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Properties of cellulosic fabrics treated by water-repellent emulsions

Amina L Mohamed, Ahmed G Hassabo, Ahmed A Nada[a] & Nabil Y Abou-Zeid

Pretreatment & Finishing of Cellulose Based Textiles Department, National Research Centre, 33 El-Bohouth St., Dokki, Giza, 12622, Egypt

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Water-repellent cotton, jute and linen fabrics have been prepared by treating them with emulsions made of beeswax/stearic acid (BW/SA) mixture. Different BW/SA ratios are tested to find out the best formulation recipe and different additives are incorporated in order to enhance emulsion stability and water repellency rating, such as alkali and metal salts. Triethanolamine (TEA) alkali has been selected for promoting the water repellency results. Cellulosic fabrics are pre-/post-treated with metal salts (aluminium chloride and zirconyl chloride) to enhance their physical attachment to the surfaces. Optimum emulsion ingredients for best results are found to be BW: SA (1:1), in presence of TEA (0.5 mole equivalent of SA) and zirconyl chloride concentration (1 g/L). Treated fabrics have been imparted with a water repellency characteristic, showing a value of 90, 80 and 80 for cotton, linen, and jute fabric respectively. Mechanical properties for treated fabrics are also demonstrated. FTIR spectra of treated fabric show no evidence of any chemical reactions between the substrate and the emulsion. Emulsions show stable rheological behavior upon storing for 3 months.

Keywords: Beeswax, Cellulosic fabrics, Hydrophobic surface, Stearic acid, Water-repellent emulsion

1 Introduction

Cellulosic substrate has always been excellent for many applications such as textile garments and packaging materials for food industry. However, unmodified substrates absorb and lose moisture easily [1], especially those designed to be used outdoor which expose to a combination of physical and chemical degradation processes due to the combined effects of sunlight, moisture, fungi, bacteria, etc[2].

Many investigations have been carried out in the past on methods for prevention of weathering degradation of cellulose substrates especially for water repellency[3,4]. Chemical modification is one of the routes for altering properties of natural polymeric materials. At present, the common water-repellent agents are polydimethylsiloxane, silica[5,6] and fluorine containing agents[7], which are chemically incorporated on fibre surfaces[8]. However, chemicals involved in direct contact with human-related materials must be carefully screened for toxicity, thus a large number of potential reagents is diminished. For instance, fluorocarbon compounds can provide excellent water repellency when applied on surfaces of materials[9]. However, the perfluorocarbon chains containing more than seven carbons can resist degradation and cause biological threats to human and animal lives[8,10].

Using fatty acids in the textile industry is dated back to long time ago[11] when they have been used in scouring and finishing fabrics[2,12]. Fatty acids show advantageous properties over many other reagents in terms of their ease of preparation from cheap recourses through conventional procedures, their ease of processing and limited toxicity. Moreover, the development of fatty acid derivatives[13] has opened up new fields in the textile industry[14,15].

Wax, made of different resources such as animal waxes, vegetable waxes, mineral waxes and petroleum waxes, has been used for centuries in cosmetics, pharmaceutical products, and coating technologies[16]. Beeswax is the most common animal wax and its chemical composition varies according to geographic region which consists mainly of esters of long-chain (lengths C 30 and C 32) fatty acids, alcohols, hydrocarbons and aliphatic aldehyde[17]. Beeswax is used as emulsion stabilizer and water-repellent enhancer to textile fabrics plus improves the roughness of their surfaces[18].This is owing to its physical properties which has a melting point of 61-66^{o}C and being in solid form at room temperature[19].

In the present work, water-repellent surface of cellulose containing fabrics (cotton, linen and jute) was developed via treatment with natural constituents,

[a]Corresponding author.
E-mail: aanada@ncsu.edu

namely beeswax/stearic acid emulsions. It is expected that due to their chemical and physical behavior, such treatment would change the surface morphology and promote water repellency on each fabrics.

2 Materials and Methods

2.1 Materials

A plain weaved and bleached cotton fabric (23 ends/cm and 23 picks/cm) was provided by Misr El – Beida Dyers, Egypt. The fabric was pre-treated by scouring in a solution containing 2 g/L sodium carbonate and 2 g/L non-ionic detergent at 70°C for 30 min. Afterwards, fabrics were rinsed with hot and cold water and then left to dry at ambient temperature. Jute fabric is provided in sheet form (60 inch wide × 2 yard long) made out of 100% jute where one square yard weight is 10 oz. Sample was purchased from local market. Linen fabric (100 %) was kindly provided by Tanta Flax and Oil Company, Mit-Hebaish El-Bahri, Tanta, Egypt.

Beeswax (BW) was purchased from local market in Egypt. Stearic acid, sodium hydroxide, hydrochloric acid, ethyl alcohol, sodium sulfate, n-hexane, ethylenediamine (EDA), ethanolamine (EA), triethanolamine (TEA), ammonium hydroxide (NH_4OH), aluminum chloride ($AlCl_3$), and zirconyl chloride ($ZrOCl_2$) were purchased from Nasr Pharmaceutical Chemicals company. All reagents were laboratory grade chemicals.

2.2 Emulsion Preparation

In order to prepare a 100 mL of the emulsion, beeswax and stearic acid in different ratios (3:1, 2:1, 1:1, 1:2 and 1:3) were heated together in a 250 mL glass beaker at 70°C. Afterwards, different amount of TEA was added gradually to the mixture. Now 85 g of hot distilled water (90°C) was subsequently added dropwise to the mixture with stirring for 5 min using homogenizer.

Metal salts play an important role in water repellency characteristic of the treated fabrics. Metal salts form insoluble metal soap in fabrics. The use of rare metals such as zirconium compounds have been reported to be more satisfactory to form such soap than the aluminum salts, because aluminum compounds dissolve in alkaline water to form aluminates while zirconium compounds do not[20].

Therefore, 1 g of metal salt (ammonium chloride – zirconium (IV) oxychloride), dissolved in aqueous solution, was added with vigorous stirring to the emulsions. Prepared emulsions were allowed to cool down and then preserved at room temperature for further use. Likewise, different emulsions were prepared by changing the emulsion stabilizer (i.e. triethanolamine, diethyleneamine, ethanolamine and ammonium hydroxide) and varying their compositions with the beeswax. Emulsion potentials were controlled through a series of tests in order to confirm their properties and stability.

2.3 Fabric Treatment

Fabrics (cotton, linen or jute) were padded in a solution containing a selective weight of the emulsion squeezing to a 100% wet-pick up. Samples were dried at 100°C for 5 min with no curing.

2.4 Test Methods

Water repellency was performed using the spray test as described by AATCC Test Method 22-2005. Water will be sprayed against a taut surface of a test specimen under controlled conditions, producing wetted patterns. Pattern size depends on the relative repellency of the fabric. Evaluation was done by comparing such patterns with pictures on a standard chart.

Tensile strength and elongation at break tests were carried out according to the ASTM Standard Test Method D–1682–1924 on a tensile strength apparatus type FMCW 500 (Veb Thuringer Industrie Werk Rauenstein 11/2612 Germany) at 25°C and 65% relative humidity. The results quoted are the mean of 5 breaks for the warp direction with test length of 20 cm at a constant breaking time of 20 s, load scale 10–50 kg. Stiffness was determined according to ASTM Test Method D 1388-96 using the cantilever apparatus. Surface roughness was monitored according to JIS 94 standard, using surface roughness measuring instrument (SE 1700) made in Japan.

The FTIR tester of Nicolet Magna-IR 560 spectrometer was used to analyze the spectrum of the untreated and treated samples. KBr was used to prepare the samples. The tester collected transmittance of the infrared in the film between 400 and 4000 cm^{-1} are examined.

3 Results and Discussion

3.1 Effect of Beeswax /Stearic Acid Ratio

Table 1 shows the effect of beeswax (BW)/stearic acid (SA) ratios on water repellency properties against the physical properties of the treated cellulosic fabrics (cotton, linen and jute). In general, the water repellency of the treated samples has improved to reach up to 80% regardless to the fabric type. The water repellency improvement is associated with decrement

Table 1 — Effect of beeswax/stearic acid ratio in the emulsion on water repellency rating of the treated fabric

Fabric[a]	Beeswax concentration %	Stearic acid concentration %	Wetting time s	Water repellency rating	Surface roughness mm	Tensile strength N/mm^2	Strain %	Bending length cm	
								Warp	Weft
Cotton	Nil (untreated)	0	2	0	17.69	13.818	7.25	3.45	2.94
	25	75	> 600	80	15.55	11.368	7.75	4.21	4.81
	33.3	66.7	> 600	80	12.66	11.368	6.25	4.61	4.85
	50	50	> 600	80	8.66	12.936	8.75	5.21	4.95
	66.7	33.3	> 600	70	7.95	13.23	8.52	3.98	4.01
	75	25	> 600	70	7.88	13.524	8.38	4.73	4.47
Jute	Nil (untreated)	0	2	0	32.53	18.816	8.00	7.16	8.85
	25	75	> 400	80	28.10	11.466	7.76	7.15	8.34
	33.3	66.7	> 400	80	25.46	11.466	7.65	7.83	8.41
	50	50	> 400	80	22.89	13.916	7.63	8.85	8.58
	66.7	33.3	> 400	70	21.01	14.014	7.40	6.76	6.95
	75	25	> 400	70	20.83	16.464	7.31	8.03	7.75
Linen	Nil (untreated)	0	4	0	20.97	11.368	7.63	5.45	5.36
	25	75	> 600	80	18.98	8.33	5.09	4.55	5.97
	33.3	66.7	> 600	80	15.15	9.016	4.11	4.98	6.02
	50	50	> 600	80	14.47	10.29	5.75	5.63	6.14
	66.7	33.3	> 600	70	13.28	10.584	11.83	4.30	4.97
	75	25	> 600	70	13.17	11.172	5.51	5.11	5.54

[a]Fabric is padded in 50 g/L of emulsion, having wet pick up of 100%, dried at 100°C/5 min, and triethanolamine: stearic acid ratio is 1:2.

in the tensile strength of the fabric. The highest rate in the water repellency value (80%) is recorded at 1:1 ratio of stearic and beeswax with acceptable tensile strength loss that decreases by 6.3%, 26 % and 9.4 % in cotton, jute and linen fabrics respectively. Such decrease in the tensile strength might be attributed to the coating of fibres by which filaments friction is decreased to facilitate filaments sliding against each other[21]. However, differences in tensile strength values of all jute samples could be for their loose weave structure. Data show that the strain values of all samples show slight changes with no trend. However, the bending length of the treated fabrics shows noticeable improvements in both warp and weft directions. It is also found from data that the bending length in both directions of all fabrics initially increases by increasing the beeswax ratio till the 1:1 proportion and then decreases afterwards. In other words, beeswax causes stiffness while stearic acid, neutralized by TEA (base), acts as a softener and influences the softness of the treated fabrics accordingly.

3.2 Effect of Base Type

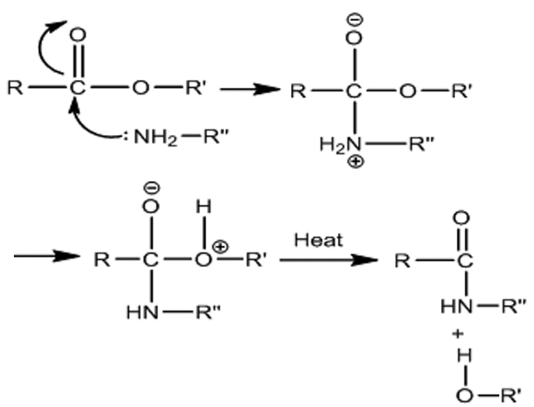
Table 2 shows the effect of base type in the emulsion effectiveness on mechanical and physical properties of the treated fabrics. Base is very important constituent in the emulsion systems by which free fatty acids are converted into ionic form ($R\text{-}CO\text{-}O^-$) in the emulsion. Table 2 shows the effect of several bases, namely ethylenediamine (EDA), ethanolamine (EA), triethanolamine (TEA) and ammonium hydroxide (AH). It is observed that the water repellency ratings of EDA, EA, AH samples are lower compared to TEA. Also, tensile strength of treated fabrics with amino-containing bases, namely EDA and EA shows notable decrement as compared to other bases. The latter phenomenon is owing to the chemical reactions occurred between the amino groups of EDA and EA with stearic acid and/ or wax esters, in the presence of heat, forming amino-ethyl-stearamide ($R\text{-}CO\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}NH_2$) and mono-ethanolamide ($R\text{-}CO\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}OH$) respectively [15]. These new compounds (Scheme 1) are hard waxy products and their penetration in the fabric is more difficult. Accordingly, the presence of such compounds in the fabric surfaces results in decrease of the filaments friction and facilitates filaments sliding against each other to ultimately show lower fabric strength.

On the other side, TEA when reacts with either stearic acid or/and beeswax's esters forms quaternized fatty acid triethanolamine esters (QFTE) which acts as surfactant and solubilizes the mono, di and tri-esters

Table 2 — Effect of base type on mechanical and the physical properties of treated fabrics

Fabric[a]	Type of amine	Wetting time s	Water repellency rating	Surface roughness mm	Tensile stress N/mm^2	Strain %	Bending length, cm	
							Warp	Warp
Cotton	Nil (untreated)	2	0	17.69	13.818	7.25	3.45	2.94
	Ethylenediamine	> 500	70	9.01	9.898	5.75	3.98	3.95
	Ethanol amine	> 500	70	8.88	12.74	6.31	4.32	4.11
	Triethanolamine	> 600	80	8.66	12.936	8.75	5.21	4.95
	Ammonium hydroxide	> 500	70	8.89	11.858	7.32	5.11	5.01
Jute	Nil (untreated)	2	0	32.53	18.816	8.00	7.16	8.85
	Ethylenediamine	> 240	70	23.82	12.446	5.01	6.76	6.85
	Ethanol amine	> 240	70	23.47	6.566	5.50	7.34	7.12
	Triethanolamine	> 400	80	22.89	13.916	7.63	8.85	8.58
	Ammonium hydroxide	> 240	70	23.50	8.918	6.38	8.68	8.68
Linen	Nil (untreated)	4	0	20.97	11.368	7.63	5.45	5.36
	Ethylenediamine	> 500	70	15.05	7.742	4.78	4.30	4.90
	Ethanol amine	> 500	70	14.84	7.938	4.15	4.67	5.10
	Triethanolamine	> 600	80	14.47	10.29	5.75	5.63	6.14
	Ammonium hydroxide	> 500	70	14.85	8.134	4.81	5.52	6.21

[a]Fabric is padded in 50 g/L of emulsion, having wet pick up of 100% of dried at 100°C/5 min, beeswax: stearic acid ratio (1: 1), amine concentration (50 % from stearic acid).



Scheme 1 — Reaction mechanism of ethylenediamine (R'' = $CH_2CH_2NH_2$) or ethanolamine (R'' = CH_2CH_2OH) with fatty acids (R' = H) and long chain esters (R' = aliphatic part)

of the beeswax. It has been reported that the latter compound shows excellent dispersing properties in water due to its superior solubility in water. Such characteristics improve the emulsion characteristics and penetration into fabric surfaces[22]. Also, QFTE possesses high biodegradability and low toxicity [23]. Therefore, TEA is preferred for environmental reasons and is chosen as the best base for the further experiments. The roughness values show up to 52%, 30 % and 31 % decrease for cotton, jute, and linen fabrics respectively. The obtained results are in sense of using the treated emulsions as fabric softeners which improves fabric handle and formability. Changes in strain values and bending length of the treated samples (cotton, jute and linen) do not show any trends.

These amide compounds are waxy hard. Two key parameters may be pointing to the former finding, viz (i) differences in the weave structure of the fabrics and (ii) varying in cellulose content of each type (cotton 99%, jute 65%, linen 92%).

3.3 Effect of Degree of Neutralization

Table 3 shows the SA neutralization effect on both physical and mechanical properties of the cellulosic fabrics. Water repellency values show a gradual increase from 50 to 80 by increasing the TEA concentrations. Such improvement is recorded at 50 % neutralization and above. However, by increasing the TEA concentration further, tensile strength values show a steep drop to reach 48 %, 25% and 75% loss in cotton, jute and linen fabrics respectively. In general, tensile strength improves only if there is proper dispersion of the filler. Otherwise, poor dispersion leads to poor mechanical properties. Likewise, increasing the base concentration provides hard and waxy emulsions which is difficult to penetrate inside fabrics evenly and finally affect the mechanical properties of the treated fabrics. On other hand, all treated fabrics show notable improvement in the surface roughness and bending length values. This is likely due to the

Table 3 — Effect of degree of neutralization (triethanol amine concentration) of stearic acid (SA) on water repellency rating of the treated fabrics

Fabric[a]	Degree of neutralization %	Wetting time s	Water repellency rating	Surface roughness mm	Tensile strength N/mm^2	Strain %	Bending length cm	
							Warp	Weft
Cotton	Nil (untreated)	2	0	17.69	13.818	7.25	3.45	2.94
	0	> 500	50	8.65	13.23	7.35	3.51	3.40
	25	> 500	70	8.65	13.034	8.21	4.28	3.99
	50	> 600	80	8.66	12.936	8.75	5.21	4.95
	75	> 600	80	8.67	10.878	7.25	5.86	5.11
	100	> 600	80	8.68	7.448	6.88	6.32	5.87
Jute	Nil (untreated)	2	0	32.53	18.816	8.00	7.16	8.85
	0	> 120	50	22.86	18.326	6.41	5.96	5.89
	25	> 240	60	23.39	18.13	7.16	7.27	6.92
	50	> 400	80	22.89	17.934	7.63	8.85	8.58
	75	> 400	80	22.92	16.954	6.32	9.95	8.86
	100	> 400	80	22.94	14.014	6.00	10.74	10.17
Linen	Nil (untreated)	4	0	20.97	11.368	7.63	5.45	5.36
	0	> 400	60	14.45	9.506	4.83	3.79	4.22
	25	> 600	80	14.79	8.526	5.40	4.63	4.95
	50	> 600	80	14.47	8.33	5.75	5.63	6.14
	75	> 600	80	14.49	4.606	4.76	6.33	6.34
	100	> 600	80	14.50	2.744	4.52	6.83	7.28

[a]Fabric is padded in 50 g/L of emulsion, having wet pick up of 100%, dried at 100°C/5 min, beeswax: stearic acid ratio (1: 1), triethanolamine as base.

softening influence of the emulsion systems used on fabrics.

3.4 Effect of Emulsion Concentration

Table 4 shows the effect of the emulsion concentrations on the water repellency rating and the physical properties of the treated fabric. Cellulosic fabrics were treated with the prepared emulsion using different concentrations (25, 50 75 and 100 g/L). Treatment of the cotton fabrics with emulsion up to (50 g/L) causes improvement in water repellency rating from zero to 90. However, continuous increase in the emulsion concentration upto 100 g/L does not further improve the water repellency rating from 90. In addition, tensile strength shows a significant decrease with increasing the concentration up to 50 g/L. Jute and linen fabrics show similar trend in cotton.

In addition, mechanical properties for all types of treated fabrics are decreased as emulsion concentration increases, and the surface roughness improves as emulsion concentration is increased.

3.5 Effect of Metal Salts on Fabric Properties

Table 5 shows the effect of metal salts on water repellency rating of the different treated fabrics. To deactivate the emulsifying agent, some salts of polyvalent metals were added to emulsion, or to the fabric before or after treatment of the fabric with the emulsion. Two metal salts ($AlCl_3$ and $ZrOCl_2$) were selected to use during this study. These salts were added in an equimolar amount to that of stearic acid. Figure 1 shows the suggested physical interactions between the metal salt with fatty acids and the fabric surface. Typically, the emulsion made from the metal salt of the fatty acid (stearic acid) adheres to the polar fabrics forming polar-nonpolar interactions, in which the polar ends of the fatty acids, produced from the base (TEA) neutralization, are attracted to metal salts at the fabric surfaces.

Addition of aluminum chloride during the preparation results in precipitating the emulsion immediately. Addition of zirconyl chloride brought about neither precipitation nor separation. So, zirconyl chloride is selected as best deactivating agent. In addition, mechanical properties for all types of treated fabrics are strongly decreased due to the salt addition before emulsion preparation. This may be attributed to the liberating hydrochloric acid which might affect the cellulose chain and destroy it. On the other hand,

Table 4 — Effect of emulsion concentration on water repellency rating and physical properties of the treated fabrics

Fabric[a]	Emulsion concentration g/L	Wetting time s	Water repellency rating	Surface roughness mm	Tensile strength N/mm^2	Strain %	Bending length cm	
							Warp	Weft
Cotton	Nil (untreated)	2	0	17.55	13.818	7.25	3.45	2.94
	25	> 500	70	12.66	13.034	6.13	3.94	3.75
	50	> 900	90	8.66	12.936	8.75	5.21	4.95
	75	> 900	90	7.95	12.838	9.12	6.32	5.26
	100	> 900	90	7.88	12.74	9.34	7.21	6.33
Jute	Nil (untreated)	2	0	32.53	18.816	8.00	7.16	8.85
	25	> 240	60	30.46	18.62	5.35	6.69	6.50
	50	> 400	80	22.89	17.836	7.63	8.85	8.58
	75	> 400	80	21.01	17.738	7.95	10.74	9.12
	100	> 400	80	20.83	17.542	8.14	12.25	10.97
Linen	Nil (untreated)	4	0	20.97	11.368	7.63	5.45	5.36
	25	> 500	70	18.15	8.82	4.03	4.26	4.65
	50	> 600	80	14.47	8.33	5.75	5.63	6.14
	75	> 600	80	13.28	5.586	5.99	6.83	6.52
	100	> 600	80	13.17	5.586	6.14	7.79	7.85

[a]Fabric is padded in X g/L of emulsion, having wet pick up of 100%, dried at 100°C/5 min, beeswax: stearic acid ratio (1: 1), triethanolamine (50 % from fatty acid).

Table 5 — Effect of salt addition on water repellency rating and mechanical properties of the treated fabrics

Fabric[a]	Salt	During emulsion			Before emulsion			After emulsion		
		WRR	BL		WRR	BL		WRR	BL	
			Warp	Weft		Warp	Weft		Warp	Weft
Cotton	No salt	80	5.21	4.95	-	-	-	-	-	-
	$AlCl_3$	-	-	--	70	2.99	2.75	60	3.35	3.11
	$ZrOCl_2$	80	4.12	3.76	90	2.86	2.46	80	3.01	2.86
Jute	No salt	80	8.85	8.58	-	-	-	-	-	-
	$AlCl_3$	-	-	-	70	5.38	5.69	70	9.85	9.33
	$ZrOCl_2$	70	8.25	8.32	80	5.11	5.02	80	8.85	8.58
Linen	No salt	80	5.63	6.14	-	-	-	-	-	-
	$AlCl_3$	-	-	-	70	1.52	1.44	70	6.27	6.68
	$ZrOCl_2$	70	5.21	5.88	80	1.34	1.94	80	5.63	6.14

WRR–Water repellency rating; BL–Bending length (cm).
[a]Fabric is padded in 50 g/L of emulsion, having wet pick up of 100%, dried at 100°C/5 min, beeswax: stearic acid ratio (1: 1), triethanolamine (50 % from stearic acid) and salt concentration (1g/L).

the treatment of fabric with salt, after the emulsion treatment, causes a decrease in the mechanical properties but still in acceptable range for the all treated samples.

3.6 FTIR Analysis of Treated Fabrics

Figure 2 shows the FTIR spectra of treated and untreated fabrics. The spectral data shows no evidence of any chemical reactions between the substrate and the emulsion. Subtle changes in the 3000 region are observed as a proof of the presence of aliphatic moieties onto the treated fabrics in the form of physical attachment.

3.7 Storage Stability

A stoppered glass bottle, containing 100 mL of the emulsion (with different ratios of beeswax/stearic acid in the presence of TEA, with and without metal salt) was stored for different periods (1, 2, and 3 months). After each period, it is found that some emulsions have settled down into two layers. It is noticed that an increase in the wax amount in the emulsion leads

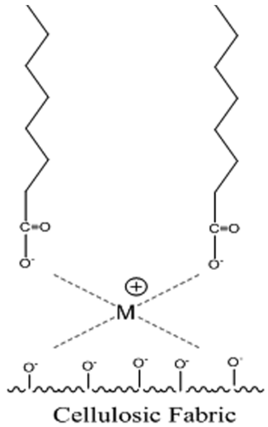


Fig.1 — Suggested mechanism of physical attraction of fatty acids and metal salt on cellulosic fabrics

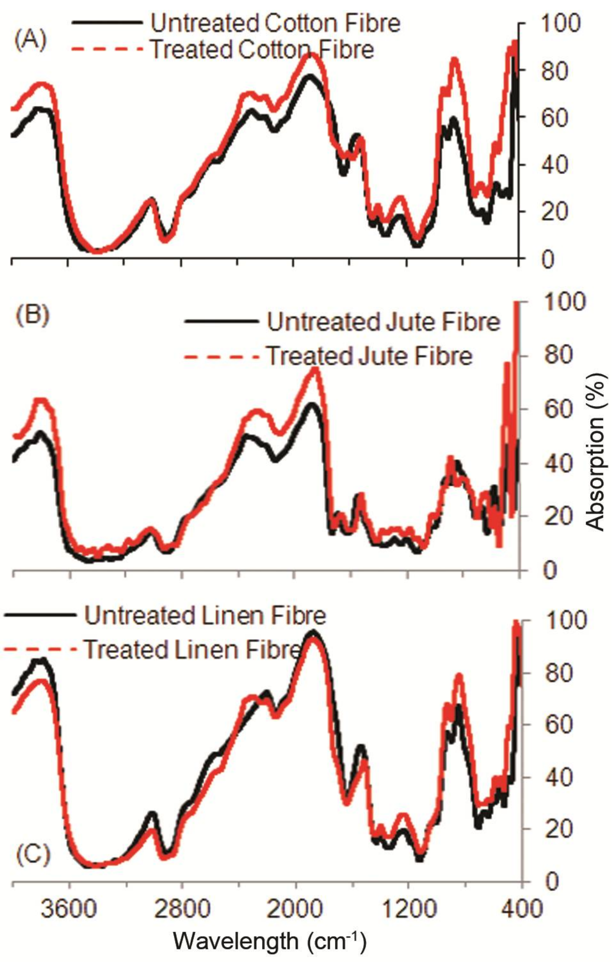


Fig.2 — FTIR spectra of treated and untreated fabrics(A) cotton fibre,(B) jute fibre, and (C) linen fibre

to a rapid separation of the emulsion into two layers. However, an increase in the amount of stearic acid in the emulsion leads to formation of a paste which is found more stable than others.

4 Conclusion

Treated fabrics have imparted a water repellency characteristic, reaching a value of 90, 80 and 80 for cotton, linen, and jute fabrics respectively. In addition, mechanical properties for treated fabrics are found to decrease as compared to the untreated fabrics, surface roughness of each fabric is enhanced because of treatment with prepared emulsion. FTIR spectra of treated fabrics have proved that the coating treatments are carried out physically with the absence of chemical reactions between the substrate and the emulsion. The treated fabrics may be used in various applications such as outdoor furniture and for packing materials.

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