

# Development of free fluorine and formaldehyde oil and water repellent finishes for cotton fabrics through polymerization of bio-based stearic acid with carboxylic acids

DOI: 10.35530/IT.071.02.1731

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## ABSTRACT – REZUMAT

### Development of free fluorine and formaldehyde oil and water repellent finishes for cotton fabrics through polymerization of bio-based stearic acid with carboxylic acids

*This research is an attempt to develop nontoxic and sustainable oil and water repellent which is fluorine and formaldehyde free. For this purpose, stearic acid was polymerized with formaldehyde free cross-linkers, such as maleic acid and acrylic acid. Sodium hypophosphite was used as a catalyst and triethanolamine as an enhancer during the polymerization. Polymerization conditions were optimized such as temperature, time and atmosphere. The prepared recipes were then applied onto the cotton fabrics. The obtained results reveal that the finished cotton fabrics achieves good oil and water repellency, crease resistance, soil resistance, and antimicrobial properties. In addition, the surface of finished cotton fabrics was characterized via SEM, EDX, FTIR, XRD, and TGA.*

**Keywords:** oil and water repellency, maleic acid, acrylic acid, functional textile, eco-friendly.

### Dezvoltarea de finisări oleofobe și hidrofobe fără fluor și formaldehidă prin polimerizarea acidului stearic bio cu acizi carboxilici pentru țesături din bumbac

*Acest studiu este o încercare de obținere a finisărilor hidrofobe și oleofobe non-toxice și durabile, care nu conțin fluor și formaldehidă. În acest scop, acidul stearic a fost polimerizat cu agenți de reticulare fără formaldehidă, precum acid maleic și acid acrilic. Hipofosfitul de sodiu a fost utilizat în calitate de catalizator, iar trietanolamina ca agent de intensificare în timpul polimerizării. Condițiile de polimerizare au fost optimizate, din punctul de vedere al temperaturii, duratei și atmosferei. Rețetele preparate au fost apoi aplicate pe țesături din bumbac. Rezultatele au arătat faptul că țesăturile din bumbac finisate sunt hidrofobe și oleofobe, prezintă rezistență la șifonare, rezistență la murdărie și proprietăți antimicrobiene. În plus, suprafețele țesăturilor din bumbac finisate au fost caracterizate utilizând SEM, EDX, FTIR, XRD și TGA.*

**Cuvinte-cheie:** hidrofob și oleofob, acid maleic, acid acrilic, material textil funcțional, ecologic

## INTRODUCTION

Cotton is one of the most abundantly available fibrous biomass materials and has been extensively used in many textile areas, as it exhibits various attractive properties [1] such as hydrophilicity, wearing comfort, breathability [2] and good mechanical strength [3]. However, it lacks oil and water repellency. To meet the demand of customers several chemical finishes are available in the market. These chemical finishes can impart function properties to the cotton fabric such as flame retardancy [4–5], ultraviolet protection [6], antibacterial activity [7], corrosion inhibition, crease recovery [8], self-cleaning properties [9], as well as water and oil repellency [10]. In order to make cotton fabric oil and water repellent its surface energy should be lowered by application of chemical finishes such as silicone repellents [11], fluorocarbon-based repellents [12], paraffin repellents [13] and polyurethanes-based repellents [14]. Most of these finishes are either expensive, noxious, non-durable or less efficient.

Among them, fluorocarbon finishes based on C8 chemistry are most attractive as they significantly lower the surface energy of the cotton fabric ( $\leq 18$  dynes/cm) to impart excellent oil and water repellency [15]. However, due to their adverse effect on the environment and potential toxic effect on human, there is an urgent need for fluorine-free oil and water repellent alternative. Moreover, C8 based perfluorinated and polyfluorinated chemicals (PFCs) are part of 11 priority chemicals that are banned to use internationally in the textile and leather process industry [16].

Nowadays, emergent research is focused on non-fluorine, eco-friendly oleophobic and hydrophobic finishes. An alternative to fluorinated compounds is long alkyl chain compounds [17]. Use of stearic acid to impart hydrophobicity has been reported in the literature. Stearic acid is an ecological, long-chain fatty acid which is used as a water repellent finish. Despite this, it lacks durability as well as higher concentration is required for effective results. In addition, it only repels water but not oil. Stearic acid is also used to

impart hydrophobicity to cotton and non-cotton fabric as reported in literature. Cotton fabric can be made more hydrophobic by treating it with titanium dioxide [18], silica nanoparticles [19], and zinc hydroxide [20] followed by dipping in stearic acid solution. However, the washing durability of the coating was not good. Hydrophobicity of non-cotton fabric such as jute fibers [21] and polyester fabric [22], can also be increased by stearic acid modification process. However, the researchers did not present the durability of coating in terms of washing. Hydrophilic behavior of recycled jute fiber treated with TiO<sub>2</sub> solutions has been shifted to hydrophobic by immersing it in stearic acid solution. There was also increase in the contact angle of the treated fabric [23]. However, stearic acid is nondurable and exhibit only water repellency.

To enhance the functional properties, durability and performance of cotton, different techniques have been introduced. Crosslinking of cellulose, with certain compounds through a chemical reaction to bridge cellulose chain for effective performance and durability is one of them [24]. Depending on chemical structure, crosslinkers are further classified as formaldehyde-based and formaldehyde-free crosslinkers. Formaldehyde-based crosslinkers dominated in past as they provide outstanding wrinkle resistance at low price but on the other hand, they reduce fabric strength, increases stiffness and release formaldehyde which is a lethal compound for human as it is now declared as confirmed carcinogenic [25]. Therefore, formaldehyde-free cross-linkers like polycarboxylic acids (PCAs) are getting more popular as they can increase washing durability and wrinkle resistance of cotton fabric without involving formaldehyde [26]. The reaction mechanism of crosslinking of PCAs with cotton is carried out in two steps: dehydration of two adjacent carboxyl groups forms cyclic anhydride, and then esterification reaction takes place between cellulose and intermediate anhydride to form ester bond [27–28].

Among all effective PCAs, BTCA is one of the most effective crosslinkers for cotton but it causes considerable damage to mechanical properties of cotton fabric and it is very expensive [29]. Citric acid is a bio-based cross-linker and it has been reported to crosslink cotton fabric [30] but its application is inhibited due to its yellowing effect [31]. Therefore, the use of cost-effective polycarboxylic acids such as maleic acid (dicarboxylic acid) [32] and monocarboxylic acid such as acrylic acid has also been reported in the literature [33]. However, carboxylic acid does not impart any oil and water repellency on their own.

Therefore, in this research stearic acid was polymerized with maleic acid and acrylic acid, in the presence of catalyst SHP and triethanolamine TEA under various polymerization conditions, temperature and time. The newly developed finish recipes were applied onto the cotton fabric and treated fabric performance were also assessed.

## EXPERIMENTAL SECTION

### Materials

Scoured, bleached and 100% pure cotton fabric was used without any other finishing processes. Lab grade stearic acid (SA), maleic acid (MA), acrylic acid (AA), sodium hypophosphite monohydrate (SHP), triethanolamine (TEA) and Isopropyl alcohol (IPA) were purchased from Sigma Aldrich. Lab grade distilled water was used as a solvent. All chemicals were used directly without any further purification.

### Chemical and fabric preparation

The polymerization reaction was carried out in a temperature and time-controlled polymerization reactor coupled with a stirrer and vacuum pump. A measured amount of fluorine-free water repellent monomer; stearic acid along with non-toxic and formaldehyde-free crosslinker such as maleic acid and acrylic acid in the presence of catalyst SHP and enhancer TEA were fed to the polymerization reactor. Optimization of the operation parameter was carried out. Finally, the reaction was carried out at optimum condition of 160°C for 3 hours in vacuum conditions for maleic acid and at 200°C for 2 hours for acrylic acid. The obtained recipes were diluted with Isopropyl alcohol and water in two different beakers. The pad-dry-cure method was used to apply finishes onto the fabric. Two roll laboratory padder with 70% pick up was used to apply the recipe onto the fabric. After that, cotton fabric was dried at 100°C for 180 seconds and cured at 180°C for 120 seconds. Prior to any testing, conditioning of all test sample was carried out for 24 hours at 20 ± 5°C and 65% of relative humidity.

### Evaluation of fabric properties

AATCC and ISO test standard methods were used to evaluate the easy-care properties of the treated fabric. For water repellency, AATCC Test Method 193 and AATCC Test Method 22 was used. For oil repellency, AATCC Test Method 118 was employed. To find the crease recovery angle and soil resistance of treated fabric, AATCC Test Method 66-2003 and AATCC Test Method 130 were used respectively. AATCC Test Method 147 was used to investigate the antibacterial properties of the fabric. British Standard BS EN ISO 13934-1 and British Standard BS EN ISO 4674 were used to determining tensile strength and tear strength of coated fabric respectively. To probe air permeability and shrinkage of treated fabric, British Standard BS EN ISO 9237 and AATCC Test Method 135 were performed respectively. The durability of the coating was inspected by washing method ISO 105-C10:2006.

## CHARACTERIZATION TO VALIDATE THE RESULTS

### Contact angle

DSA 30 was used to find wet contact angle (WCA) of modified and un-modified cotton fabric. A camera was attached with a computer interface to capture

and assess the shape and contact angle of drop placed on the fabric. The contact angle of control fabric and the treated fabric was measured.

### FTIR analysis

FTIR spectroscopy technique was employed to determine the degree of ester crosslinking between cellulose/stearic acid/maleic acid and cellulose/stearic acid/acrylic acid. FTIR spectrum was recorded with a scan range of 500–2500 cm<sup>-1</sup> and a resolution of 4 cm<sup>-1</sup>.

### Thermogravimetric analysis

Thermogravimetric analysis (TGA) of samples was performed to record the mass loss during heating from 25°C to 600°C with a heating rate of 10°C /min. A NETZSCH TG 209F1 Libra (Germany) evolution analyzer was used. The sample mass of 3–5 mg was placed in an alumina crucible in the presence of air.

### X-ray diffraction

The diffractogram of the samples was recorded using X'Pert Pro diffractometer (Netherland) with Cu K $\alpha$  radiation ( $\lambda=0.1540$  nm) and a generator was running at 45 kV and 40 mA. One of the most important characteristics of cellulose that contribute to its chemical, physical and mechanical properties is its crystallinity. XRD is an analytical technique that provides information on the molecular structure of the finished fabric by measuring the crystallinity index of the samples. Segal crystallinity index was calculated

based on the area of amorphous cellulose peak  $A_{AM}$  and the total area of all peaks  $A_{TOT}$  of diffractogram [34].

$$CI\% = 1 - A_{AM} / A_{TOT} \quad (1)$$

### SEM analysis

The morphology of cotton fabric before and after application of polymer onto the fabric was observed by scanning electron microscope.

### Energy dispersive spectroscopy (EDX)

Elemental analysis of treated and untreated cotton fabric was carried out by EDX analysis with beam's energy at 5 keV. Contents of carbon, oxygen, and fluorine on the cotton fabric surface were determined by EDX.

## RESULTS AND DISCUSSION

In this research, a long-chain fatty acid, stearic acid is polymerized with crosslinkers such as maleic acid and acrylic acid to impart hydrophilicity and oleophobicity to the cotton fabric. The behavior of stearic acid as oil and water repellent was observed by applying it on the cotton fabric without any polymerization. The solution of stearic acid was made in water and an organic solvent Isopropyl alcohol. Stearic acid was only fairly soluble in water at a higher temperature range from 80 to 90°C with zero oil and water repellency rating. However, water repellency rating of "2" was achieved when 15% of stearic acid was dissolved in Isopropyl alcohol, as shown in table 1. The

Table 1

WATER AND OIL REPELLENCY RATING OF THE COTTON FABRIC TREATED WITH STEARIC ACID AND CROSSLINKERS WITHOUT POLYMERIZATION							
Sample	Oil and water repellent	Cross-linker	Catalyst (SHP)	Enhancer (TEA)	Solvent	Water repellency rating	Oil repellency rating
Recipe A1 (Control fabric)	-	-	-	-	-	w	w
A2 (Nuva-3585)	3%	-	-	-	H <sub>2</sub> O	8	5
A3	1% SA	-	-	-	H <sub>2</sub> O	w	w
A4	3% SA	-	-	-	H <sub>2</sub> O	w	w
A5	5% SA	-	-	-	H <sub>2</sub> O	w	w
A6	-	3% MA	-	-	H <sub>2</sub> O	w	w
A7	-	3% MA	-	-	IPA	w	w
A8	-	3% AA	-	-	H <sub>2</sub> O	w	w
A9	-	3% AA	-	-	IPA	w	w
A10	-	-	-	3%	H <sub>2</sub> O	w	w
A11	1% SA	-	-	-	IPA	2	w
A12	3% SA	-	-	-	IPA	2	w
A13	5% SA	-	-	-	IPA	2	w
A14	15% SA	-	-	-	IPA	2	w
A15	25% SA	-	-	-	IPA	3	w
A16	30% SA	-	-	-	IPA	3	w
A17	3% SA	5% MA	5%	5%	IPA	2	w
A18	3% SA	5% AA	5%	5%	IPA	2	w

increased concentration of stearic acid to 25% results in a higher rating of “3” for water repellency. Further increase in the concentration of stearic acid does not affect water repellency rating. The solution of maleic acid and acrylic acid in water and Isopropyl alcohol showed zero oil and water repellency rating. It clearly indicates that carboxylic acid on their own cannot impart any oil and water repellency.

### Effect of operational parameters on oil and water repellency rating

#### Effect of the selection of monomers on water and oil repellency rating

Combination of stearic acid with crosslinker maleic acid or acrylic acid in the presence of catalyst SHP and enhancer TEA under vacuum conditions exhibit water repellency rating of 4 and 3 respectively as shown in table 2. Monomers were selected by performing number of experiments in vacuum condition. Results related to dosage of stearic acid, polymerization time and temperature are described in the figures 1–3.

Vacuum condition exhibited superior results as compared to atmospheric conditions due to lesser side

reactions and by-products as shown in table 3. There is an improvement of one rating of water repellency when polymerization was carried out between stearic acid and either maleic acid or acrylic acid under vacuum and non-vacuum conditions.

#### Effect of dosage of stearic acid on water and oil repellency rating

The concentration of stearic acid has a vital effect on water and oil repellency rating. At different concentrations of stearic acid; 11%, 16%, 25 %, and 50%, experiments were performed to find out the optimum value. Figure 1 clearly depicted that with an increase in dosage of stearic acid up to 25%, water and oil repellency rating was also increased for maleic acid for both solvents; water and Isopropyl alcohol. However, at very higher concentration of 50%, the trend remained straight due to saturation effect. For acrylic acid, the same trend as that of maleic acid had been observed for water repellency rating but it exhibits zero rating for oil repellency for both solvents.

Table 2

SELECTION OF MONOMERS FOR POLYMER SYNTHESIS UNDER VACUUM AT 160°C AND THEIR EFFECT ON OIL AND WATER REPELLENCY RATING OF COTTON FABRIC								
Sample	Oil and water repellent (SA %)	Cross-linker (%)	Catalyst (SHP %)	Enhancer (TEA %)	Solvent	Polymerization temperature (°C)	Water repellency rating	Oil repellency rating
B1	25	-	-	5	IPA	160	3	w
B2	25	5% MA	5	-	IPA	160	3	w
B3	25	5% MA	5	-	IPA-H <sub>2</sub> O	160	3	w
B4	25	5% MA	-	5	IPA	160	2	w
B5	25	5% MA	-	5	IPA-H <sub>2</sub> O	160	2	w
B6	25	5% MA	5	5	IPA	160	4	1
B7	25	5% MA	5	5	IPA-H <sub>2</sub> O	160	4	1
B8	25	5% AA	5	5	IPA	160	3	w
B9	25	5% AA	5	5	IPA-H <sub>2</sub> O	160	3	w

Table 3

COMPARISON OF OIL AND WATER REPELLENCY RATING OF THE FINISHED COTTON FABRIC IN ATMOSPHERIC AND VACUUM POLYMERIZATION AT 160°C								
Sample	Oil and water repellent (SA %)	Cross-linker (%)	Catalyst (SHP %)	Enhancer (TEA %)	Solvent	Polymerization temperature (°C)	Water repellency rating	Oil repellency rating
C1 (atm)	25	5% MA	5	5	IPA	160	3	w
C2 (atm)	25	5% MA	5	5	IPA-H <sub>2</sub> O	160	3	w
C3 (vac)	25	5% MA	5	5	IPA	160	4	1
C4 (vac)	25	5% MA	5	5	IPA-H <sub>2</sub> O	160	4	1
C5 (atm)	25	5% AA	5	5	IPA	160	2	w
C6 (atm)	25	5% AA	5	5	IPA-H <sub>2</sub> O	160	2	w
C7 (vacc)	25	5% AA	5	5	IPA	160	3	w
C8 (vacc)	25	5% AA	5	5	IPA-H <sub>2</sub> O	160	3	w

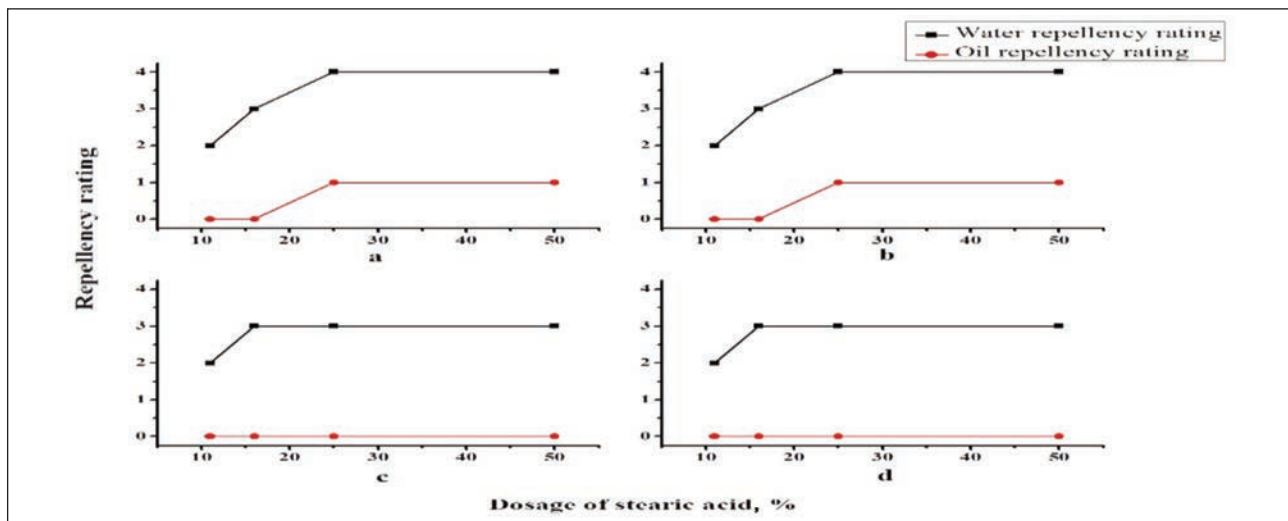


Fig. 1. Optimum dosage of stearic acid at 160°C with: a – Maleic acid + IPA; b – Maleic acid + IPA + H<sub>2</sub>O; c – Acrylic acid + IPA; d – Acrylic acid + IPA + H<sub>2</sub>O

### Effect of temperature on water and oil repellency rating

Figure 2 reflects the influence of temperature on the oil and water repellency rating. It exhibits that as the temperature of reaction raised, water and oil repellency rating increased firstly and then decreased. At lower temperature range, crosslinking efficiency of monomers were low. Literature reports that carboxylic acid esterification reaction starts around 150 °C and it was also reported that greater the temperature better will be the esterification. In our experimentation we also observed that after 150 °C repellency rating was improved. The optimum value was observed at a temperature of 160 °C for a combination of stearic acid and maleic acid and 200 °C for a combination of stearic acid and acrylic acid.

It is important to note that at the temperature of 100 °C, very less amount of solid melted and it was difficult to apply recipe onto the fabric. As the polymerization temperature further increased after 200 °C, a viscous liquid was formed that makes the fabric very sticky thus decreasing the repellency

rating. After the further increase in temperature above 200 °C up to 450 °C, excessive evaporation started and due to this, the polymerization reactor pressure was also increased and resulted in decreased oil and water repellency rating.

### Effect of time on water and oil repellency rating

Figure 3 exhibited that water and oil repellency rating was first increased and then curve remained constant as the reaction time increased. At the initial stage of the polymerization reaction, more crosslinking occurred between monomers and conversion ratio of monomers to polymer continued to increase. So, water and oil repellency rating increased with the increase of time. The optimum time of polymerization reaction was found to be 3 hours for stearic acid and maleic acid while it is 2 hours for stearic acid and acrylic acid. It is mainly due to the fact that rate of reaction between stearic acid and acrylic acid was high due to the presence of a vinyl group. Nevertheless, at a very prolonged time of 5 hours, water and oil repellency rating remained constant.

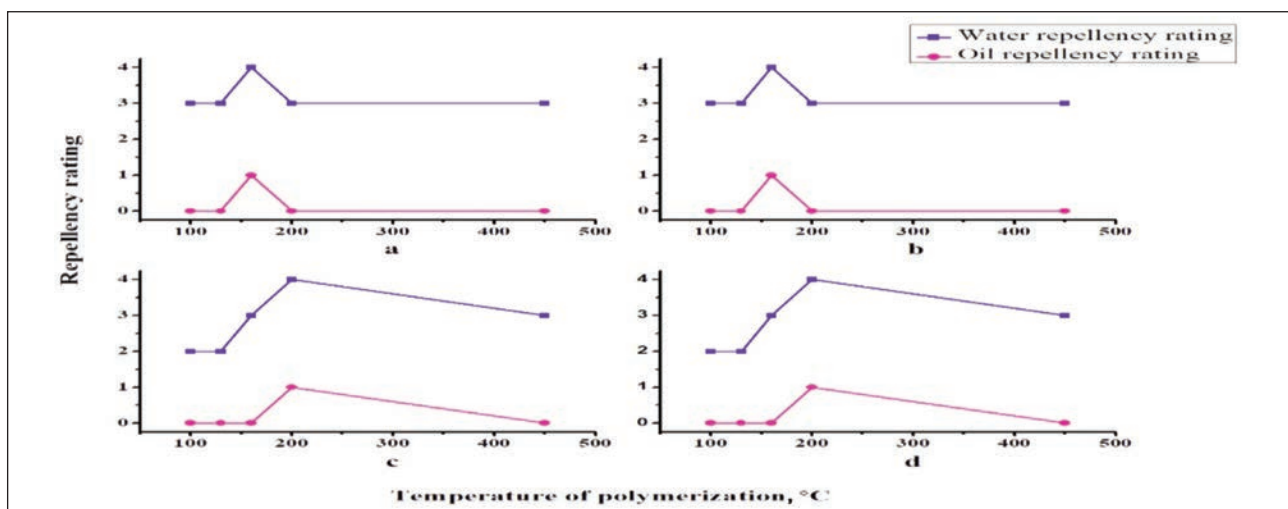


Fig. 2. Optimum temperature for polymerization of stearic acid with: a – Maleic acid + IPA; b – Maleic acid + IPA + H<sub>2</sub>O; c – Acrylic acid + IPA; d – Acrylic acid + IPA + H<sub>2</sub>O

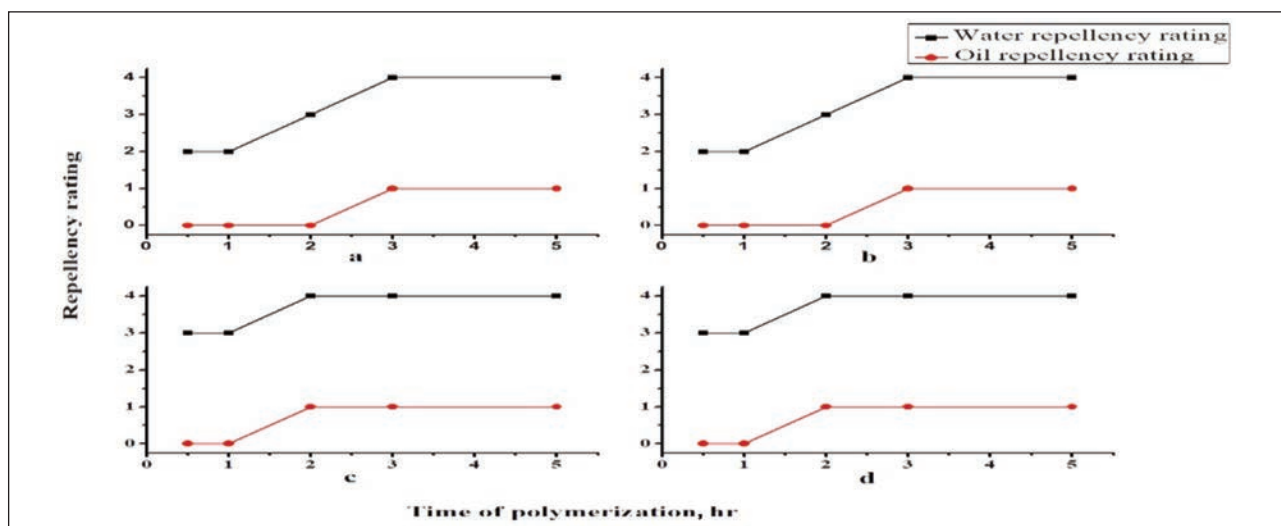


Fig. 3. Optimum time for polymerization of stearic acid with: a – Maleic acid + IPA; b – Maleic acid + IPA + H<sub>2</sub>O; c – Acrylic acid + IPA; d – Acrylic acid + IPA + H<sub>2</sub>O

### Water and oil repellency

Commercial recipe of Nuva 3585, a C6 based fluorocarbon exhibits water repellency rating of 7 before any wash and it was reduced to 3 after 20 washes for an un-pressed sample. Nevertheless, in case of oil repellency, the fluorocarbon achieved a rating of 2 for the pressed sample after 20 washes. Sample A15, which contain alone stearic acid exhibit water repellency rating of 3 before any wash, but it became wet after 5 washes. Therefore, it can be concluded that stearic acid can only impart water repellency.

### Functional properties of the finished fabric

Use of cotton fabric in various household and industrial application makes the cotton fabric among one of the most widely used fabrics. To assess the diverse application of newly developed recipes, various easy-

care and performance properties were evaluated after application of finishes.

### Spray test

Spray test was performed to measure the ability of the cotton fabric to repel water. Hydroxyl group present in cellulose are responsible for its water absorbency. After application of the newly developed recipes the spray rating of the treated fabric was improved. Table 4 shows that sample E6, E7, E8, and E9 were rated 70 by comparing with spotted patterns on the standard spray test rating chart. Benchmark sample A2 also rated 70 at rating chart. However, spray test rating for control fabric, sample A15, A7, and A9 was 0.

### Crease recovery angle (CRA)

Crease recovery of the cotton fabric is one of the most important property which the apparel industry is

Table 4

FUNCTIONAL PROPERTIES OF FINISHED AND CONTROL COTTON FABRIC AT OPTIMUM TEMPERATURE, THE DOSAGE OF MONOMERS AND TIME UNDER VACUUM CONDITION									
Sample	Spray test rating	Contact angle (degree)	Air permeability retention (%)	Soil release rating	CRA (W+F) (degree)	Shrinkage (%)		Tensile strength retention (%)	Tear strength retention (%)
						Warp	Weft		
A1 (Control Fabric)	0	0	100	1	144	4	3	100	100
A2 (Nuva-3585)	70	145	71	3	165	3	2	84	81
A15 (SA)	0	101	76	3	150	3	2	87	94
A7 (MA)	0	0	80	4	191	3.2	1	80	75
A9 (AA)	0	0	84	3	185	3.7	1.8	82	76
E6 (SA+MA+SHp+TEA+IPA)	70	142	78	4	178	3.1	1.2	81	75
E7 (SA+MA+SHp+TEA+IPA+H <sub>2</sub> O)	70	139	77	4	172	3.1	1.2	79	73
E8 (SA+AA+SHp+TEA+IPA)	70	136	82	4	169	3.5	1.5	84	81
E9 ((SA+AA+SHp+TEA+IPA+H <sub>2</sub> O)	70	132	70	4	164	3.3	1.6	83	78

looking for. Cotton fabric lacks crease resistance due to the amorphous region and weak hydrogen bonding between the chains. The crease recovery behaviour of the cotton fabric can be improved by the formation of a covalent bond with crosslinking agents. Table 4 shows the crease recovery behaviour of the treated and untreated cotton fabric. CRA has a higher value of 191° and 185° for maleic acid and acrylic acid respectively due to the esterification reaction between the cotton fabric and carboxylic acids. Maleic acid has higher CRA as it has two carboxylic acid groups as compared to one carboxylic group of acrylic acid. Similarly, recipes E6, E7, E8, and E9 show better crease recovery as compared to untreated cotton fabric. The commercial benchmark sample of A2 exhibited lower CRA as compared to optimized recipes of maleic acid and acrylic acid. It is quite obvious as maleic acid and acrylic acid are cross-linkers, therefore, impart superior crease recovery properties as compared to commercial oil and water repellent recipes.

#### Air permeability

Passage of air through cotton fabric is related to another important property which is known as air permeability. It is basically related to the comfort of clothes. The air permeability of the control fabric is set as 100%. As finishes were applied onto cotton fabric, the passage of air through treated fabric decreases to a certain low value as presented in table 4. The reduced value of air permeability for recipe E6 was 78% and for recipe E8 it was 82%. However, the commercial recipe of A2 exhibited the least air permeability of 71%.

#### Soil release

Table 4 shows that soil release of grade 1 was obtained by control fabric and it has been increased to grade 4 for samples E6, E7, E8 and E9 due to the presence of the carboxylic acid group. Soil release rating of 3 was achieved by using the benchmark commercial recipe of A2. Stearic acid and acrylic acid exhibited the soil release grade of 3 whereas maleic acid has demonstrated a grade of 4. It is mainly due to the reason that maleic acid has two carboxylic acid groups consequently it can repel the negatively charged soils in a better way.

#### Strength

Tensile and tear strength retention of untreated cotton fabric was considered as 100%. Typically, cross-linkers impart loss in strength due to crosslinking at the intermolecular and intramolecular level. Therefore, stress distribution among all molecules is not equal and load withstanding capacity is reduced. Samples treated with maleic acid imparted slightly more reduction in tensile and tear strength retention as compared to acrylic acid. It is mainly due to greater cross-linking of maleic acid in comparison with acrylic acid recipes, table 4.

#### Shrinkage

Shrinkage is associated with a change in the dimension of cotton fabric in warp and weft direction after washing. After the application of the newly synthesized finishes, shrinkage test was performed. Cotton fabric treated with acrylic acid exhibit more shrinkage in warp direction having a value of 3.7% as compared to maleic acid having a value of 3.2%. Again, maleic acid being the better cross-linker will lead to lesser shrinkage as compared to acrylic acid. Sample E6 and E7 both have shrinkage value of 3.1% in warp direction which was less as compared to the cotton fabric which stands at a value of 4% in warp direction as shown in table 4. Shrinkage of the commercial recipe A2 is more than the newly developed recipes.

#### FTIR analysis

The strong peaks of carbonyl stretching and ester bond formation between stearic acid, maleic acid and cellulose (E6) as well as stearic acid, acrylic acid with cellulose (E8) appeared at 1703  $\text{cm}^{-1}$  and 1730 and  $\text{cm}^{-1}$  respectively as depicted in figure 4. Whereas the peak at 1156  $\text{cm}^{-1}$  and 1152  $\text{cm}^{-1}$  corresponds to C-O stretching for sample E6 and E8 respectively. These peaks confirmed the ester linkages between recipes and cellulose. However, these ester peaks were not present for control fabric as well as for samples A9 and A7.

#### TGA analysis

To evaluate the thermal stability of control fabric and treated ones, thermogravimetric analysis (TGA) was performed. Figure 5 shows the TGA curves for control fabric and fabric treated with maleic acid, and fabric treated with acrylic acid respectively. Mass loss of

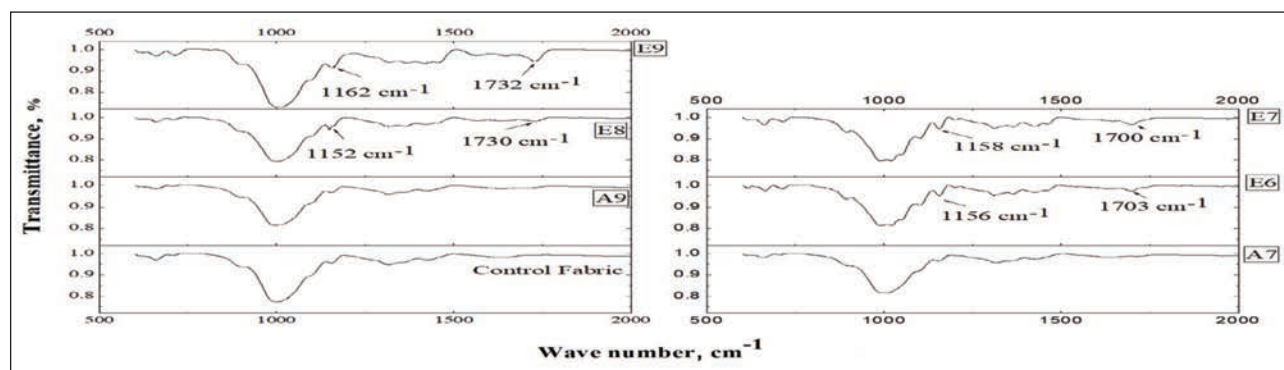


Fig. 4. FTIR spectrum of untreated control fabric and cotton fabric treated with A9, E8, E9, A7, E6, E7

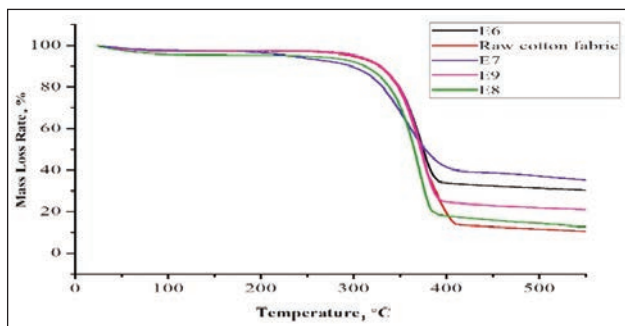


Fig. 5. TGA thermograms for control and modified cotton fabric

thermogram was divided into three regions. In the first region, the dehydration of polymer takes place and the mass loss rate is less than 5%. In the second region, mass loss was due to decomposition caused by pyrolysis and in the last region, there was the conversion of remaining material to carbon residue. The melting point of cellulose is in the range of 260–270°C. So, in TGA analysis pyrolysis of cotton fabric starts at 265°C. Maleic acid have the melting point of 135°C. Therefore, cotton fabric treated with E6, E7, E8 and E9 start decomposing at 261, 219, 262 and 264 respectively.

#### XRD analysis

Cellulose showed its diffraction peaks at  $2\theta = 15.2^\circ$  and  $22.9^\circ$  corresponding to 101 and 002 diffraction planes, respectively. Miller indices were used to label the peaks. Segal crystallinity index was estimated in two steps. In the first step, the subtraction of the background signal was carried out and then height ratio is considered between crystalline peak intensity and total intensity. The high degree of crystallinity was achieved with a more regular chain of finished cotton fabric and larger crystalline area. Figure 6 show the diffractogram for untreated cotton fabric and cotton fabric treated with maleic acid and acrylic acid. No considerable difference was noticed between all spectrums. Finished fabric treated with maleic acid has high crystallinity index due to the presence of two carboxyl acid groups that will form a more regular chain and better water and oil repellency as compared to acrylic acid (table 5).

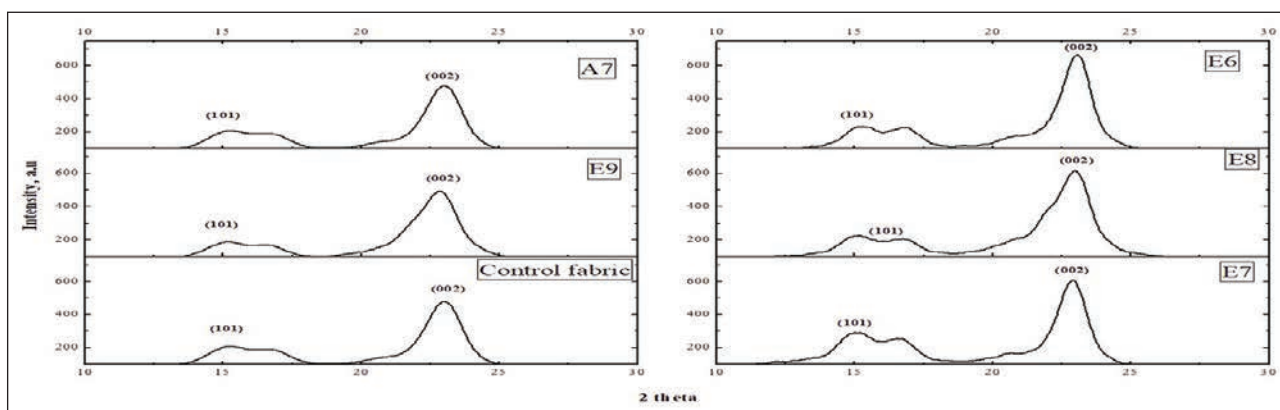


Fig. 6. XRD spectrum for control cotton fabric and modified cotton fabric with maleic acid and acrylic acid

Table 5

CRYSTALLINITY INDEX OF UNTREATED COTTON FABRIC AND COTTON FABRIC TREATED WITH BEST RECIPES	
Sample	Crystallinity Index (%)
A1(Control fabric)	60
E6 (SA+MA+ SHP+TEA+ IPA)	82
E7 (SA+MA+ SHP+TEA+IPA+H <sub>2</sub> O)	76
E8 (SA+AA+ SHP+TEA+ IPA)	78
E9 ((SA+AA+ SHP+TEA+ IPA+H <sub>2</sub> O)	75

#### SEM analysis

The surface morphology of raw cotton, stearic acid-maleic acid-cotton and stearic acid-acrylic acid-cotton samples were studied by scanning electron microscope analysis. Figure 7 present that untreated cotton fabric surface has no coating and it was plain and smooth. However, the newly synthesized finishes E6 and E8 coating can be clearly observed on the surface of cotton fabric.

#### EDX analysis

Commercial recipe of A2, a C6 based fluorocarbon indicates the fluorine peak at an energy level of 0.677 KeV showing counts of 91. EDX spectrum of samples A1, A15, A7, A9, E6, E7, E8 and E9 exhibited no peak for fluorine showing that control fabric and newly synthesized recipes were free of fluorinated compounds. Highest counts of carbon 669 and oxygen 550 elements can be observed in E6 having maleic acid diluted with isopropyl alcohol due to the presence of more carboxyl groups. Figure 8 showed the EDX spectrum of control fabric compared with cotton fabric coated with newly synthesized fluorine-free recipes.

#### Contact angle

Since the cotton fabric is hydrophilic in nature, therefore, water droplet placed on it is spread immediately as shown in figure 9, a. Modified cotton fabric with stearic acid showed contact angle of  $101^\circ$ , as stearic acid (A15) lowers the surface energy of treated cotton fabric but the coating was non-durable.



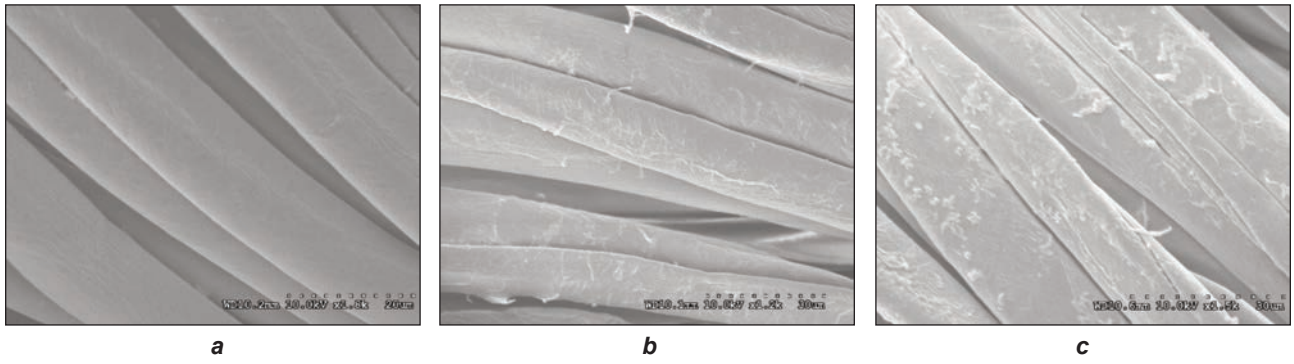


Fig. 7. SEM analysis of: a – control fabric; b – coated fabric with E8; c – coated with E6 recipes

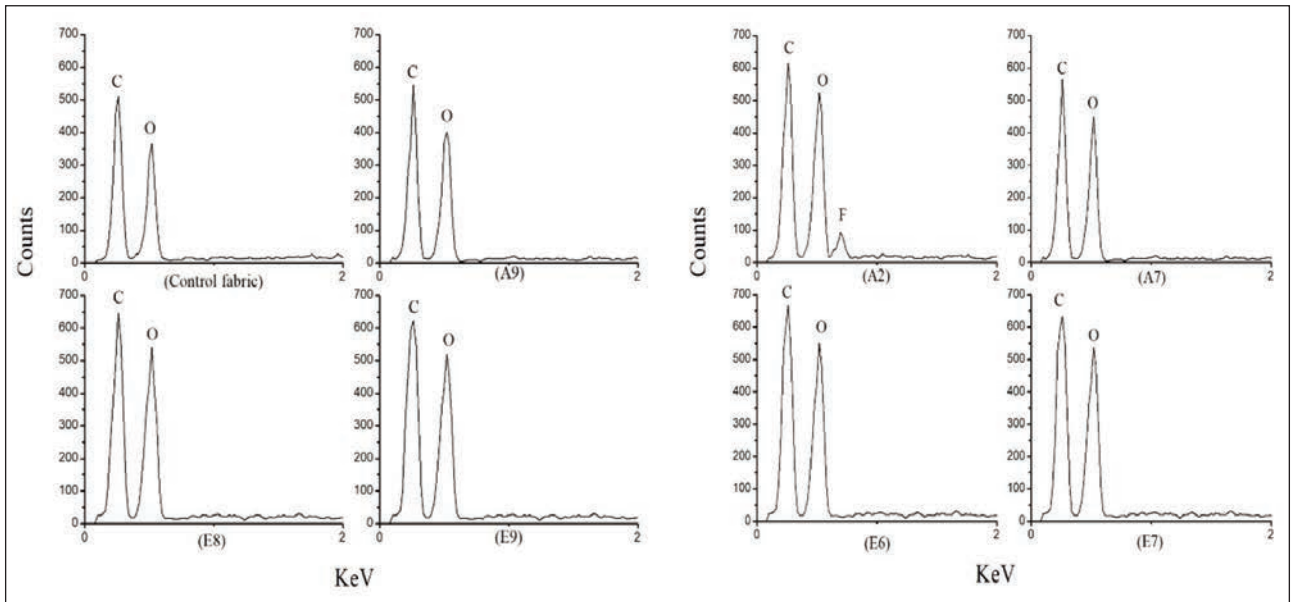


Fig. 8. EDX spectrum for control cotton fabric and modified cotton fabric with maleic acid and acrylic acid

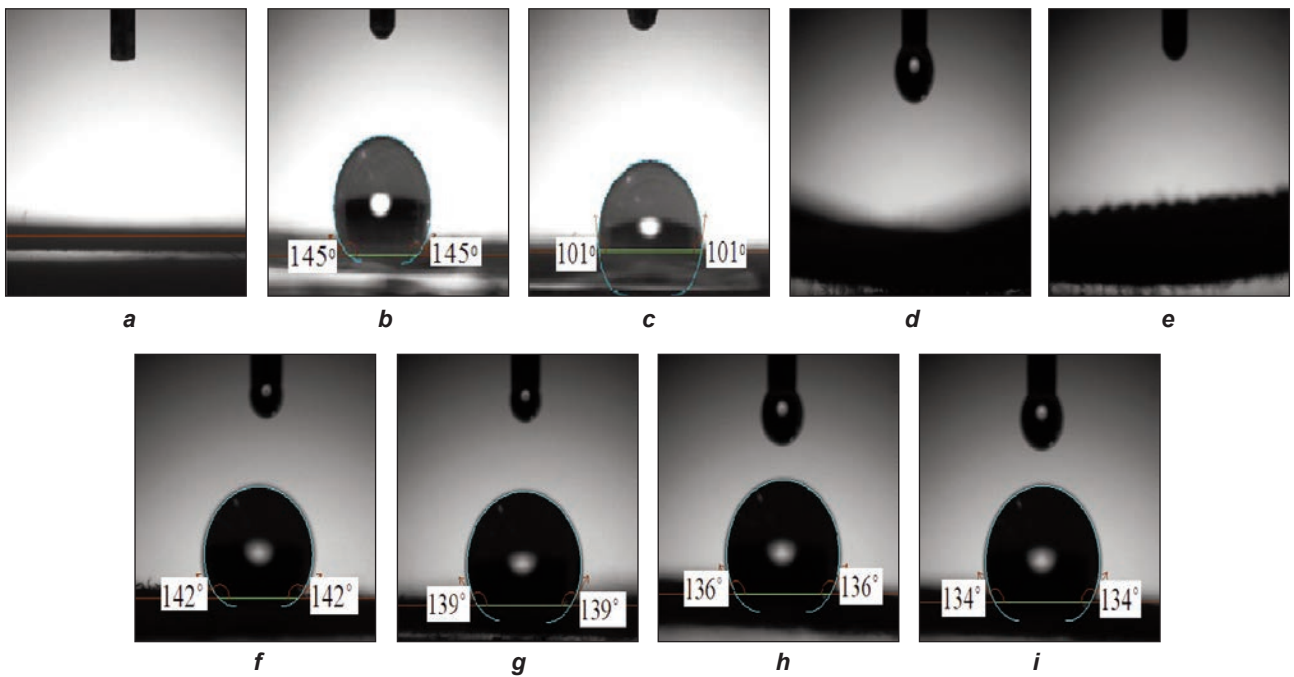


Fig. 9. Contact angles of: a – control fabric; b – A2 (bench mark); c – A15 (stearic acid); d – A7 (maleic acid); e – A9 (Acrylic acid); f – E6; g – E7; h – E8; i – E9

Crosslinkers such as maleic acid (A7) and acrylic acid (A9) showed 0° contact angle when applied alone on cotton fabric. Sample E6, E7 showed contact angle 142° and 139° respectively due to a combination of stearic acid with maleic acid.

Incorporation of cross-linker such as maleic acid with stearic acid increases washing durability of the coating as well as contact angle as shown in table 4. Polymerization of acrylic acid with stearic acid (E8, E9) also improves washing durability of coating and contact angle. However, better and comparable results with benchmark having a contact angle of 145° were obtained with maleic acid due to the presence of two carboxyl groups. The contact angle of sample E8 and E9 was 136° and 134° respectively.

#### Antimicrobial potential

Table 6 shows the antibacterial activity of different sample against *E. coli* and *S. aureus*. Raw cotton showed no antibacterial resistance, however, cotton fabric modified with maleic acid and acrylic acid exhibited antibacterial performances. Sample E6 exhibit better antimicrobial properties against gram-positive and gram-negative bacteria as compared to E8 due to the presence of two carboxylic acid groups.

Table 6

INHIBITION ZONE OF SAMPLE E6 AND E8 FOR <i>E. COLI</i> AND <i>S. AUREUS</i> BACTERIA		
Samples	Inhibition zone (cm)	
	<i>E. coli</i>	<i>S. aureus</i>
A1 (control fabric)	0	0
E6 (SA+MA+IPA)	0.23	0.18
E8 (SA+AA+IPA)	0.17	0.16

## CONCLUSIONS

The presented cross-linkers maleic acid and acrylic acid along with stearic acid yielded a successful synthesis of fluorine and formaldehyde-free oil and water repellent for cotton fabric. The newly polymerized recipes application onto the cotton fabric lead to improved crease-resistance, antimicrobial properties, soil release properties, contact angle and oil and water repellency up to 20 washes. Polymerization conditions such as time, temperature and dosage of monomer were optimized. Best results were achieved when 25 % of stearic acid was polymerized with 7% of maleic acid in the presence of catalyst SHP and enhancer TEA. Combination of stearic acid with maleic acid yielded water repellency rating of 4 and oil repellency rating of 1 before any wash and it attained a value of 3 and 1 respectively after 20 washes. Stearic acid with acrylic acid attained water and oil repellency rating of 4 and 1 prior to any wash, however after 20 washes both of these ratings reduced to 2 and zero respectively. The contact angle of modified cotton samples E6 and E8 was increased to 142° and 136° respectively due to a combination of stearic acid with maleic acid and acrylic acid respectively. Ester bond formation was confirmed by FTIR analysis. EDX analysis confirmed the absence of fluorine in the newly synthesized recipes. SEM affirms the coating of newly developed polymer onto the cotton fabric. Therefore, newly developed and optimized recipes can give a good alternative to the current toxic fluorine and formaldehyde-based oil and water repellents.

## ACKNOWLEDGEMENTS

Authors are thankful to UET Lahore for funding this research project (No. ORIC/100-ASRB/1990).

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