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Antifriction aminopropyltriethoxysilane films on thermoplastic elastomer substrates using an APPJ system

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ABSTRACT

The study of friction coefficients has long been of great importance in the automotive industry where some areas of the vehicle are subject to slippage. One example is the space between the window channels and the glass. The polymeric materials that are used in these areas, like thermoplastic elastomers (TPE), involve a high degree of friction. So, in order to decrease the friction coefficient of the TPE, companies are using such techniques as flocking. However their high energy consumption, irregular distribution of fibers and poor adhesion are drawbacks. In order to overcome these drawbacks, this work attempts to obtain a SiOx-based thin film over a TPE substrate using aminopropyltriethoxysilane (APTES) with similar or lower friction coefficients and the same durability. Since TPE is heat-sensitive, an atmospheric-pressure plasma jet system (APPJ) with a dielectric barrier discharge (DBD) was used in this study. The influence of the plasma power and number of passes was characterized by Profilometry, Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) Spectroscopy, X-Ray Photoelectron Spectroscopy (XPS), Water Contact Angle (WCA) measurements and friction coefficient. The average surface temperature of the samples and the coating thickness seem to be the key variables in determining the friction behavior. Successful samples (those that have a lower friction coefficient than those of the current industrial solutions - flocked seals and polyamide tap) were coated at an average surface temperature of <92 °C and thicknesses of the coatings were >1000 nm. Sample coated in six passes and the lowest power (350 W) proved to have the best friction performance. This sample has a friction coefficient that is 46% lower than that of the flocked seals. The results of this research permit one to conclude that a promising antifriction technology using APPJ with a DBD could be an alternative to the current industrial solutions.

1. Introduction

The study of friction coefficients and wear mechanisms has long been of great importance in the operation of many mechanical systems. In fact, many industrial applications require low friction coefficients. In the automotive industry, some areas of the vehicles are subjected to slippage. These include the space between the window channels and the glass, and between the wind-shield and the wind-shield wipers, where a low friction coefficient is necessary to prevent jams. Furthermore, a high hydrophobicity would be desirable in order to evacuate the stored water in the operation. The polymeric materials that are used in these areas, like thermoplastic elastomers (TPEs), intrinsically involve high friction [1]. So, in order to improve friction performance, companies are using two different techniques, such as flocked seals and a polyamide tape affixed to the tape seals. Today, the flocked method is widely used in the automotive sealing industry due to its low friction coefficient. The high energy consumption and long installation lines, together with an irregular distribution of fibers, poor fiber orientation and poor adhesive distribution are the main drawbacks of this technology [2].

Plasma technology is becoming more and more popular as a means to modify the intrinsic properties of substrate materials by coating or activation [3–5]. Operating at atmospheric pressure in a dielectric barrier discharge configuration is particularly suitable for the treatment of temperature-sensitive materials, such as polymers, since it generates cold plasmas [5,6].

The friction and wear of a material depend primarily on its surface properties [7]. Previous studies of plasma-polymerized siloxane coatings, like hexamethyldisiloxane (HMDSO) or aminopropyltriethoxysilane (APTES), have demonstrated a reduction in the friction coefficient on different substrates [8–10].

This paper deals with the synthesis and characterization of SiOx-based coatings that are deposited on TPE substrates that have been produced by an Atmospheric Pressure Plasma Jet (APPJ) system. The main purpose is to obtain a coating that has friction coefficients that are

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similar to, or lower than, the current industrial solutions (flocked seals and polyamide tape) with the same or greater durability. It would be desirable also to obtain a wettability behavior that is similar to or better than those of these industrial solutions. In addition, this coating method would reduce considerably the manufacturing cost, which is one of the most important concerns when developing a viable coating for an industrial application [11].

The influence of the different process parameters, mainly plasma power and deposition time (number of passes), in depositing coatings on TPE was characterized from morphological, chemical and mechanical points of view by Profilometry, Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) spectroscopy, X-Ray Photoelectron Spectroscopy (XPS), Water Contact Angle (WCA) measurements and friction coefficient.

2. Experimental details

2.1. Materials and sample deposition

SiO_2-based coatings of various thicknesses were deposited on flat TPE substrates of 100 mm × 50 mm × 2 mm that were vulcanized from pellets of Santorene™ 121-67 W175 (ISO 18064).

A schematic diagram of the atmospheric pressure plasma jet (APPJ) system of PlasmaSpot® that was used to coat the samples is shown in [1]. This system consists of an Al_2O_3 dielectric tube between two cylindrical electrodes; the outer electrode is connected to high voltage during operation and the inner electrode is grounded.

The jet moved across the sample's surface at a scanning speed of 6 m/min and a track pitch of 2 mm. The gap between the discharge plasma and the substrate was set at 6 mm. Nitrogen was used as the plasma gas at 80 slm. The chemical precursor, 3-aminopropyltriethoxysilane (APTES), was purchased from Sigma Aldrich and used as received. A fine aerosol of liquid APTES was created using an atomizer. The inlet gas for the atomization was nitrogen at 1.5 slm and the size of the generated droplets ranged from 10 nm to 300 nm. With the aim of preventing a direct contact of APTES fumes with the plasma operator, due to its toxicity, the coating process was implemented using a fume hood. The ozone generated from the air during the atmospheric pressure process is evacuated with the same system. The APTES fume from the atomizer is directly transported to the inner electrode via a silicone tube. At the bottom of the inner electrode, the APTES fume contacts with the plasma.

Twelve different samples were coated as Table 1 shows. For each sample the coating process consisted of two steps, in which the same plasma power at a frequency of 68 kHz was used. In the first step, the sample was scanned once to activate the surface. During this activation step, no precursor was introduced into the jet. Only nitrogen was used as plasma gas. With the aim of studying the effect of the activation step, three activated samples with different plasma power (A1/350, A1/450 and A1/550) were analyzed (see Table 1). After activation, a process of plasma-polymerization with APTES was carried out. Depending on the sample, the jet was moved across the substrate surface as many times as Table 1 indicates (number of passes).

In order to evaluate the effect of surface temperature on the properties of the coated samples, the temperature was measured continuously during the coating process using a temperature sensor that was taped to the sample's surface for the 18-pass samples (S18/350, S18/450 and S18/550).

2.2. Sample characterization techniques

The thickness of the coatings has been evaluated by surface profilometry using a Taylor Hobson Surtronic 25 profilometer, which provides data analysis and images captured by scanning. The scanning length that was chosen was 4 mm and the range was 100 μm. Before coating the samples, the TPE's surface was partially covered by a mask. After the coating process, the mask was removed and the step's height was measured by the mechanical profilometer. The average coating thickness of five measurements from each sample was determined.

An XE-70 Atomic Force Microscopy system (AFM) (Park systems) was used to explore the surface topography and the roughness of the samples. Areas of 40 μm × 40 μm were scanned in non-contact mode with a silicon cantilever (Nanosensors™ PPP-NCHR). Data processing was done by applying a plane fit algorithm. The root mean square (RMS) roughness was calculated as the average value of the measurements of three different spots per sample by means of NanoScope Analysis 1.4 software.

The surface morphology of all the samples was examined by use of a Scanning Electron Microscope (SEM) HITACHI S-2400 at an operating voltage of 18 kV. Samples that were analyzed were made conductive by gold-palladium sputtering before introduction to the SEM chamber to prevent charging during SEM analysis. An energy dispersive X-ray spectroscopy (EDX) that was installed in the SEM was used to study the atomic chemical composition of the uppermost layer of the coatings and the wear tracks.

Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) spectroscopy spectra were recorded on a Bruker Tensor 27 spectrometer that was equipped with a single reflection ATR accessory for chemical bond characterization of the samples. For each spectrum, 32 scans were collected and averaged in the range of 600–4000 cm^{-1} at a 4 cm^{-1} resolution.

The atomic chemical surface composition of the samples was monitored using a Physical Electronics PHI 5700 spectrometer with a multi-

Table 1
Sample identification and deposition conditions of each sample.

Sample	Power (W) (activation and polymerization)	Number of passes (activation)	Number of passes (polymerization)	Deposition time (s) (polymerization)	Average surface temperature (°C)
A1/350	350 W	1	–	–	68.3
S2/350		1	2	75	70.0
S6/350		1	6	224	75.3
S12/350		1	12	449	79.5
S18/350		1	18	673	82.4
A1/450	450 W	1	–	–	81.7
S2/450		1	2	75	83.8
S6/450		1	6	224	90.5
S12/450		1	12	449	94.6
S18/450		1	18	673	97.6
A1/550	550 W	1	–	–	98.0
S2/550		1	2	75	101.1
S6/550		1	6	224	108.0
S12/550		1	12	449	113.1
S18/550		1	18	673	116.3