



# Investigations on the use of nanoclay for generation of superhydrophobic coatings

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## ABSTRACT

Organically modified layered silicate nanoclay particles were dispersed into a sol–gel silica matrix to obtain a formulation for generating a superhydrophobic coating. Dimethyldiethoxy silane, tetraethoxysilane and hexamethyldisilazane were used as precursors. Commercially available organically modified montmorillonite clay, Cloisite® 25A was used as the source of nanoclay. The loading of Cloisite® into the hybrid silica sol was varied and coatings were generated by dip coating technique on soda lime glass substrates. Heat treatment was carried out in air at 250 °C for 2 h. In some cases, spray coating was also employed and pigmented coatings were deposited on aluminum substrates and cured using the same conditions as employed for coatings generated using dip coating. Coatings were characterized for their transmittance, haze, thickness, water contact angles, surface morphology using scanning electron microscopy, atomic force microscopy and resistance to weathering. The present investigation explored for the first time, a pathway towards practical applications of nanoclay dispersion in silica matrix for generation of environmentally friendly superhydrophobic coatings in a cost effective manner. Water contact angles as high as  $170 \pm 2^\circ$  could be generated using optimized compositions and heat treatment conditions of sol and nanoclay fillers.

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## 1. Introduction

Barthlott and Neinhuis discovered in 1997 [1] that the self-cleaning property of lotus leaf is due to its nano and micro roughened surface along wax, acting as a surface tension lowering agent. This phenomenon is known as “lotus leaf effect” [1], which explains the rolling of the water droplet on the lotus leaf or the phenomenon called superhydrophobicity. While the high density of nano surface protrusions does not allow any water molecule to get absorbed on the surface, water drops roll from the leaf surface thereby cleaning the dust present on the surface. The phenomenon exhibited here is called as “self-cleaning”. It is now understood that superhydrophobic, self-cleaning surfaces can be achieved by a synergistic combination of low surface energy materials (chemical composition) and hierarchical surface roughness (geometrical structure) in the micrometer or nanometer scale [2–5]. In the past decade, different methodologies have been reported in the literature on the fabrication of super hydrophobic surfaces, which are characterized by water contact angles (WCA) > 150° and low contact angle hysteresis. Such surfaces have been drawing a lot of interest for industrial applications as well as for pursuing basic R&D because of their practical applications in antifouling paints [6,7],

micro-fluidics [8], self-cleaning coatings [9], waterproof textiles [10], etc.

Fluorosilanes, polyvinylidene fluoride, Teflon coatings etc. have generally been used along with organically modified silanes for generation of hydrophobic coatings [11–15]. The presence of fluorine on the surface allows chemical modification and thereby provides low surface free energy. These fluorinated precursors can be replaced by environmentally friendly materials which can also be economical for the preparation of hydrophobic materials [16,17]. Recently Jeevajoithi et al. investigated on the generation of transparent, non-fluorinated hydrophobic surface [18, 19]. However, the reported hydrophobic surfaces though with better mechanical properties, could not exhibit superhydrophobicity [19], probably due to absence of dual-scale roughness on the surface, which is a required condition for achieving superhydrophobicity as explained in [9].

The theoretical maximum contact angle achievable for water on a smooth surface is 120° [20,21]. As mentioned above, generation of superhydrophobic surfaces requires generation of a dual-scale roughness on a hydrophobic surface. Nanoclays can be used as fillers into a hydrophobic sol, in order to create roughness when deposited on a surface. The use of cost-effective precursors like nanoclay for generation of sol–gel nanocomposite coatings for a variety of applications has recently been attracting attention [22–26]. Since sol–gel process is a convenient and versatile method for generating hydrophobic coatings and fine microstructures at low temperature, it can be expected that superhydrophobic surfaces can be created through use of nanoclay in

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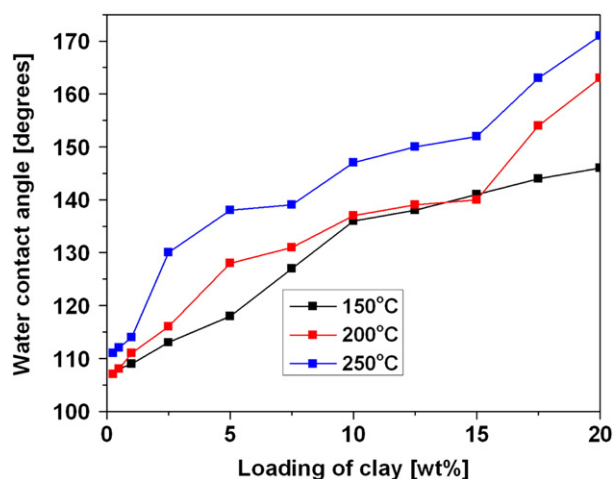


Fig. 1. Effect of nanoclay loading and heat treatment temperature on water contact angles of coated glass substrates.

a sol–gel matrix. The present investigation was carried out with this objective and reports for the first time on the feasibility of generating environment friendly and cost-effective superhydrophobic coatings using sol–gel matrices along with commercially available nanoclay fillers like Cloisite® 25A. Possibilities of generating pigmented superhydrophobic nanoclay-based coatings were also explored with a view to replace the currently used Teflon coatings for non-stick applications.

## 2. Experimental

### 2.1. Materials

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), ethanol ( $C_2H_5OH$ , Hong Yang chemicals, China), hydrochloric acid (HCl, Qualigens Fine Chemicals, India), nanoclay (Cloisite® 25A, Southern Clay Products, USA) and de-ionized water. The above-mentioned chemicals were used without further purification throughout the experiments. Soda lime glass sheet of dimensions 75 mm × 25 mm × 2 mm and with a nominal composition of the major metallic elements in weight % Na–15.5%, Mg–4.2%, Si–63.3%, Ca–14.3%, and Al–1.4%, was used as the substrate. In some cases, pure aluminum coupons (3 cm × 2 cm) as supplied by Q-Lab Inc., USA were also used as the substrates.

### 2.2. Synthesis

Silica matrix sol was prepared by adding the chemicals namely DMDEOS, TEOS, ethanol, HMDS in the molar ratio of 1:0.5:12.71:1 respectively in 0.1 M HCl and deionized water. The mixture was stirred at room temperature for 24 h. The resultant sol was clear and homogeneous and will henceforth be referred to as sol-A and the coating from sol-A will be called as coating A. To the above sol, nanoclay Cloisite® 25A was added followed by ultrasonication to form the nanocomposite. Cloisite® 25A is an organically modified montmorillonite clay i.e., a quaternary ammonium salt modified natural montmorillonite polymer additive. The surface modified nanoclay can be easily dispersed in a hybrid sol–gel matrix due to the compatibility of the organic groups on the surface of the nanoclay particle with the organic–inorganic sol–gel matrix. A pre-treatment was carried out for Cloisite® 25A prior to its usage in order to avoid agglomeration due to moisture absorption. For this purpose, a mixture of the clay and acetone was ultrasonicated for 30 min, followed by air drying at 150 °C for 6 h. Using this method,

a fine dispersion of clay in the sol could be achieved. The parameters such as withdrawal rate, sonication time, clay loadings, effect of different solvents used for dilution, surface pre-treatments, drying temperature, coating deposition technique, heat treatment temperature and ambience were systematically varied and optimized.

Nanoclay was added to this mixture by varying weight percentages such as 0.25, 0.5, 1, 2.5, 5, 7.5, 10, 12.5, 15, 17.5, and 20. The sol after addition of clay is referred as Sol C and the clay loadings are referred as C1–11 respectively. In case of Sol C, the formulation tends to become viscous after the addition of nanoclay. So the sol was subjected to ultrasonication with different times varying from 10 to 150 min, with 30 minute interval, prior to coating deposition. Atmospheric air plasma surface pre-treatment was carried out on some of the cleaned glass substrates so as to verify whether coating wettability could be improved if deposited on a plasma pre-treated surface. The coatings were deposited using dip coating technique. The substrate was withdrawn from the sol at different rates such as 1 mm/s, 3 mm/s, 5 mm/s, and 10 mm/s so as to optimize the withdrawal rate. The coatings were cured in air at different temperatures such as 150 °C and 250 °C for 1 h. The curing was carried out under vacuum in some cases, to study the effect of heat treatment ambience on the property of the coating. Some of the clay loaded sols were also deposited using spray coating technique after addition of pigments, namely mica black and carbon black particles dispersed in the sol-C, to check the feasibility of generating pigmented coatings on large scale for industrial applications. Details regarding the morphology of the pigments are as given elsewhere [27].

### 2.3. Characterization

The crystallinity of the nanoclay used was analyzed using a Bruker D8 ADVANCE diffractometer using  $Cu K_{\alpha}$  radiation ( $\lambda = 0.154178$  nm), 40 kV voltage and 40  $\mu A$  current. Thermogravimetric analysis of the as-received Cloisite® was carried out using a Netzsch Thermoanalyzer. Surface hydrophobicity of coated and uncoated substrates was evaluated by static contact angle measurement using a Drop Shape Analyzer (DSA) (Krüss GmbH, Germany). The surface morphology of the coatings was studied by using field emission scanning electron microscope (FESEM-Hitachi S3400N and SEM-Thermo electron cooperation S3400N) along with EDAX analysis (Ametek) and atomic force microscope (XE7, Park Systems, Korea). Coating thickness was measured by carrying out the SEM analysis of the cross-section of the coated samples.

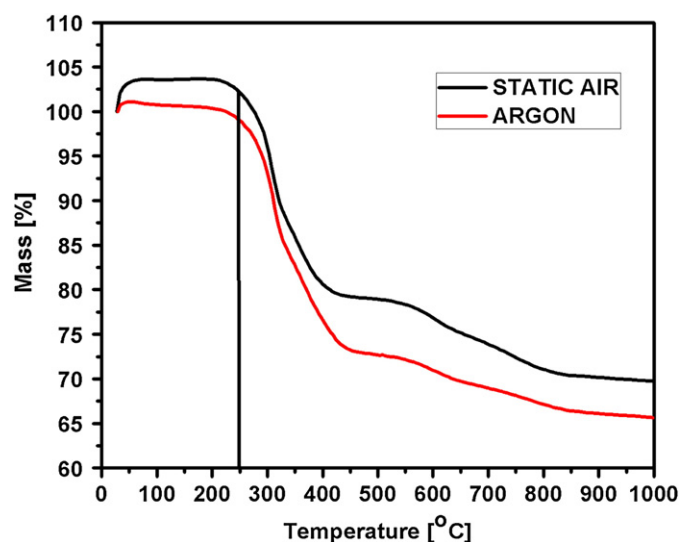


Fig. 2. Comparison of the results of the thermogravimetric analysis of Cloisite®-25A in static air and argon.

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