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Fabrication of a Superhydrophobic Nanofibers by Electrospinning

Meikandan Megaraj and Malarmohan Keppannan

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Abstract

The major work of this research work is fabrication and investigation of the surface characteristics of a hydrophilic polycaprolactone (PCL) and superhydrophobic 1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane (PFDTES)-AgNO₃-modified PCL fibrous membranes through the electro spinning technique. The surface properties of the PCL fibrous were modified from hydrophilic to superhydrophobic by adding (0.05 vol%) PFDTES-AgNO₃ solution into a mixed with a solvent of PCL and chloroform. The electrospun PFDTES-modified PCL fibrous showed a maximum water contact angle (WCA) of 158° due to increase in surface roughness when compared with the PCL fibrous roughness, having a maximum WCA of 81° and an average fiber diameter of 400–700 nm.

Keywords: electrospinning, polycaprolactone (PCL), nanofiber, water contact angle (WCA), superhydrophobic

1. Introduction

The superhydrophobic surface normally states, mixture of the static contact angle more than 150° with a contact angle hysteresis lesser than 5°. It is categorized into two types agreeing to water rolling angle; an enormously adhesive superhydrophobic surface that permits water droplets to adhere the surface, even when the surface is turned upside down and less adhesive superhydrophobic surface with a rolling angle less than 10° [1–3]. Electrospinning has been keenly exploited as a simple and flexible method for producing ultrathin fibers made of several materials. Countless advancement had been made in latest years with concern to the theory for electrospinning and mechanism of the orientation of electrospun fibers [4]. Electrospinning is an efficient and simple method for fabrication of constant nanofibrous with high surface

bumpiness and the surface-to-volume ratio of the driving force of an outward electric field on polymer solutions or polymer liquefies [5]. Since polymeric structures allow the numerous everyday applications areas of nanoparticles are as additives to polymers used in the motorized and aerospace division were vehicle parts for lesser weight and greater performance, packaging including food and biomedical to keep and preserve the reliability of the product by controlling the obstacle, mechanical, optical and respiration properties, in textiles industries increases in strength, water resistance, self-cleaning, fade resistance and special care merchandises UV shield, deep dispersion skin cream emulsions. Many of these functionalities can be exchanged from one use to another. For example, the similar technology used for transparent UV protective coatings such as sunscreens in personal care products can be used for UV protection in food packaging, paints, and textiles [6]. Coming together or altering the basic frame with another component for the electrospinning applications, one can produce modified nanocomposite hybrid fibers for the variety of day to day applications. So far, a number of techniques have been effectively expressed for generating rough surface structures. Among others, electrospinning as a low-cost, continual, scalable nanomanufacturing technique has been widely engaged for fabricating continuous nanofibers/microfibers of a huge variety of natural and synthetic polymers, polymer derived carbon, metals, metal oxides and ceramics, etc. [7–12].

There have also been many noteworthy models describing the production of low energy hydrophobic and superhydrophobic surfaces by electrospinning. Jiang et al. produced superhydrophobicity of Fe_3O_4 -filled carbon nanofibers through sintering electrospun [13]. Cao et al. fabricated a superhydrophobic surface on calcined electrospun SiO_2 nanofibers using a tridecafluoro-1,1,2,2-tetrahydrooctyldimethyl-chlorosilane layer [14]. Ma et al. defines low surface energy fibers produced by electrospinning polystyrene–polydimethylsiloxane copolymers which were unclean with polystyrene homopolymer. Relatively more content of low surface energy siloxane polymer caused in fibers with water contact angles of 163° [15]. Rutledge et al. stated that chemical vapor deposition coating of polytetrafluoroethylene having superhydrophobic properties [16]. Miyauchi et al. fabricated a biomimetic superhydrophobic surface including micro-nanoporous poly styrene microfibers by the use of electrospinning technique [17]. Jiang et al. electrospun polystyrene from DMF/THF to give a fiber mat with contact angles of 139.1° and went on to spin/spray a dilute solution of polystyrene to give a film of porous microparticles which gave a water contact angle of 162° [18]. Acatay et al. used a fluorinated comonomer, present at up to 50 wt% to attain superhydrophobic surfaces via an electrospinning process using a copolymer of acrylonitrile and α,α -dimethyl meta-isopropenyl benzyl isocyanate and 50 wt% of a perfluorinated diol [19]. Borner et al. used a one-step process to produce poly(lactic-co-glycolic acid) nanofiber interconnects with surfaces improved biofunctional peptides by spinning a homogeneous mixture of PLGA and a polymer-peptide conjugate [20]. Bianco et al. spun polyamide 6 nanofibers in the occurrence of fluorinated acridine. They identified that the addition of increasing volumes of the acridine (2–6 wt%), static contact angles with water on the fibers improved gradually from 62° for unchanged polyamide to 123° [21]. Considering the fascinating features of superhydrophobic surface an attempt is made in the present work to develop a superhydrophobic surface of polycaprolactone and PFDTES-modified polycaprolactone nanofibrous through an electrospinning technique. The surface characterization studies such as morphological feature, chemical composition, and water contact angle were analyzed and reported.

2. Experimental details

The reagents used in the present study were polycaprolactone (PCL), chloroform, 1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane (PFDTES), ethanol and acetone. All other chemicals were of analytical grade and were used as received purchased from Sigma Aldrich, India.

Electrospinning is a simple and flexible method for producing ultrathin fibers. Altering the basic frame with another component for electrospinning, can produce modified nanocomposite hybrid fibers for various applications. So far, a number of techniques have been effectively expressed for generating rough surface structures. Among others, electrospinning is a low-cost, continual, scalable nanomanufacturing technique and is widely used for fabricating continuous nanofibers/microfibers of a huge variety of natural and synthetic polymers; polymer derived carbon, metals, metal oxides and ceramics, etc.

The reagents used in the present study are polycaprolactone (PCL), silver nitrate (AgNO_3), chloroform, ethanol, PFDTES, and acetone. All other chemicals are of analytical grade and purchased from Sigma Aldrich, India. The photographic and schematic view of electrospinning setup that was used in this preparation method is shown in **Figure 1(a)** and **(b)**, it consists

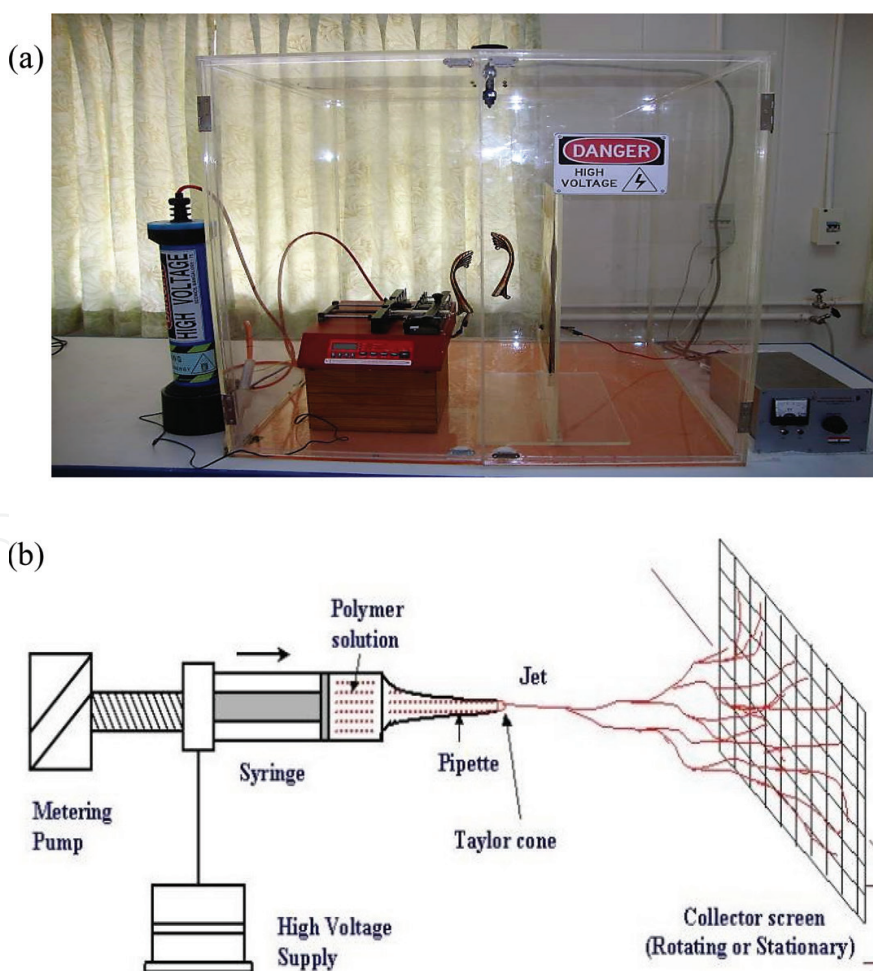


Figure 1. (a) Photographic view of electrospinning setup and (b) schematic view of electrospinning setup.

of a high-voltage supplier, grounded target board and a syringe pump. The polymer solution was flowing through a needle of 1 mm inside diameter. Solutions were prepared by liquefying the desired amount of polymer (according to concentration) in a solvent (chloroform). Solutions are prepared in beakers. Glass beaker was protected with aluminum foil and plastic sheet throughout the process of suspension to prevent solvent evaporation. The process of liquefying was continued using magnetic stirrer. PFDTES-AgNO₃-modified PCL solutions are prepared in the same way which was followed by the addition of PFDTES.

Initial experiments were carried out to find best conditions for electrospinning PCL and PFDTES-AgNO₃ modified PCL fiber membranes were obtained by varying solution concentration (5–15% W/V), feed rate (5, 10, 15, and 20 ml/h) and voltage (5, 15, and 25 kV). The needle to tip collector distance (NCD) was 10 cm and a 10 ml syringe fitted with a 0.838 mm inside diameter and stainless steel needle (Sigma Aldrich) was used. PCL and (0.05% W/V) PFDTES-AgNO₃-modified PCL nanofibers were prepared with electrospinning technique with 10 & 15% W/V concentration using chloroform as an organic solvent. The applied dc voltage was kept at 10 kV, tip target distance was maintained at 10 cm and the flow rate was kept at 0.01 ml/min.

3. Results and discussion

3.1. Nanofibers by electrospinning

The solvent used for electrospinning plays a vital role in the morphology of the subsequent electrospun polymer fibers. Nanofibers achieved by electrospinning frequently exhibit beaded fiber structures, which are significantly influenced by the solution properties. Initially, the concentration of polymer solution plays a significant role in the formation of beads. At dilute concentration, mostly beads are produced because of lack of sequence entanglement in polymer solution, beaded fiber structure is generated in the medium concentration. Normally, beaded fibers have been considered as unwanted or faulty products. Therefore, at a concentrated solution the continuous fiber structure, without bead is attained. The morphology of electrospun PCL fiber membrane and PFDTES-AgNO₃-modified PCL fiber membrane is shown in **Figures 2–4**. The PCL fibers and PFDTES-AgNO₃-modified PCL fibrous membrane, having widely distributed fiber diameters, were randomly oriented as a porous membrane. Furthermore, the fibers exhibited smooth fibers and they have an average fiber diameter of 400–700 nm.

The wettability of prepared substrate was measured, in relations of contact angle, by means of a Goniometer based on sessile drop technique. A drop size of 5 µl was used and the contact angle measurement was done at six different locations in a sample conserved at room temperature. A water droplet placed on PCL fibrous membrane is shown in **Figure 5**. The water droplet was straightaway absorbed by this fibrous membrane.

After PFDTES-AgNO₃ modification, the PCL fibers membrane still maintained the fiber shape. Smooth fibers observed from **Figure 6(a) and (b)** show a water droplet placed on PFDTES-AgNO₃-modified PCL fiber membranes. It can be found that a high surface hydrophobicity WCA lies in between 150 and 158° of fibrous membranes was obtained after the PFDTES-AgNO₃ modification.

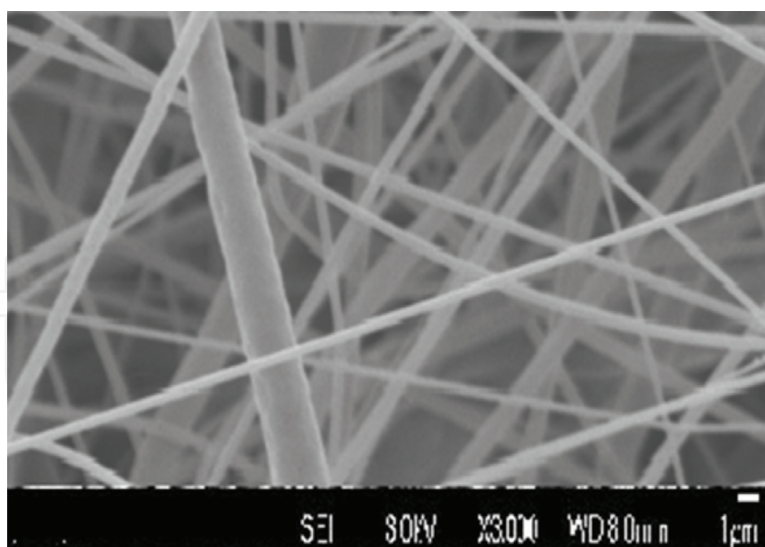


Figure 2. Influence of PCL solution concentration of 15% W/V observed under SEM.

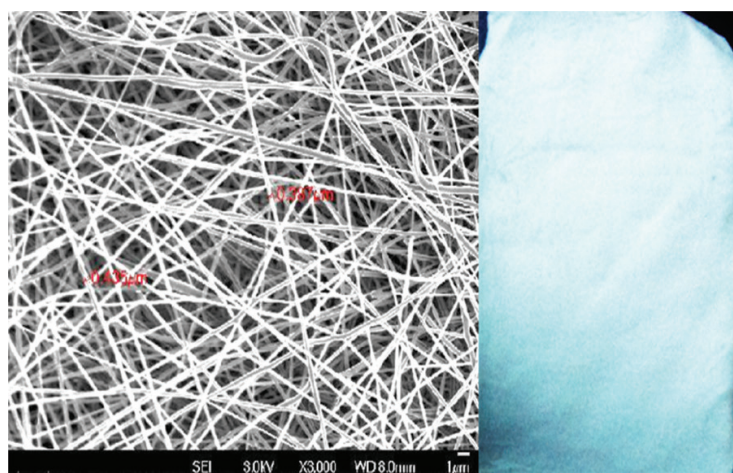


Figure 3. Influence of PFDTES-AgNO₃-modified PCL solution concentration of 15% W/V observed under SEM.

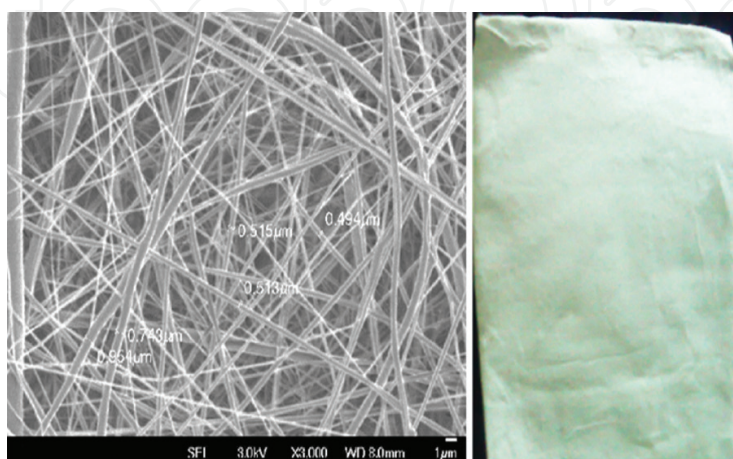


Figure 4. Influence of PFDTES-AgNO₃-modified PCL solution concentration of 10% W/V observed under SEM.

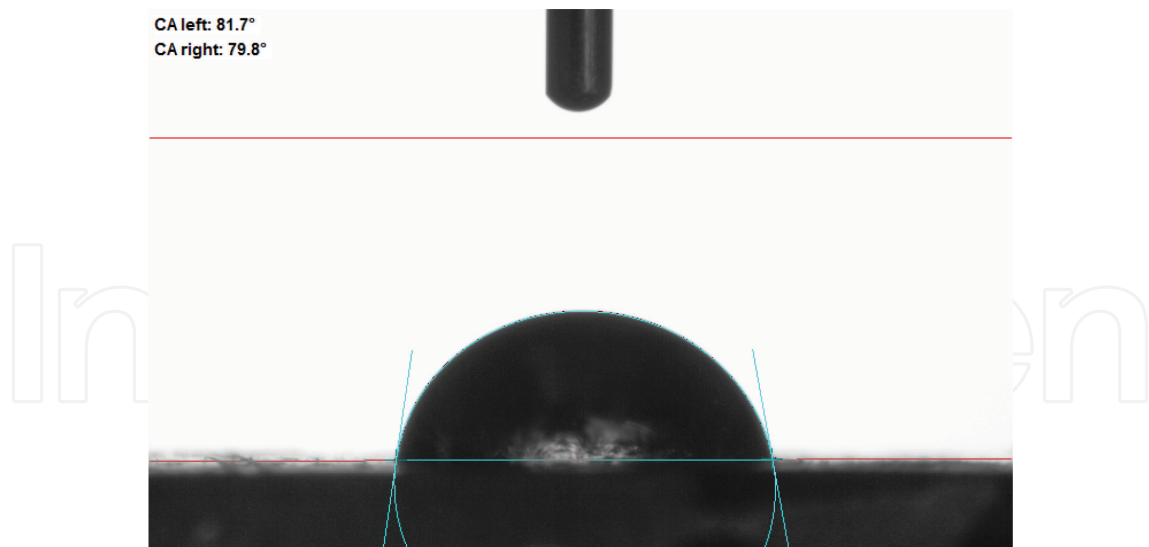


Figure 5. Water droplet on PCL fibers membrane.

The PFDTES-AgNO₃ modification it was proved to be effective to increase the membrane hydrophobicity. PFDTES is a well-known low-surface-energy material. From the above results, the surface coated with PFDTES improves the superhydrophobicity through the formation of micro/nano metric arrangement and these structures are stable. However, entrapment of air between the fibrous membranes allows the water drops to roll off the surface with ease.

Surface profilometer top view images (10 × 10 μm) and cross-section profiles of PFDTES-AgNO₃-modified PCL fibers membrane are displayed in **Figures 7–9**. The electrospun fibrous membrane shows high surface roughness due to the random deposition of the fibers on the collector end.

The stability of hydrophobicity nature aimed at PFDTES-AgNO₃-modified PCL fiber membranes were deliberate and analyzed under ambient, low 10°C and high temperature 110°C

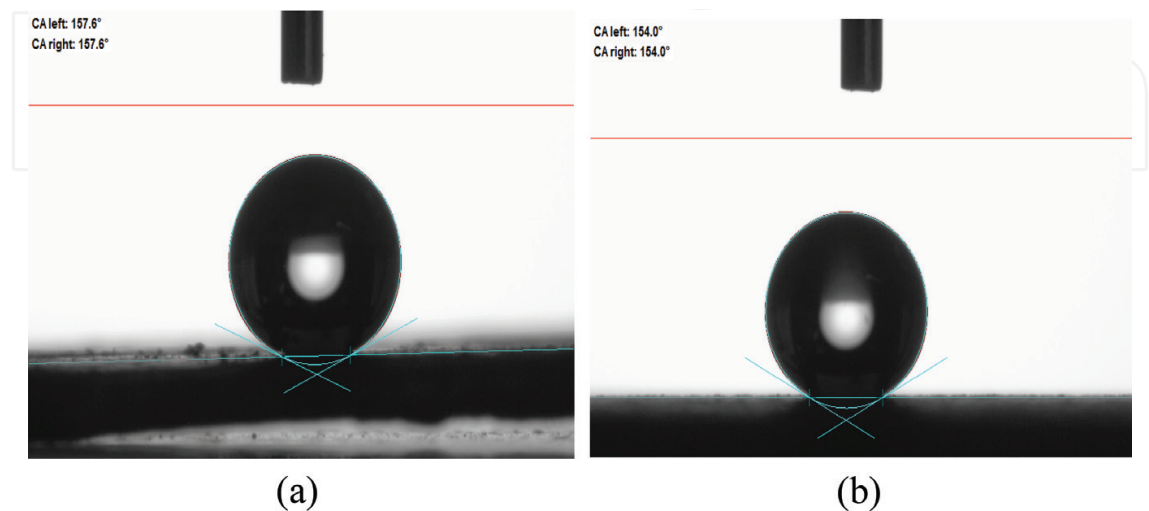


Figure 6. (a and b) Water droplet placed on PFDTES-AgNO₃-modified PCL membrane.

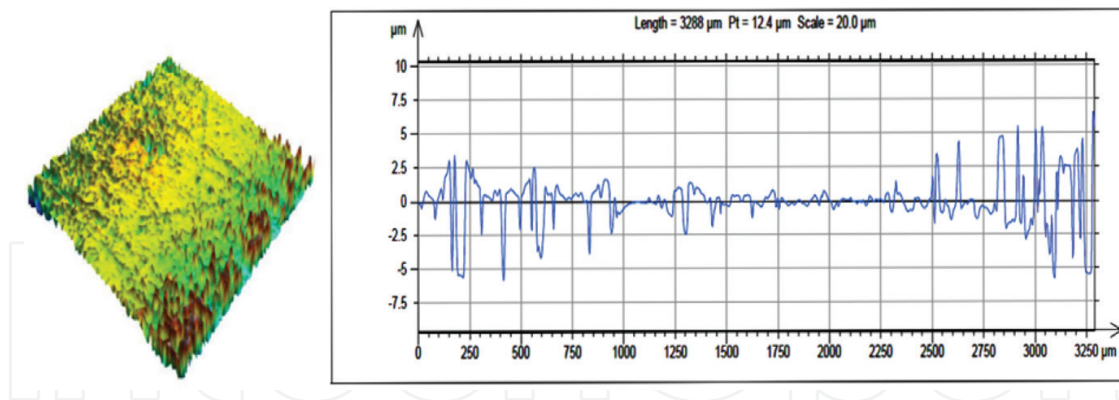


Figure 7. PFDTES-AgNO₃-modified PCL fibers membrane with roughness value of 1.52 μm.

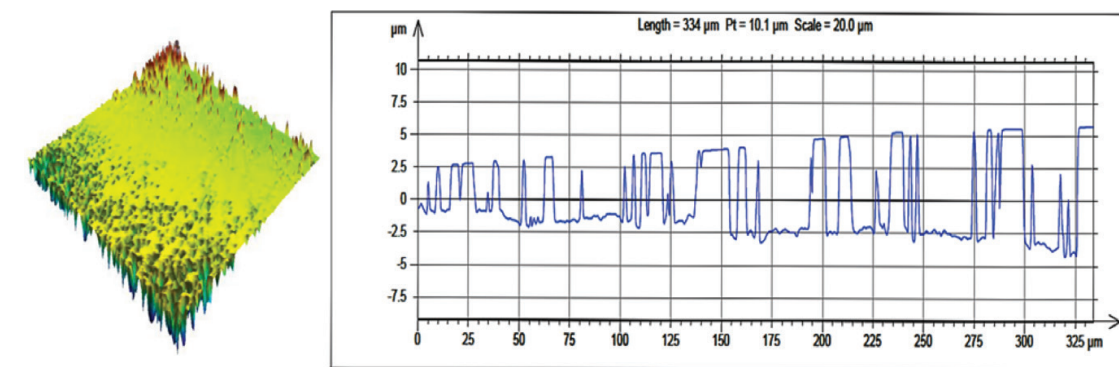


Figure 8. PFDTES-AgNO₃-modified PCL fibers membrane with roughness value of 1.85 μm.

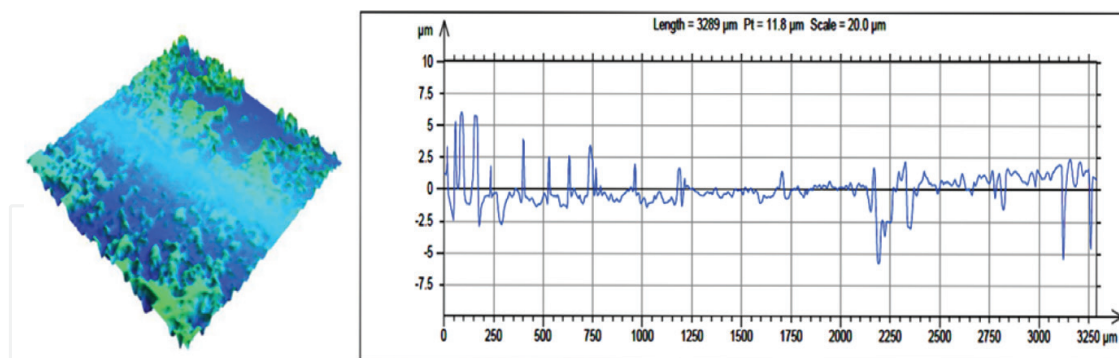


Figure 9. PCL fibers roughness value is 0.82 nm.

conditions for 60 days correspondingly. It is resolved from the **Figure 10** that for all the given temperatures, hydrophobicity nature for PFDTES-AgNO₃-modified PCL fiber membrane reduced only by 7°. Based on the discussion, it is understood that the proposed electrospinning is best for developing hydrophobic/superhydrophobic surface. However, after the stability tests at various temperatures it is observed flaking or pops on the top layer of nanofibers. Unfortunately the fibers flake out with the simplest touch or with simple air pressure, and results in dust over the system.

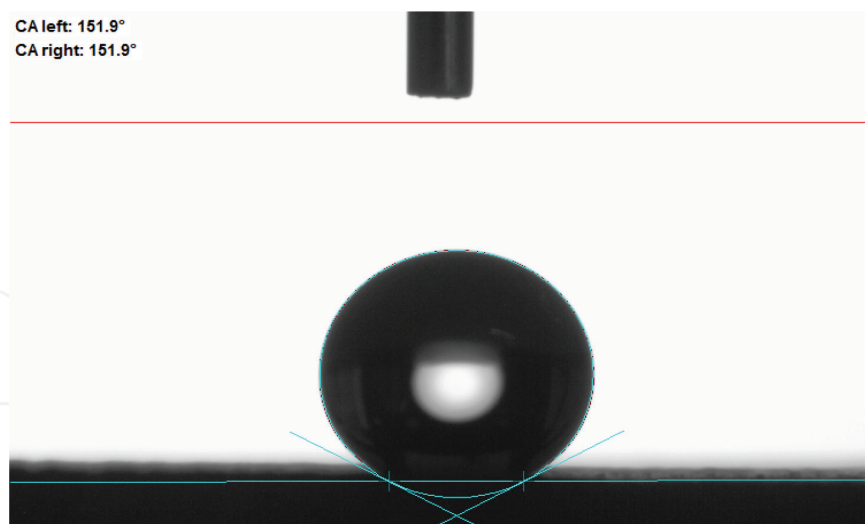


Figure 10. Superhydrophobic nature of PFDTES- AgNO_3 -modified PCL fibers after durability test.

4. Conclusion

The hydrophilic and superhydrophobic fibrous membranes were fabricated by electrospinning using polycaprolactone (PCL) and 1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane (PFDTES)-modified polycaprolactone. Surface roughness of the PFDTES-modified polycaprolactone nanofibers was controlled using a variety of chloroform solvent mixtures. The addition of PFDTES to the solvent mixture affected the surface morphology of polycaprolactone fibrous and enhanced the WCA of the polycaprolactone fibrous without altering the smoothness of fibers. The electrospun PFDTES-modified polycaprolactone fibrous showed a maximum water contact angle (WCA) of 154° due to increase in surface roughness when compare with the polycaprolactone fibrous roughness, which showed a maximum WCA of 81° and an average fiber diameter of 400–700 nm.

4.1. Drawbacks

- Although electrospinning coating technique achieved enhancement in heat transfer, their durability still needs to be improved to prevent observed flaking or pops after the heat transfer tests.
- Polymer coatings with higher stability on substrates have larger thickness. It involves in larger thermal resistance of the substrate, hence heat transfer characterizes values were not reported.

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