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Modification of epoxy resin, silicon and glass surfaces with alkyl- or fluoroalkylsilanes for hydrophobic properties

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ABSTRACT

Preparation of superhydrophobic materials inspired by nature has attracted a great scientific interest in recent decades. Some of these materials have hierarchical lotus-like structures, i.e. micro- and nano-objects coated by hydrophobic compounds. A major challenge of applying the superhydrophobic surfaces for the self-cleaning coatings preparation is their improved efficiency in varying atmospheric conditions, e.g. UV light. The objective of this research work was to investigate the effect of the different chemical structure and the surface free energy on the hydrophobic and tribological properties of the alkylsilanes and fluoroalkylsilanes deposited on silicon wafers, glass slides and epoxy resin. Tribological and hydrophobic properties of the modified surfaces were correlated with their chemical structures. Chemical structures of the deposited materials were examined by using Fourier transform infrared (FT-IR) spectroscopy and hydrophobic properties were investigated by water contact angle (WCA) and surface free energy (SFE) measurements. The modified surfaces exhibited water contact angles of above 100° for the selected modifiers. It was noticed that the replacement of hydrogen atoms by fluorine atoms in alkyl chain caused an increase in the water contact angle values and a decrease in friction coefficients. The obtained results showed that the carbon chain length of a modifier and its chemical structure can strongly affect the hydrophobic and tribological properties of the modified surfaces. The highest values of WCA, lowest values of SFE and coefficient of friction were obtained for samples covered by fluorinated compounds. Moreover, some preliminary aging test was performed to give an insight into the effectiveness of deposited alkylsilanes and fluoroalkylsilanes coatings. After accelerated UV exposure, no significant changes in the chemical structure, hydrophobic and tribological properties of the modified surfaces were noticed. The samples degradation was not observed and hydrophobic effect was maintained in UV light what can be promising in efficient self-cleaning coatings obtaining.

1. Introduction

Wetting and non-wetting phenomena are ubiquitous in the natural and technological worlds. Examples include droplet spreading on solids such as a spraying of paint, penetration of ink in paper, and liquid absorbency or repellency of fabrics. Numerous surface modification techniques are used to control wettability and adhesion on the obtained surfaces. A promising strategy to regulate wetting behavior is the combination of the surface patterning and the chemical surface modification [1–7]. It is known that high wear resistant properties of polymeric material and well defined modification process are needed to prepare superhydrophobic surfaces with high application potential [3,8,9]. Physicochemical processes such as physical vapour deposition, plasma enhanced PVD, chemical vapour deposition, wet chemical reactions can be used for surface modification. For example, fluorinated silanes or fluoropolymers can be used for hydrophobization to obtain superhydrophobic lotus-like surfaces by using modification process based on chemical bath deposition (CBD) [10–12]. Moreover, fluorinated compounds can also influence the reduction in friction coefficient of modified surfaces [13]. Wettability of the solid surface is a unique property of the materials and strongly depends on both the surface energy and the surface roughness. At the same time, the hydrophobicity is a fundamental property of a solid surface that can play an important role in many applications. It is defined on the basis of the water contact angle (WCA), sliding angle (SA) and the surface free

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energy (SFE). Surfaces with a high surface free energy (SFE) exhibit a high wettability. The surface tension γ has two components: the dispersive component γ^{LW} (Van der Waals interactions) and the acid–base component γ^{AB} (hydrogen bonding interactions) [14]. The superhydrophilic materials are characterized by low water contact angle (WCA), even close to zero degrees. On the other hand, superhydrophobic materials exhibit WCA values exceeding 150°, as a result of low surface free energy, coupled with low water-surface contact area that is provided by appropriate hierarchical surface roughness. Researchers are inspired by nature, for example the lotus leaf [1,15–17] and have made an effort to adopt it to many applications e.g.: self-cleaning, antifouling or potentially icephobic coatings for airplane surfaces [1,16,18]. Whereas many research works have been published on hydrophobicity, up to date there is little information concerning correlation between chemical structure of modifiers and properties of the modified surface. Investigations on the chemical modification and wear resistance of smooth silicon surface are necessary to select an adequate modifier in terms of covering the hierarchical surfaces by coatings with intentional water-repellent and tribological properties.

In this work, the influence of various alkylsilane modifiers on hydrophobic and tribological properties of the obtained surface is investigated. This paper reports the improvement of the frictional properties of three different substrates, i.e. glass slides, silicon wafers and epoxy resin modified by two groups of compounds, i.e. alkylsilanes and fluoroalkylsilanes with different amount of carbon atoms in the molecule. The hydrophobic surfaces with water contact angles of above 100° were obtained and tested in terms of chemical structure, roughness and tribological properties. The obtained results showed that chemical modification with compounds containing long alkyl chain length caused the surface roughness to be increased and hydrophobic properties to be improved, especially for fluoroalkylsilanes used as modifiers. The results presented in this work shed some new light on constantly growing demand for compounds used to produce self-cleaning or anti-icing systems.

2. Experimental

2.1. Materials and sample preparation

Glass slides, silicon wafers and epoxy resin were used as substrates. Cyclohexane (99.8%) was supplied by Chempur and modifiers of 97% purity were obtained from ABCR GmbH & Co. KG. Hydrophobic thin films were obtained using cyclohexane as a solvent and two groups of modifiers, i.e. alkylsilanes and fluorosilanes with different amount of carbon atoms in the molecule. Liquid phase deposition was applied as a chemical modification method to obtain a thin film of silanes (1% of modifier in cyclohexane solution) on glass slides, silicon wafers and epoxy resin. The following silanes were applied:

Alkylsilanes
- n-Octyltrichlorosilane (OTS) – C_8
- n-Decyltrichlorosilane (DTS) – C_{10}
- Dodecyltrichlorosilane (DDTS) – C_{12}
- n-Hexadecyltrichlorosilane (HDTS) – C_{16}
- n-Octadecyltrichlorosilane (ODTS) – C_{18}
- Docosyltrichlorosilane (DCTS) – C_{22}

Fluoroalkylsilanes
- 1H,1H,2H,2H-Perfluorooctyltrichlorosilane (PFOTS) – C_8
- 1H,1H,2H,2H-Perfluorodecyltrichlorosilane (PFDTS) – C_{10}
- 1H,1H,2H,2H-Perfluorotetradecyltriethoxysilane (PFTDS) – C_{14}

Unmodified samples are labeled as C_0.

According to Haensch et al. [18] plasma activation was applied before chemical modification by chloroalkylsilanes to obtain an activated surfaces with hydroxyl groups (—OH). The low pressure air plasma system (Diener Electronic Plasma-Surface-Technology, Zepto, 40 Hz, 100 W) was used for 20 min to remove impurities and generate reactive —OH groups on the surfaces. The samples were modified by 1% of silane in cyclohexane solution at room temperature for 30 min. Then, the surfaces were washed out with cyclohexane, dried with nitrogen gas and thermally treated at 40 °C for 24 h. Chemical modification process was carried out according to a procedure developed in our earlier research work [19].

2.2. Materials characterization

The surface topography of the coatings was investigated using atomic force microscopy (AFM, Solver P47, NT-MDT) in oscillation mode (tapping mode), operating in air under ambient conditions. The unmodified and modified silicon wafers (Si) or epoxy resin surfaces was examined using a Si3N4 tip with a radius of curvature of less than 10 nm and a spring constant of about 14 N/m. A scan of 5 μm × 5 μm in size was used to not exceed the surface roughness of AFM scanner's vertical range of 4 μm. Tapping mode were applied to avoid damage of soft polymer surface structures during measuring step. The AFM topographical images were analyzed by using Image Analysis 2 SPM image processing software (NT-MDT). Surface image flattening corrections were applied, first order line fitting (1D) and second order plane subtraction (2D). The 3D roughness parameters were calculated according to the ISO 25178 standard and were averaged over three independent measurements for each sample.

The hydrophobic properties of the surfaces were examined using a DSA-100 Drop Shape Analysis System (KRÜSS GmbH). The water contact angle (WCA) and sliding angle (SA) values were measured at room temperature by applying the Laplace–Young fitting algorithm to the images recorded with a CCD camera. A water drop of 5 μl from a syringe was placed on the modified surface. Five drops have been deposited on each coating sample, giving the average WCA values. The SFE value was calculated using the van Oss–Good method, from contact angle values measured for deionized water, diiodomethane and glycerine droplet.

Chemical analysis of the modified samples were performed using infrared spectrophotometer with GATR starter and MCT detector cooled by liquid nitrogen in the measuring range of 4000–700 cm^{-1}. Essential FTIR software was applied to perform and analyze spectra.

Frictional measurements (CoF) were performed using homemade microtribometer designed and constructed at the Department of Chemical Technology and Environmental Protection, University of Lodz. Three independent measurements were conducted at the same conditions, and one after another to obtain the final friction coefficient. Tribological tests were performed for unmodified and modified substrates with suitable compounds listed above. Applied zirconia ball characterized by high hardness has provided small changes in geometry during friction measurements. A high stability of counterbody enabled to obtain comparable friction measurements for various types of modifiers used to prepare thin coatings on different substrates. At the beginning of each measurements, the ball has been cleaned with cotton cloth soaked with ethanol or acetone to remove impurities and solid wear products that could be accumulated during previous runs. To obtain the most reliable results, the substrate has been purified under a stream air. Friction test have been performed on a distance of 5 mm with velocity of 42 mm min^{-1}. The initial value of the load was 30 mN, which at 7 measurements cycles with the load interval of 10 mN, gave a final value of load 90 mN. Real value of

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