Methyltrichlorosilane polysiloxane filament growth on glass using low cost solvents and comparison with gas phase reactions

Emine Gozde Atici [a], Esra Kasapgil [a], Ilke Anac [a,*], H. Yildirim Erbil [b,*]

[a] Gebze Technical University, Department of Materials Science and Engineering, TR-41400 Gebze, Kocaeli, Turkey
[b] Gebze Technical University, Department of Chemical Engineering, TR-41400 Gebze, Kocaeli, Turkey

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ABSTRACT

Fluorine free, transparent, superhydrophobic polysiloxane filament coatings on glass were successfully prepared using methyltrichlorosilane (MTCS) both via liquid phase reactions using standard hydrocarbons in an open system and gas phase reactions under controlled humidity environment. Wettability, morphology and transparency of the obtained coatings were characterized by contact angle measurements, scanning electron microscopy and UV–vis spectrometer transmittance tests respectively. Superhydrophobic polysiloxane nanofilament coatings were obtained for the first time in an open system using standard petroleum ether having advancing contact angle values (θ_a) between 156 and 168°. Surfaces having contact angle hysteresis as low as 9° were obtained by varying the reaction time and MTCS concentration in petroleum ether. On the other hand, the relative humidity was found to be the most important factor when compared with the factors such as reaction time and silane concentration to change the morphology and the contact angles of the coatings in the gas phase where 38% RH was found to be the optimum for the growth of polysiloxane nanofilament coatings on glass. Polysiloxane nanofilaments having diameters ranging from 34 up to 42 nm and θ_a values between 166 and 168° were obtained in the gas phase reactions. The transparency of the surfaces prepared in the gas phase was higher than the ones prepared in the liquid phase.

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1. Introduction

Artificial superhydropobic surfaces have attracted much attention since the "lotus effect" has been reported in 1997 [1–4]. These surfaces have a wide variety of potential applications in various fields such as self-cleaning, anti-fogging, anti-icing, drag reduction, drop transport and so-on [4–6]. Superhydrophobic surfaces can be synthesized by either introducing high roughness onto surfaces using low surface energy materials or the modification of rough surfaces with materials having low surface energy [2–6]. The formation of a Cassie-Baxter wetting state is required to obtain superhydrophobicity through water contact angles larger than 150° and roll-off angles lower than 5° [3–8].

Reactive organosilanes having a hydrolysable group ($R_{3 - n}SiX_{n + 1}$, where X = Cl, OR and NMe_2) have been widely used to modify the surface properties of inorganic materials [9–12] due to their low surface free energy, biocompatibility and chemical stability. Depending on the reaction conditions and the type of the organosilane used (mono-, di- or tri), a number of different structures can be formed on surfaces having hydrolysable OH groups [13,14]. Synthesis of superhydrophobic and superoleophobic surfaces by coating a mono- or polylayer of alkylfluorosilanes on various surfaces have been reported many times

in the literature [2,4,6,15]. However, such methods are expensive due to the micropattern pre-formation and mostly used in academic studies. In 2006, the first successful synthesis of the one-dimensional superhydrophobic polysiloxane nanofibers via surface initiated polymerization of methyltrichlorosilane (MTCS) in the gas phase [16] and in solution phase under controlled humidity environment [17] were reported by Seeger and coworkers and by McCarthy and coworkers respectively. These coatings were transparent, superhydrophobic and the applied procedure was not expensive. However, the mechanical resistance of these coatings is still poor similar to most other superhydrophobic surfaces. Nevertheless, the synthesis of transparent superhydrophobic coatings is needed for many industrial applications where mechanical weakness is not a problem [4,6] however, this task is difficult because increasing the roughness of a surface can enhance the water repellence due to the introduction of more air pockets, but the transparency will be decreased due to light scattering losses. In order to maintain transparency on a surface, the size of the roughness of the films should not be greater than approximately 25% of the visible light wavelength, that is, 100–200 nm [18]. Since the coating of polysiloxane nanofibers onto the glass surface can result in transparent superhydrophobic coatings with a low cost procedure, this method attracted many researchers. Several reports have been published on the formation of polysiloxane nanofibers using MTCS [19–28], vinyltrichlorosilane (VTS) [29,30], methyltriethoxysilane (MTES)

* Corresponding authors.
E-mail addresses: ilkeanac@gtu.edu.tr (I. Anac), yerbil@gtu.edu.tr (H.Y. Erbil).

[31,32], methyltrimethoxysilane (MTMS) [31] and organosilanes with long alkyl groups [33] on silicon wafers, glass slides, silica particles and other surfaces such as textiles either in gas phase or solution phase. Two recent reviews were published on these extremely water repellent and fluorine-free polysiloxane nanofiber coatings which was prepared on technologically important materials [27,34].

In all of the previous publications, the effect of the presence of water in the reaction system was stated. The surface of a glass substrate was not completely anhydrous in all cases since a thin film of surface-condensed water is present on the glass and this water layer is necessary for the formation of the siloxane monolayer and also the subsequent nanofiber growth by polycondesation [10,11,16,17]. However if more water is present in the system, the rate of hydrolysis and condensation reactions changes resulting in formation of surface structures having unexpected morphology. Thus, the control of water content in the liquid or vapor medium and also on the substrate surface is very important. It is well-known that when MTCS, dimethyldichlorosilane and trimethylchlorosilane were reacted on glass or other silicone surfaces in the gas or solution phases under very dry (but not anhydrous) conditions, the obtained surfaces had water contact angles that were lower than 108° indicating that no one dimensional nanofiber but a two-dimensional mono- or polylayer formed on the surface [10,14]. As a practical solution of controlling the water content, all of the solution phase polysiloxane nanofiber productions already reported in the literature were carried out in closed systems to avoid water vapor absorption from the humid medium. Dried toluene was the first used and the most preferred solvent for this purpose [17,21–23,25,28]. The effects of time, silane concentration and water content on the polycondensation of siloxanes in toluene were well-studied [21,22]. Nano-architectures by the polymerization of MTCS in toluene with varying shape and size have been prepared by Khoo et al. by changing the synthesis conditions such as MTCS concentration, reaction time and relative humidity (RH) in the closed chamber which will affect the water content in the dry toluene [21]. Jin et al. have fabricated organosilane surfaces with tunable geometry using MTCS in toluene-anhydrous toluene mixtures in a closed glass vial [22]. The preparation of toluene having a known amount of dissolved water is a difficult process since toluene is prone to absorb water vapor from the medium if any leakage occurs in the closed system. Silicone nanofilaments having different size and morphology have been prepared on glass slides by Zhang et al. by varying solvent type and composition using MTCS where the reactions were ran in a custom made closed chamber in order to control the water content of the solvents such as cyclohexane, t-butylbenzene, dioxane, paraffin oil, acetonitrile, p-xylene, hexadecane, methyl ethyl ketone, ethyl ether and DMSO and acetone and it was found that toluene and its homologues are ideal solvents for the growth of nanofibers, whereas hydrophilic solvents and molecules containing N and/or O elements seriously hinder their growth [28]. Unfortunately the effect of reaction time and concentration of MTCS were not tested in that study [28]. Chen et al. prepared hydrophobic silicone nanofiber coatings using MTES and MTMS in petroleum ether in an open system, however they did not try MTCS in that study [31].

Although the water content of the solvent is a very important factor in the silicone filament growth process, the low cost technical aliphatic hydrocarbon solvents having very small water contents in open medium were not tested for that purpose in the literature. Then, we decided to use standard petroleum ether where the solubility of water is very low (30–60 ppm water content due its high hydrophobicity) with MTCS for the formation of polysiloxane nanofibers on glass slides without using closed liquid phase reaction systems. If the polysiloxane nanofibers can be grown in standard petroleum ether in open laboratory conditions, then these fiber growth reactions can be done practically in any large cup which is open to the air in industry. We also planned to compare our results obtained in the liquid phase reactions of MTCS with the results obtained in the gas phase polycondensation of MTCS on glass where a closed system is used.

The preparation of polysiloxane nanofibers on glass or other surfaces using MTCS in the gas phase have been published by several research groups [16,27,35,36]. Artus et al. prepared polysiloxane nanofibers in the gas phase using MTCS on different substrates [16] and scaled up the gas phase reaction using glass panes up to 2.4 m × 1.1 m [36]. Zimmermann et al. showed that polysiloxane nanofibers prepared on glass by gas phase reactions were found to be stable in organic solvents, neutral, mildly acidic aqueous solutions and mildly acidic detergent solutions over a period of at least 6 months and the coatings deteriorate fast in strong basic media [37]. Korhoren et al. prepared superhydrophobic polysiloxane nanofibers on silicon and proposed a growth model for the polysiloxane coating [27]. Rollings et al. grew polysiloxane nanofibers using VTS in the gas phase and studied the effect of substrate composition, substrate activation, reaction time and water content and also proposed a growth mechanism for the fiber forming process [29,30]. Unfortunately, the effects of the parameters such as silane concentration in the closed volume, RH of the system and reaction time on the structure and size of polysiloxane nanofibers in the gas phase reactions using MTCS as a silane agent were not studied by any group in the literature.

This paper describes the growth of polysiloxane nanofibers on glass using MTCS via both solution and gas phase reactions where the reaction conditions were varied systematically. MTCS is chosen as the precursor to be used in the solution and gas phase reactions since it is more reactive than MTMS and MTES and have a lower boiling point (66 °C) than MTMS (103 °C) and MTES (143 °C) which will facilitate the polycondensation reactions at room temperature. The surface topography and wettability of obtained polysiloxane nanofibers on glass were characterized by scanning electron miscroscopy (SEM) and equilibrium, advancing and receding contact angle measurements. Solution phase reactions were conducted in standard petroleum ether and also in toluene at room temperature, and effect of reaction time and MTCS concentration on the shape, morphology and contact angles were investigated and the findings are compared with the results of polysiloxane nanofibers reported in the literature. In addition, gas phase reactions were conducted at room temperature under the controlled humidity environment using MTCS as the silane precursor in order to compare the results with the results obtained by the solvent phase reactions. The effect of reaction time, MTCS concentration and RH on the coatings' morphology and contact angles in the gas phase conditions were also investigated systematically and compared with the findings reported in the literature.

2. Experimental details

2.1. Materials

Sulfuric acid (95–97%), hydrogen peroxide (30%), ethanol (HPLC grade) and toluene (99,8%) were purchased from Merck. Methyltrichlorosilane (MTCS, ≥97%) was purchased from Sigma-Aldrich. Petroleum ether (40–70 °C) was purchased from Riedel-de Haën (Germany). All chemicals were used as received. Glass microscope slides (25 mm × 76 mm × 1 mm) were obtained from ISOLAB GmbH (Wertheim, Germany) cut into 25 mm × 35 mm × 1 mm pieces. Water was purified using a Elga Option Q15system that involves pretreatment, reverse osmosis and ion exchange steps (18.2 MΩcm^{-1}), and we refer to water which was purified by this method as "deionized water". The hygrometers were purchased from TFA Dostmann (Wertheim-Reicholzheim, Germany).

2.2. Cleaning and activation of glass slides

Glass slides were cleaned by ethanol and dried under nitrogen flow before activation. They were then submerged into the piranha solution consisting of a 7:3 v:v mixture of concentrated H_2SO_4 and 30% H_2O_2 at 80 °C for 2 h and then left at room temperature overnight. Afterwards,