefficient of TPE, this work analyzes the characteristics of coating films that are based on aminopropyltriethoxysilane (APTES) over a TPE substrate. Since this material is heat-sensitive, it is necessary to use a technology that permits the deposition of coatings at low temperatures without affecting the substrate integrity. Thus, an atmospheric-pressure plasma jet system (APPJ) with a dielectric barrier discharge (DBD) was used in this study. The coated samples were analyzed by Scanning Electron Microscopy, Atomic Force Microscopy, Fourier-Transform Infrared with Attenuated Total Reflectance Spectroscopy, X-ray Photoelectron Spectroscopy and tribological tests (friction coefficient and wear rate). The studies showed that the coated samples that contain a higher amount of forms of silicon (SiOSi) and nitrogen (amines, amides and imines) have lower friction coefficients. The sample coated at a specific plasma power of 550 W and an APTES flow rate of 1.5 slm had the highest values of SiOSi and nitrogen-containing groups peak intensity and atomic percentages of Si2p and SiO_4, and the lowest percentages of C1s and average friction coefficient. The results of this research permit one to conclude that APPJ with a DBD is a promising technique to use in coating SiO_x and nitrogen-containing groups layers on polymeric materials.

1. Introduction

The use of elastomer-based materials has increased due to their high performance and relatively low cost [1]. Thermoplastic elastomer (TPE) refers to a series of commercial plastic materials that are both relevant and interesting [2]. TPEs are multifunctional polymeric materials that combine the processability of thermoplastics and the elasticity of vulcanized rubber. In general, they are biphasic materials that [a] possess the combined properties of the glassy or semi-crystalline thermoplastics and soft elastomers and [b] enable rubbery materials to be processed as thermoplastics [2–5]. TPEs are characterized by moderate cost, excellent mechanical properties (high elasticity, good flexibility, hardness, etc.), high tensile strength, oxidation and wettability [5]. These elastomers are widely used in the automotive sealing industry to produce components for different automotive parts (door glass edges, glass run weather strips, door weather strips, roof rail weather strips, quarter window weather strips, deck lid seals, secondary seals, inner and outer beltstrips, etc.).The elasticity and high friction coefficient of these elements ensure that they are water tight, dust proof and noise proof. Nevertheless, this high friction coefficient can be a serious problem in some areas of the vehicle, such as the window channels, which, for instance, are usually flocked. The present work concentrates on an analysis of the deposition of plasma polymer thin films that are based on silicon oxides (SiO_x) and nitrogen-containing groups by using aminopropyltriethoxysilane (APTES) as a precursor, to reduce the friction coefficient of the elastomer's surface. Some instances of the deposition of siloxane-based coatings using APTES as a precursor to improve the tribological properties of hydrogenated nitrile butadiene rubber can be found in the literature [6,7].

The SiO_x coatings deposited by means of such methods as chemical vapor deposition (CVD), are known for their specific properties, such as their chemical structures and protective coating [8]. However, these coating methods are unsuitable for products that are made from heat-sensitive materials, such as TPEs, because of their high processing temperatures [9].

The low-temperature, plasma-enhanced, chemical vapor deposition (PE-CVD) method is characterized by deposition temperatures that are considerably lower than experienced in other methods [10]. However, in spite of its excellent coating efficiency, the use of this technique is limited due to the restricted volume of the plasma reactor, the requirement for one or more chemical cycles and the need for a vacuum pressure environment.

The cold atmospheric-pressure, plasma jet systems (APPJ) are well-known in the literature and used increasingly in industry [11]. The use of a low temperature and low pressure plasma for deposition

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of coatings over polymers has become increasingly common. Since these systems do not require a vacuum pressure environment, the cost of the process is reduced significantly. Furthermore, the coatings that are used to improve the tribological properties of the materials affect only the outer layers of the substrate that are exposed to the plasma.

Previous works by these authors [12] demonstrated the feasibility of reducing the friction coefficient of Ethylene Propylene Diene Monomer (EPDM) substrates – another popular material used in the automotive sealing industry – with plasma-polymerized tetraethoxysilane (TEOS) films that are based on silicon oxides and deposited using an APPJ system [13] (PlasmaPlus®, Plasmatreat GmbH, Germany). In this study, a different APPJ system and different process parameters (flow rate, plasma-power values, ionization gas, number of passes, etc.), substrate (TPE) and precursor (APTES) were used. More precisely, the selected APPJ system is the Plasma Spot® technology from VITO (Belgium), which is a plasma torch working at atmospheric pressure [14]. Furthermore, this study analyzes the influence that the nitrogen-containing groups, in addition to SiO_x groups, have on tribological properties.

The original contribution of this paper is in presenting the relationships between: [a] the plasma-polymerization process parameters — plasma power and precursor (APTES) flow rate, [b] the chemical structure of the coating and [c] the average friction coefficient and wear rate. In order to understand the relationships between the essential plasma-polymerization process parameters and the chemical and functional characteristics of the deposited APTES films on TPE surfaces, the coated samples were analyzed by Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), Fourier-Transform Infrared with Attenuated Total Reflectance Spectroscopy (FTIR-ATR), X-ray Photoelectron Spectroscopy (XPS), as well as tribological tests.

2. Experimental procedure

As mentioned above, the samples were coated using an APPJ system with a dielectric barrier discharge. It employs a plasma torch system at atmospheric pressure, which is contained in a gun [12]. This device (Fig. 1) was moved across the surface of the samples in a scanning motion. The established speed of the gun was 6 m/min and the track pitch was 2 mm. Each sample was treated first with plasma without using any precursor in order to activate the surface. Immediately after activation, the sample was coated in a three-pass process. That is, the gun was passed over the substrate surface three times with a duration of 37 s for each pass. During the activation and coating processes, different settings of plasma power of 75 kHz were used (350, 450 and 550 W). Nitrogen gas (99.99%) was used as the ionization gas at a flow rate of 80 slm. Liquid APTES precursor was nebulized with an atomizer to produce a fine aerosol. Droplet sizes were distributed in the range of 10–300 nm with a maximum concentration around 50 nm [6]. Nitrogen gas was also used as the carrying gas. In this case, three different flow rates were applied 1, 1.5 and 2 slm. These flow rates correspond with an atomizer pressure of 5×10^4, 1×10^5 and 1.5×10^5 Pa, respectively. The N_2 that carries the aerosol was directly injected in the afterglow through a 0.5 mm opening. Otherwise, coating deposition inside the gun would have occurred and caused many problems. Since the N_2 used for the atomization did not go through the plasma, the amount of active species did not increase. The distance between the jet and the substrate was maintained at 6 mm. During the coating process, the temperature of the substrate surface did not exceed 90 °C.

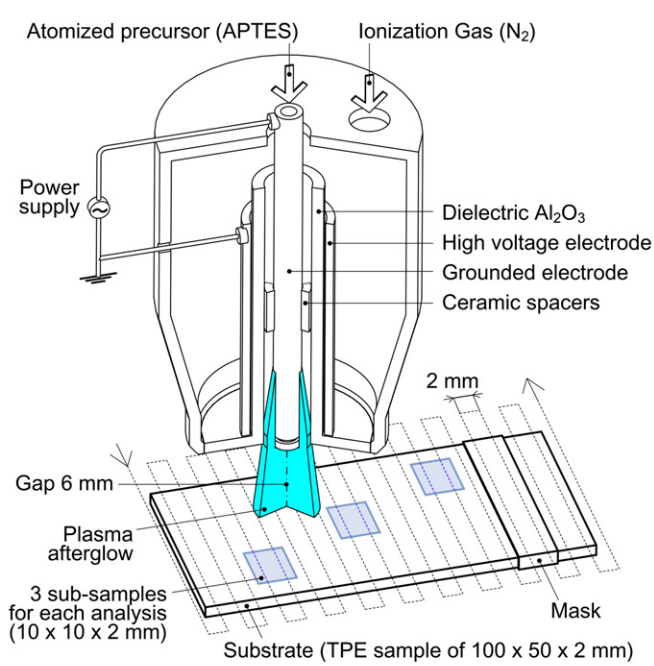

Fig. 1. Schematic diagram of the APPJ system (PlasmaSpot®, VITO, Belgium).

The material used as a substrate in this work was produced from pellets of Santorene™ 121-67W175, that has an ISO 18064 code of TPE-(EPDM + PP). This means that the elastic phase is EPDM and the plastic phase is Polypropylene (PP). The raw material was provided by an automotive sealing factory, Standard Profil SA (Spain). Pellets were injected into a mold to produce sheets of 300 × 200 × 2 mm. Samples were prepared by cutting to dimensions of 100 × 50 × 2 mm. Table 1 shows the label of each analyzed sample, as well as the flow rate and plasma power used during the coating process. For each sample, three sub-samples were used to conduct the present study (see Fig. 1).

The following equipment was used to perform the tests necessary to study the behavior of the coated samples. The film's surface was observed by the use of a JEOL JSM-840 scanning electron microscope under the operating voltage of 10 kV. The wear track produced during the tribological tests was observed by the use of an HITACHI S-2400 scanning electron microscope under the operating voltage of 18 kV. In order to make the surface of the samples conductive, they were gold-coated. The morphology of the film's surface was analyzed by use of a Veeco Instruments, Multimode AFM, operating in tapping mode. The scanning area of the final samples was 10 μm × 10 μm. The thickness of the coatings was measured by optical profilometry (ConScan profilometer, CSM Instruments), using the following procedure. First, the film's surface was partially covered with a mask (see Fig. 1). Second, the sample was coated with a plasma-polymerization process. Finally, the mask was removed and the height of the step was measured by profilometry. A BRUKER IFS 66 FTIR spectrometer with a Specac Golden Gate ATR accessory based on a single bounce diamond prism was used to record the FTIR-ATR spectra. For every ATR spectrum, 64 scans were made at a resolution of 2 cm^{-1}. Deconvolution of FTIR-ATR spectra was accomplished by use of the spectral analysis program PeakFit version 4.12 (SPSS Inc.). The FTIR-ATR spectra were fitted with bands described by a mixture of Gaussian and Lorentzian

Table 1
Label of each sample according to the flow rate and plasma power used during the coating process.

Sample label	APTES flow rate (slm)	Plasma power (W)
$S_{1/350}$	1	350
$S_{1/450}$	1	450
$S_{1/550}$	1	550
$S_{1.5/350}$	1.5	350
$S_{1.5/450}$	1.5	450
$S_{1.5/550}$	1.5	550
$S_{2/350}$	2	350
$S_{2/450}$	2	450
$S_{2/550}$	2	550
TPE	–	–