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Nanoscale morphology for high hydrophobicity of a hard sol–gel thin film

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ABSTRACT

It is challenging to obtain a hydrophobic smooth coating with high optical and mechanical properties at the same time because the hydrophobic additives are soft in nature resulting in reduced hardness and durability. This paper reports a durable hydrophobic transparent coating on glass fabricated by sol–gel technology and a low volume medium pressure (LVMP) spray process. The sol–gel formula consists of a pre-linked hydrophobic nano-cluster from hydroxyl-terminated polydimethylsiloxane, titanium tetraisopropoxide and a silica-based sol–gel matrix with silica hard fillers. Polydimethylsiloxane (PDMS) is uniformly distributed throughout the coating layer providing durable hydrophobic property. Mechanical properties are achieved by the hard matrix and hard fillers with the nano-structures. Due to the surface nano-morphology, a high degree of hydrophobicity was maintained with only 10 vol.% PDMS, while the hardness and abrasion resistance of the coatings were not significantly compromised. Chemical analyses by FTIR confirmed the uniform distribution of the PDMS and surface morphology analyses by atomic force microscopy (AFM) displayed the nano-surface structures that enhanced the hydrophobicity. The special surface nanostructures can be quantified using surface Kurtosis and ratio between asperity peak height to distance between peaks. The LVMP process influences the spray droplet size resulting in different surface structures.

1. Introduction

Water repellent coatings providing high water repelling function and higher abrasion resistance are increasingly used on inorganic surfaces, such as glass and ceramics, for a wide range of applications including coatings for automotive windows, building surfaces, bathroom surfaces, and green house glass pennels. Hydrophobic coatings made from perfluoroalkylsilanes by sol–gel technology [1–3] have been intensively investigated, and have been used on automotive windshield and sidelights by Nippon Sheet Glass for 10 years [4]. Although three generations of coatings have been introduced, further improvements on hydrophobicity and abrasion resistance will lead to expended market and wider application fields. Other hydrophobic reagents including long-chain organosilane compounds were reported [5–8]. Contact angles in the range of 95–115° were reported on smooth surfaces, and up to 141° on rough surfaces. It is well known that the water contact angle cannot be increased beyond 120° by a purely chemical process on smooth surface [9]. Further enhancement of contact angle is due to an increase in surface roughness. Some authors [10–12] defined superhydrophobic surfaces as those having water contact angle higher than 150°. Others [13–15] believed that contact angle hysteresis (the difference between the advancing and receding contact angles), rather than the static contact angle, controls the water repellency. Studies on textiles [16,17] showed that hysteresis was caused by kinetic barriers to contact line movement, both advancing and receding. On smooth surfaces, these barriers are usually from the roughness and chemical heterogeneity. It was suggested that hydrophobicity should be quantified by providing the advancing angle (θ_A) and receding angle (θ_R) and calculating the force required for a water droplet to move over the surface using the value of $\gamma_{LV}(\cos\theta_R - \cos\theta_A)$. It must be noted that increasing surface roughness decreases the transparency because of the light scattering at the rough surface. Therefore, it is always challenging to obtain high hydrophobicity on a transparent surface.

A sol–gel formulation consisting of a pre-linked hydrophobic nano-cluster from hydroxyl-terminated polydimethylsiloxane (PDMS) and titanium tetraisopropoxide (TIP), and a silica-based sol–gel matrix with silica hard fillers was developed and reported by us previously [18]. A contact angle of 133° was achieved by 50 vol.% PDMS. However, the coating hardness was reduced to 0.2 GPa from 0.85 GPa of the original sol–gel silica coating. In this paper, we further report the optimization of the chemical composition and spraying process

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towards nanoscale structures to maximize hydrophobicity with balanced mechanical, optical and surface properties. The surfaces with different PDMS contents were characterized on their chemical groups, morphologies (surface Kurtosis (Ku), peak height and distance between peaks), stationary contact angles, advancing and receding angles. Abrasion resistance and nano-indentation hardness values were tested for optimizing the mechanical properties.

2. Experimental procedures

2.1. Materials

The coating system consists of the following components and raw materials:

- hydrophobic additive: hydroxyl-terminated PDMS, average molecular weight 550, viscosity 25 cSt,
- metal alkoxide as linker for the PDMS: titanium tetraisopropoxide,
- modifier for TIP to reduce the hydrolysis and condensation reaction rate: ethyl acetoacetate (EAcAc),
- sol–gel matrix to provide the primary strength of the coating: methyl-triethoxysilane (MTES) and tetraethyl orthosilicate (TEOS),
- silica nano-filler: 20 nm colloidal particles suspended in *iso*-butanol (pH 7),
- catalysts: acetic acid (HAc) or hydrochloric acid (HCl),
- solvents: ethanol (EtOH) and 1-propanol (PrOH).

All materials were purchased from leading chemical suppliers without further purification.

2.2. Synthesis procedures

Detailed procedures were described in our earlier publication [18]. In short, TIP/PDMS solution was prepared by mixing TIP, 1-propanol, EAcAc, PDMS and deionized water in molar ratios of TIP:PrOH:EAcAc:PDMS:H_2O = 1:6:2:2:2, which was stirred for 24 h. A stock solution of MTES and TEOS was prepared by hydrolysing these precursors in acidic water (pH 3 by adding HCl in water), followed by an addition of colloidal silica. The molar ratios of the components are: MTES:TEOS:H_2O = 1:0.016:4.4. The colloidal silica is acidified by HCl to pH 4, and added at 30 vol.% with respect to the volume of the cured solid coating. The calculation procedures for the volume percent of each component in cured solid coating was described in reference [18], and the same method was used to calculate the PDMS vol.% in this paper. The TIP/PDMS mixture was added to the MTES/TEOS stock solution in various ratios to form the final coatings with 10, 20 and 30 vol.% PDMS, in order to study the hydrophobicity and mechanical properties of the coatings.

2.3. Coating and curing processes

Coating was applied on glass substrate by a spraying process. The glass substrate was cleaned by ethanol and blown dry with N_2 gas. The air spray gun is a low volume medium pressure (LVMP) gun, which makes higher transfer efficiency and better atomization with less air consumption. This is necessary to ensure fine spray droplets and maintain a uniform transparent coating. The coated glass was dried in an oven at 80 °C for 40 min. then cured at 200 °C for 90 min. In order to fairly compare the properties of the coatings made of different chemical compositions, the coating thickness was well controlled by measuring the weight of the wet coating during spraying. The number of spraying stocks were kept the same at first, then the weight increase of the coated sample was measured, additional spraying was performed if the weight is not enough. Since the solvent content in all the coatings were the same, the cured coatings had similar thickness between 4 and 5 μm.

2.4. Coating characterization

Coatings' hydrophobicity is measured using the VCA Optima (VCA-2500XE AST products, Inc.) contact angle machine. The image of the water drop is obtained when a pre-determined amount of water (0.5 μl) is dropped on the surface under test. The program then analyses the image of the drop and gives the contact angle value. The advancing angle is measured by dispersing additional 0.2 μl of water into the first water drop, while the receding angle is measured by withdrawing 0.2 μl of water from the drop. The difference between these two angles is the contact angle hysteresis. The force needed to move the water drop on the surface is then calculated by $F \sim \gamma_{LV}(\cos\theta_R - \cos\theta_A)$.

The chemical bonds in the coating layers were analysed by Fourier transform infrared spectroscopy (FTIR, Bio-Rad Excalibur Series). Infrared absorption spectra of the coatings in the range of 4000–600 nm wavelengths were analysed by FTIR using the attenuated total reflectance (ATR, with Ge crystal) method. An infrared radiation is passed through an infrared transmitting crystal with a high refractive index, allowing the radiation to reflect within the ATR element several times. The absorption of radiation is related to fundamental vibrations of the chemical bonds, therefore, provides information related to the presence or absence of specific functional groups in the coatings.

The surface morphology is analysed by atomic force microscopy (Veeco Scanning Prob Microscope). The 3D image of the surface topography is plotted and the surface Kurtosis and the surface area ratio (*R*, ratio between real surface area taking the height into consideration to the apparent area of flat plane) were measured. The surface Kurtosis describes the peaked-ness (peak sharpness) of the surface topography as defined by SPIP^{TM} (Scanning Prob Image Processor, http://www.imagemet.com/). For Gaussian height distributions, Ku approaches 3.0. Smaller values indicate broader height distributions and *vice versa* for values greater than 3.0. The mean surface roughness (R_a) of all the samples were measured by a Tayler–Hobson Stylus Profilometer. Section analyses were performed on the topographies of the samples by AFM, and 10-point height (R_z) and distance between peaks (d) were measured. Coating's light transmittance was measured by UV–vis spectrophotometer (SHIMADZU UV-3101PC UV–vis–NIR scanning spectrophotometer).

Coating's hardness is evaluated by nano-indentations (NanoTest from Micro Materials Ltd., U.K.). The nano-indenter is a diamond Berkovich type with tip radius of 50–100 nm. The load was controlled below 0.5 mN. The resultant displacement of the indenter into the surface is monitored with a sensitive capacitive transducer and displayed in real time as a function of load. The hardness and elastic modulus are then calculated by the established equations [19] by the software. The indentation depth is controlled to be at most 10% of the coating thickness to reduce the influence from the substrate. The abrasion resistance was measured by a pin-on-disc Tribometer (ISC-200 Tribometer from Implant Sciences Corp.) using a standard Wearaser CS10 (from TABER Industries) according to ASTM D 4060. The Wearaser is in cylinder shape with a flat tip of diameter 6 mm, which is made of alumina abrasive particles embedded in resilient material. A load of 100 g was applied on the Wearaser. The test sample rotates at a speed of 500 rpm. A circular wearing track with radius about 12 mm is formed on the surface. The weight loss of the sample after