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Short communication

Transparent, non-fluorinated, hydrophobic silica coatings with improved mechanical properties

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Abstract

Non-fluorinated, hydrophobic silica coatings were generated on soda lime glass substrates using dimethyldiethoxysilane (DMDEOS), tetraethoxysilane (TEOS) and a silylating agent hexamethyldisilazane (HMDS) using sol–gel process. To improve the mechanical properties of the coating, epoxy modified nanosilica particles were added to the sol of dimethyldiethoxysilane, tetraethoxysilane and hexamethyldisilazane followed by sonication prior to coating. Coatings were characterized for their water contact angles, thickness, UV–Vis transmission, pencil hardness and surface morphology. The concentrations of the nanosilica particles as well as the sonication times were optimized to obtain a transparent, hydrophobic coating with improved pencil scratch hardness. An optimized coating composition with 1: 0.5 M ratio of the nanosilica particles and sol synthesized from DMDEOS, TEOS and HMDS sonicated for 60 min yielded coatings that exhibited a water contact angle of $125 \pm 2^\circ$ with a pencil scratch hardness of HB and average visible light transmittance of 89%.

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

1. Introduction

Hydrophobic surface generation has recently received much attention due to the large industrial demand in the need for easy-to-clean surfaces. The wettability of a surface strongly depends on both the surface chemical composition as well as the surface roughness [1]. Sol–gel process has been widely used to generate hydrophobic coatings due to its unique advantages such as low temperature processing, easy functionalization of surfaces and high homogeneity of final products. Fluorosilanes [2–4], polyvinylidene fluoride [5] are usually used in small amounts along with organically modified silanes to synthesize low surface free energy sols for chemical modification of any surface. Since fluorinated materials are not eco-friendly in addition to being expensive, other surface modifying materials like silylating agents are being investigated as alternatives for generating hydrophobic/superhydrophobic coatings [6–8]. It is challenging to obtain a smooth hydrophobic coating with high optical and mechanical properties at the same time because the hydrophobic additives are usually soft and do not provide good hardness and durability. Recently Jeevajothi et al. [9] investigated on generation of non-fluorinated hydrophobic silica surfaces using tetraethoxysilane (TEOS) and hexamethyldisilazane (HMDS) as silylating agent. Transparent hydrophobic surfaces were obtained with moderate scratch hardness. Lakshmi et al. [10] reported on generation of non-fluorinated, hydrophobic silica coatings using methyltriethoxysilane (MTEOS), colloidal silica along with fumed silica and claimed superhydrophobic surfaces with better scratch hardness. However, the reported hydrophobic surfaces with better mechanical properties did not exhibit high transmittance, since it is difficult to obtain transparent, superhydrophobic surfaces with good mechanical properties. Hence, the present investigation was carried out and reports for the first time on generation of transparent, non-fluorinated hydrophobic surface using dimethyldiethoxysilane (DMDEOS), HMDS and surface modified nanosilica particles for improving the mechanical

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properties. The reason for using surface modified nanoparticles instead of only nanoparticles was to obtain a better linkage between the nanoparticle and the organic–inorganic hybrid network.

2. Experimental

2.1. Materials

Five different silica sols were synthesized in the present study using the following chemicals: Dimethyldiethoxysilane (DMDEOS, GELEST Inc., USA), tetraethoxysilane (TEOS, ABCR GmbH and co., Germany), hexamethyldisilazane (HMDS, Sigma-Aldrich® chemie GmbH, Germany), epoxy modified nanosilica (Nanopox® C 680, particle size: 20 nm, nanoresins AG, Germany), isopropyl alcohol (IPA, Qualigens Fine chemicals, India), and hydrochloric acid (HCl, Qualigens Fine chemicals, India).

Soda lime glass sheet of dimensions 75 mm × 25 mm and with a nominal composition of the major metallic elements in wt% as Na = 15.5%, Mg = 4.2%, Si = 63.3%, Ca = 14.3%, Al = 1.4%, was used as the substrate.

2.2. Synthesis

Five different organically modified silica sols were prepared by the following methods and will henceforth be referred to as sols A, B, C_1, C_2, and C_3. Sol A was synthesized by using DMDEOS: TEOS: IPA: H_2O in the molar ratio of 1: 0.5: 12.7: 3.5 and HCl (0.1 M) was used as a catalyst. The mixture was allowed to stir for 24 h. Sol B was prepared by using the same chemicals as used in sol A, but with an addition of HMDS to the sol A. The molar ratio of DMDEOS: HMDS was 1: 1 and mixture was allowed to stir for 5 h. Sol C was prepared by using the same chemicals used in sol B. In addition Nanopox® C 680 was added to the sol B in three different ratios (i.e., nanosilica: sol B, to be 1: 0.5, 1: 0.25 and 0.5: 1) and these sols are denoted as sol C_1, sol C_2, and sol C_3. Before the addition of the sol, Nanopox® C 680 was dispersed in IPA. Then the total mixture was allowed to stir for 1 h. In the case of sol C_1, different ultrasonication times of 10 min, 30 min and 60 min duration were employed to optimize conditions to obtain a transparent coating. The sols A, B, C_1–C_3 were coated on the cleaned glass substrates by dip coating employing a withdrawal speed of 5 mm/s. The films were dried at 150 °C for 1 h.

2.3. Characterization

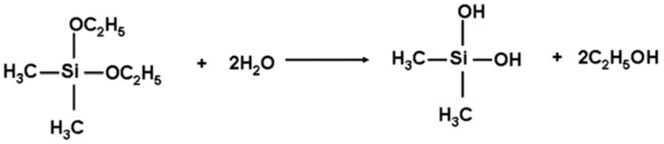
The water contact angles were measured using a Drop Shape Analyzer (DSA) (Krüss GmbH, Germany). The volume of water droplet was ~4 μl and the average of 10 measurements is reported as the water contact angle. The surface morphology of the silica coatings was studied by using Field Emission Scanning Electron Microscope (FESEM) (Hitachi S3400N). Transmittance of the coating was measured by Varian Cary 5000 UV–Vis–NIR Spectrophotometer. Coating thickness was measured using Filmetrics Inc. F20 equipment and pencil scratch hardness of the coatings measured according to ASTM D 3363-05. **The coating roughness was measured using a Mahr profilometer.**

3. Results and discussion

The proposed reaction mechanisms for the synthesis of the five different sols are given below:

In case of sol A, usual hydrolysis and condensation reactions of DMDEOS (Eqs. (1)–(3)) and similarly, the hydrolysis and condensation reactions for TEOS gives rise to an organically modified silica sol A [11], as shown by Eq. (4).

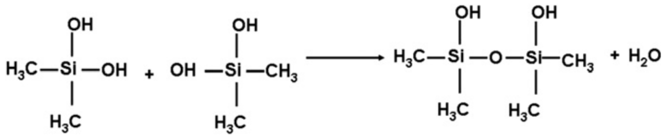
Hydrolysis of DMDEOS:



$$\mathrm{H_3C{-}\overset{OC_2H_5}{\underset{H_3C}{Si}}{-}OC_2H_5 + 2H_2O \longrightarrow H_3C{-}\overset{OH}{\underset{H_3C}{Si}}{-}OH + 2C_2H_5OH} \quad (1)$$

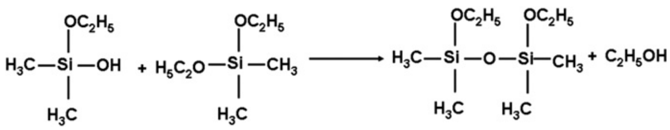
Condensation:

(a) Water condensation of DMDEOS:



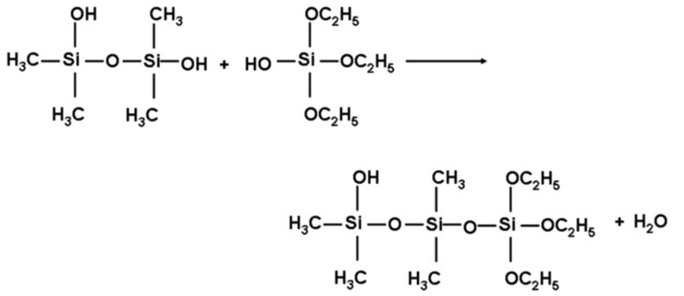
$$\mathrm{H_3C{-}\overset{OH}{\underset{H_3C}{Si}}{-}OH + OH{-}\overset{OH}{\underset{H_3C}{Si}}{-}CH_3 \longrightarrow H_3C{-}\overset{OH}{\underset{H_3C}{Si}}{-}O{-}\overset{OH}{\underset{H_3C}{Si}}{-}CH_3 + H_2O} \quad (2)$$

(b) Alcohol condensation of DMDEOS:



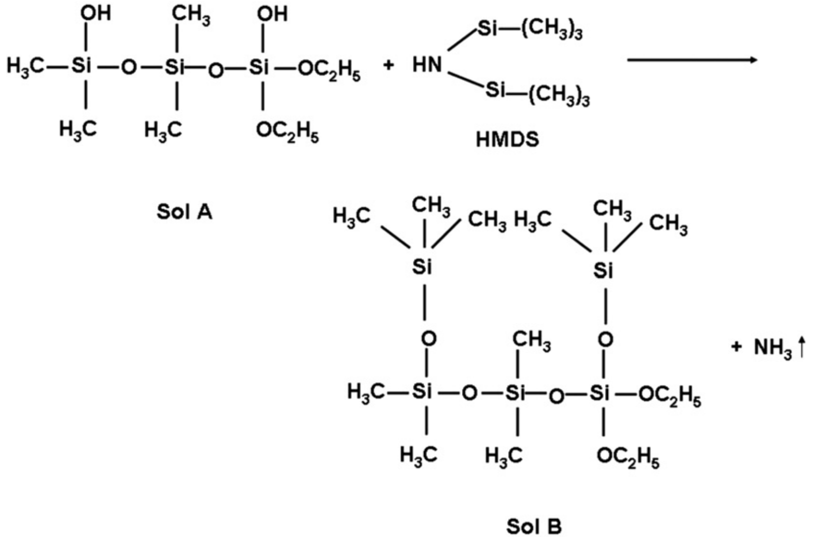
$$\mathrm{H_3C{-}\overset{OC_2H_5}{\underset{H_3C}{Si}}{-}OH + H_5C_2O{-}\overset{OC_2H_5}{\underset{H_3C}{Si}}{-}CH_3 \longrightarrow H_3C{-}\overset{OC_2H_5}{\underset{H_3C}{Si}}{-}O{-}\overset{OC_2H_5}{\underset{H_3C}{Si}}{-}CH_3 + C_2H_5OH} \quad (3)$$

(c) Co-condensation of intermediates after hydrolysis/condensation of DMDEOS and TEOS:



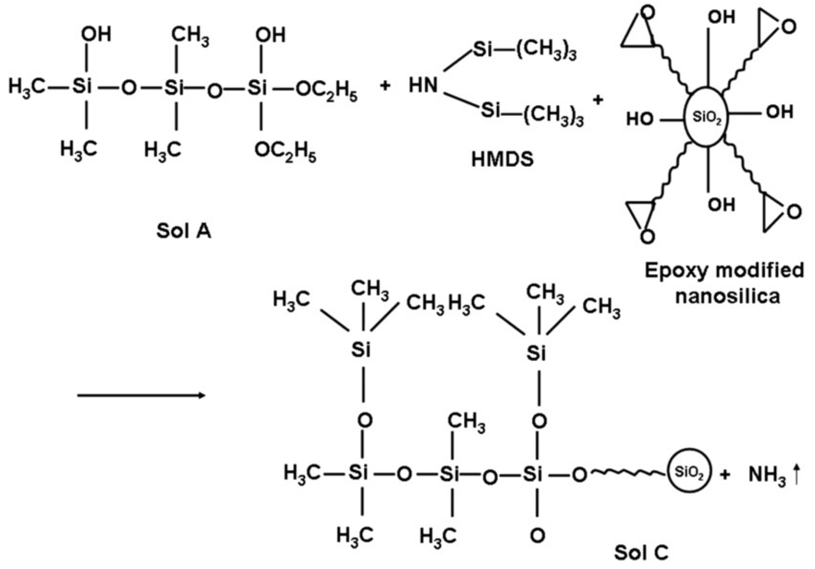
(4)

The proposed reaction mechanism after addition of HMDS to sol A to give sol B is given below [9]:



(5)

The following mechanism is proposed for the sol C from sol B after the addition of epoxy modified nanosilica:



(6)

The above mechanism is similar to that reported by Park et al. [12], who studied the characteristics of organic–inorganic hybrid coating films synthesized from colloidal silica–silane sol. In the present investigation, a surface modified silica nanoparticle suspension was added to the sol synthesized from DMDEOS and TEOS instead of colloidal silica as reported in [12].

The properties of coatings derived from the five sols are summarized in Table 1. Coating A exhibits contact angles of 93 ± 2° because of the presence of non-polar methyl groups on the surface. In coating B, contact angle was 104 ± 2° because of the surface modification due to HMDS which provides additional $-CH_3$ groups that yields contact angles greater than 100°. It does not show a super hydrophobic behavior though because of possible steric hindrance caused due to the large number of methyl groups on the surface which may even obstruct the silylation taking place according to Eq. (5). In the case of coatings A and B, sonication of sols was not necessary, because the films were transparent.

When Nanopox® C 680 was added to sol B in 1: 0.5 ratio, the viscosity immediately increased and the sol could not be used for coating. This sol C_1 was sonicated for 10 min and coating could be deposited though films were not transparent and not of very good quality, and the WCA was 133 ± 2°. Then the same sol was sonicated for 30 and 60 min and coatings deposited. After 60 min of sonication, the obtained coatings were transparent whose WCA was 125 ± 2°. It should be noted that obtaining films with good transparency and stability depends on the ultrasonication time. Contact angle of the coating films decreased with increasing in sonication time. This is because increase in sonication time increased the dispersion of nanoparticles. So roughness of the surface decreases from 0.55 μm (10 min ultrasonication) to 0.03 μm (30 min ultrasonication) to 0.017 μm (60 min ultrasonication) due to better dispersion as seen from Fig. 1 and contact angle was reduced as seen from Table 1. From the results obtained, an ultrasonication time of 60 min was chosen to be the optimized time for getting a transparent coating from sol C_1.

To compare and study the effect of nanosilica addition to the mechanical properties of the coatings, the nanosilica and sol C was taken in three different ratios labeled as sol C_1 (1: 0.5), sol C_2 (1: 0.25), and sol C_3 (0.5: 1). Required amounts of epoxy modified nanosilica to synthesize C_1, C_2, and C_3 were dispersed in IPA and added to sol C followed by ultrasonication for the optimized time of 60 min. The reactive nanosilica particles contributed to the hardness of the coatings. From the properties of coatings derived from C_1, C_2, and C_3 (as shown in table 1), it could be seen that C_1 coating was transparent, stable, hydrophobic with a scratch hardness of HB, whereas for the other ratios C_2 and C_3, though the coatings obtained were transparent, either there was a wetting problem or the coating had a lower scratch hardness. Hence C_1 was chosen to be the optimized ratio of Nanopox® C 680: sol B.

Surface morphology of the coatings B and C_1-60 as examined by FESEM is shown in Fig. 2. For coating from sol C_1, (fig. 2b), the image shows dense arrangement of silica nanoparticles on the surface which is the reason for the coating to exhibit improved mechanical properties than coatings without the nanosilica. The UV–Vis transmission of the coatings from sol C_1 after 10 and 60 min ultrasonication showed that the average optical transmission from 400–800 nm increased from 9% to 88% respectively

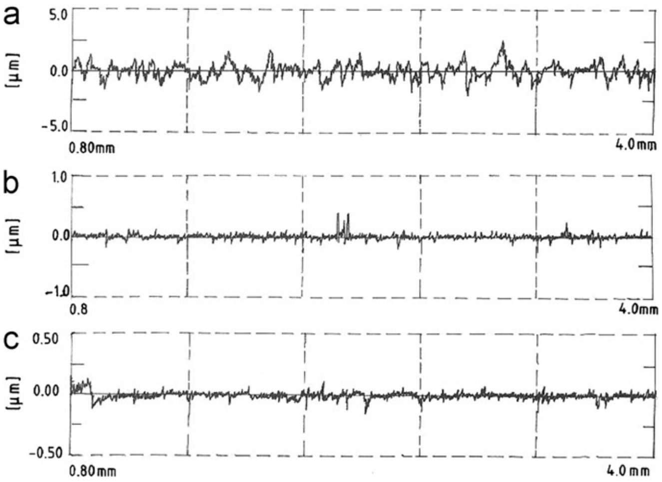


Fig. 1. Roughness profiles of Sol C_1 (a) after 10 min (b) after 30 min and (c) after 60 min of ultrasonication.

Table 1
Properties of coatings obtained from sols A, B, C_1-10, C_1-30, C_1-60, C_2, and C_3. (C_1=1: 0.5; C_2=1: 0.25; C_3=0.5: 1 M ratio of Nanopox® C680: sol).

Sol composition	Sonication time [min]	Coating properties		
		WCA [deg]	Scratch hardness	Other remarks
A	0	93 ± 2	7H	Transparent, no wetting problem
B	0	104 ± 2	B	Transparent, no wetting problem
C_1	10	133 ± 2 (R_a=0.55 μm)	< 9B	Non-transparent, wetting problem
C_1	30	127 ± 2 (R_a=0.03 μm)	< 9B	Non-transparent, wetting problem
C_1	**60**	**125 ± 2** (R_a=0.017 μm)	**HB**	**Transparent, no wetting problem**
C_2	60	118 ± 2	F	Transparent, wetting problem
C_3	60	113 ± 2	B	Transparent, no wetting problem

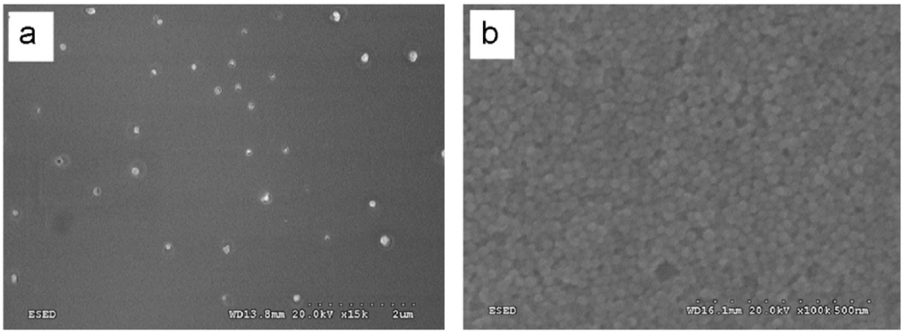


Fig. 2. Surface morphology of coatings from (a) Sol B and (b) Sol C_1 after 60 min ultrasonication.

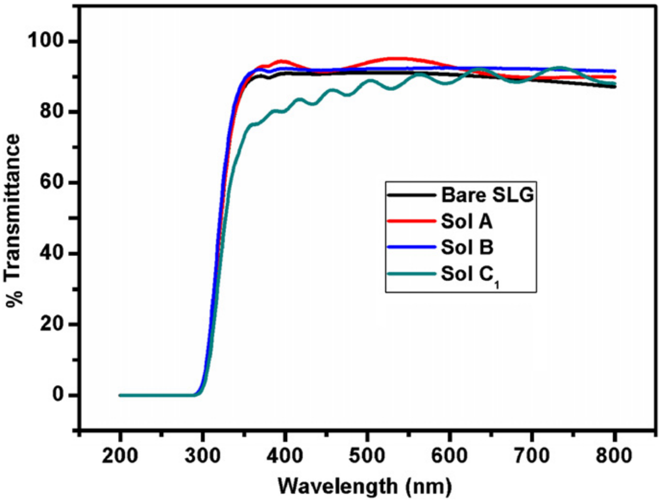


Fig. 3. Transmittance spectra for bare, sol A, B, and C_1-60 coated SLG.

with increase in sonication time. The uncoated substrate showed an average optical transmission of 90%. Fig. 3 shows a comparison of transmission of coatings from sol A, sol B and sol C_1-60. For sol A and sol B, the transmittance of 92% was more than that of the bare substrate. In case of sol C_1-60, the transmittance was maintained 88% even after the addition of silica nanoparticles. The thickness of coatings generated was 0.34 μm, 0.40 μm and 1.75 μm for the sols A, B and C_1-60 respectively. Silica coatings from sol A exhibited a pencil hardness of '7H' but with a WCA of only $93 \pm 2°$. The HMDS modified coating B showed a hardness of 'B', with a contact angle greater than 100°. When the surface modified silica nanoparticles were added and ultrasonicated for 60 min (C_1-60), coatings showed a hardness of 'HB', which is one order higher than the hardness of B. This clearly showed an improvement in the scratch hardness of the hydrophobic coatings after the addition of surface modified nanoparticles, which contributed to the improving hardness of the coatings and also maintained the coating transparency. It should be mentioned here that in our earlier investigations on generation of non-fluorinated hydrophobic coatings using TEOS and HMDS, the scratch hardness obtained was only 2B [9]. The coatings obtained in the present investigation were found to possess improved mechanical properties than those reported in Ref. [9].

4. Conclusion

Non-fluorinated, water repellent, transparent silica coatings with improved scratch hardness were prepared from DMDEOS, TEOS, HMDS and epoxy modified nanosilica particles. Coating with 1: 0.5 M ratios of the nanosilica particles and sol synthesized from DMDEOS, TEOS and HMDS exhibited a WCA of $125 \pm 2°$. This WCA was attributed to low surface energy because of the presence of methyl groups on the surface due to precursors used and surface roughness created from the surface modified silica nanoparticles. The hybrid nanocomposite coatings showed good adhesion and scratch hardness. The present investigation showed that transparent, non-fluorinated, hydrophobic silica surfaces with improved scratch hardness could be achieved using surface modified silica nanoparticles in combination with organically modified silica sol and a silylating agent. The present method is eco-friendly and also suitable for large area application on various substrates.

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