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Atmospheric plasma-polymerization of hydrophobic and wear-resistant coatings on glass substrates

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ABSTRACT

In order to find a coating that promotes both the wear resistance and the hydrophobicity of glass, a non-thermal atmospheric jet plasma-polymerization system with mixtures of two precursors at different proportions were used. (Heptadecafluoro-1,1,2,2-tetrahydrodecyl)trimethoxysilane (FLUSI) was used to promote the hydrophobicity, due to its fluorocarbon chain. Aminopropyltriethoxysilane (APTES) was used to enhance the wear resistance of the surface. The key aspect of the present work consists of determining the optimal mixture of precursors that produces a satisfactory coating in both characteristics; since coatings based on FLUSI have a low wear resistance and those based on APTES have a hydrophilic character. Scanning electron microscopy (SEM), atomic force microscopy (AFM), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), lap-shear tests, static water contact angle (WCA), tribological tests, profilometry measurements and energy dispersive X-ray spectroscopy (EDX) were used to analyze the coatings. It is believed that the upper limit of hydrophobicity that can be attained by modifying of the surface chemistry (WCA of ~120°) has been achieved. It was observed that the wear resistance depends on the thickness and the SiOSi content of the coatings. These appear to be directly related to the proportion of APTES in the mixture. The sample that was coated with 50% of APTES and 50% of FLUSI provided the best combination of hydrophobicity and wear resistance. It showed the highest WCA (123.2° ± 1.5) because it has a high fluorocarbon content and the highest CF_3 content. Its wear resistance is considerably better than that of the uncoated glass and is one of the highest exhibited by the hydrophobic samples.

1. Introduction

Improving the hydrophobicity of various materials has been a popular topic of research in recent years [1–6]. A high hydrophobicity is useful for a variety of products and industrial uses, such as self-cleaning fabrics and windows, friction reduction in microfluidic devices, glass windshields that quickly evacuate the water for better visibility in adverse weather conditions, and solar panels [1]. Yim et al. [2] deposited hydrophobic coatings with water contact angles in the range of 90–116° on a polymer substrate, using fluorine-based liquid precursors and an atmospheric pressure plasma enhanced vapor deposition process. Recent studies of the self-cleaning ability of presently available hydrophilic and hydrophobic products reveal a higher effectiveness of hydrophilic surfaces for external applications. However, these studies emphasize the importance of the research and development of superhydrophobic surfaces, with water contact angles (WCA) that exceed 150°, because of the excellent self-cleaning ability that they have shown [7]. Generally, the hydrophobicity is improved by two different methods or a combination of both: (1) creation of a rough structure on an intrinsically hydrophobic substrate or (2) modification of a rough surface with low-surface-energy materials [3,8].

For example, Ji et al. [3] used a one-step hydrothermal method to create hierarchical textured morphologies on glass surfaces with water ammonia, and a subsequent modification of the chemical composition with vinyltriethoxysilane. This resulted in superhydrophobic glass surfaces with a water contact angle of 155°. Wu el al. [9] used a sol–gel formula containing hydrophobic polydimethylsiloxane (PDMS) to coat a glass substrate by spraying, in seeking a balance between wear resistance and hydrophobicity. They reported that the wear resistance declined, and the water contact angle increased, as the solution's percentage of PDMS increased. Their optimum PDMS content was 10% by volume. This resulted in a wear resistance that was not significantly compromised, and a high water contact angle (118°) due to the nanoscale surface morphology of the coating obtained.

The development of hydrophobic and wear-resistant surfaces on glass is of particular interest to us because this material is widely used in vehicles and architecture [10]. It is used particularly in photovoltaic

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cells and parabolic mirrors for photothermal plants in the renewable energy field. The theoretical efficiency limit of solar panels is around 33.7% [7]. Thus, it is very important to approach this limit as closely as possible in order to realize their full capability. This capability is directly reduced as the surface becomes more opaque due to the deteriorating effect of weather agents, cleaning or maintenance work, or by the deposition of dirt and snow. Consequently, the objective of the present work is to study the application of a coating on these surfaces that promotes their hydrophobicity and wear resistance.

For this purpose, the application of different mixtures of liquid precursors has been investigated. (Heptadecafluoro-1,1,2,2-tetrahydrodecyl) trimethoxysilane (FLUSI), is a precursor that is characterized by its low surface energy, due to its fluorocarbon chain. This makes FLUSI a suitable material to increase the hydrophobicity of various substrates. However, these fluorocarbon-based materials can cause problems due to their poor adhesion to metal or inorganic material substrates [11], such as glass. For this reason, it is convenient to combine the fluorinated precursor with an additive that promotes its adhesion and whose behavior governs the mechanical response of the surface [12]. Aminopropyltriethoxysilane (APTES) is one of the materials that are known as aminosilanes. It is the most commonly used reagent to functionalize silica surfaces with amine groups. Aminosilanes have been widely used to promote the adhesion of proteins or different types of molecules to glass or SiO_2 surfaces [13]. Siloxane (SiOSi) is usually formed when aminosilanes are used to apply coatings. Masuko et al. [14] studied the tribological performance of self-assembled monolayers (SAMs) with different numbers of siloxane bonds on smooth silicon substrates. They found that the SAMs with higher numbers of siloxane bonds had stable low friction coefficients and superior durability. Therefore, in our present work, we use APTES to promote the adhesion of the hydrophobic coating and to improve the wear resistance of the surface.

Among the technologies available for the application of these coatings, the use of a cold or non-equilibrium plasma is especially interesting. This technology allows one to carry out the process at atmospheric pressure and room temperature. In addition, it allows one to control the features of the coatings by the parameters of the plasma-polymerization process, such as gas flow rate and plasma power. This is a versatile technology that is suitable for integration in an in-line process that can apply coatings without altering the substrate's bulk material properties [15,16]. A non-thermal atmospheric jet plasma system will be used, as it is effective for applications, such as depositing coatings that are based on silicon oxide, increasing scratch-resistance and enhancing barrier properties against gases, polyolefins or water [17].

Therefore, we will study various coatings deposited on glass substrate by non-thermal atmospheric jet plasma-polymerization of APTES and FLUSI. In order to find a coating that provides the best balance between hydrophobicity and wear resistance, both precursors will be used individually and mixed in different proportions.

2. Experimental

Glass samples of 100 mm × 50 mm × 3.9 mm were coated by the non-thermal atmospheric jet plasma system, PlasmaSpot® (VITO) [18] . It employs a gun that contains a plasma torch system at atmospheric pressure. This system is equipped with coaxial, cylindrical electrodes and a dielectric barrier of Al_2O_3 between them. The gun moved over the surface of the samples at a fixed speed of 6 m/min, keeping a track pitch of 2 mm and a distance of 6 mm from the substrate. All of the samples, except one that was kept uncoated, were subjected first to a surface activation phase by exposure to one pass of plasma without using a precursor. Secondly, each sample was coated by two passes of plasma-polymerization. Nitrogen gas (99.99%) at a flow rate of 80 slm was used as a supply gas for activation and plasma-polymerization. The generator's power was set at 450 W, and the frequency was set at 68 kHz. The samples were coated using (Heptadecafluoro-1,1,2,2-tetrahydrodecyl)trimethoxysilane (FLUSI, $CF_3(CF_2)_7(CH_2)_2Si(OCH_3)_3$) and aminopropyltriethoxysilane (APTES, $H_2N(CH_2)_3Si(OC_2H_5)_3$) as liquid precursors, both individually and mixed in different proportions as indicated in Table 1.

The specified proportions of the precursors were mixed together in the same container before atomization. An atomizer (model 3076, TSI) was used to nebulize the liquid precursors, producing a fine aerosol. Nitrogen gas at a flow rate of 1.5 slm was used to carry the precursors through the atomizer to the afterglow. This gas flow rate corresponds to a flow rate of approximately 0.06 mL/min for the precursor mixture. The precursors carried by nitrogen gas were admixed perpendicularly to the afterglow through a 0.5 mm opening at the end of the central tube of the gun.

In order to obtain convincing results, some of the analyses were performed on four different sub-samples of 10 mm × 10 mm × 3.9 mm from different locations of each 100 mm × 50 mm × 3.9 mm sample type. The thickness of the coatings was quantified with surface profile measurements using a WYKO NT3300 non-contact surface profiler in phase-shifting interferometry (PSI). Four measurements were taken from each sample in order to obtain an average thickness. Surface images of the samples were taken by a JEOL JSM-840 scanning electron microscope (SEM) at an operating voltage of 10 kV. The wear tracks generated during the tribological tests were observed by a HITACHI S-2400 scanning electron microscope at an operating voltage of 18 kV. A qualitative analysis of the elemental composition of the wear tracks was carried out using an energy dispersive X-ray spectroscope (EDX) Bruker, Quantax 200 with an XFlash 5010/30 detector and microanalysis software ESPRIT 1.9. The surfaces of the samples were coated with gold by sputtering to make them conductive.

Atomic Force Microscopy (AFM) measurements were undertaken in order to study the morphology of the coated and uncoated surfaces. For this purpose, a Multimode AFM from Veeco Instruments operating in tapping mode with a Nanoscope V controller was used. An area of 10 μm × 10 μm was scanned on each sample and the root mean square (RMS) roughness of each sample type was calculated from the images obtained.

Chemical characterization of the coatings was achieved by Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) analyses. For the FTIR analysis of the coatings, the same coating process with the same precursors in Table 1 was employed using silicon wafers of 1 cm^2 area as substrates. An uncoated silicon wafer that was subjected to surface activation by one pass of plasma was used as the reference for the comparison of the FTIR spectra. The FTIR spectra were obtained by a BRUKER IFS 66 FTIR spectrometer in transmission mode. The spectrum of each sample was averaged over 64 scans in the range of 400–4000 cm^{-1} with a resolution of 2 cm^{-1}. The FTIR spectra of all samples were normalized according to the peak at 611 cm^{-1}, which is related to the Si–Si of the substrate. To better study the chemical structure of the coatings, the FTIR spectrum of the uncoated substrate was subtracted from those of the coated samples. X-ray photoelectron spectra were obtained using a Physical Electronics PHI 5700 spectrometer with a multi-channel hemispherical analyzer and a MgKα X-ray source (1253.6 eV) operating at 15 kV and 300 W. The spectra were acquired at a constant pass energy of 29.35 eV.

Table 1
Sample identification based on the proportions of APTES and FLUSI.

Sample	Precursors (%)	
	APTES	FLUSI
F100	0	100
A25/F75	25	75
A50/F50	50	50
A75/F25	75	25
A100	100	0
Uncoated glass	–	–

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