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Modification of silk surface by polymerization of fluoro-monomer in fluoro-surfactant solution

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Non-wettability is a renowned avenue for designing a vast array of smart and advanced materials. In this context, water-repellent surfaces have been prepared. Thin polymer coatings were successfully fabricated on silk surfaces through the admicellar polymerization technique by using fluoro-surfactant and 1*H*,1*H*,2*H*,2*H*-perfluorodecyl acrylate (PFDA monomer) system and potassium persulfate ($K_2S_2O_8$) as an initiator. The water-repellent properties induced to the treated surface were examined by analyzing the halting-time of the waterdrop on its surface and its contact angle values. The structural morphology of the fabricated surface was assessed by SEM (Scanning Electron Microscope) studies. FTIR (Fourier transform infrared) analysis was done to elucidate the structural changes of the surface after the surface modification. Results authenticated that a substantial degree of hydrophobicity has been imparted to the silk surface.

Keywords: Admicellar polymerization, contact angle, fluoro-surfactant, hydrophobicity, modified fabric.

Introduction

Textiles are polymeric materials that have been subjected to polymerization since the ancient time[1,2]. Polymerization can account for creating advanced fibers. It can also increase the performance aspect of silk fibers[3,4]. Recent studies revealed the enormous application of polymers having biodegradable properties[5]. Research showed that thin-film polymers, hydrogels, and polymer composites can be deployed as a support for the substrates, reagents, catalysts, enzymes, photosensitizers, supramolecular assembly, and drug delivery[5–9].

Silk, extracted from the cocoons of the silkworms, is a proteinaceous fiber in origin. The name 'queen' has been conferred on the silk fiber. Such naming is imputed to the exceptional traits it possesses – soft texture, gleaming aspect, easy-care, comfortable to be worn, and biodegradability. The polar groups (-OH, -COOH, and $-NH_2$) in silk, account for its hydrophilic structure, thereby, rendering it susceptible to bacterial and fungal attacks[10]. Silk fabric gets easily damaged by environmental factors – sunlight, grime, and detritus. Therefore, the main concern lies in fabricating the silk surfaces with water-resistant coatings to protect them from spattering and wetting. In the last decennary, there has been a gradual advancement in surface modification of silk textile by chemically bound polymers with the tailoring of the surface properties that have resulted in substantially improved intrinsic properties such as good mechanical property, increased hydrophobicity, favorable processability, and biocompatibility[11–13]. The hydrophobic property of the surface is greatly influenced by its chemical functional groups, physical geometry, and surface energy.

Many techniques such as dip coating[14], solution immersion[15], sol-gel coating[16–18], foam coating[17], etc. have been sizably used to coat the surface of silk fabric and render functional finishes by availing different agents (paraffin, silicones, fluorocarbons, and nanoparticles) which are impervious to water. Research exemplified that fluorocarbon agents intensified the oil and water-repellent properties and augmented the surface roughness by diminishing the surface energy[19]. Among the several methods available for modifying the surface properties of the fabric, solvent-based procedure employing alkyl or partially fluorinated alkyl compounds prevails the most[19,20]. Hydrophobicity can be procured by fabricating the silk surface by cladding it with fluorinated polymers[21]. Studies revealed that silk fabrics modified with SF_6 plasma amplified the hydrophobicity due to the replacement of H by F[22–25]. The hydrophobicity was enhanced by treating with atmospheric pressure plasma in an environment containing helium-fluorocarbon gases, He/1,3-butadiene, and He/dodecyl acrylate[26–28]. Research showed that hydrophobicity can be procured by plasma deposition of polytetrafluoroethylene (PTFE)[29]. The hydrophobicity gets enhanced and the surface energy gets diminished by escalating the quantity of fluorine-carbon bonds of the coated structure[25]. Active research has been conducted to deposit nano-coatings of ZnO, Cu, TiO_2, DLC, etc. on the silk surface to enhance the hydrophobicity[30–35].

Recently, an advanced technique of adsorption of surfactant molecules by the admicellar polymerization method has been deployed for creating a fine coating of a polymeric layer on the material. It's an effective and easy method of surfactant-assisted polymerization. By this process, in the aqueous medium, an ultra-thin film (dimension of 10 nm order) can be deposited on the silk surfaces[36] keeping its soft texture, breathability, and glossy appearance intact. CMC (critical micelle concentration) plays a prime role in surfactant aggregation in the admicellar polymerization technique. Lower the CMC, lower is the concentration, i.e. lesser is the surfactant necessary to be adsorbed at the solid/liquid interface. Thus, it lowers the overall cost of fabrication. Wu *et al.* (1987) followed this procedure to deposit an ultra-thin layer of polystyrene on alumina in sodium dodecyl sulfate (SDS) solution[37]. Essumi *et al.* (1989) employed surfmers to design a fine polymeric layer on alumina (having dimension 200 nm) through this method[38]. A fine coating on surfaces, like, polystyrene on alumina[39] and cotton[40], poly(methyl methacrylate) on alumina pigment[41], polypyrrole on mica[42] has been easily achieved by this technique. The simple procedure and economical aspect make the admicellar polymerizations advantageous.

Our main objective is to impart a hydrophobic coating on the silk fabric through a simple admicellar process by using a fluoro-monomer, fluoro-surfactant, and an initiator.

Materials and methods

Chemicals:

The fluoro-monomer used was 1*H*,1*H*,2*H*,2*H*-perfluorodecyl acrylate (PFDA). It was acquired from Sigma Aldrich. The fluoro-surfactant FS31 + NaCl was acquired from DuPont India. The potassium persulfate (initiator) used was bought from Merck.

Preparation of hydrophobic silk fabric by admicellar polymerization:

Pure silk was bought from a local shop. Silk was cut to a particular size (4.5×5.5 cm). It was immersed in a 10% NaOH solution for about 2 h.

Next, it was thoroughly rinsed. The silk was then air-dried. The admicellar polymerization technique was used to perform surface modification. The steps of admicellar polymerization are depicted in Fig. 1. Numerous sample compositions were examined by the trial and practice method. Here, we are discussing the composition that gave the best result: homo-polymerization of 0.5 mL of 8 mM PFDA solution on silk surface (4.5×5.5 cm) was executed in a 30 mL vial accommodating 20 mL solution of 0.5 mL FS31 + NaCl solution (at the CMC 2500 ppm) and pH 4 water. Next, it was

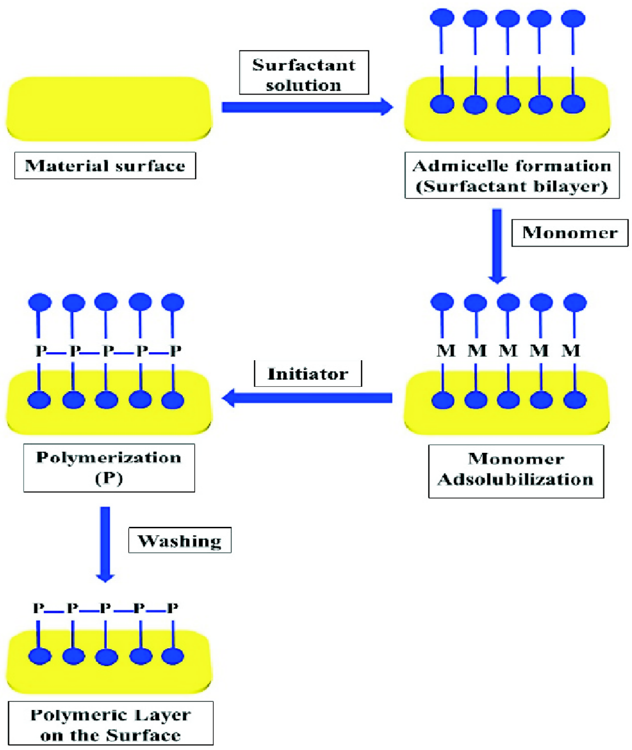


Fig. 1. Pictorial representation of ADPM.

positioned in the shaking water bath at 50°C for 1 h. Then initiator potassium persulfate (0.5 mL) was added to initiate the reaction. Next, it was positioned inside the shaking bath again, at 70°C for 1 h. Next, the vial was cooled and the silk was slowly taken out and rinsed thoroughly to eliminate the excess surfactant solution. The silk fabric was then kept in an oven at 70°C and dried completely.

Determination of hydrophobic (water-repellent) properties:

Waterdrop test:

The initial characterization carried out was the water-repellent test to appraise the hydrophobic film on the treated silk surface. The waterdrop test was effectuated by placing a small drop of 10 µL distilled water from a 20 µL syringe on the treated silk surface.

Water contact angle measurement:

The optical tensiometer (TL100 Theta) was used to calculate the water contact angle at 23°C by the sessile drop method. A micropipette having deionized water (surface tension 72.75 mN/m) was rested 2 cm above the silk surface. From it, a 20 µL drop was placed on the treated silk surface. Readings were taken at 5 mins interval and the mean value was noted by taking measurements at four different positions of the surface.

Surface characterizations:

Surface morphology study by scanning electron microscope (SEM):

Here, we have studied different surface morphologies of the modified and unmodified silk fabrics after drying in the oven. For this purpose, Scanning Electron Microscope (SEM) (Model No. Jeol JSM 5800) was used. Prior to scanning, the fabrics were gold-sputtered. SEM images revealed the surface micro/nanostructures.

Fourier transform infrared (FTIR) analysis:

ATR (attenuated total reflection) mode of Perkin-Elmer (L1600300 Spectrum two Lita S.N.96499) FTIR-ATR spectrometer was used to record the IR peaks of the unmodified and fabricated silk fabrics. The IR spectra were recorded in the range of 3500–500 cm^{-1} which revealed the functionalities of the surfaces.

Results and discussion

Hydrophobic (water-repellent) properties:

Our present study focuses on the process of designing hydrophobic film on the fabric surface using polymerizable fluoro-monomer (perfluorodecyl acrylate), initiator, and fluoro-surfactant. The monomer homo-polymerization is illustrated in Fig. 2. Waterdrop stay-time test, contact angle measurements were done to appraise the hydrophobicity engendered on the fabricated surface in contrast to the unmodified one.

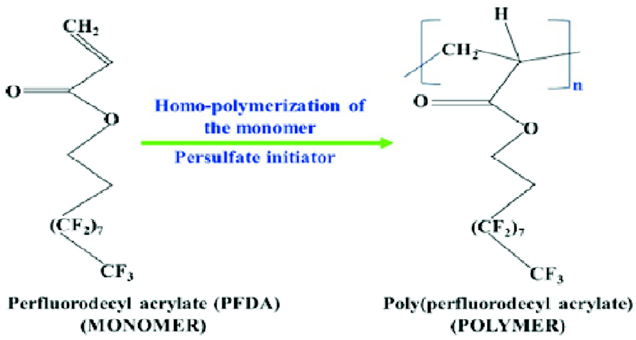
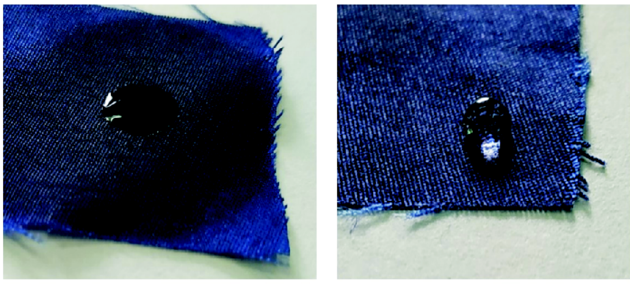


Fig. 2. Fabrication of poly(perfluorodecyl acrylate) on silk fabric surface by admicellar polymerization.

Wetting is the process of spreading of a liquid on a solid due to intermolecular interactions in between them. The admicellar-treated silk fabric was kept on a fixed base and drops of water were carefully added. The unmodified silk fabric absorbed the waterdrop completely (Fig. 3a), while, a perfectly spherical waterdrop was formed on the fabricated silk surface indicating the fine hydrophobic coat generated on it (Fig. 3b), which prevents the penetration of water or moisture through it. The wettability factor is contingent on the balance acting between the two forces – adhesive and cohesive forces. The wetting of the solid by the liquid results from the adhesive forces. While cohesive forces reduce the area of interaction, thereby, reducing the surface tension, thus, making the droplets spherical[43]. The measured contact angle is depicted in Fig. 4. For the untreated silk, the waterdrop got entirely absorbed within just 5 s. But the modified silk surface showed distinct and perfectly spherical waterdrop on its surface indicating a good hydrophobic coat-



(a) (b)

Fig. 3. (a) Waterdrop absorbed by the unmodified silk fabric and (b) perfectly spherical waterdrop resides on the modified silk fabric.

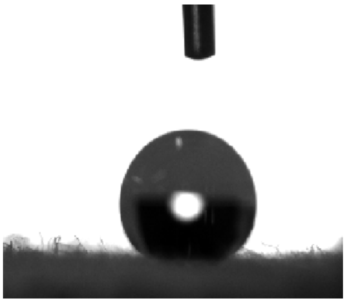
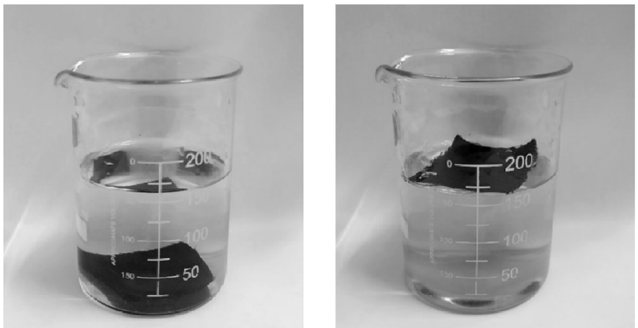


Fig. 4. Contact angle (129±2°) of modified silk fabric as measured by tensiometer.

ing formed on its surface. The gleaming surface beneath the waterdrop indicates that it might have mimicked fish-scale like appearance. Results also indicated that the untreated silk fabric is completely immersed into the water (Fig. 5a), while, the modified silk fabric floats freely (Fig. 5b). The shiny surfaces indicate that air has been trapped between the solid-liquid interface. The silk fabric retained its dryness even after being taken out of water. Following Young's equation,

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG} \cos \theta$$

(where γ_{SG} is the solid-gas surface tension, γ_{SL} is the solid-liquid surface tension, γ_{LG} is the liquid-gas surface tension, and θ is the water contact angle), the surface tension and contact angle are inversely related to each other. Therefore, low surface tension is inevitably the pre-requisite to achieve hydrophobicity. This confirms that the fluoro-polymerization has perfectly altered the silk surface.

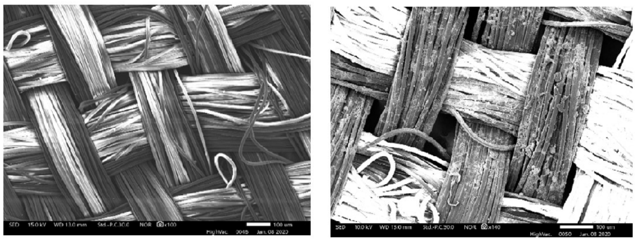


(a) (b)

Fig. 5. (a) Image of unmodified silk fabric immersed in water and (b) image of modified silk floating on the water surface.

Surface morphology study by Scanning Electron Microscope (SEM):

Hydrophobicity is greatly enhanced by fluoropolymers[43]. The higher electronegativity and greater bond strength of C-F than the C-H bond are responsible to lower the surface energy. As the roughness increases, the surface energy decreases, depicted by the SEM images in Fig. 6. The images show the stratified rough structure, rendering the hydrophobicity to the modified surface (Fig. 6). Different natural hydrophobic rough surfaces such as fish-scale, lotus leaf, lizard legs have inspired to design artificial surfaces. There exist trapped air spaces between the waterdrop and the rough surface. The state at which a liquid sit on the rough base



(a) (b)

Fig. 6. SEM images of silk fabrics. (a) Plain silk fabric before modification at high magnification and (b) silk fabric after admicellar-treatment on the surface at high magnification.

creating air pockets (that shines underneath each droplet, mimicking fish-scale like properties) between the surface and the liquid is given by the famous Cassie-Baxter equation,

$$\cos \theta_{CB} = r_f f \cos \theta_0 + f - 1$$

in which, θ_{CB} is the recorded contact angle (129±2°) and θ_0 is the inherent water contact angle (0°), f is the fraction of surface beneath the droplet, and r_f stands for the roughness factor. In the present study, we have designed a rough, fluoro-polymeric layer on the silk surface to increase its roughness (r_f) and hydrophobicity than the untreated wetted surface, as exhibited in Fig. 6.

The gleaming, transparency underneath the droplet symbolizes the voids filled with trapped air. Smaller the contiguity between the fabricated surface and the droplet, higher is its contact angle. The untreated silk surface bears an even appearance without any bumpy aggregation being formed on it, as exhibited in Fig. 6(a). A thin coating having significant roughness was achieved when the silk underwent admicellar polymerization and subsequent drying at 70°C. The SEM image in Fig. 6(b) shows several nano-scaled polymeric aggregations and bumpy appearances distributed uniformly on its surface. The hierarchical nano-scaled bumpy coated appearance on the silk surface engendered the roughness and hydrophobicity.

Fourier transform infrared (FTIR) analysis:

The FTIR spectra of the fabricated and untreated silk fabrics are illustrated in Fig. 7. The spectra exhibited minor changes, exemplifying that the polymerization process has not affected its internal bonding. The modified fabric showed a band at 1700 cm^{-1} and at 1250 cm^{-1} which are indicative of the C=O bond and C-O bond of the ester group. The modified silk showed a band at 1080 cm^{-1}, which is the characteristic of the C-F bond. Sourav *et al.* (2018) have evinced

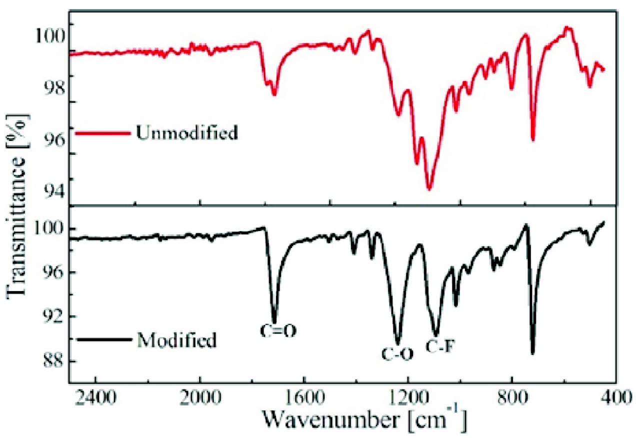


Fig. 7. FTIR spectra of unmodified and modified silk fabrics.

the C-F peak at 1010 cm^{-1} [44]. The unmodified silk spectrum is devoid of any C-F stretching band. The C-F stretching band in the modified fabric spectrum is indicative of a strong carbon-fluorine interaction between the silk and the fluoro-polymer. Thus, the treated fabric spectrum ensures that the fluoro-monomer homo-polymerization has enabled the attainment of the desired hydrophobicity and water-repellent property.

Conclusion

We have conveniently fabricated a hydrophobic silk surface by admicellar polymerization using a little quantity of fluoro-monomer. The 129±2° water contact angle justified the remarkable hydrophobic property created on its surface. SEM studies illustrated the roughness created by the admicellar-treatment of fluoro-monomer on the silk surface. The attachment of fluorine moiety has been affirmed by the FTIR studies.

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