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Synthesis and application of modified vegetable oils in water-repellent finishing of cotton fabrics

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ABSTRACT

Fluorine containing water-repellent agents—fatty acid trifluoroethyl esters were prepared by modification of different vegetable oils—castor oil, palm oil, and soybean oil via a reaction of hydrolysate of vegetable oil with 2,2,2-trifluoro ethanol. The structures of the modified vegetable oils were characterized by FT-IR. With contact angle, time for water to disappear, whiteness, and breaking strength as indicators, the optimum finishing processes of cotton fabrics with each modified vegetable oil were studied. The results showed that the cotton fabrics treated with the modified vegetable oils demonstrated excellent water repellency, while the whiteness and breaking strength of the fabrics reduced a little. The fabrics treated with modified palm oil exhibited the highest water repellency among all treated fabrics. All the treated fabrics showed good durability of water repellency after 5 cycles of washing, the contact angle remained about 90° or even higher, among which the durability of fabric treated with modified soybean oil was the best.

1. Introduction

Water-repellent finishing is an important process in the textile industry. Hydrophobic cotton fabrics are in great demand in a variety of functional applications including outdoor gear, rainwear, stain resistant products, and bandages. Water-repellent agent on hydrophilic fabrics such as cotton could prevent drops of water from spreading on the surface. The drops should stay on the surface and easily be wiped off (Abidi & Hequet, 2004; Sahin, 1996; Singh, 1987).

Water-repellent agent achieves its properties by reducing free energy at the fiber surface. There are different ways to incorporate water-repellent agents to surfaces of fibers. Traditionally, the mechanical incorporation of paraffin waxes or paraffin emulsion was used, however, there are some disadvantages, including stiff handle, lack of air and vapor permeability, and consequently poor wear comfort (Hagenmaier & Shaw, 1991). At present, the most widely used water-repellent agents are polydimethylsiloxane and fluorine containing agents, which are chemically incorporated on fiber surfaces. However, silicones increase pilling, and their wastewater are harmful to aqua-life (Lee et al., 2005; Mazurek, Kinning, & Kinoshita, 2001; Yahaya, Brisdon, Maxwell, & England, 2001). Fluorocarbon compounds can lower surface energy when applied on surfaces of materials and bring remarkable water repellency (Lee, Jin, Park, & Park, 2004; Malshe & Sangaj, 2005; Ming et al., 2001; Raslan & Bendak, 2005; Xie, Hou, & Shi, 2008; Xie, Hou, Shi, & Yu, 2007). However, the perfluorocarbon chains containing more than seven carbons, especially perfluorooctanoic acid (PFOA) and perfluorooctane sulfonates (PFOS), can resist degradation and cause bio-accumulate in human and animal tissue, posting long biological threats to human lives (Andersen et al., 2008; Aringer & Smolen, 2003; Berger, Machackova, & Berger, 2005). Therefore, more research activities presently have focused on developing environmental friendly alternative fluorinated materials to replace the traditional reagents associated with PFOA.

Vegetable oils are bio energy resources (Bala, 2005; Pinto et al., 2005), and because of the long carbon chains, they are somewhat water repellent. Introduction of C–F bond to the oil can further reduce surface energy at fiber surface, which may produce fabrics with improved water repellency.

In this study, different fluorine containing fatty acid esters were synthesized from three vegetable oils, through alkaline hydrolysis, acidification, acylation and reaction with 2,2,2-trifluoro ethanol. The structures of the esters were characterized by FT-IR. The effect of the modified oils was studied by measuring contact angle, time for water to disappear, whiteness, and breaking strength of the treated cotton fabrics.

2. Experimental

2.1. Materials

Vegetable oils (castor oil, palm oil, and soybean oil) were supplied by Taobao Co., Ltd (Zhejiang, China). 2,2,2-Trifluoro ethanol

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was purchased from Shanghai Record Pharmaceuticals Co., Ltd, China. Thionyl chloride, sulfuric acid, sodium hydroxide, sodium chloride, and 4-dimethylaminopyridine were supplied by Sinopharm Chemical Reagent Co., Ltd., China. All of them were used without further purification. Cotton fabrics, supplied by Test Fabrics (Shanghai, China), were thoroughly scoured and bleached according to AATCC Test Method 124-1996, then rinsed thoroughly in tap water, and dried in air before use.

2.2. Preparation of fatty acids

Vegetable oil (0.1 mol) was reacted with NaOH (0.3 mol) solution in hot water at 80 °C, stirred until uniform solution was formed. NaCl was added to the solution to separate fatty acid sodium from the by-product, glycerol. H_2SO_4 (0.15 mol) was added to the fatty acid sodium solution, then the fatty acids (about 84 g, different vegetable oils had different yields) were collected, rinsed with distilled water to remove excess H_2SO_4.

2.3. Preparation of fatty acid chlorides

The fatty acids (60 g) were added to the $SOCl_2$ (40 mL) dropwise over 20 min. Reaction was carried out at room temperature for 40 min, heated to 45 °C, and kept for 50 min. Excess $SOCl_2$ was removed under reduced pressure on a rotary evaporator at 40 °C. The product (about 60 g, different vegetable oils had different yields) was used in the next step without further purification.

2.4. Preparation of fatty acid trifluoroethyl esters

The fatty acid chlorides (50 g) were added to a three necked flask equipped with a magnetic stirrer, a thermometer, a nitrogen bubbling tube, and a water condenser, heated to 50 °C, 2,2,2-trifluoro ethanol (30 g), with 4-dimethylaminopyridine (0.5 g) dissolved in it was added with an injector slowly under reflux conditions, heated to 60 °C and kept for 4 h. The reactions of synthesis are shown in Scheme 1.

2.5. Treatment of cotton fabrics with fatty acid trifluoroethyl esters

Cotton fabrics were impregnated into different fatty acid trifluoroethyl ester solutions with ethyl ether as a solvent. The pressure on the mangle was adjusted to give 90% wet pickup, and pad proceeded with 2 dips (3 min for one dip) and 2 nips; then the samples were dried directly at 100 °C for t_1 min in a Rapid baker, then heated to T °C and cured for 3 min.

2.6. Measurement of the results

The structures of fatty acid trifluoroethyl esters were characterized with FT-IR. The whiteness of cotton fabrics was measured according to standard GB/T 8424.2-2001. The breaking strength was measured according to GB/T 3923.1-1997. Hydrophobic properties of the cotton fabric surfaces were estimated by measuring contact angles using a contact angle goniometer (JY-82). The measurement of the contact angle was carried out using the sessile drop method. The contact angle value was acquired 10 s after the dropping of a distilled water drop (about 5 μL) on the fabrics. More than ten readings were averaged to obtain one representative contact angle for each sample. The time for water to disappear was measured with a standard dropper (25 drops/mL), time for one drop (from 3 cm away) to change from sphere to hemisphere was measured. All the measurements were carried out at 24 °C.

3. Results and discussion

3.1. FT-IR analysis

The FT-IR spectra of castor oil, fatty acid hydrolyzed from castor oil, fatty acid chloride and fatty acid trifluoroethyl esters synthesized from castor oil are given in Fig. 1. The peak at 3006 cm^{-1} (C═C) confirmed the presence of unsaturated carbons. The peaks at 2925 and 2851 cm^{-1}, which arose from C–H asymmetric stretch in $-CH_3$, C–H asymmetric stretch in $-CH_2-$, and C–H asymmetric stretch in both $-CH_2-$ and $-CH_3$, respectively, indicated the presence of long chain alkyl groups.

The peak at 1742 cm^{-1} in (a) was attributed to the carbonyl group from castor oil. Formation of the free fatty acids was confirmed by (b). The FT-IR spectrum (b) showed an intense carbonyl stretch at 1711 cm^{-1} that corresponded to the free carboxylic acid, which replaced the original ester carbonyl stretch of the starting material at 1742 cm^{-1}. The intense signals centered on 1172 cm^{-1} (C–O stretch) associated with the glyceryl moiety had disappeared. Formation of the acid chlorides was confirmed by the presence of an intense carbonyl absorption at 1800 cm^{-1} and the absence of the broad O–H band of the acid in the region of 3500–2500 cm^{-1}. Formation of the fluorine containing new ester was confirmed by the presence of the peak at 1754 cm^{-1} in (d) and the peak at 1245.55 cm^{-1}, which is attributed to the strong stretching vibration of C–O–C, and the narrower and sharp absorption band at approximately 1168.17 cm^{-1} originates from the C–F symmetric stretching.

Figs. 2 and 3 show similar phenomena to Fig. 1, indicating that fluorine containing new esters have been synthesized from palm oil and soybean oil. The peaks at about 1741 cm^{-1} still remained in Figs. 2b and 3b after hydrolysis, because there are some unsaponifiable matters in both palm oil and soybean oil. But the unsaponifiable matters do not have much impact on the product, since in Figs. 2d and 3d we can see the peak of C═O of the vegetable oil is neglectable in comparison with the peak of C═O of the new ester.

3.2. Water repellency assessment

3.2.1. The effect of concentration on water repellency

Table 1 shows the effect of concentration of different modified vegetable oils on water repellency. It can be seen that cotton fabrics treated with three esters all showed water repellency compared with those untreated cotton fabrics. At the same concentration, the fabrics treated with modified palm oil showed higher contact angle than those treated with modified castor oil and soybean oil. The contact angle of the cotton fabrics treated with modified castor oil increased with the increase of concentration of esters, the contact angle was more than 120° when the concentration was more than 30 g L^{-1}. The contact angle of the cotton fabrics treated with modified palm oil and soybean oil decreased when the concentration of ester was higher than 40 and 50 g L^{-1}, the maximum was 125° and 123.5°, respectively.

The time for water to disappear of fabric treated with 40 g L^{-1} modified castor oil was as long as 32.17 min, although its contact angle was not the biggest. The tendency of the time for water to disappear of fabrics treated with modified palm oil and soybean oil was almost the same as that of contact angle, the maximum was 113.1 and 86.27 min, respectively.

The time for water to disappear firstly increased then decreased with the increase of concentration, since agents of high concentration brought damage and fiber breakage to the fabrics which also caused decrease in contact angle. Again, the modified palm oil provided the best water repellency.

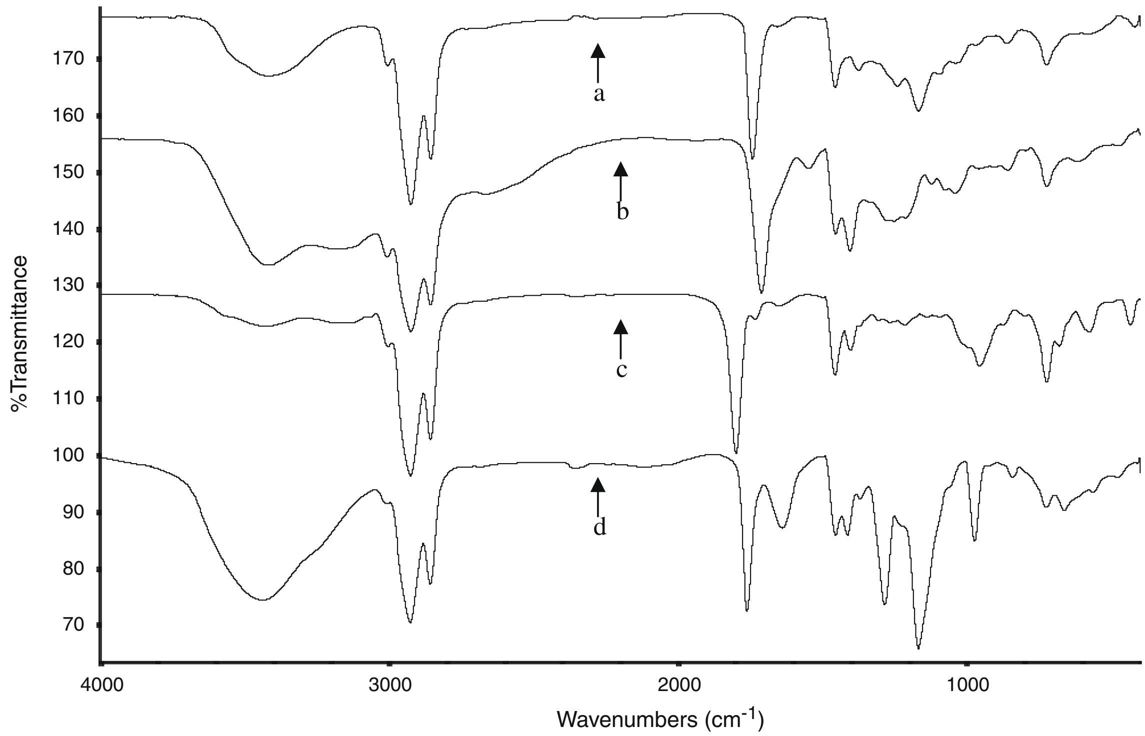


Fig. 1. FT-IR spectra of (a) castor oil, (b) fatty acid hydrolyzed from castor oil, (c) fatty acid acyl chloride, and (d) fatty acid trifluoroethyl esters synthesized from castor oil.

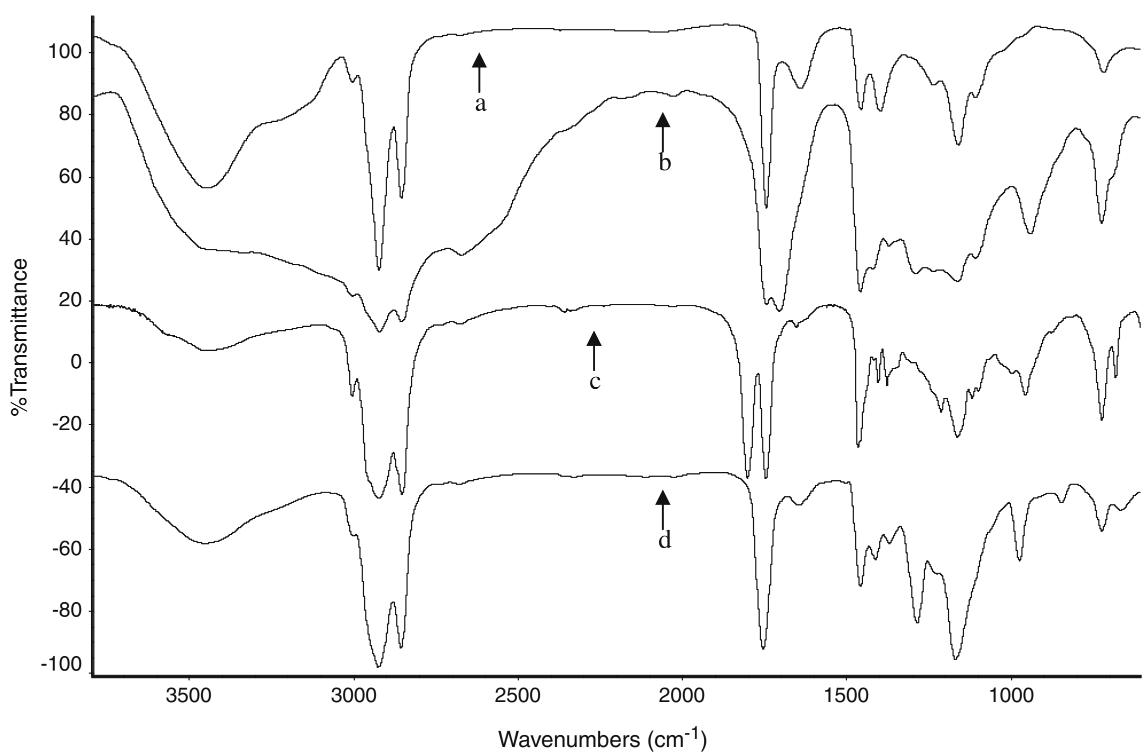


Fig. 2. FT-IR spectra of (a) palm oil, (b) fatty acid hydrolyzed from palm oil, (c) fatty acid acyl chloride, and (d) fatty acid trifluoroethyl esters synthesized from palm oil.

The whiteness and breaking strength of treated cotton fabrics decreased in comparison with untreated fabrics, the higher the concentration, the lower the whiteness and breaking strength.

It can be concluded that the optimum concentration is different to different esters synthesized from different oils. Higher concentration gave better water repellency, but also brought some harmful effects to whiteness and breaking strength. From the whole aspect, the modified palm oil provided the best water repellency.

3.2.2. The effect of drying time on water repellency

Table 2 shows the effect of drying time of different modified vegetable oils on water repellency. The contact angle increased at

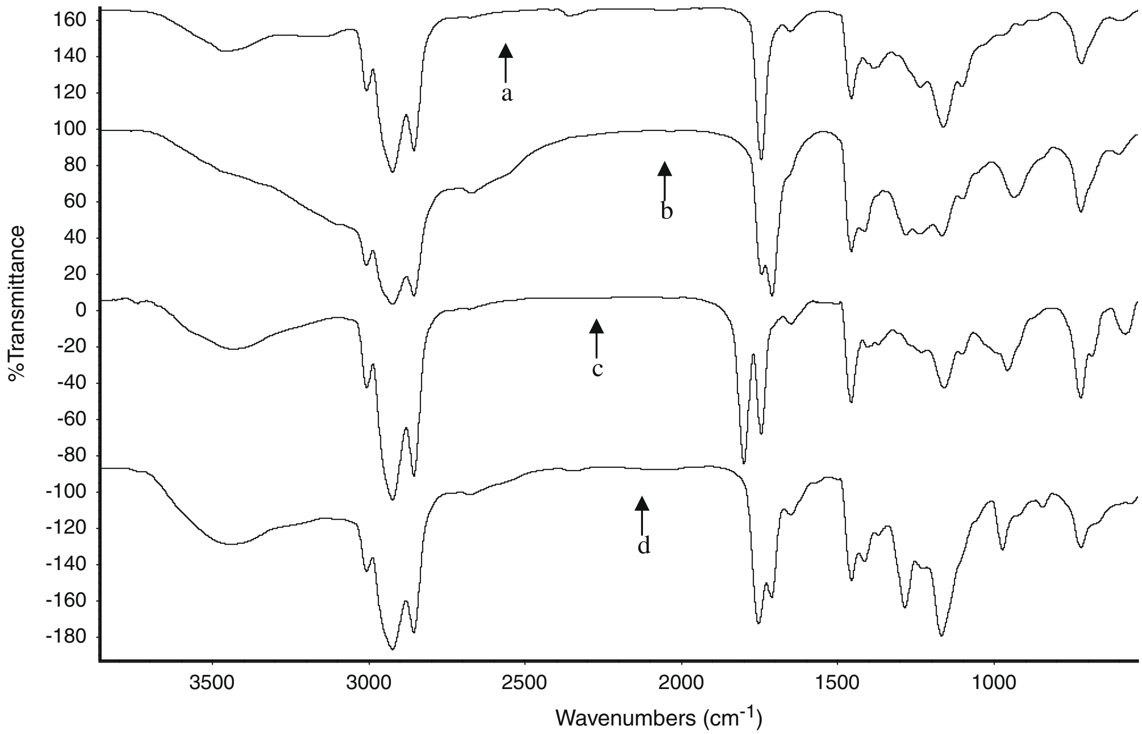


Fig. 3. FT-IR spectra of (a) soybean oil, (b) fatty acid hydrolyzed from soybean oil, (c) fatty acid acyl chloride, and (d) fatty acid trifluoroethyl esters synthesized from soybean oil.

Table 1
The effect of concentration of different modified vegetable oils on water repellency.

Modified vegetable oils	Concentration ($g L^{-1}$)	Contact angle (°)	Time for water to disappear (min)	Whiteness[a]	Breaking strength (N)[b]
Modified castor oil	10	108.3	1.96	76.8	315.7
	20	116.0	2.42	75.7	311.4
	30	119.7	13.34	72.4	310.6
	40	121.2	32.17	69.6	309.7
	50	121.3	31.50	66.2	306.8
	60	122.5	29.22	60.1	275.5
Modified palm oil	10	121.5	4.42	73.5	293. 0
	20	122.0	8.00	72.4	282.3
	30	122.7	111.67	69.7	270.2
	40	125.0	113.10	69.3	260.6
	50	122.8	88.00	65.7	259.5
	60	122.0	32.83	60.1	251.0
Modified soybean oil	10	93.0	1.37	76.6	287.7
	20	108.0	1.99	76.0	283.3
	30	108.5	2.92	75.3	274.8
	40	120.0	13.97	75.0	270.5
	50	123.5	86.27	69.3	264.3
	60	119.5	10.64	68.9	239.6

[a] The whiteness of untreated cotton fabric is 80.0.
[b] The breaking strength of untreated cotton fabric is 329.2 N.

Table 2
The effect of drying time of different modified vegetable oils on water repellency.

Modified vegetable oils	Drying time (min)	Contact angle (°)	Time for water to disappear (min)	Whiteness[a]	Breaking strength (N)[b]
Modified castor oil	20	116.0	6.15	76.4	310.7
	30	119.0	8.64	71.9	310.1
	40	128.1	36.82	71.2	311.3
	50	123.2	36.64	65.5	301.7
	60	119.3	26.80	63.5	297.3
	80	116.6	224.42	61.2	286.8
Modified palm oil	20	117.6	6.23	77.0	323.6
	30	123.0	14.34	76.2	320.3
	40	129.0	37.58	74.8	288.2
	50	127.0	31.56	74.5	328.5
	60	125.2	26.00	73.6	325.2
	80	125.0	16.30	71.7	304.5
Modified soybean oil	20	108.9	5.11	77.9	300.8
	30	111.0	6.23	76.9	280.7
	40	119.8	21.18	75.4	274.7
	50	120.30	23.79	74.7	298.6
	60	117.6	22.07	73.0	276.9
	80	118.2	16.30	71.6	250.7

[a] The whiteness of untreated cotton fabric is 80.0.
[b] The breaking strength of untreated cotton fabric is 329.2 N.

first with the increase of drying time, and then it decreased once the drying time exceeded certain value. For the fabrics treated with modified castor oil and palm oil, drying for 40 min gave highest contact angle, 128° and 129°, respectively. While for fabric treated with modified soybean oil, the optimum drying time was 50 min and the maximum contact angle was 120.3°. From the whole aspect, when drying for the same time, the modified palm oil provided higher contact angle than those treated with modified castor oil and soybean oil.

The tendency of the time for water to disappear was almost the same as that of contact angle. When drying for 40 min, both the modified castor oil and palm oil provided rather long time for water to disappear, 36.82 and 37.58 min, respectively, compared with that of soybean oil, 23.79 min.

The whiteness of cotton fabrics treated with the three esters decreased in comparison with untreated fabrics, the longer the drying time, the lower the whiteness. When drying for the same time, the whiteness of cotton fabrics treated with modified soybean oil was the best while that of the castor oil was the lowest.

The breaking strength of the cotton fabrics treated with the three esters decreased at first and then increased and then decreased again. Because with the drying time prolonged, more and

Table 3
The effect of curing temperature of different modified vegetable oils on water repellency.

Modified vegetable oils	Curing temperature (°C)	Contact angle (°)	Time for water to disappear (min)	Whiteness[a]	Breaking strength (N) [b]
Modified castor oil	130	0.0	0.15	75.5	315.9
	140	119.0	1.33	74.1	310.6
	150	111.1	11.07	73.9	296.9
	160	115.9	23.75	72.4	298.5
	170	119.8	32.75	71.0	296.5
	180	115.0	10.05	65.9	275.8
Modified palm oil	130	87.1	4.53	77.6	311.3
	140	94.0	5.11	76.7	309.6
	150	108.1	17.88	75.7	298.7
	160	117.0	24.43	75.0	260.6
	170	121.2	36.65	74.4	258.1
	180	125.0	22.18	74.0	251.0
Modified soybean oil	130	0.0	0.10	78.3	305.5
	140	71.9	1.18	77.1	297.9
	150	106.1	5.35	75.7	279.9
	160	112.3	14.51	75.1	270.5
	170	120.1	22.58	74.8	256.9
	180	114.0	12.67	73.2	239.8

[a] The whiteness of untreated cotton fabric is 80.0.
[b] The breaking strength of untreated cotton fabric is 329.2 N.

more esters could adhere to the fabrics, forming a film and leading to increase of the breaking strength. When the drying time exceeded some limit, the destructive effect surpassed the enhancement effect of the esters, so the breaking strength decreased again.

It can be concluded that the optimum drying time is different for the fabrics treated with different esters. Longer drying time gave better repellency, but also brought some harmful effects to whiteness. Again, the modified palm oil provided the best water repellency on the fabrics when dried for the same time.

3.2.3. The effect of curing temperature on water repellency

Table 3 shows the effect of curing temperature of different modified vegetable oils on water repellency. The contact angle of fabrics treated with modified palm oil increased with the increase of curing temperature, the maximum was 125° at 180 °C, while the

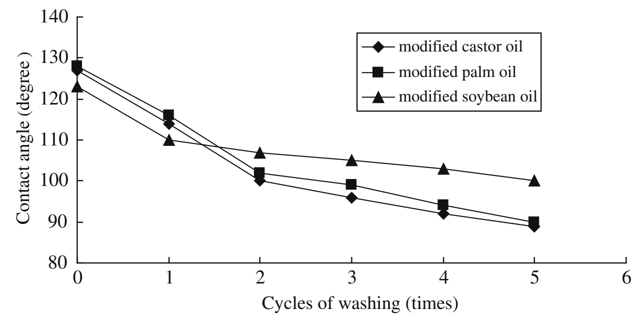


Fig. 4. Durability of water repellency of cotton fabrics treated with different modified oils.

contact angle of fabrics treated with modified castor oil and soybean oil both reached the maximum of about 120° at 170 °C.

The time for water to disappear of all the treated fabrics reached the maximum at 170 °C. This fact, together with the fact of contact angle, indicated that high curing temperature could cause damage and fiber breakage to the fabrics, so their contact angle and time for water to disappear could decrease.

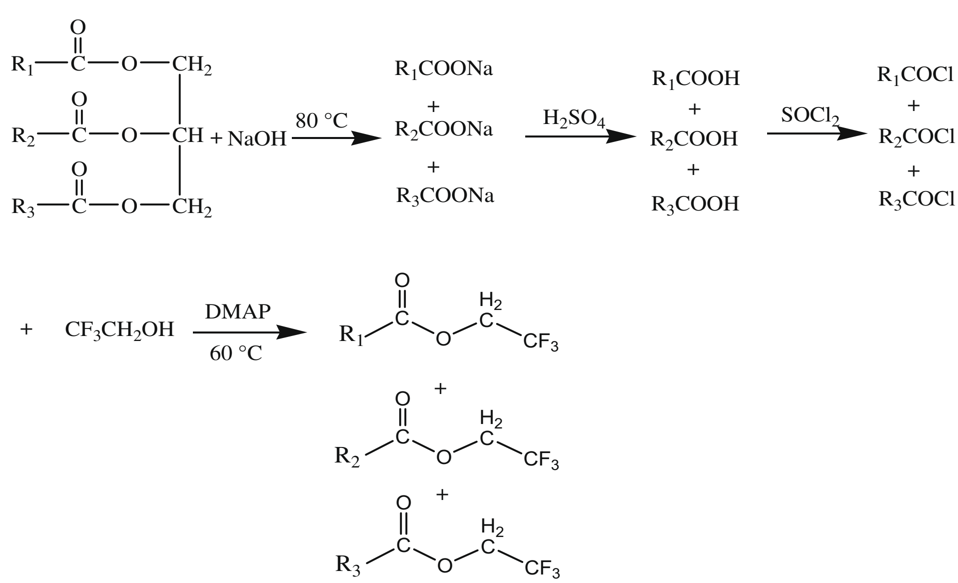
The whiteness of all the fabrics treated with esters decreased compared with the untreated fabric (whiteness about 80.0). When cured under the same temperature, the whiteness of fabrics treated with modified castor oil was the lowest, there was no obvious difference of whiteness between fabrics treated with modified palm oil and soybean oil.

The breaking strength of cotton fabrics treated with the three esters decreased with the increase of curing temperature, which was due to the higher temperature brought damage and fiber breakage to the fabrics.

Results showed that curing temperature of 170 °C can bring good water repellency, and acceptable whiteness and breaking strength.

3.3. Durability of water repellency

The durability of water repellency of the fabrics treated with three esters was tested. The cotton fabrics were immersed into 2 g L^{-1} soap solution, washed at 40 °C for 10 min, then rinsed for



Scheme 1. Synthesis of fatty acid trifluoroethyl esters.

2 min. After that, the fabrics were cured at 170 °C for 3 min. This was the first cycle of washing. The contact angle was tested after washing for different cycles. The results are shown in Fig. 4.

After 5 cycles of washing, the contact angle remained about 90° or even higher, indicating the durability of water repellency was good. The modified soybean oil provided the best durability of water repellency among all samples.

4. Conclusion

New water-repellent agents were synthesized from different vegetable oils and 2,2,2-trifluoro ethanol. FT-IR shows the C–F bond was introduced to the vegetable oils.

The optimum finishing conditions of cotton fabrics with different modified oils were discussed with contact angle, time for water to disappear, whiteness, and breaking strength as indicators. The results showed that all these modified oils could provide great water repellency and good durability to cotton fabrics with little adverse effect on its whiteness and breaking strength. The modified palm oil provided better water repellency than modified castor oil and soybean oil. After 5 cycles of washing, the contact angle of all treated samples remained about 90° or even higher. The modified soybean oil showed the better durability of water repellency than modified castor oil and palm oil.

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