Study on the Wettability and Optical Properties of Polydimethylsiloxane-SiO_2 Nano-composite Surfaces

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Abstract: In this paper, the effects of different weight percentages of silica nano-particles on the wettability and optical properties of polymer based surfaces were investigated. The Polydimethylsiloxane (PDMS)-SiO_2 nano-composites containing 0.5, 1, 2, 3 and 4 wt% silica were prepared and coated on the fabric surfaces by immersion technique at the ambient conditions. Then, the characterization of nano-composite coated samples was carried out by water contact angle technique, scanning electron and atomic force microscopes and diffuse reflectance spectroscopy. It was found that increasing the silica content caused to increase the water contact angle of sample to 158° which results in an improvement in the water repellency property. This can be due to the aggregation of silica nano-particles which led to higher surface roughness of sample. The AFM and SEM images validated the results of surface roughness. However, Silica-PDMS composite coated sample exhibited a lower transmittance value (57%) in comparison to the uncoated sample (90%). This can be ascribed to the light scattering by silica nano-particles.

Keywords: Polydimethylsiloxane, SiO_2 Nano-Particles, Super-Hydrophobic, Transmittance, Water Contact Angle

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1 INTRODUCTION

In recent years, super-hydrophobic surfaces due to significant properties such as anti-icing, anti-sticking, anti-contamination, and self-cleaning have been attractive both in the academy and industry fields [1-4]. To prepare super-hydrophobic surfaces, roughness and surface energy factors are very important [5]. According to the researches, higher roughness and lower energy surfaces demonstrated hydrophobic behavior [6]. Polydimethylsiloxane (PDMS) showed a good water repellent, so that the contact angle of 110° for surfaces coated with PDMS was obtainable [7-9]. The roughness of PDMS coated surfaces should be increased to perform more hydrophobic behavior. Materials such as silicon, silica, polyelectrolyte/silica, polyelectrolyte/metal, and raspberry-like particles were utilized to prepare a surface with a double structured roughness [10-11]. Polymer matrix nano-composite is a new generation of material that contains percentage of nano-meter reinforcement. Nano-meter reinforcement due to high specific surface area to volume ratio compared to conventional reinforcement, improves polymer properties [12]. Moreover, nano-particles, as reinforcement were presented to create the rough surfaces of polymer matrix nano-composite. The SiO_2 nano-particles constructed hierarchical structures on the PDMS surface [13-16]. These particles exhibited high chemical inertness, high thermal resistance and a fairly good mechanical strength. Particularly, some of silica-based materials are generally transparent [17]. However, the obstacles in the application of SiO_2 particles were low compatibility and consequentially, undesirable dispersion. In addition, the SiO_2 particles exhibited strong tendency to aggregate in solvent system [18].

Wang et al. [18] prepared SiO_2-PTFE mixture which was coated to carbon steel surfaces by spraying. The effectiveness of organic PTFE and inorganic SiO_2 particles on super-hydrophobic property were comparatively investigated. Liu et al. [19] reported a novel approach to develop raspberry like super-hydrophobic silica coating for self-cleaning applications. The hydrophobic silica particles were obtained by simple condensation of fluoroalkoxysilane in ethanol at room temperature. These silica particles were embedded into the sol-gel processed silica matrix and deposited on glass plates which showed super-hydrophobic properties. Hejazi et al. [20] investigated the interrelationship of super-hydrophobicity with surface morphology in spray-coated polyurethane/silica nano-composites. Wang et al. [21] presented a simple and inexpensive method for forming a super-hydrophobic surface using polystyrene and an acetone based suspension of perfluorosilane coated silica nano-particles. The combination of partially-embedded nano-particles and hierarchical structure resulted in the robustness of as-prepared surface, which could withstand tape-peeling test (24.50 kPa) for at least 80 times and sandpaper abrasion (7.84 kPa) for 6.75 m without losing super-hydrophobicity. According to the researches, PDMS exhibited the hydrophobicity nature and chemical compatibility with silica nano-particles in comparison to other polymer matrix such as polystyrene [22]. Liu et al. [6] prepared super-hydrophobic coating through spraying the mixture of PDMS and hydrophobic nano-silica on the glass slide. The coating kept super-hydrophobic property after a calcination process. Li et al. [23] investigated the effects of calcination temperature on the microstructure and wetting behavior of PDMS/SiO_2 coating. They found that the wetting behaviour of coating was changed to super-hydrophilicity with water contact angle of nearly 0° by increasing the calcination temperature over 500°C. Basu et al. [24-25] fabricated an oleophobic and super-hydrophobic PDMS-silica coating by applying a topcoat fluoroalkyl silane (FAS). Ke et al. [26] examined the mechanical properties of a super-hydrophobic surface by using a shear test. It was found that the hierarchical SiO_2 based PDMS films retained superhydrophobicity after 48 kPa shear stress. Öztürk et al. [27] studied the effect of PDMS polymer (3 wt%) and polystyrene-silica particles (1 wt%) on the hydrophobicity of a microporous layer. The water contact angle and surface roughness of 122° and 2.63 µm were measured, respectively.

In the present study, the effects of silica nano-particles on the properties of the hydrophobic silica based polymer matrix nano-composite were investigated to achieve optimal super-hydrophobicity. Firstly, the PDMS-Silica nano-composites containing 0.5, 1, 2, 3 and 4 wt% silica were prepared. Then, the composite mixtures were coated on the fabric surfaces by immersion method at ambient conditions. Secondly, Water Contact Angle (WCA) technique was used to investigate the hydrophobicity behavior of samples. The morphology and distribution of nano-particles in the composite coatings were investigated by Scanning Electron Microscopy (SEM). The Atomic Force Microscopy (AFM) was also used to study the surface topography of samples and measure the surface roughness. Finally, the transparency of PDMS-Silica nano-composite coatings was evaluated using Diffuse Reflectance Spectroscopy (DRS). According to review of the literature, the effects of different weight percentages of silica nano-particles on the wettability and optical properties of PDMS-SiO_2 nano-composites have not been reported so far. Moreover, a dip-coating process as a low-cost fabrication technique was used in this research. This method has advantages including higher controllability to produce thin films in comparison to other methods such as spin-coating technique.

2 MATERIAL AND METHODS

Two ingredients of PDMS (Dow corning, Sylgard 184) were mixed with a ratio of 10:1. Then, a certain amount of ethyl acetate (Merck, Germany) was added to the mixture. After stirring the solution for two minutes by magnetic stirrer, a certain amount of ethyl silicate and DBTDL (Dibutyltindilaurate) were added to the mixture in order to increase the hydrophobicity and adhesion of components. The mixture was stirred by magnetic stirring to achieve the uniformity. Subsequently, the mixture was divided into five sections and nano-composite materials with 0.5, 1, 2, 3 and 4 wt% nano-silica (20 nm, purity 99.5%) were prepared. Moreover, the 8 cm × 3 cm pieces of conventional fabric were prepared. The SEM image of fibers structure in the fabric is shown in “Fig. 1”. Each fabric piece was immersed in a nano-composite mixture for five minutes, and then removed from mixture and dried at ambient conditions.

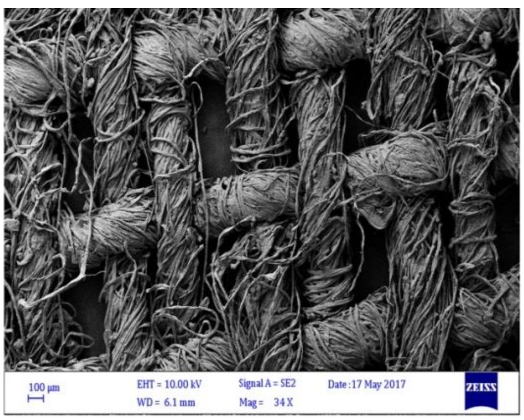


Fig. 1 SEM image of fibers structure in the fabric.

The microstructure, size and distribution of silica nano-particles of PDMS-Silica nano-composite samples were observed by scanning electron microscopy (Agar Scientific-UK). To evaluate the surface topography and roughness of PDMS-Silica nano-composite coatings, atomic force microscopy in the contact mode (Model Dualscop C-26-DME Germany) was used. In the AFM contact mode, as a common mode, the tip scans the sample in close contact with the surface. The force on the tip is repulsive with a mean value of 10^{-9} N. Since the original composites were extremely rough, the mixtures were diluted by twenty times decreasing in silica amounts and then coated on the glass slides and dried at ambient conditions. The water contact angle measurement was accomplished by using Tensio tester (Model CA-ES10). In this method, water drops with a volume of 4 micro-liters were deposited on the substrate and a high resolution CCD camera was used to image the drops. In order to investigate the optical absorbance and transmittance of PDMS-Silica nano-composite coating, Diffuse Reflectance Spectroscopy (DRS) was performed by UV-VIS spectrophotometry (Model V-670-JASCO Japan). In this analysis, the absorption and transmission spectrums were measured over the spectral range of 300-800 nm. Since the fabric substrate used in this research was not able to pass the light, the best weight percent silica nano-composite (4 wt%) was selected and coated on the glass slide for DRS analysis. To prepare the coated glass slide, a clean glass slide (bare glass) was selected and one surface was preserved by using the tape. Then, the glass slide was dipped in the 4 wt% silica composite and removed from the mixture and dried in the air condition without heat treatment. In addition, the optical absorbance and transmittance of coated glass slide was compared with those of bare glass slide.

3 RESULTS AND DISCUSSION

Figure 2 shows WCA values of PDMS-Silica nano-composites coatings with varying silica content. According to the figure, the WCA value of composite coatings increases with increasing the nano-silica content. This can be attributed to higher value of surface roughness for the nano-composite coating with higher concentration of silica particles [28-30].

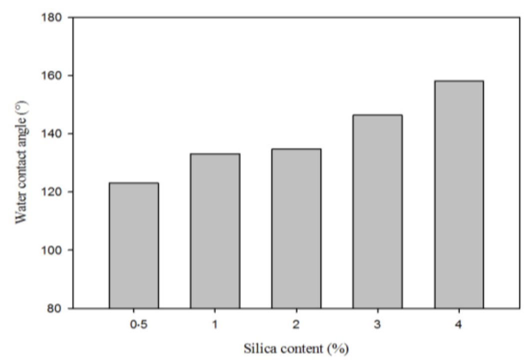


Fig. 2 Water contact angle values of PDMS-Silica nano-composites coatings as a function of silica content.

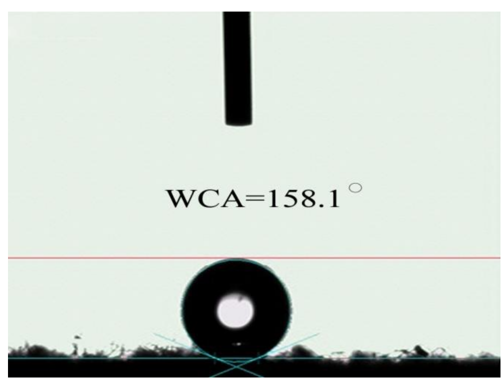
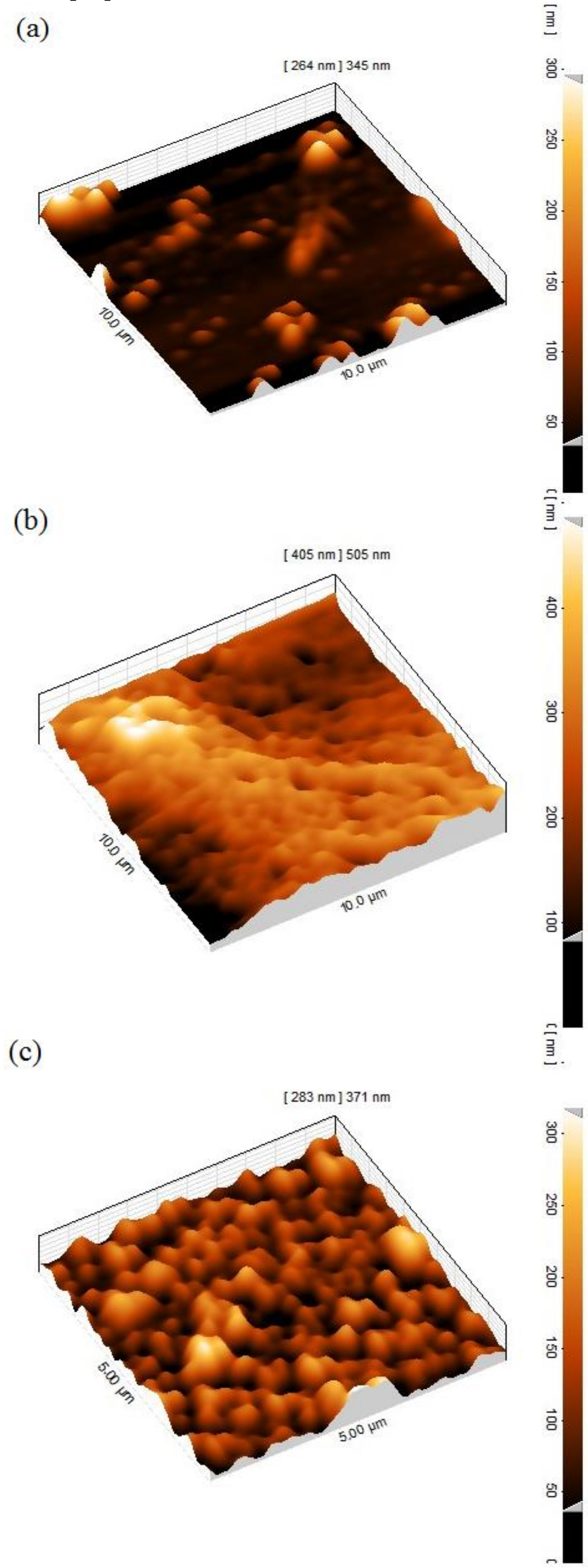


Fig. 3 Water contact angle image of 4% Silica-PDMS composite coated on the fabric.

It seems that the roughness of surface causes air pockets trapping and prevents direct contact the surface with the water [31].



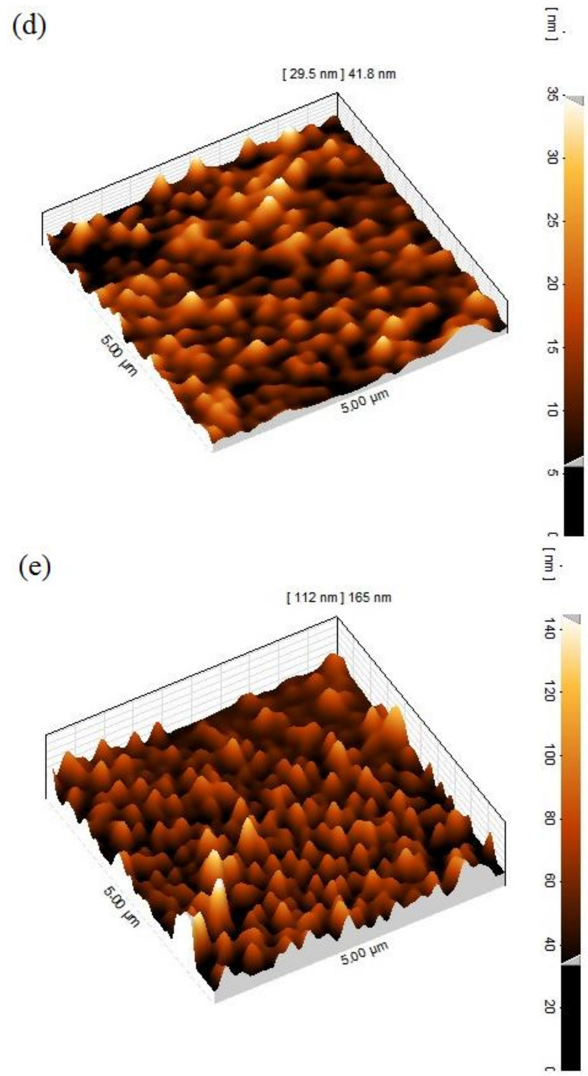


Fig. 4 AFM 3D topography images of PDMS-Silica nano-composite coatings with: (a): 0.5, (b): 1, (c): 2, (d): 3 and (e): 4 wt% silica nano-particles.

The samples with silica content up to 3 wt%, exhibited hydrophobic behavior with WCA values higher than 90°; however, 4 wt% silica composite sample with WCA larger than 150° ("Fig. 3") demonstrated super-hydrophobic behavior. The AFM images of PDMS-Silica nano-composite coatings validated the results of WCA analysis. 3D surface topography plots of samples and roughness profiles obtained by AFM are shown in "Fig. 4 and Fig. 5", respectively.

The nano-particle aggregation is seen for all samples. Moreover, this aggregation is increased with increasing the silica nano-particle content. According to the AFM images, the formation of roughness peaks is seen on the surface of all tested samples. This can be due to the shrinkage of PDMS matrix during the drying process [32].

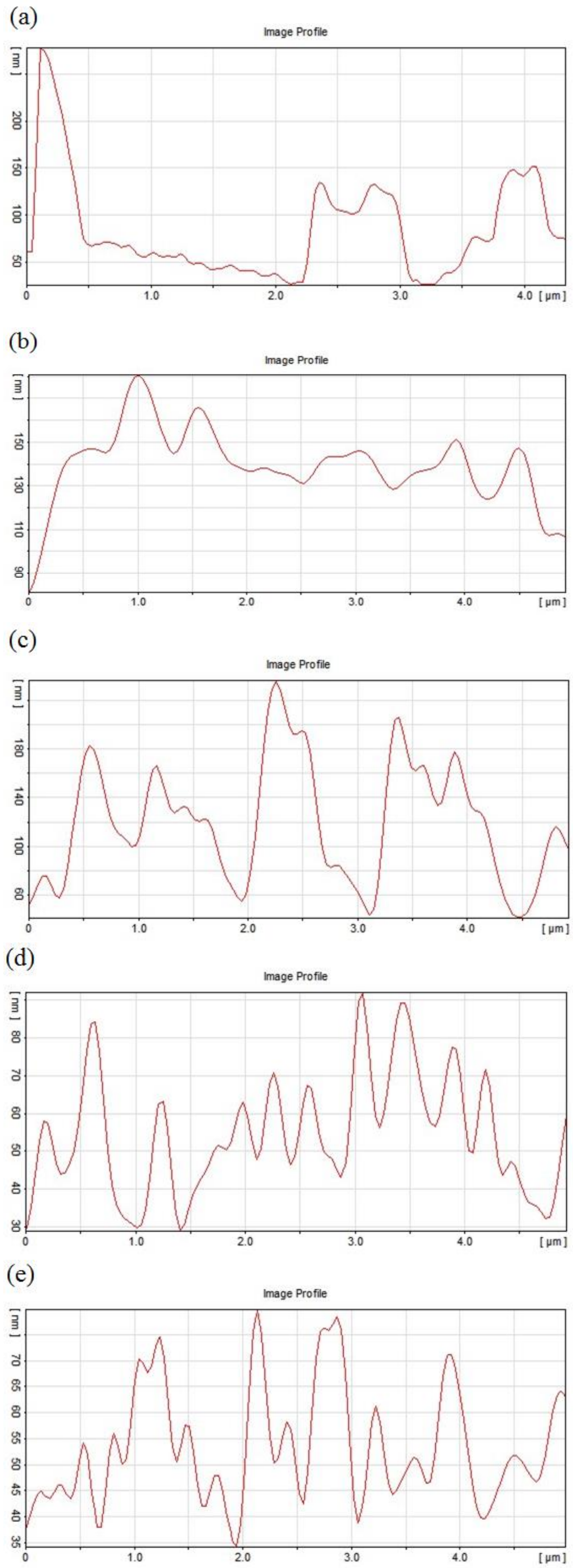


Fig. 5 AFM roughness profiles of PDMS-Silica nano-composite coatings with: (a): 0.5, (b): 1, (c): 2, (d): 3 and (e): 4 wt% silica nano-particles.

The Root Mean Square (RMS) roughness values of composite surfaces as a function of silica content of PDMS nano-composites coatings are shown in “Fig. 6”. The results confirmed that the surface roughness is increased with increasing the silica content of nano-composite coatings. Increased surface roughness can lead to more water repellency and super-hydrophobicity behavior [6], [33-34]. This means that silica nano-particles can develop a rough surface on the structure of hydrophobic surface. Higher silica content was found to be advantageous to the hydrophobicity of PDMS layer [19].

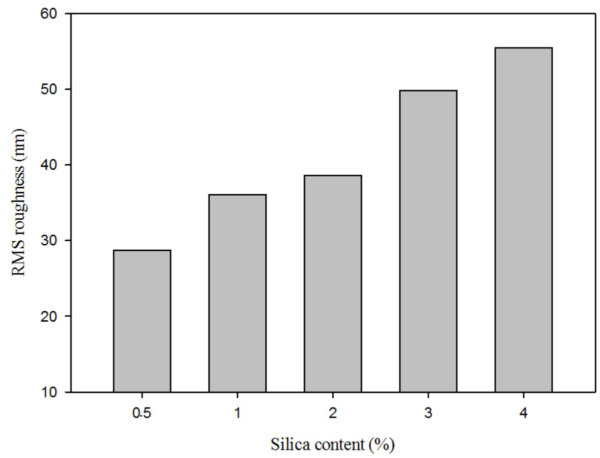
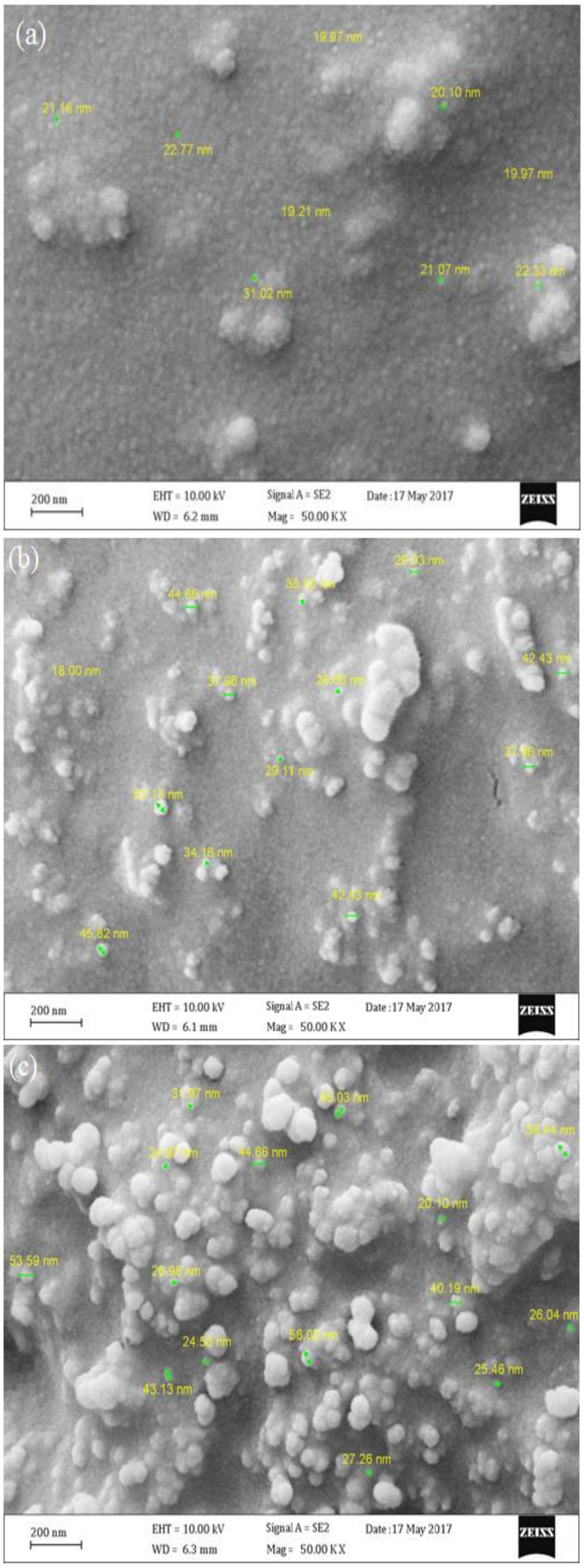


Fig. 6 Roughness values of PDMS-Silica nano-composite coatings as a function of silica content.

Figure 7 shows the SEM images of PDMS nano-composites with different amount of silica nano-particles as filler coated on the usual fabrics. The images showed the bumps which are randomly distributed over the surface. These bumps were due to the distribution and aggregation of silica nano-particles which created the roughness of surface.

It can also be seen from the SEM images that the nano-particle aggregation was increased with increasing the nano-particle content. For 0.5 wt% composite, silica nano-particles (20-31 nm) exhibited a good distribution in the matrix. While, for 1 wt% composite, some agglomerations of nano-particles (18-52 nm) are seen that are connected to each other with matrix. Furthermore, 2 and 3 wt% composites exhibited the same silica size distribution (20-58 nm) but more silica content in 3 wt% composite led to more bumps and aggregations of surface, therefore creating a rougher surface and more hydrophobicity. 4 wt% composite had the largest average size of particles (41-68 nm) and almost narrow size distribution which showed a super-hydrophobic behavior.



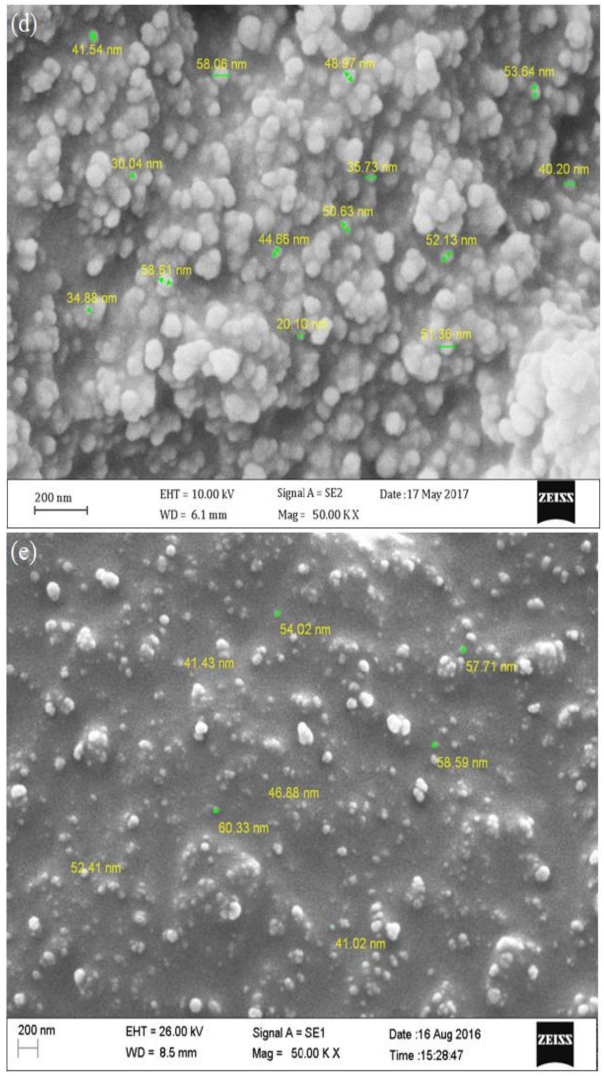


Fig. 7 SEM images of PDMS-Silica nano-composite coatings with: (a): 0.5, (b): 1, (c): 2, (d): 3 and (e): 4 wt% silica nano-particles.

Figure 8 shows the optical absorbance and transmittance spectral values of bare glass slide and 4% Silica-PDMS composite coated glass slide, respectively. It can be seen that the absorption of visible light (in the range of 400 to 800 nm) on the coated glass slide increased 3.5 times in comparison to the bare glass slide. Furthermore, the coated glass slide exhibited the transmittance value of 50% to 57%, while the transmittance value for the bare glass slide was 87.9% to 90%. The decreasing in the transparency of coated glass slide in comparison to bare glass slide can be attributed to the absorption of light by PDMS and silica nano-particles and the light scattering by silica nano-particles [33], [35].

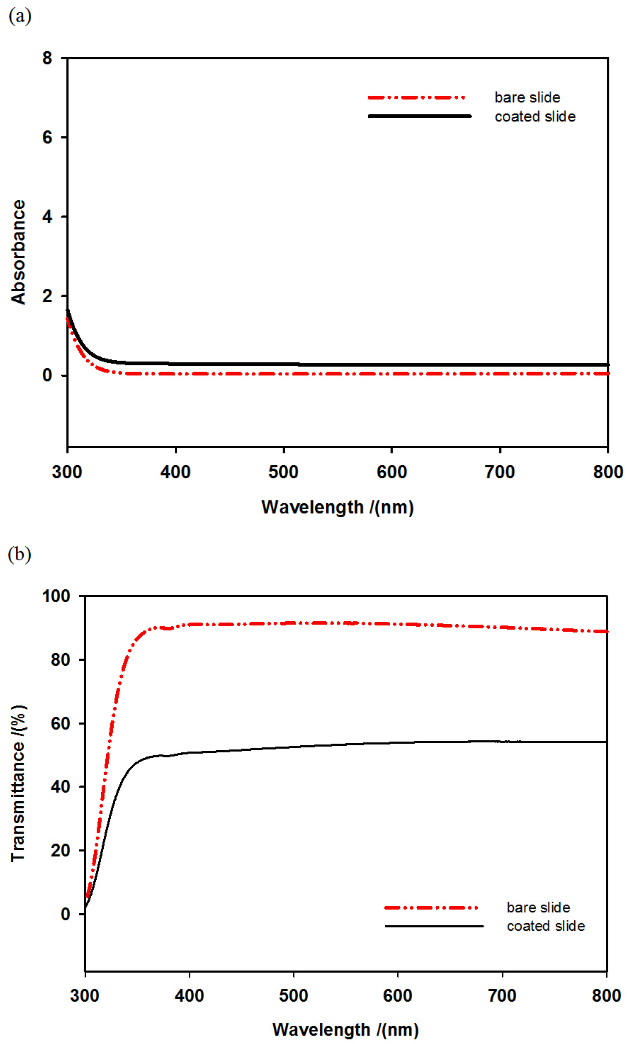


Fig. 8 (a): Optical absorbance spectral values and (b): optical transmittance spectral values of bare glass slide and glass slide coated with 4% Silica-PDMS composite.

4 CONCLUSION

In this study, PDMS-SiO_2 composite surfaces with varying silica nano-particles contents were prepared. The results showed that the water repellency improved by increasing the silica content. AFM images showed an increase in the surface roughness value with increasing the nano-particle concentration.

In fact, the rough surface causes the air pocket trapping and prevents the direct contact of the surface with the water. The SEM images also indicated the distribution of the nano-particle in the polymer matrix coating. Moreover, the spectral transmittance value of PDMS-SiO_2 composite coated glass with higher surface roughness was decreased in comparison to that of the bare glass.

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