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Superhydrophobic clothes: preparation and characterization

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ABSTRACT: A superhydrophobic surface is coated on the surface of a cloth by MTCS (methyltrichlorosilane) nanoparticles and then, it is modified by SiO_2–m–FTCS (1H,1H,2H,2H-Perfluorododecyltrichlorosilane) nanoparticles. This surface is characterized by SEM(scanning electron microscopy), and FT-IR (Fourier transform-infrared microscopy) and also its contact angle is investigated in various conditions and an optimized condition is identified for industrial utilization.

Keywords: *Hydrophobic copolymers; Nanoparticles; SiO_2–m–FTCS; Silicon nanoparticles; Superhydrophobic*

INTRODUCTION

Most of the technologies which exist today have been inspired by nature. One of these technologies is self-cleaning phenomenon which is of commercial importance. In our natural world most of the surfaces, such as butterfly's wing and the leaf of some plants like water lily possess self-cleaning properties. This interesting technology because of tremendous applications in clothing, windows, solar cells and loom industry has drawn significant attention in recent decades (Azimi, *et al.*, 2013, Lyon, *et al.*, 2015, Moyano,*et al.*, 2014). Self-cleaning technology causes the decrease in costs related to keeping and the amount of time to keep instruments clean and also gives rise to the increase in their durability.Self-cleaning surfaces are classified into two main categories: hydrophilic self-cleaning surfacesand hydrophobic self-cleaning surfaces(Moyano, *et al.*, 2014, Tian,*et al.*, 2013, Guo, *et al.*, 2013, Qu,*et al.*, 2014). It is noteworthy that these two categories clean themselves by water. In hydrophilic self-cleaning surfaces, water spreads on the surface. In this way, it could transport dirty and other impurities and remove them. While, in the hydrophobic self-cleaning surfaces, water droplets slide on the surface and clean the surfaces. However, hydrophobic self-cleaning surfaces due to the affordable technologies have more applications in comparison with hydrophilic ones. Since centuries, the removal of water and oil has been one of the most important goals of researchers and manufacturers in loom industry. Various ways of yarn surface treatment to reach the least hydrophobicity confirms it. However, there is enough space to research and study on this field to reach the least repellence between water and other liquids. Nature has guided researchers to reach a contact angle more than 150° by unifying chemistry and physics. These kinds of surfaces are known as superhy-

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(*) Corresponding Author - e-mail: mohammadjavadtaghizadeh31@yahoo.com drophobic or ultrahydrophobic surfaces (Nishimoto, *et al.*, 2013, Hu, *et al.*, 2014, Patankar, *et al.*, 2016). In fact, Superhydrophobicity is the ability of a surface to repel water. It is a relatively recent field of investigation which has drawn significant attention from both industry and academia. For the first time Barthlott and Neinhuis, and Jiang's group demonstrated that the superhydrophobicity of natural surfaces is a consequence of a combination of the synergetic effects of their dual scale structure as well as the low surface energy of the relevant material. Then, many researchers have tried to artificially reproduce such intricate structures by using the concept of biomimetics(Papadopoulos, *et al.*, 2013). Many superhydrophobic surfaces which exist in nature have developed their unique properties as a result of having to adapt the conditions of their environment. Researchers by analyzing various morphologies present in both plant and insect natural surfaces have realized that dynamic loading (such as rainfall pressure) determines nanostructure size, while static loading determines the number of hierarchical levels (Checco, *et al.*,2014, Li, *et al.*, 2015).By studying the plants which have such properties, researchers have reached this point of view that to make such a surface, in addition to materials to reduce the surface energy, another factor which is creating roughness on the surface is demanded. To create rough surfaces tremendous attempts have been carried out and diverse methods have been used such as sol-gel, lithography, chemical etching, chemical vapor deposition (CVD) and powder spraying.

MATERIALS AND METHODS

All the solvents, chemicals and reagents were purchased from Merck, Fluka and Aldrich. IR spectra were recorded on a Shimadzu IR-470 spectrometer by the method of KBr pellet. SEM images were obtained on a Seron AIS 2100. The products were identified by comparison of their spectroscopic and analytical data with authentic samples.

Synthesis of silicon nanoparticles

Silicon nanoparticles were synthesized by Stober method.In a 250 mL round bottom flask 50 mL ethanol and 2 mL distilled water was loaded. Then, 5 gr (0.024 mol)tetraethyl orthosilicate was added to the flask and the mixture was stirred by a magnetic stirrer till the mixture was completely homogeneous. Then the flask temperature was raised to 50°C by oil bath and 1 mL ammonia 28% (as a catalyst) was added to the solution until its reached pH 11. The reaction was continued for 5 hrs. Next, the reaction mixture was cooled to reach room temperature and the white precipitate was separated from the solution by centrifuge. The obtained precipitate was washed with ethanol 3 times. In the final step, the precipitate was placed in an oven to be dried completely.

Synthesis of silicate nanoparticles modified by FTCS

0.5 gr synthesized white powder silicon nanoparticles and 4 mL FTCS were loaded into a round bottom flask and then it was placed under ultrasound waves to completely be homogeneous. The flask was placed at 50°C and was stirred magnetically for 30 min. 1 mL ammonia 25% was added to the reaction mixture for making the mixture basic.The reaction continued for 12 hrs. The flask was cooled and white precipitate was separated by centrifuge. To remove unreacted silanes, the obtained precipitate was washed by ethanol two times and at last the product was separated and dried at 50°C.

Preparation of cotton surface for coating

To prepare cotton surface for coating, diverse methods and various materials were used. To make sure that the cotton surface has no contaminants, contact angle was measured before and after washing. If contact angle is less than 4o, the surface is clean and is ready for coating. To coat the clothes by silicate nanoparticles, two methods, wet and dry, have been used. Initially, cloth was washed by water and detergents and then it was placed in a concentrated solution of washing surfactants to remove any contaminants and oils completely. Next, the cloth was washed with distilled water and placed under ultrasound waves for 15 min. Then, it was washed with distilled water and dried.

Preparation of hydrophobic cover by methyltrichlorosilane (MTCS) via chemical vapor deposition (CVD)

Previously prepared clothes were placed in an isolated system. In a small pot placed in this system, 1 mL MTCS was loaded and 2 mL ethanol 5% was added to the bottom of the system. The system's cap was fastened and placed on a heater at 50°C for 24 hrs. In this condition, the clothes werehydrophobic by CVD. Then, the clothes were prepared for measurement of their contact angles.

Hydrophobic surface modification by modified SiO_2-FTCS nanoparticles in various weight percents

In this step, after measuring contact angle to compare with modified condition,hydrophobic clothes were modified by submerging in the considered solution. SiO_2-FTCS solutions with weight percent ranging 0.1–0.9 were dissolved in ethanol and were placed under ultrasound waves for 30 min then the prepared hydrophobic clothes were submerged in these solutions for 5-15 min.after pulling the clothes out of the solution, they were dried and their contact angle were measured. Time and concentration were optimized with considering contact angle.

Modification of surface for durability of superhydrophobic nanoparticles by spraying hydrophobic copolymers

At this stage a 5% solution of methyl methacrylate and dodecyl methacrylate was dissolved in dichloromethane and then it was sprayed on the cloth containing nanoparticles. This stage increases the durability of nanoparticles on the cloth. It is noteworthy that it causes a decrease in contact angle.

Measuring contact angle with water

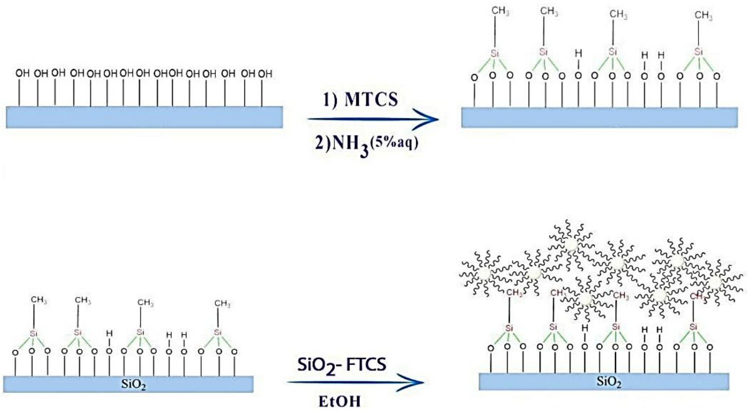
Contact angles of hydrophobic clothes were measured by contact angle instrument. 2 μL water was placed on the cloth surface by Hamilton syringe and a photo was captured and then contact angle was measured by software.

Measurement of contact angle with surfactants

Surfactants were prepared in specified concentrations and their contact angle with surface was measured so that 2 μL of surfactants were placed on the surface by Hamilton syringe. Surface contact angle was compared with anionic and cationic surfactants and the mixture of cationic and anionic surfactants with water and also the interaction between the surface and nanostructured surfactants was investigated. This test on the clothes was carried out to maintain their stability in case of being in touch with detergents and surfactants specially in case of being washed.

RESULTS AND DISCUSSION

To verify chemical structure of SiO_2, modified nanoparticles and modified silicon nanoparticles, FT-IR spectroscopy was used. FT-IR spectrum of silicon nanoparticles and modified silicon nanoparticles are depicted in Fig. 1. In Fig.1,the peaks at 804 cm^{-1} and 1100 cm^{-1} are related to unsymmetrical and symmetrical stretching vibrations of Si-O-Si bond. In the FT-IR spectrum of modified silicon (Fig.1), the peaks at 2856 cm^{-1} and 2927 cm^{-1} are related to unsymmetrical and symmetrical stretching vibrations of $–CH_2$ groups



Scheme 1: Synthesis of superhydrophobic surface

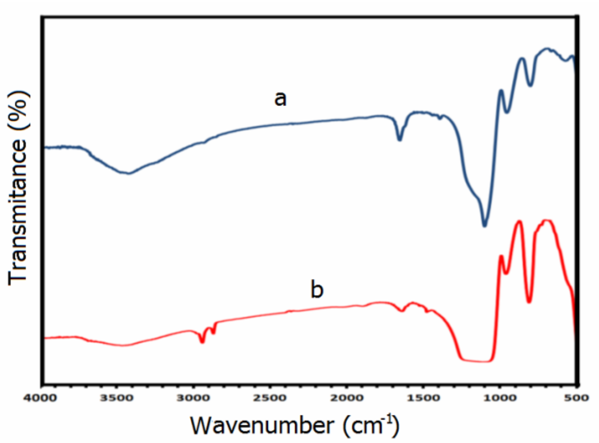


Fig. 1.FT-IR spectrum of a) silicon nanoparticles and b) silicon nanoparticles modified by FTCS

present at FTCS carbon chain added to nanoparticles surface which confirm their surface modification by these groups.

The contact angle of water droplet with hydrophobic surface is the most important criterion in order to confirm the superhydrophobicity of the produced surface. As it was mentioned before, the surfaces which their contact angle is more than 150o are defined as superhydrophobic surfaces. The cloth surface which has been hydrophobic by methyltrichlorosilane and SiO_2-m-FTCS nanoparticles in various percent, which have been used to improve the hydrophobicity of the cloth, were prepared and their contact angle were measured. Fig.2 shows contact angle picture of the cloth coated by MTCS. By using of the software related to contact angle measuring instrument, contact angle could be measured. According to the picture, its contact angle is 129.7°, that by considering the classification of surfaces in the basis of contact angle, it can be concluded that the surface coated by MTCS is hydrophobic. Fig. 2 shows the diagram of obtained hydrophobic surface contact angle in the basis of nanoparticles percent increase. It is obvious that the contact angle of the surfaces coated by nanoparticles is raised increasingly and the hydrophobic cloth with 0.9 weight percent from nanoparticles was selected to investigate the interaction of surfactants with that.

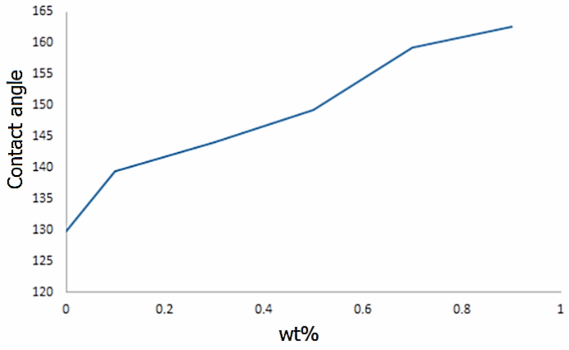


Fig. 2. Diagram of contact angle in the basis of the increase in modified nanoparticles weight percent

Fig.3 shows the contact angles of hydrophobic cloth surface improved by nanoparticles in various weight percent. According to contact angles it is obvious that the maximum contact angle is related to the cloth containing 0.9% (wt%) of nanoparticles and has contact angle 162.5° which shows the cloth surface is superhydrophobic. In addition, the minimum contact angle is related to the coated cloth containing 0.1% (wt%) of nanoparticles and has contact angle 139.5°. Obtained images and presented diagram demonstrated that with the increase in contact angle the percent of SiO_2-m-FTCS increases.

To study the morphology of superhydrophobic surface and also to observe the roughness of its surface, scanning electron microscopy (SEM) was used (Fig.4). Figs 4a and 4b,which have been obtained in sizes 200 and 50 µm respectively, show that the surfaces are similar. It is obvious that in addition to rough-

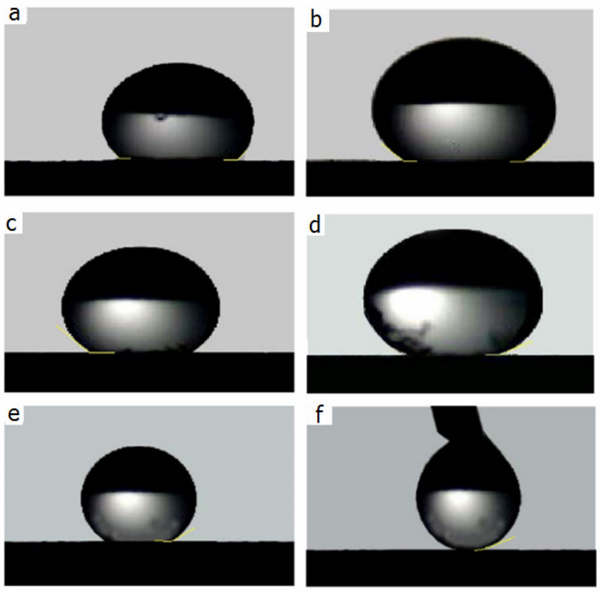


Fig.3. Contact angle images of hydrophobic surfaces modified by SiO_2-m-FTCS with percent: a) pure MTCS, b) 0.1% (wt%) of SiO_2-m-FTCS, c) 0.3% (wt%) of SiO_2-m-FTCS, d) 0.5% (wt%) of SiO_2-m-FTCS, e) 0.7% (wt%) of SiO_2-m-FTCS, f) 0.9% (wt%) of SiO_2-m-FTCS

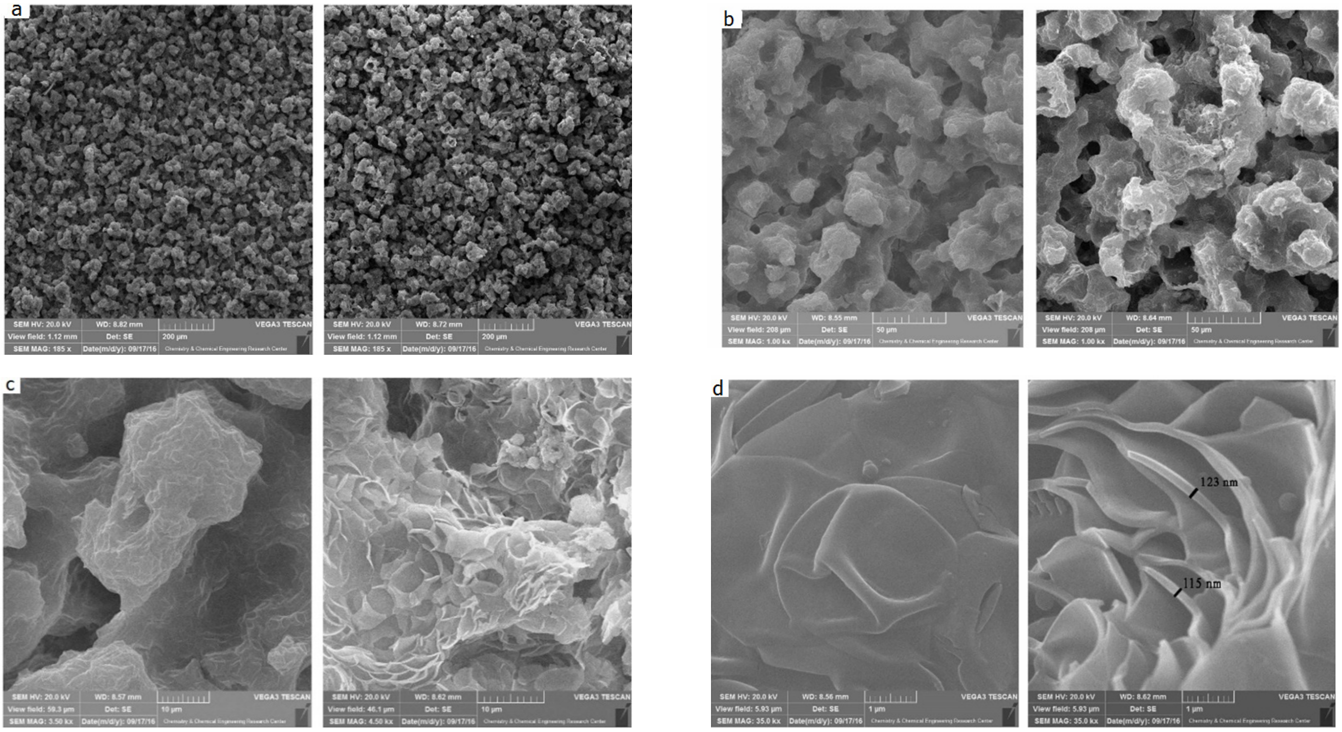


Fig.4.SEM images of the hydrophobic surface obtained by MTCS (left) and modified by SiO_2-m-FTCS 0.9% (right): a) 200 µm, b) 50 µm, c) 10 µm, d) 1 µm

ness of the surface, the presence of the particles with low level energy, has given rise to the creation of superhydrophobic surface. Figs 4c and 4d, show the differences between MTCS and SiO_2-m-FTCS (0.9%)in sizes 10 µm and 1 µm. In addition to above mentioned factors, the presence of the layers ranging 115-123 nm on the surface roughness of SiO_2-m-FTCS (0.9%) is an obvious reason for why it is superhydrophobic in comparison with MTCS.

One of the other unique features of these surfaces is the stability of coating in case of being placed in high quantities of water. Contact angle test, is a test in which a tiny droplet of water is placed on the surface. This test may not be a true criterion to investigate superhydrophobicity of the surface for practical use. Fig.5 demonstrates the performance of superhydrophobic surface in high quantities of water. It is obvious from the image that the surface resists against wetting very well and after pulling out of water, the cloth is completely dry.

Fig.5. Images of the obtained superhydrophobic surface

CONCLUSIONS

Hydrophobic surface was prepared on the cloth surface via CVD and by using of nanoparticles. In order to coat the surface, CVD and submerging, which is inexpensive, creates homogeneous cover and has high performance, was applied. The performance of this film was investigated through various tests and it was concluded that it could be used as industrial covers. Contact angle of this cover was more than 150o. In addition, this cover possessed self-cleaning property which is of commercial interest.

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