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Enhancement of cotton hydrophobicity through modified styrene admicellar polymerization

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A novel modified admicellar polymerization (ADPM) technique has been proposed for achieving hydrophobicity on cotton fabrics by synthesizing an ultrathin layer of polystyrene on them. The effect of ethanol and methanol on styrene ADPM has been investigated and polymerization time is halved by using methanol at a concentration as low as 0.3 M. Evaluation of the hydrophobic effect is performed through drop tests, contact angle measurements and durability tests. Contact angle of water is as high as ~ 130° and water droplets are repelled for more than 30 min. ADPM delivers hydrophobicity which is comparable with commercially available water repellents based on stearic acid melamine resins. Characterization through SEM confirms the formation of ultrathin layers of polystyrene on cotton. Thus, the findings successfully exhibit a modified ADPM process as a potential water repellent finish affording conservation of time and chemicals.

Keywords: Admicellar polymerization, Contact angle, Cotton hydrophobicity, Polystyrene, Surfactants

1 Introduction

Admicellar polymerization (ADPM) is an innovative form of polymerization, wherein admicelles (surfactant bilayers)[1] are formed on the substrate surface. Accommodation of monomer and initiator entities within the admicelles leads to polymerization. Ultrathin layers of desired polymers can be efficiently formed on the surface without altering the intrinsic properties of the substrate. ADPM can also be described as a surface analogue of emulsion polymerization and is represented pictorially in Fig. 1[2,3]. ADPM can be explained sequentially with the help of the following four steps:

Step 1 – Formation of Admicelles on Substrate Surface

The first and the most important step of ADPM comprises the admicelle formation. When cotton is immersed in water, it attains a negative zeta potential[4] which attracts the hydrophilic part of the surfactant moieties. This leads to arrangement of the surfactants on the fabric surface with their hydrophilic head down and hydrophobic tail directing upward. A second layer of surfactant also starts getting formed on this, however, this time the hydrophobic tails get attracted to that of the first layer and the hydrophilic heads face the bulk of the solution. This whole entity is known as an admicelle and the concentration of the surfactant at which this occurs is known as the Critical Admicelle Concentration (CAC)[5], which needs to be maintained throughout the ADPM process.

Step 2 – Adsolubilization

The process of accommodation of monomers into the admicelles is known as "adsolubilization" or monomer adsolubilization. The hydrophobic nature of the monomers allows their arrangement in the space available in between the hydrophobic tails of the two layers of the surfactants facing each other in the admicelle. The monomer size and the nature of the functional groups present on it affect the process of adsolubilization[6,7]. Greater the size of the monomer more tedious is the adsolubilization. The greater the hydrophobicity of the monomer, smoother is the process of adsolubilization.

Step 3 – Polymerization

This step comprises the entry of the initiator molecules into the admicelles and their strategic positioning therein. Polymerization commences when conditions suitable for it become available viz. time, initiator, decomposition temperature, initiator concentration, etc. The mass transfer of monomers, from the bulk to the admicelles as and when they get consumed in the polymerization process, plays a crucial role in the overall polymerization process.[5]

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Step 4 – After Treatment

After completion of polymerization, the upper surfactant layer is washed off using water or other suitable solvent. Unreacted monomer is also removed in a similar manner.

ADPM has been widely used for achieving water repellency[8-14], stain resistance[15], flame retardancy[16-18], UV protection[6,19,20], anti-microbial effect[21,22], ozone resistance[23], etc. on various substrates. It can also be used to enhance dyeability by cationizing cotton[24] and to enhance conductivity of textile substrates[25,26]. Styrene, in the form of its polymer, has been instrumental in imparting hydrophobicity to textile substrates. Various methods like chemical graft co-polymerization[27], atom transfer radical polymerization[28], coating through use of nanocomposites[29], radiation induced grafting[30,31], drop coating[32], or the conventional pad-dry-cure method[33] have been investigated for attaining hydrophobicity on cotton.

The basic principle behind water repellency is to lower the surface energy of the fabric or fibre surface in such a way that the cohesive forces available in the water droplet remain higher than the adhesive forces between the fabric/fibre and the droplet. This causes the droplet to retain itself and prevents its spreading on the fabric/fibre. Polystyrene produces hydrophobicity by providing $–CH_2$, $–CH_3$ groups on the surface of cotton, thereby lowering its surface energy[34].

This paper reports the results of water repellency achieved on cotton fabric through ADPM of styrene. Solvents such as ethanol and methanol were used to bring about an appreciable decrease in the polymerization time. Hydrophobicity, thus attained, was evaluated using drop tests and contact angle measurements. Industrial competency of the finish was evaluated by comparison with water repellents currently existing in the market. Durability of the finish was investigated and the characterization of the ADPM treated fabric was done using SEM. Thus, a complete study of ADPM application on cotton was realized, resulting in a hydrophobic finish with sustainable use of time and chemicals.

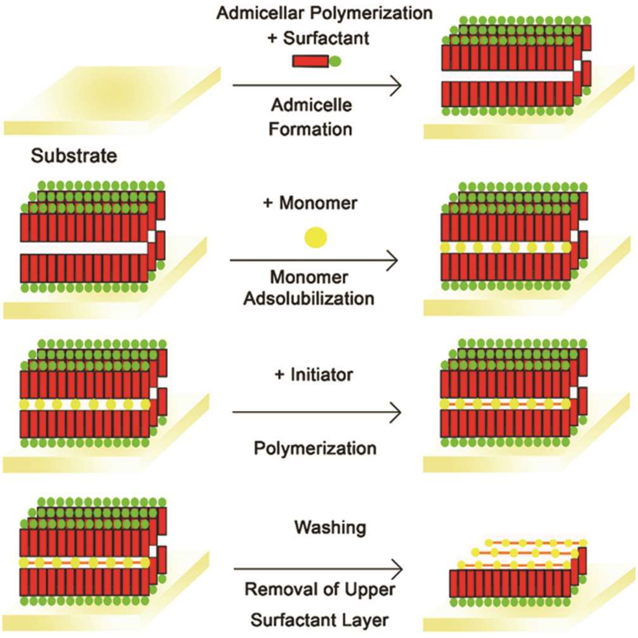

Fig. 1 — Pictorial representation of admicellar polymerization[2]

2 Materials and Methods

2.1 Materials

A plain weave, medium weight (105 GSM), ready for dyeing (RFD) cotton fabric was obtained from Piyush Syndicate, Mumbai, India. Styrene monomer (99.94 % purity) was provided by Accord Chemical Corporation, Mumbai. Sodium dodecylbenzene sulphonate (SDBS), sodium persulphate, sodium chloride, hydrochloric acid (conc.), and methanol, all of LR grade, were provided by S D Fine Chemicals, India. Distilled water was used for all the experiments. Table 1 shows a list of commercial water repellents procured from Huntsman International India Pvt. Ltd, Mumbai, India, along with their brief description.

2.2 Methods

2.2.1 *Admicellar Polymerization*

One mM of SDBS solution was taken along with 0.15 M NaCl and the *p*H was adjusted to 4 using 0.1 N HCl. Increasing concentrations of ethanol and methanol were added to this solution (Table 2). Five mM styrene was then added and cotton fabric was immersed. The contents were stirred continuously for varying times at 30 °C to suit the monomer adsolubilization process. Polymerization was brought about by adding 5 mM initiator ($Na_2S_2O_8$) and raising the temperature to 80 °C. The temperature was maintained for 2 h with continuous stirring. After completion of the polymerization process,

Table 1 — List of commercially available water repellent chemicals used in the current research work

Chemical	Based on	Padding bath concentration g/L
Oleophobol®CP-C	C6 fluorocarbon	20
Oleophobol®7713	C8 fluorocarbon	20
Phobotex®JVA	Dispersion of a fat modified melamine resin and paraffin	50
Phobotex®APK	Aluminium salt of paraffin dispersion	40
Phobotex®ZAN	Zirconium salt of paraffin dispersion	60

Table 2 — Experimental parameters of polymerization

Experiment No.	Ethanol, M	Methanol, M	Combined SA and MA (CSAMA)	Liquor ratio	Apparatus
1a	0.3	-	30 °C, 3 h	500	Glass
1b	0.5	-	30 °C, 3 h	500	Glass
1c	0.7	-	30 °C, 3 h	500	Glass
1d	0.7	-	30 °C, 4 h	500	Glass
2a	-	0.1	30 °C, 3 h	500	Glass
2b	-	0.2	30 °C, 3 h	500	Glass
2c	-	0.3	30 °C, 3 h	500	Glass
2d	-	0.5	30 °C, 3 h	500	Glass
2e	-	0.7	30 °C, 3 h	500	Glass
3	-	0.3	30 °C, 3 h	50	Stainless steel (SS-316)

SA – Surfactant adsorption, MA – Monomer adsolubilization.

the fabric was taken out, thoroughly washed with distilled water to facilitate removal of the upper layer of surfactant and then washed with ethanol to remove unreacted styrene. The fabric was then washed again and dried in an oven at 60 °C. Figure 2 (a) depicts the schematic diagram of ADPM experimental set up involving glass apparatus while Fig 2 (b) shows a stainless steel SS-316 plate – cotton fabric – horizontal water shaker bath combination for lower liquor ratio ADPM experiments. The horizontal water shaker bath was filled with water to a certain depth which acted as a heating medium for the polymerization process and a reciprocating motion was provided to the steel plate kept inside it which substituted for the stirring motion provided in the former ADPM experiments.

2.2.2 Weight Add-on Testing

The weight add-on of polymer was calculated by using the formula:

$$\text{Weight add} - on = \left(\frac{Wf-}{Wi}\right) \times 100$$

where Wf and Wi are the weights of the fabric after and before ADPM.

2.2.3 Drop Test

All the hydrophobic fabrics were subjected to a drop test, wherein they were held in a tout condition using an embroidery loop and a 3 μL drop of distilled water was placed on them using a micropipette. Time was noted down for the complete absorption of this water droplet.

2.2.4 Measurement of Contact Angle

Using a Goniometer (Ramé-Hart CA 190-F2), static contact angles of water on the hydrophobic fabric were measured. The amount of distilled water used to form the water droplet was 3μL. Contact angles were measured 1 min after the water droplet was placed on the fabric.

2.2.5 Tensile Strength Testing

The ADPM treated fabric was tested as per Breaking Force and Elongation Grab Test ASTM D 5034, 2001. The machine used for this purpose was Universal Tensile Machine (Tinius Olsen HT400, USA).

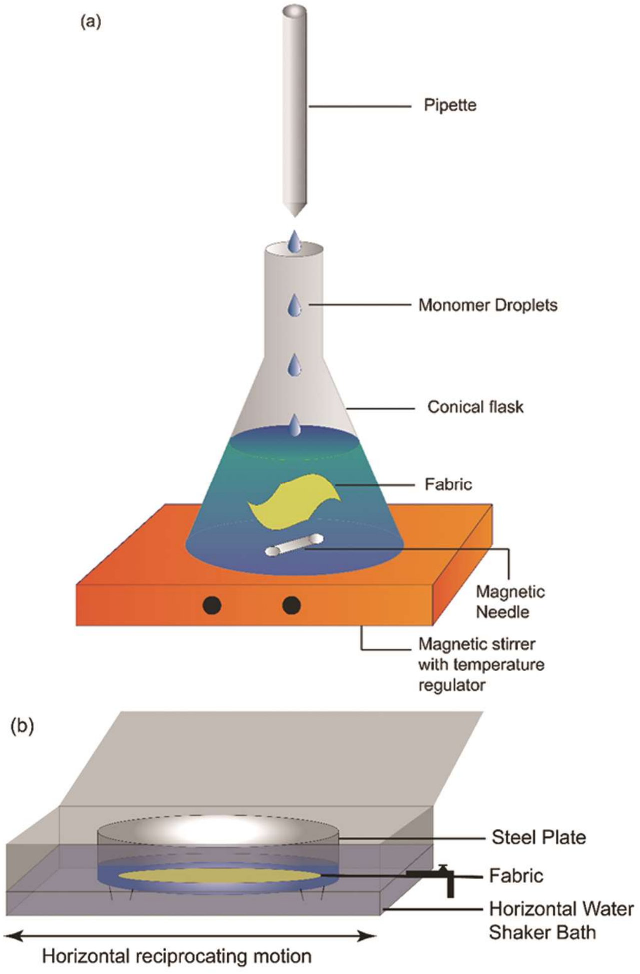

Fig. 2 — Experimental setup for admicellar polymerization (a) MLR 1:500 and (b) MLR 1:50

2.2.6 Durability of Finish Testing

Durability in Water

Treated cotton fabric (5 × 4 cm) was added to 50 mL distilled water and washed for 10 min in a Rota

Dyer machine (R B Electronic and Engineering Pvt Ltd, Mumbai). The washed fabric was kept in an oven at 60 °C. The cycle of washing and drying was repeated 8 times. Another 5 × 4 cm treated cotton fabric was washed with distilled water in the Rota Dyer continuously for 3 h. Pieces of the treated cotton fabric were placed in 200 mL boiling distilled water for 5, 10, 15, 20, 25 and 30 min each and dried in air later.

Durability in Hard Water and Resistance to Dry Heat

Hard water concentrate was prepared as per AATCC 162. One mL of hard water concentrate was diluted to 50 ml using distilled water to get a solution containing 150 ppm Ca^{2+} and 100 ppm Mg^{2+}. ADPM treated cotton fabric (5 × 4 cm) was added to this solution and agitated in the Rota Dyer for 10 min. ADPM treated cotton fabric was also subjected to dry heat of 160 °C for 3 min to study resistance to dry heat.

2.2.7 Comparison with Commercially available Water Repellent Chemicals

The concentrations of the commercially available water repellency chemicals used for application are given in Table 1. Padding with one dip-one nip method was used with 60 % expression. Fabrics were dried at 110 °C for 2 min and then cured at 150 °C for 3 min.

2.2.8 Characterization through SEM

SEM images were obtained for the untreated and ADPM treated fabrics (methanol 0.3 M). The machine used for SEM was Philips XL 30 SEM. Moisture was removed from the fabric by exposing it to infrared radiation for 5 min. The samples were then mounted on an aluminium stub with the help of an adhesive carbon tape and coated with gold, a process commonly known as sputtering. Accelerating voltage of 10 kV was used and the magnification was × 1500.

3 Results and Discussion

The ADPM experimental parameters are provided in Table 2. One mM is the critical admicelle concentration for SDBS[8]. During the ADPM experiments, it is observed that styrene monomer requires atleast 5 h to get solubilized in the aqueous surfactant solutions and further 3 h are required for their adsolubilization in the admicelles. Enhancing the solubilization of styrene in aqueous solutions is one of the methods to bring down the process time of SDBS-Styrene-Cotton ADPM. Hence, alcohols are used, as they have proven efficiency in solubilizing organic molecules.

3.1 Ethanol Experiments

An increase in concentration of ethanol from 0.3 M to 0.7 M simultaneously improves the hydrophobicity on the cotton fabric (Table 3). In presence of 0.3 M ethanol, water droplets are absorbed instantaneously by the cotton fabric. As the concentration of ethanol is increased to 0.5 M and then 0.7 M, resistance to water droplets upto 10 s and 4 min is achieved respectively. Hence, in the next set of experiments, the concentration of ethanol is kept at 0.7 M and the adsolubilization time is increased. However, an increase in adsolubilization time decreases the hydrophobicity of the fabric and instead of 4 min, water droplets could be repelled for only 2 min. Also, even though process time is brought down by ethanol, the finish produced by ethanol is found uneven.

3.2 Methanol Experiments

The concentration range of methanol used in ADPM experiments is 0.1 – 0.7 M. As concluded from the ethanol experiments, the adsolubilization time is maintained at 3 h. For methanol concentrations of 0.1 M and 0.2 M, styrene remains insoluble in the reaction bath. At 0.3 M methanol, styrene dissolves within an hour and uniform hydrophobicity is realized. In this case, water droplets could be repelled uniformly throughout the treated fabric for 30 min. Unevenness is observed when the concentration of methanol is increased to 0.5 M and 0.7 M. At some places on the treated fabric, the water droplets are repelled for 2 min and at other places they are repelled for more than 35 min. Thus, it is concluded that the optimum methanol concentration for SDBS-Styrene-Cotton ADPM is 0.3 M and the optimum adsolubilization time is 3 h.

3.3 Lower Liquor Ratio Experiments

For experiments 1a – 1d and 2a – 2e (Table 2), glass apparatus is used and material–to–liquor ratio (MLR) is 1:500. Since textile industry is water

Table 3 — Hydrophobicity results of admicellar treated fabrics

Experiment No.	Drop test results	Contact angle, deg
1a	0	-
1b	10 s (Uneven finish)	-
1c	4 min (Uneven finish)	135.4
1d	2 min (Uneven finish)	111.5
2a	0	-
2b	0	-
2c	= 30 min	113.8
2d	Uneven finish[a]	-
2e	1 min (Uneven finish)	-
3	> 30 min	131.1

[a] In this case, water was repelled for 2 min at some places and at others it was repelled for > 35 min.

intensive in nature, our next step is to reduce water consumption during ADPM which could be brought about by a decrease in the MLR. It is necessary to change the MOC (material of construction) of the apparatus to facilitate the aforementioned step. There have been several reports of ADPM being carried out on glass (alone or in combination with isoprene) using SDBS[35-39]. This proves that SDBS is capable of forming admicelles on the surface of the glass apparatus. On the contrary, SDBS cannot form any micelles on SS-316 at concentrations < 2mM[40]. In our ADPM experiments, SDBS concentration is maintained at 1 mM, hence the MOC of the apparatus is changed from glass to SS-316 which results in remarkable improvements in the hydrophobicity obtained on the fabrics. The contact angle of water increases from 113.8° to 131.1° when steel (SS-316) apparatus is utilized without any alteration in the other polymerization parameters. Also, the MLR now reduces to 1:50 which used to be 1:500 in the earlier experiments. Thus, prevention of a competing substrate enhances the efficiency of ADPM on cotton by increase in hydrophobicity and decrease in water usage.

3.4 Comparison of Contact Angles of Water attained with ADPM

Figure 3 illustrates the contact angles of water achieved for Experiment No. 2c and 3. Contact angles of water for admicellar treated fabrics have been tabulated in Table 3. Thus, the contact angle for ADPM treated cotton fabrics increases from 113.8° to 131.1° due to the use of SS-316 apparatus.

3.5 Performance Testing of ADPM Treated Fabric

After the initial success of forming ultrathin hydrophobic layers on cotton fabric, it is necessary to evaluate its performance as a daily use garment. The average weight add-on for the ADPM treated fabrics is found to be only 0.2%. Thus, with a negligible addition to the weight of the fabric, its functionality is improved radically. ADPM can hence provide water repellent breathable fabric because the ultrathin layers formed on cotton are feather light and do not block the pores of the fabric. The durability of the ADPM finish is tested against laundering treatments too. It is observed that the treated fabric could withstand more than 8 wash and dry cycles. Even when the fabric is washed continuously for more than 3 h, there is no adverse effect on its hydrophobicity. The water repellency remains unaffected in boiling water for up to 25 min. The ADPM fabric could resist dry heat of 160 °C for upto 3 min. Water repellency of the treated fabric continues to remain intact even after treatment of hard water. Mechanical strength testing shows that the tensile strength of the fabric decreases by 37% after ADPM treatment, however, the % elongation is increased by 17%. The increase in % elongation supports our earlier results that ADPM does not add stiffness to the treated cotton fabrics and continues to maintain its comfort properties.

3.6 Comparison of Water Repellency of ADPM Treated and Commercial Sample

The water repellent chemicals prevalent in the market are based on:

- Paraffin
- Stearic acid melamine
- Silicones
- Fluorochemicals

Paraffin based water repellents are one of the earliest types of water repellents and are marketed as emulsions of aluminium or zirconium salts of fatty acids. The metal salt attaches itself to the polar surfaces of cotton and the hydrophobic alkane chain protrudes outwards, thus providing water repellency to the fabric. However, the water repellency provided by them is less durable to laundering and dry cleaning. They decrease the air and vapour permeability of the treated fabric. Also, presence of paraffin adds to the flammability of fabric.

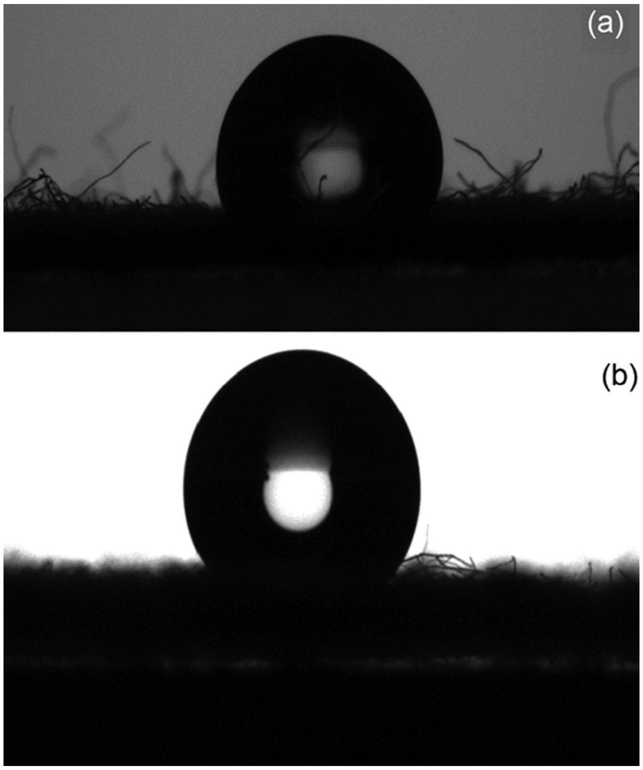

Fig. 3 — Contact angle of water for admicellar treated sample using methanol with (a) MLR 1:500 and (b) MLR 1:50

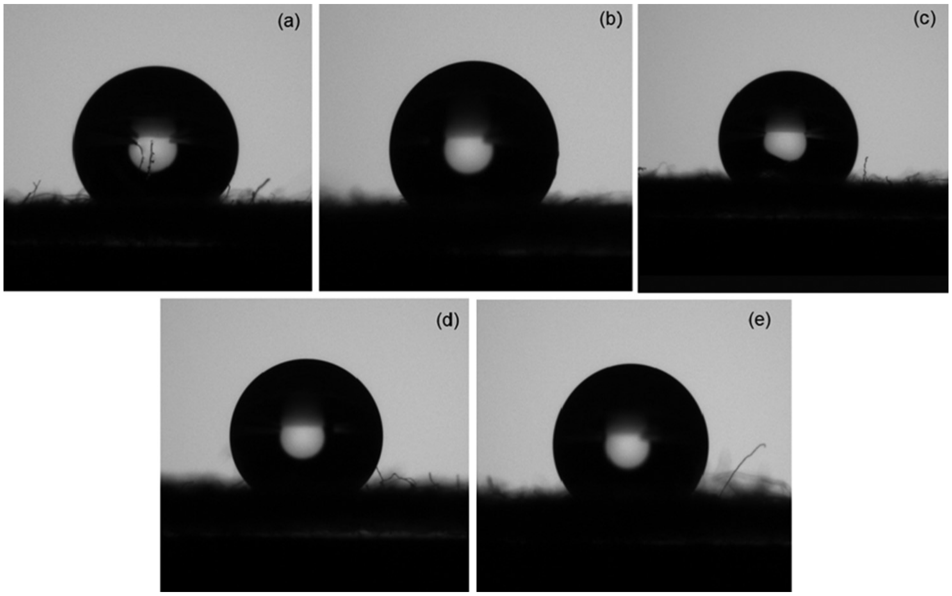

Fig. 4 — Contact angles of water (a) C6 fluorocarbon chemistry, (b) C8 fluorocarbon chemistry, (c) fat modified melamine resin and paraffin dispersion, (d) aluminium salt of paraffin dispersion and (e) zirconium salt of paraffin dispersion

Water repellency of stearic –acid melamine based products is due to the presence of N-methylol groups. These chemicals face the drawback of release of formaldehyde during the use of the fabric.

Silicone based water repellents are required in low amounts during application and provide a soft handle to the treated fabric. Water repellency from silicones has moderate durability to laundering and the residual baths from silicon application industries are known to be toxic for aquatic life.[41]

Fluorochemicals have currently captured the water repellent textile market due to the high water repellency offered by them. They comprise long carbon chains carrying $–CF_3$ or $–CF_2$ groups. Initially they are based on C8 chemistry, which implies that the alkane chain carrying the fluorogroups has 8 carbon atoms. However, it is soon realized that C8 fluorocarbon chains break down in the environment to produce perfluroalkyl ocatnoic acid (PFOA) and perflurooctyl sulphonate (PFOS) which are bio persistent and bio accumulative in nature. Therefore, the chain is reduced to 6 carbon atoms (C6 fluorochemistry) which makes biological break down of the fluorocarbons a bit easier. Nevertheless, the increasing amount of fluorocarbons in human environment continues to remain a cause of concern for the conservationists[42].

On the other hand, water repellency achieved through combination of ADPM and polystyrene has no known environmental hazards. It makes use of easily available surfactants and chemicals and does not contribute to the flammability of the fabric.

Table 4 — Comparison of performance of admicellar treated fabrics with commercial water repellent treated fabric

Parameter	Contact angle of water, deg	AATCC 22 spray test
Experiment 1 (ADPM 4 days process)	132.8	-
Experiment 2 (ADPM 10 h process)	124.7	-
Experiment 4c (ADPM, Methanol 5 h process LR = 50)	131.1	50
C 8 Fluorocarbon chemistry	133.6	70
C 6 Fluorocarbon chemistry	148.5	90
Aluminium salts of paraffin dispersion	137.5	90
Zirconium salts of paraffin dispersion	131.6	100
Stearic acid melamine resin and paraffin dispersion	131.3	50

We tested the performance of our ADPM treated fabrics with the aforementioned water repellent chemicals through measurement of the respective contact angles of water and AATCC 22 spray test ratings. Observations reveal that the contact angles of water for ADPM fabrics are comparable with zirconium salts of paraffin dispersion, stearic acid melamine resin and C8 fluorocarbon chemistry. In spray ratings also, the performance of ADPM treated fabrics is found at par with stearic acid melamine resins. The overall best performance is achieved by C6 fluorocarbon chemistry. Detailed results provided in Table 4 and Fig. 4 depict contact angle of water images for all the commercially available finishes.

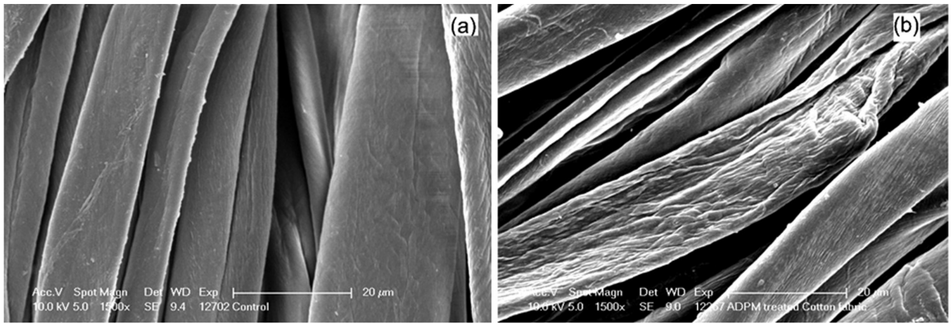

Fig. 5 — SEM images of (a) untreated cotton and (b) admicellar treated cotton

3.7 Characterization of ADPM Treated Cotton Fabric

Figure 5 depicts the SEM images of untreated and ADPM treated cotton fibres (0.3 M methanol). Smooth surfaces of untreated cotton fibres are clearly visible in Fig.5 (a), whereas a distinct coating of polystyrene can be seen on the ADPM treated fibres in the form of ridges [Fig.5 (b)].

4 Conclusion

The findings show that ADPM is a novel technique for achieving water repellency on cotton and possesses immense potential for industrial applications. Long polymerization times reported in literature are brought down to half of their values by using ethanol and methanol. Methanol, at a concentration as low as 0.3 M is found instrumental in providing a uniform finish in reduced time. Stainless steel proves to be a better material of construction for the equipment rather than glass for ADPM experiments involving polystyrene. Characterization of the hydrophobic cotton is done through SEM, indicating distinct ultrathin layers of polystyrene on cotton. Drop tests and contact angle measurements are used to measure the efficiency of hydrophobicity achieved on the cotton fabrics. Strength of the fabric is tested after polymerization and the durability of the hydrophobic finish is tested to various agents. The performance of ADPM fabrics is comparable with commercially available water repellents based on zirconium salts of paraffin dispersion, stearic acid melamine resin and C8 fluorocarbon chemistry. ADPM treated fabrics find wide usage in hospitality industry where they can be used as table cloths. Breathable water repellent trousers and shirts can also be manufactured using ADPM cotton fabrics, as the ADPM finish doesn't add to the weight of the fabric and doesn't alter the porosity of the same. Thus, ADPM can be fruitfully used for achieving high quality and light weight water repellent cotton fabrics.

References

1 Harwell J H, Hoskins J C, Schecter R S & Wade W H, *Langmuir*, 1 (1985) 251.
2 Ulman K N & Shukla S R, *Adv Polym Tech*, 35 (2016) 307.
3 O'Haver J, Grady B P, Harwell J H & O'Rear E A, in *Reactions and Synthesis in Surfactant Systems*, edited by J Texter (Surfactant Science Series 100, Marcel Dekker, New York), 2001, 537.
4 King D, in *Cotton: Science and Technology*, edited by S Gordon & Y-L Hsieh (Woodhead Publishing, Cambridge) 2007, 355.
5 Wu J, Harwell J H & O'Rear E A, *J Phys Chem*, 91 (1987) 623.
6 Tragoonwichian S, O'Rear E A & Yanumet N, *J Appl Polym Sci*, 108 (2008) 4004.
7 Tragoonwichian S, Kothary P, Siriviriyanun A, O'Rear E A & Yanumet N, *Colloids Surf A*, 384 (2011) 381.
8 Pongprayoon T, Yanumet N & O'Rear E A, *J Colloid Interface Sci*, 249 (2002) 227.
9 Pongprayoon T, O'Rear E A, Yanumet N & Yuan W-L, *Langmuir*, 19 (2003) 3770.
10 Metachan B, Pongprayoon T, Yanumet N & O'Rear E A, *AATCC Rev*, 2 (8) (2002) 60.
11 Pongprayoon T, Yanumet N, O'Rear E A, Alvarez W & Resasco D, *J Colloid Interface Sci*, 281 (2005) 307.
12 Boufi S & Gandini A, *Cellulose*, 8 (2002) 303.
13 Maity J, Kothary P, O'Rear E A & Jacob C, *Ind Eng Chem Res*, 49 (2010) 6075.
14 Kothary P, Yanumet N & O'Rear E A, *Fiber Polym*, 14 (2013) 710.
15 Hanumansetty S, Maity J, Foster R & O'Rear E A, *App Sci*, 2 (2012) 192.
16 Siriviriyanun A, O'Rear E A & N. Yanumet N, *J Appl Polym Sci*, 109 (2008) 3859.
17 Siriviriyanun A, O'Rear E A & Yanumet N, *Cellulose* 15 (2008) 731.
18 Siriviriyanun A, O'Rear E A & Yanumet N, *Polym Degrad Stab*, 94 (2009) 558.
19 Tragoonwichian S, O'Rear E A & Yanumet N, *Colloids Surf A*, 329 (2008) 87.
20 Tragoonwichian S, O'Rear E A & Yanumet N, *Colloids Surf A*, 349 (2009) 170.
21 Ren X, Kou L, Kocer H, Zhu C, Worley S, Broughton R & Huang T, *Colloids Surf A*, 317 (2008) 711.
22 Ren X, Kou L, Kocer H, Worley S, Broughton R, Tzou Y & Huang T, *J Biomed Mater Res Part B Appl Biomater*, 89B (2009) 475.

23 Pongpilaipruet A & Magaraphan R, *Mater Chem Phys*, 160 (2015) 194.

24 Pisuntornsug C, Yanumet N & O'Rear E A, *Color Technol*, 118 (2002) 64.

25 Lekpittaya P, Yanumet N, Grady B & O'Rear E A, *J Appl Polym Sci*, 92 (2004) 2629.

26 Yang H & Wang L, *Adv Mater Res*, 113-116 (2010) 2030.

27 Shukla S R & Athalye A R, *Polymer*, 33 (1992) 3729.

28 Hutchings L R, Narrianen A P, Thompson R L, Clarke N & Ansari I, *Polym Int*, 57 (2008) 163.

29 Qing Y, Zheng Y, Hu C, Wang Y, He Y, Gong Y & Mo Q, *Appl Surf Sci*, 285B (2013) 583.

30 El Salmawi K, El Naggar A M & Attia S E, *Polym Int*, 44 (1997) 181.

31 Zohdy M H, Sahar S M, Hassan M S, Khalil E M, El-Hossamy M & El-Naggar A M, *Polym Int*,48 (1999) 515-525.

32 Zhang M, Wang C, Wang S & Li J, *Carbohydr Polym*, 97 (2013) 59.

33 Zhao T, Zheng J & Sun G, *Carbohydr Polym*, 89 (2012) 193.

34 Holme I, in *Textile Finishing*, edited by D Heywood (Society of Dyers and Colorists, Bradford), 2003, 135.

35 Grady B P, O'Rear E A, Penn L & Pedicini A, *Polym Compos*, 19 (1998) 579.

36 Barraza H, Hwa M, Blakley K, O'Rear E A & Grady B P, *Langmuir*, 17 (2001) 5288.

37 Barazza H, Olivero K, Hamidi Y, O'Rear E A & Altan M, *Compos Interfaces*, 9 (2002) 477.

38 Barazza H, Aktas L, Hamidi Y, Long J, O'Rear E A & Altan M, *J Adhes Sci Technol*, 17 (2003) 217.

39 Blakley K, Grady B P & O'Rear E A, *Polym Compos*, 25 (2004) 82.

40 Zhang J & Meng Y, *Tribol Lett*, 56 (2014) 543.

41 Schindler W & Hauser P, *Chemical Finishing of Textiles* (Woodhead Publishing Ltd, Cambridge, England), 2004.

42 http://www.europeanoutdoorgroup.com/files/DWR-Study_Alice_Davies__digital_.pdf (accessed on 10th April 2017).