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FABRICATION OF A SUPERHYDROPHOBIC NANOFIBRES BY ELECTROSPINNING

M. MEIKANDAN*, K. MALARMOHAN
Department of Mechanical Engineering, Anna University, Chennai – 600025

The focus of the present work is to fabricate and investigate the surface characteristics of a hydrophilic polycaprolactone (PCL) and superhydrophobic 1H, 1H, 2H, 2H-Perfluorodecyltriethoxysilane (PFDTES)-modified polycaprolactone fibrous membranes through simple electro spinning techinique. The surface properties of the polycaprolactone fibrous were modified from hydrophilic to super-hydrophobic with an addition of a small amount (0.05 vol%) PFDTES solution into a mixed solvent of polycaprolactone and chloroform. The morphology of the nanofibirous was observed by scanning electron microscopy (SEM). The electrospun PFDTES-modified polycaprolactone fibrous showed a maximum water contact angle (WCA) of 158^0 due to increace in surface roughness when compare with the polycaprolactone fibrous roughness, which showed a maximum WCA of 81^0 and an average fiber diameter of 400-700 nm.

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1. Introduction

The superhydrophobic surface normally states, mixture of the static contact angle more than 150° with a contact angle hysteresis lesser than 5º. 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 10º [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 nano manufacturing technique has been widely engaged for fabricating continuous nano-

*Corresponding author: meikandan013@gmail.com

/micro fibers of a huge variety of natural and synthetic polymers, polymer derived carbon, metals, metal oxides and ceramics,etc [7-11].

There have also been many noteworthy models describing the production of low energy hydrophobic and superhydrophobic surfaces by electrospinning. Jiang et al, produced super-hydrophobicity of Fe3O4-filled carbon nanofibres through sintering electrospun [12]. Cao et al, fabricated a super-hydrophobic surface on calcined electrospun SiO2 nanofibers using a tridecafluoro-1,1,2,2- tetrahydrooctyldimethyl-chlorosilane layer [13]. Ma et al, defines low surface energy fibres produced by electrospinning polystyrene – polydimethylsiloxane copolymers which were unclean with polystyrene homopolymer . Relatively more content of low surface energy siloxane polymer caused in fibres with water contact angles of 163 degrees [14]. Rutledge et al, stated that chemical vapour deposition coating of poly-tetrafluoroethylene having super-hydrophobic properties [15]. Miyauchi et al, fabricated a biomimetic super-hydrophobic surface including micro-nanoporous poly styrene microfibres by the use of electrospinning technique [16]. Jiang et al, electrospun polystyrene from DMF/THF to give a fibre mat with contact angles of 139.1 degrees 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 degrees [17]. 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 [18]. 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 [19]. Bianco et al, spun polyamide 6 nanofibres 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 fibres improved gradually from 62 degrees for unchanged polyamide to 123 degrees [20]. 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. Materials and Methods

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.

2.1. Experimental setup

The electrospinning apparatus that was used in this study is shown in figure 1 , it consists of a a high-voltage supplier, grounded target board and a syringe pump. The polymer solution was flowing through a needle of 1 mm inside diameter.

Fig. 1. Electrospinning setup.

2.2. Electrospinning

Solutions were prepared by liquefying the desired amount of polymer (according to concentration) in a solvent. Solutions were prepared in earlier washed glass 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-modified polycaprolactone solutions were prepared in same way which was followed by the addition of PFDTES.

2.3. Electrospinning Conditions

Initial experiments were carried out to find best conditions for electrospinning Polycaprolactone and PFDTES-modified polycaprolactone fibrous membranes were obtained by varying the following parameters. solution concentration (5 to 15% w/v), feed rate (5, 10, 15, and 20 ml per hour) and voltage (5, 15, and 25kV). The needle to tip collector distance (NCD) was 10 cm and a 10ml syringe fitted with a 0.838mm inside diameter and stainless steel needle (Sigma Aldrich) was used. Polycaprolactone and (0.05 vol%) PFDTES-modified polycaprolactone nanofibrous prepared with electrospinning technique with 10 wt%, 15 wt% 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 0.01ml/min.

2.4. Measurements

The surface morphology of all samples was examined by scanning electron microscope (Tescon vega-3) and their roughness was measured by a surface profilometer (Talysurf Cci Lite). The wettability of the substrate was measured, in terms of contact angle, using a Goniometer (Data physics–OCA 20) based on sessile drop measuring method.

3. Result and discussion

The solvent used for electro-spinning plays a vital role in the morphology of the subsequent electrospun polymer fibers. Nanofibers achieved by electro-spinning 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 polycaprolactone fibrous membrane and PFDTES-modified polycaprolactone fibrous membrane is shown in figure 2. The polycaprolactone fibres and PFDTES-modified polycaprolactone fibrous membrane, having widely distributed fibre diameters, were randomly oriented as a porous membrane. Furthermore, the fibres exhibited a smooth fibres and they have an average fibre diameter of 400-700 nm.

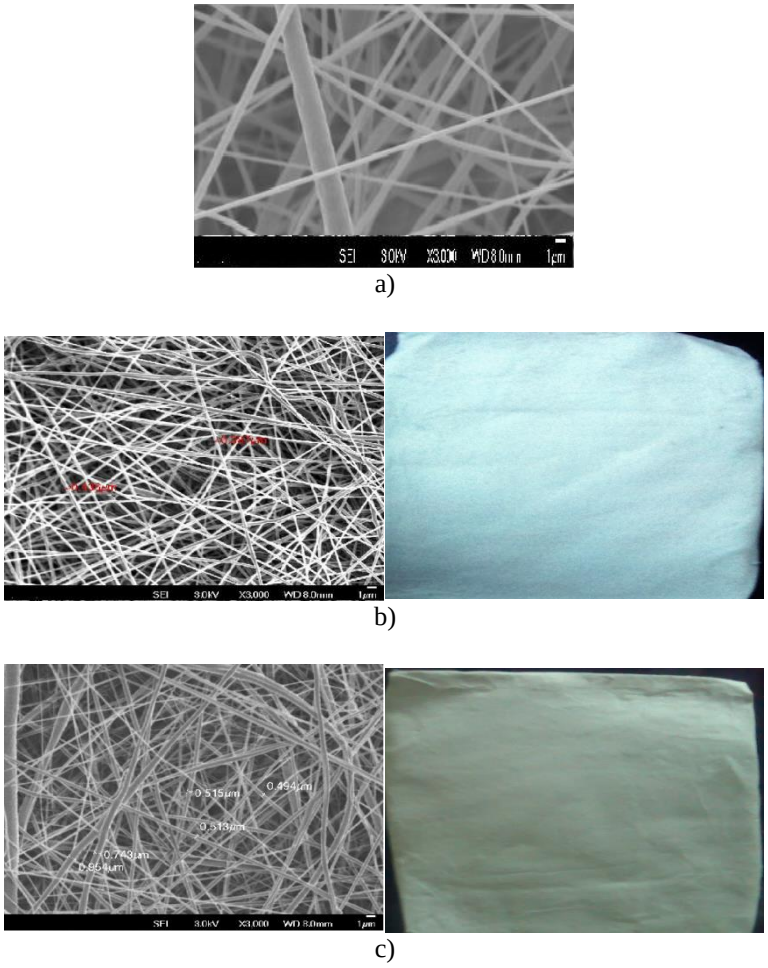


Fig. 2. Influence of polycaprolactone and PFDTES-modified polycaprolactone solution concentration observed under SEM: a) 15wt%; b) 15wt%; c) 10wt%

The wettability of the substrate was measured, in terms of contact angle, using a Goniometer (Data physics–OCA 20) based on sessile drop measuring method. A droplet size of 5 µl was taken and the contact angle was measured at six different positions in a sample maintained at a room temperature. A water droplet placed on polycaprolactone fibrous membrane is shown in figure 3. The water droplet was straightaway absorbed by this fibrous membrane. After PFDTES-modification, the polycaprolactone fibrous membrane still maintained the fibre shape and smooth fibres observed from figure 4(a). Figure 4(b) shows a water droplet placed on PFDTES-modified polycaprolactone fibrous membrane. It can be found that a high surface hydrophobicity WCA lies in the range between 150º to 158º of fibrous membranes was obtained after the PFDTES modification. The PFDTES 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 with PFDTES coating enhance the superhydrophobicity through the creation of micro/nano metric structures and these structures are stable. However, entrapment of air between the fibrous membranes that enables the water droplet to roll off the surface more simply.

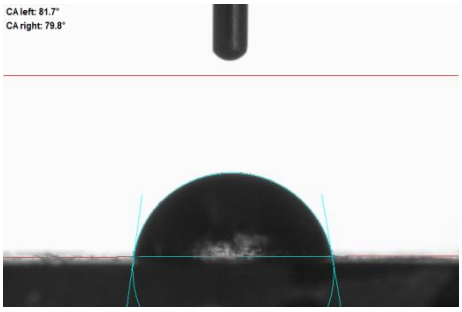
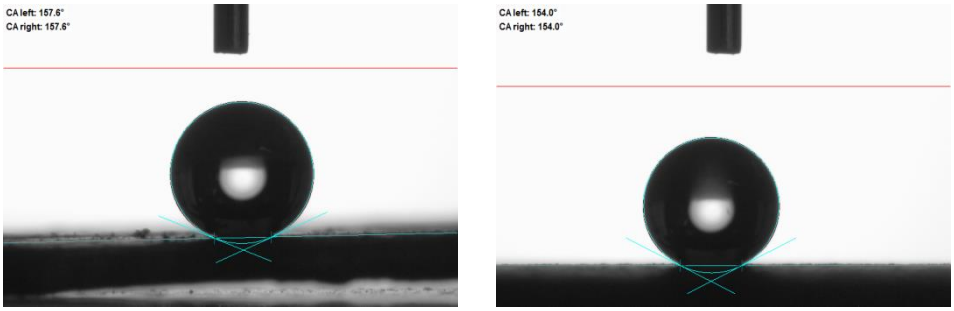


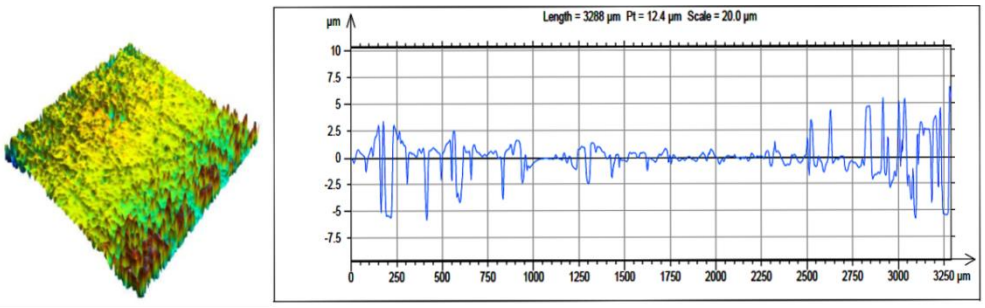
Fig. 3. Water droplet on polycaprolactone fibrous membrane



a) b)

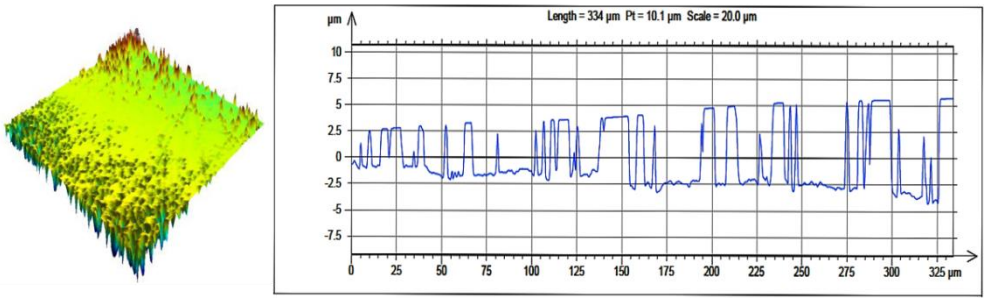
Fig. 4. a) and b) shows water droplet placed on PFDTES-modified polycaprolactone fibrous membrane

Surface profilometer top-view images (10 × 10 µm) and cross-section profiles of PFDTES-modified polycaprolactone fibrous membrane displayed in figure 4. The electrospun fibrous membranes showed high surface roughness due to the random deposition of the fibres on the collector end. As seen in figure 5 (a) and (b), the PFDTES-modified polycaprolactone fibrous membrane presented a high surface roughness, with root-mean-square (RMS) roughness value of 1.52 µm, 1.85 µm and figure 6, without PFDTES-modification roughness value is 0.82nm respectively.



a)

Fig. 5 a) PFDTES-modified polycaprolactone fibrous membrane with roughness value of 1.52 µm



b)

Fig. 5 b), PFDTES-modified polycaprolactone fibrous membrane with roughness value of 1.85 µm

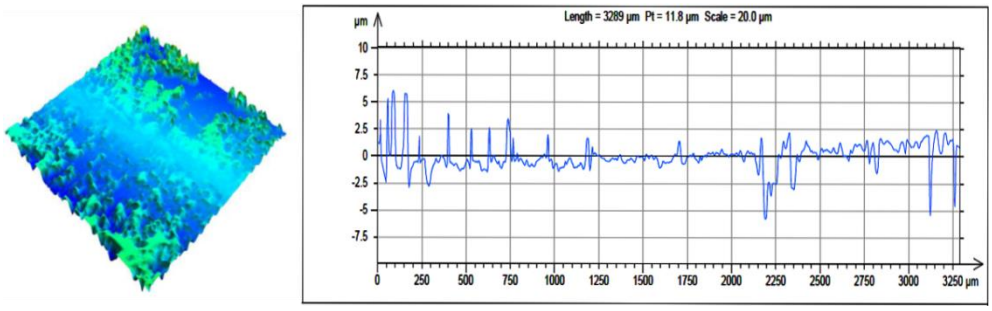


Fig. 6 Without PFDTES-modification roughness value is 0.82 nm

The durability of hydrophobicity nature for PFDTES-modified polycaprolactone fibrous membranes were studied and analyzed under ambient, low 10ºC and high temperature 110ºC conditions for 60 days respectively. It is concluded from the figure 7 that for all the temperature conditions the hydrophobicity nature for PFDTES-modified polycaprolactone fibrous membrane reduced only 7^0. Based on the above discussion, it is interpreted that the proposed electrospinning is the most beneficial in developing the superhydrophobic surface.

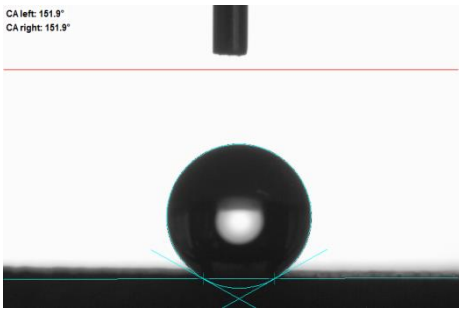


Fig. 7 Super- hydrophobic nature of PFDTES-modified polycaprolactone fibrous after durability test

4. Conclusions

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 fibres. The electrospun PFDTES-modified polycaprolactone fibrous showed a maximum water contact angle (WCA) of 154^0 due to increace in surface roughness when compare with the polycaprolactone fibrous roughness, which showed a maximum WCA of 81^0 and an average fiber diameter of 400-700 nm.

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