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Non-fluorinated, room temperature curable hydrophobic coatings by sol–gel process

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Abstract

Non-fluorinated hydrophobic silica surfaces were generated on soda lime glass (SLG) substrates using hexamethyldisilazane (HMDS) as a surface modifying agent. Silica coatings were fabricated by dip coating of a sol derived from base catalyzed hydrolysis and condensation of tetraethoxysilane (TEOS). Two methodologies were adopted to generate the hydrophobic surface; one where the hydrophilic silica coated surface was treated by immersion into different concentrations of alcoholic solutions of HMDS varying from 2.5 wt% to 15 wt%. In the other method, HMDS was directly added to a mixture of TEOS, water, ethanol, and ammonium hydroxide and coatings were deposited using this sol by dip coating and spray coating. Water contact angles (WCA) were measured to study the effect of HMDS treatment times and concentrations on hydrophobicity in the first case, and in the second case, WCA were measured for dip and spray coated samples. UV–visible transmission, scratch resistance, and thermal stability of the coatings were determined. The WCA increased from $66 \pm 2^\circ$ to $125 \pm 4^\circ$ after the treatment of the silica coatings with HMDS. In case of coatings generated from direct addition of HMDS to silica sol, WCA varied from $145 \pm 2^\circ$ to $166 \pm 4^\circ$ for dip and spray coated surfaces respectively. Surface morphology was studied to explain the difference in hydrophobicity of coatings generated using the two methods.

Keywords: A. Sol–gel processes; A. Films; B. Surface; C. Optical properties; E. Functional applications

1. Introduction

Hydrophobicity is a property that provides water repellency and non-wettability of a solid surface. The fabrication of hydrophobic coatings is an active area of research in recent years because of its wide range of applications. Sol–gel process has been widely used in the research area of superhydrophobicity due to its unique advantages such as low temperature processing, easy functionalization of surfaces and high homogeneity of final products. Chemical modification of smooth surfaces can lead to a hydrophobic surface with water contact angles up to $\sim 130^\circ$ [1–4]. Fluorosilanes [1–3], polyvinylidene fluoride [4] are used in small amounts along with organically modified silanes to synthesize low surface free energy sols for chemical modification of any surface. However, fluorinated materials are not eco-friendly and hence, other surface modifying materials like silylating agents are being investigated as alternatives for generating hydrophobic coatings.

A silica surface can be made hydrophobic by chemical reaction (referred to as functionalizing, grafting, or silylating) with certain coupling agents to form trimethylsilyl (TMS, $-Si(CH_3)_3$) surfaces. Rao et al. [5] studied the silylation using dimethylchlorosilane (DMCS) on silica coatings derived from methyltrimethoxysilane (MTMS). They reported that the hydrophobicity increased with increase in concentration of DMCS. Mahadik et al. [6] studied the effect of using trimethylchlorosilane (TMCS) as silylating agent on the silica coatings prepared from methyltriethoxysilane (MTES) and trimethylmethoxysilane (TMMS). They reported that the hydrophobicity increased with increase in treatment (silylation) time [6]. Latthe et al. [7] reported on silylation of silica sols derived from tetraethoxysilane (TEOS) and vinyltrimethox-

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ysilane (VTMS). They showed that when molar ratio (M) of VTMS/TEOS was varied, surface structure and hydrophobicity also changed [7]. TMS functionalization of silica surfaces can also be done by a different method by reaction of silica sol with silylating agent like hexamethyldisilazane (HMDS) or chlorotrimethylsilane in the vapor phase [8–13]. Suratwala et al. [14] however used a different approach to generate hydrophobic coatings. Silica sols synthesized by Stöber process were treated with silylating agent HMDS to produce TMS functionalized colloids. HMDS was reacted with these silica sols in suspension to produce highly hydrophobic, TMS functionalized sols. They reported that the variation in starting surface species, the HMDS reaction time, and concentration strongly affect the amount of TMS coverage that takes place [14]. Bhagat et al. [15] also used HMDS as silylating agent and prepared a sol by changing the molar ratio of tetramethoxysilane (TMOS)/methanol and adding the HMDS to the sol to achieve hydrophobicity. Li et al. [16] have reported that superhydrophobic nanosilica can be prepared by surface modification using HMDS.

In most of the investigations where silylating agents were used to modify silica coatings, the coatings were derived from tetramethoxysilane (TMOS) precursor. Since TEOS as a precursor is more suitable for large scale production of silica coatings when compared to TMOS (which yields methanol on hydrolysis and alcohol condensation), silica sol using TEOS was synthesized in the present study. Moreover all the previous reports on the silylation of surfaces mention the use of toxic hexane and decane as solvents to make HMDS solutions. In the present study, isopropyl alcohol (IPA) was used along with HMDS which has not been reported so far. Two methods were adopted to generate the hydrophobic surface; one by treating the hydrophilic silica coating with HMDS as silylating agent and the other by addition of HMDS to silica sol which was coated on the substrate. The coatings were assessed for their hydrophobicities and UV–visible light transmission.

2. Experimental

2.1. Materials

The silica sols in the present study were prepared by the conventional sol–gel process using the following chemicals: tetraethoxysilane (TEOS, ABCR GmbH and co.), hexamethyldisilazane (HMDS, Sigma–Aldrich® Chemie GmbH), ethanol (EtOH), isopropyl alcohol (IPA) (Qualigens Fine Chemicals), and ammonium hydroxide (NH_4OH, Assay – 25 wt%, Finar Chemicals (India) Pvt. Ltd.).

Soda lime glass with a nominal composition of the major metallic elements as Na = 15.5 wt%, Mg = 4.2 wt%, Si = 63.3 wt%, Ca = 14.3 wt%, Al = 1.4 wt% was used as the substrate.

2.2. Sol synthesis and deposition of thin films

Two methods were adoped to prepare the hydrophobic films

(a) Silica films treated with silylating agent

The silica sol was synthesized using the following chemicals TEOS:EtOH:H_2O:NH_4OH in the molar ratio of 1:36.4:6.6:0.25 and NH_4OH (6 M) used as a catalyst. The mixture was allowed to stir for 24 h at 25 °C and the cleaned glass substrates were dipped vertically into the sol for 1 min and withdrawn at a speed of 5 mm/s. The films were dried at 25 °C and annealed at 300 °C for 1 h followed by room temperature treatment in alcoholic HMDS solution with the concentrations varying from 2.5 wt% to 15 wt% HMDS in IPA. All the films were prepared at room temperature and the treatment time was varied from 1 h to 3 h. The surface treated silica films were annealed at 150 °C for 1 h in air using a drying oven.

(b) Silylating agent added to silica sol

The sol was prepared by mixing TEOS:EtOH:HMDS:H_2O:NH_4OH in the molar ratio of 1:36.4:1:6.6:0.25 respectively. HMDS was added to the silica sol and stirred for 24 h. The SLG substrates were dipped vertically in the sol for 1 min and withdrawn at a speed of 5 mm/s. Manual spray coating was also carried out. Both the dip coated and spray coated films were dried at an ambient temperature of 25 °C and annealed at 150 °C in air using a drying oven.

2.3. Characterization

Hydrophobicities of the coatings as well as the wettabilities of substrates prior to coating were measured using a Drop Shape Analyser (DSA) (Krüss GmbH Germany). Contact angles were measured by fitting a mathematical expression to the shape of the water drop, and then calculating the slope of the tangent to the drop at the liquid–solid–vapor interface line. The volume of water droplet was ~4 μl and at least ten measurements were taken. Average of these values was reported as water contact angle (WCA) on the substrate. In case of surface treatment of silica films with HMDS, contact angles were measured before and after treating with HMDS. The surface morphology of the silica coated thin films was studied by using Scanning Electron Microscope (SEM) (Hitachi S3400 N). Transmittance of the coatings was measured by Varian Cary 5000 UV-Vis-NIR Spectrophotometer. Thickness of the transparent coatings measured using Filmetrics Inc. F20 equipment. Hardness of the coatings was evaluated by Pencil scratch tester (Sheen Instruments Ltd. Wolff Wilborn pencil tester GEF 720N) according to ASTM D 3363-05.

3. Results and discussion

3.1. Reaction mechanism

The proposed reaction mechanism for the coatings generated using the two methods are given below:

(a) Silica films treated with silylating agent