



Radius ratio rule for surface hydrophilization of polydimethyl siloxane and silica nanoparticle composite



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ABSTRACT

Polydimethyl siloxane (PDMS) and Silica (SiO₂) nanoparticle composite blocks of three different batches (CB1–CB3) made by varying the size of SiO₂ nanoparticles (NP), are studied for the degree of hydrophilization and retainability after oxidation by contact angle measurements (CA) and force distance spectroscopy (FDS) using Atomic Force Microscope (AFM). While CA measurements have shown high hydrophilization and retainability for CB3, F-D spectroscopy has reiterated the observation and has shown long range interactive forces and high Debye length of the electrostatic double layer formed. These results are in agreement with the radius ratio rule of binary sphere system for high density packing in the composite and thereby for strong hydrophilization and retainability due to reinforcement and restricted diffusion of uncured polymer.

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1. Introduction

Microfluidic devices are going to be next generation diagnostic technology. Stability and reliability of micro fluidic devices is still a concern due to several challenges like coagulation, low zeta potential and low electro osmotic flow (EOF). Even though Poly dimethyl siloxane (PDMS) has lower zeta potential compared to glass and silicon, it is found to be more suitable for making microfluidic devices and point of care diagnostics due to its low cost and ease of micro fabrication. PDMS is natively hydrophobic [1–3] and can be easily rendered hydrophilic. The untreated PDMS specimens exhibit highest contact angle (~110°) [4–6]. Zeta potential is the electrokinetic potential at the shear plane that separates the immobilized surface and mobilized fluid. Electro osmotic flow (EOF) velocity is proportional to the zeta potential for a paired liquid–solid interface. Therefore, higher applied electric fields are needed for PDMS than for glass or silicon materials in order to achieve similar pumping flow rates [7,8]. This has several disadvantages of local heating and bubble formation due to electrolysis which in turn obstructs the fluid flow. To improve zeta potential of PDMS surface, several surface treatment methods were adapted. Apart from Oxygen plasma and UV treatment [2,9,10] which makes PDMS hydrophilic, there are several other surface treatment approaches, which include,

corona discharge, charged surfactants, polyelectrolyte multilayer coatings, covalent modifications (such as silanization), chemical vapor deposition, pre-doping PDMS with chemicals etc. [11–16]. The presence of these functional groups determines the effectiveness of a surface treatment method and thus may improve the zeta potential of PDMS. Apart from the degree of hydrophilization, the retainability of the same for longer duration is another important factor for the reliability of micro fluidic devices. Hence sufficient effort was put not only in improving zeta potential but also in retaining it. For PDMS surface exposed to plasma it was found that the hydrophilic condition deteriorates with time and can be retained up to 3 h at the maximum [17–19], due to surface diffusion of uncured PDMS, removing the functionalization with time.

In the present study we used the functionalization capability of SiO₂ NPs in improving the hydrophilization by making composite of PDMS/SiO₂. Silica surface is the best and suitable surface for microfluidic devices due to its ease of functionalization and high surface electro negativity.

We studied the degree and retainability of hydrophilization by both contact angle measurements and force spectroscopy under Atomic Force Microscope (AFM). Force distance spectroscopy (FDS) is the best method of studying different types of interaction between two surfaces and the underlying physics. Based on DLVO theory, the interaction of AFM tip with PDMS surface can be best explained by F-D Spectroscopy. AFM is capable of detecting several interactive forces like Coulombic, Vanderwaal's, dipolar and

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solvation forces [20]. It is the perfect system to study the zeta potential of modified PDMS and has the feasibility of studying the behavior in different media which portrays the real situation in microfluidic channels [21].

2. Experiment

PDMS/SiO₂ composites are prepared with different size of SiO₂ nanoparticles (NP) system and hydrophilized to study both the surface hydrophilicity and its retainability by measuring Contact angle and by doing F-D spectroscopy. F-D spectroscopy is an easy and simple technique to study zeta potential and is required to standardize the PDMS surface condition for potential microfluidic devices.

Sylgard 184 Silicone elastomeric kit from Dow Corning was used in making PDMS composites. Silica nanoparticles were synthesized by Stöbers method [22]. Three different size and combination of SiO₂ NPs (B1–B3) are synthesized by varying methanol to ethanol ratio during the hydrolysis of Tetra ethyl ortho silicate (TEOS). PDMS/SiO₂ NP composite blocks of three different batch CB1, CB2 and CB3 are prepared by mixing 4.8% (w/w) of each batch silica NPs with PDMS (10:1 of base:curing agent), followed by degassing for 30 min in a vacuum desiccator. Even though the weight percentage of silica NPs is low compared to PDMS, due to their low density and high porosity, the volume percentage is higher [23]. The mixture is cured in an oven at 70 °C for 1 h. Oxidation of PDMS blocks were done by dipping in base Piranha of NH₄OH and H₂O₂ of 1:1 ratio at 70 °C for 10 min. SEM imaging for morphology and size distribution of SiO₂ NPs is done by Field Emission Scanning Electron Microscope (FESEM) (Make: Zeiss, Model:Supra 40VP). The resolution of the instrument is 1.3 nm @ 15 kV. A contact angle setup which was built indigenously was used for the measurement of contact angle before and after oxidation. Contact angle measurements on the captured images were done using open ware software Image J using low bond axi-symmetric drop shape analysis (LBDSA) method based on the fitting of the Young-Laplace equation to the image data [24]. A Multimode V AFM with Nanoscope V controller (Bruker Ltd.) was used for doing F-D spectroscopy. Si₃N₄ cantilevers with a spring constant 0.06 N/m were used for F-D spectroscopy. The deflection sensitivity of cantilever was measured on sapphire surface after performing F-D spectroscopy on the samples. For engaging AFM tip normal to the surface and avoid drag in the x-direction, the AFM tip was engaged with an x-rotation of 12°. To minimize the errors, all the measurements were carried out without disturbing the laser alignment on the cantilever.

3. Results and discussion

Fig. 1 shows SEM images of three different batch silica NPs along with their size analysis. These NP's are produced by Stöbers process by varying the hydrolyzing reagent from methanol to ethanol during synthesis. Fig. 1a shows SEM image of SiO₂ NPs prepared by using completely methanol as hydrolyzing reagent (B1). SiO₂ NPs produced are highly monodisperse in size and are around 200 ± 10 nm. For SiO₂ NPs prepared by using 50:50 methanol to ethanol ratio (B2), two different sized nanoparticles of size 550 ± 20 nm and 400 ± 15 nm, respectively are obtained as shown in SEM image of Fig. 1b. For complete ethanol based synthesis (B3), Fig. 1c, nanoparticles of diameter 320 ± 10 nm and 200 ± 15 nm are obtained respectively. By varying ratio of methanol to ethanol, different hydrolysis and condensation rates are achieved due to alkoxy exchange with TEOS, which leads to different seed size, resulting in different nanoparticle diameters [25]. Stirring conditions during synthesis also could also determine the nucleation and growth of these particles.

The presence of two different sized nanoparticles for batch B2 and B3 resembles the system of binary hard sphere. Based on the radius ratio rule, such system has known to have high packing density. The packing could be denser than fcc structure at radius ratio less than 0.64. Above this radius ratio, there will be frustration in crystallization leading to two separate fcc phases [26].

Fig. 1d shows the analysis of the size of nanoparticles based on this model. Left y-axis in Fig. 1d shows bar diagram of the diameter of different batch nanoparticles plotted against the percentage ratio of methanol to ethanol during synthesis. Right y-axis shows the radius ratio of nanoparticles of different batch. The radius ratio for batch B2 nanoparticle system is found to be 0.73, where as the radius ratio for batch B3 is 0.63. From the above analysis, batch B3 nanoparticle system falls within the radius ratio peak for highly dense packing.

Surface hydrophilization properties of PDMS strongly depend on the functionalization groups present in it. Bare PDMS cannot retain hydrophilic state more than half an hour due to diffusion of hydroxyl ions by uncured PDMS polymer. SiO₂ NPs are known to have high electro negativity and strong binding energy with different functional groups [27].

Hence PDMS/SiO₂ NP composite should enhance the surface hydrophilization property of PDMS. To study the effect of addition of SiO₂ NPs to PDMS, three batch PDMS blocks, CB1, CB2 and CB3 are prepared by mixing SiO₂ NPs B1, B2 and B3 respectively. All these PDMS blocks along with bare PDMS are hydrophilized in base Piranha and are analyzed for their contact angle as shown in Fig. 2.

The contact angle of these PDMS composites before oxidation have shown very little variation from bare PDMS except for CB3 which has shown a CA ~100°. Fig. 2a shows the contact angle setup used for the measurement. Inset in Fig. 2a shows the image of droplet on one such PDMS block captured and analyzed for the contact angle. Fig. 2b shows the variation of contact angles of three different composites along with bare PDMS, up to 2 h and at an interval of half an hour. Immediately after oxidation, bare PDMS, composite CB1 and CB3 have measured roughly same CA ~95° where as CB2 has shown minimal effect of oxidation. Fig. 2b also shows the retainability of hydrophilization with time. Bare PDMS recovers very fast after hydrophilization (black line) where as CB1 recovers eventually. But PDMS composite CB3 retains the hydrophilization longer, even after 2 h. On the contrary, composite CB2 attains hydrophobicity very quickly. This shows that both the frustration in packing and competition in hydrophilization of methyl to ethyl groups make CB2 not efficient for hydrophilization. High monodispersity of CB1 makes it hydrophilic easily but will not be able to retain for long. Hence CB3 is the best system for both hydrophilization and retainability due to high packing density of SiO₂ NPs. Also due to reinforcement, the matrix of SiO₂ NPs in PDMS acts like diffusion barriers for uncured PDMS, preventing the loss of hydrophilization. This restriction on polymer diffusion due to high density packing increases the retainability of functionalization for CB3 sample.

To further strengthen the observation of enhancement and retainability of functionalization, force spectroscopy on these samples was done using AFM. Fig. 3 shows the FD spectroscopy analysis of the PDMS composites after 2 hrs of oxidation. All the curves in Fig. 3a are the average of 5 such FD plots. All the measurements are found to be within an uncertainty of ±2 nN. These are the approach curves rather than retract as these curves give information about electrostatic interactions rather than adhesion during pull off. As shown in Fig. 3a, CB3 sample has shown maximum interaction between AFM tip and the surface. The noticeable thing observed from FD curve for CB3 is the long range interactive force. The variation of the force of interaction for all the samples is shown in the plot of Fig. 3b. The hydrophilization of PDMS surfaces induces a net charge and during interaction with AFM tip, the concentration of

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