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Synthesis and applications of vegetable oil-based fluorocarbon water repellent agents on cotton fabrics

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ABSTRACT

Vegetable oil-based fluorocarbon water repellent agents were prepared by chemical modifications of different vegetable oils – soybean and linseed oils through several reactions, including saponification, acidification, acylation of vegetable oil and trans-esterification with 2,2,2-trifluoroethanol and 2,2,3,3-tetrafluoropropanol. The resulted fluorocarbon agents were then copolymerized with styrene. The structures of the vegetable oil based agents were characterized by FT-IR and NMR. By evaluating water contact angle and time of water disappearance on cotton fabrics, as well as whiteness and breaking strength of cotton fabrics that were treated by these agents, optimum fabric finishing conditions were explored. The cotton fabrics finished with the vegetable oil-based fluorocarbon agents showed excellent water repellency, while other properties of the cotton fabrics declined to certain level. The linseed oil-based tetrafluoropropanol water repellent agent displayed the highest water repellency among all modified oils. All the treated fabrics exhibited good durability of water repellency. The linseed oil-based tetrafluoropropanol water repellent agent demonstrated the best durability among all repellent agents.

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1. Introduction

The hydrophobicity of material surface has attracted more attentions in research in recent years, owing to its wide range of potential applications (Hsieh, Lai, & Cheng, 2009). Fluorocarbon compounds confer extreme hydrophobicity and water insolubility to polymers, and can increase their thermal and oxidative stability when applied on the surfaces (Guner, Yagci, & Erciyes, 2006; Sharma & Kundu, 2006). The fluorocarbon bonds generate very strong interchain interactions and prevent the polymer from dissolving in any common solvents and interacting with other chemicals (Mokhtar, Abd-Elaziz, & Gomaa, 2010). The polydimethylsiloxane and organic fluorocarbon agents, which can be chemically incorporated onto fiber surfaces, have ever been prevalent as water repellent finishing agents for textiles. However, the silicone repellents could increase pilling on fabrics, and the wastewater generated in the finishing process is harmful to human and environment (Ren & Zhao, 2010). Up to now, the fluorocarbon compounds used widely are fluoroacrylate compounds which are copolymers of several non-fluorinated and fluorinated monomers (Espinosa & Meier, 2011). Among these fluorinated polymers, polyacrylate with perfluoroalkyl moieties in the side chains has been one of the most hydrophobic and oleophobic polymers (Schmidt et al., 1994). However, poly(fluoroalkyl acrylate)s with long perfluoroalkyl groups could degrade and produce perfluorooctanoic acid (PFOA) or perfluorooctanesulfonic acid (PFOS), which is more resistant to degradation and can bioaccumulate in human and animal tissues, possessing long biological half lives (Andersen et al., 2008; Berger, Machackova, & Berger, 2005). Therefore, these materials are concerned by public and have accordingly been either banned or voluntarily withdrawn by the manufacturers from the market. Fluorinated compounds exhibit the lowest surface energies, which has been employed in the development of water and oil repellency applications, but the products often were coupled with many of the other special or extreme properties of fluorinated compounds (Johns & Stead, 2000).

Due to the concerns on environmental impact of fluorocarbon compounds, vegetable oils were considered as a suitable alternative as water repellent agents, as they are hydrophobic, biodegradable, nontoxic, and 'Generally Regarded as Safe' (GRAS) products (Huang, Meng, & Qing, 2007; Kahraman, Bayramoglu, & Boztoprak, 2009; Li, Wu, & Han, 2002; Timeperley et al., 2003). Because of hydrophobicity, vegetable oils possess certain level of water repellency (Sacristan, Ronda, Galia, & Cadiz, 2010; Shen & Dai, 2007). Further lowering their surface energy could improve their water repellency and serve as good water repellent agents. Thus, researches

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on modification of vegetable oils (soybean oil, castor oil and palm oil) with trifluoroethanol have been conducted (Ren & Zhao, 2010). However, the water repellency of the modified oils was still unsatisfactory, the contact angle of finished cotton fabric was just about 120° and the laundry durability of the treatment was poor. In this study, different kinds of short fluorocarbon chain containing fatty acid esters were synthesized from different unsaturated vegetable by saponification, acidification, acylation and esterification of the oils, and copolymerization of the modified oils with styrene. Similarly, we evaluated the effect of these agents on cotton fabric by means of water contact angle and time of water disappearance on fabrics, and whiteness and breaking strength of the treated fabrics. Moreover, the performance of these reagents after repeat launderings was also evaluated. Water repellency of the fabric treated with the modified vegetable oil polymer was improved largely based on the results of contact angle and washing fastness.

2. Experimental

2.1. Materials

Vegetable oils (soybean oil and linseed oil) were supplied by Taobao Co. Ltd (Home-grown, Shanghai, China). 2,2,2-Trifluoroethanol and 2,2,3,3-tetrafluoropropanol were purchased from Shanghai Record Pharmaceuticals Co. Ltd., China. Sodium hydroxide, sodium chloride, ethanol (99%), sulfuric acid, methyl oleate, boron trifluoride diethyl etherate, styrene, 1,2-dichloro ethane, thionyl chloride, and 4-dimethylaminopyridine were supplied by Sinopharm Chemical Reagent Co. Ltd., China. 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. General procedure of saponification reaction

A typical reaction of preparing vegetable oil sodium soap was carried out in a conical flask equipped with a mechanical agitator, a water condenser and a thermometer under the following conditions: vegetable oil (0.01 mol), NaOH (20 mL, 2 mol/L), ethanol (20 mL, 99%), reaction time 50 min; an oil bath was heated to 120 °C; the mixture was stirred until a uniform solution was formed. The solution was heated directly to remove ethanol. Then hot saturated saline solution was added to the solution to separate fatty acid sodium salt from the other product, glycerol. The upper layer was fatty acid sodium salt (sodium soap) after the mixture was sufficiently cooled.

2.3. Preparation of fatty acids

H_2SO_4 (15 mL, 2 mol/L) was added to the fatty acid sodium salt solution. The mixture was heated directly with magnetic stirring while distilled water was added in several times. After precipitation of the fatty acid, the solution was rinsed with distilled water to remove excess H_2SO_4. The fatty acids were adequately dried at 85 °C.

2.4. Production of fatty acid chlorides

The fatty acids after drying at 85 °C in the oven were added to a four necked flask equipped with a magnetic stirrer, a water condenser, a thermometer, and a pressure equalizing dropping funnel, which was kept anhydrous to prevent side reaction of $SOCl_2$. The mixture of 5 mL $SOCl_2$ and 5 mL 1,2-dichloroethane was dropped slowly into the flask under an ice-bath. Then the mixture was kept for 4 h under room temperature. The rotary evaporator was used to remove excess $SOCl_2$. The prepared fatty acid chlorides were used in next step reactions without additional treatment.

2.5. Preparation of fatty acid fluorinated ester

The fatty acid chlorides and fluorinated alcohol (2,2,2-trifluoroethanol or 2,2,3,3-tetrafluoropropanol) were reacted at 65 °C for 6 h under nitrogen environment. Then the fluorine containing esters were concentrated in a rotary evaporator under 70 °C to remove excess 2,2,2-trifluoroethanol or 2,2,3,3-tetrafluoropropanol. The nomenclatures adopted for the products are: soybean oil-based fluorinated ester from 2,2,2-trifluoroethanol (STE), soybean oil-based fluorinated ester from 2,2,3,3-tetrafluoropropanol (SFE), linseed oil-based fluorinated ester from 2,2,2-trifluoroethanol (LTE), and linseed oil-based fluorinated ester from 2,2,3,3-tetrafluoropropanol (LFE), respectively.

2.6. Polymerization of fatty acid fluorinated ester with styrene

The fatty acid fluorinated esters (0.03 mol) were added to a four necked (100 ml) flask equipped with a magnetic stirrer, a thermometer, a nitrogen bubbling tube and a water condenser under room temperature. A mixture of methyl oleate (0.006 mol) and boron trifluoride diethyl etherate (0.0066 mol) was added to the flask, and then styrene (0.06 mol) was dropped into the reactor slowly, then the mixture was heated to 55 °C and reacted for 26 h. The vegetable oil-based fluorocarbon water repellent agents were collected by reduced pressure distillation. The nomenclatures adopted for the products are: soybean oil-based fluorocarbon water repellent agent from 2,2,2-trifluoroethanol (STP), soybean oil-based fluorocarbon water repellent agent from 2,2,3,3-tetrafluoropropanol (SFEP), linseed oil-based fluorocarbon water repellent agent from 2,2,2-trifluoroethanol (LTP), and linseed oil-based fluorocarbon water repellent agent from 2,2,3,3-tetrafluoropropanol (LFP), respectively.

2.7. Water repellent property of vegetable oil-based fluorocarbon water repellent agents on cotton fabric

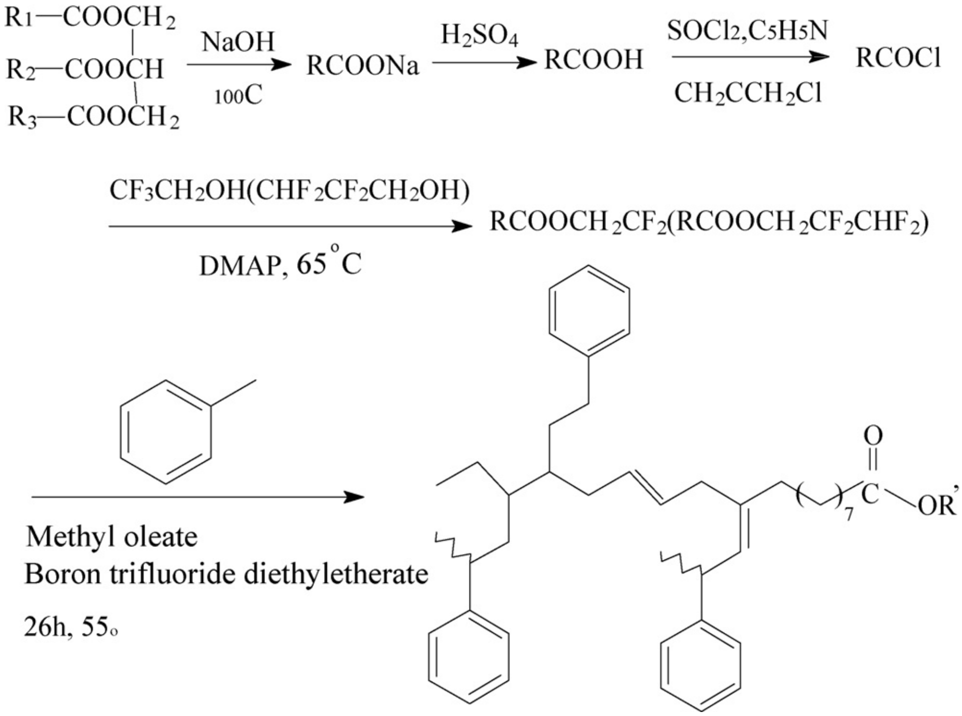
Cotton fabrics were impregnated in these water repellent agents, and then padded at a 90% wet pickup. The process was repeated to achieve 2 dips (3 min for one dip) and 2 nips. A preliminary drying was set at 100 °C for *t* minutes in a rapid baker, then heated to *T* °C and cured for 3 min at that temperature.

2.8. Characterizations

The structures of vegetable oil-based fluorinated esters were characterized with nuclear magnetic resonance (NMR) (Bruker Av400, Switzerland). The structures of all products during the whole reaction were characterized with a Fourier transform infrared spectrometer (FT-IR) (JSM-5600LV, Japanese JEOL). The whiteness of treated fabrics was obtained through standard American Association of Textile Chemist and Colorist (AATCC) 110-2005. The breaking strength of the fabrics was measured according to ASTM D2261. The water contact angle on fabrics was measured with a contact angle measurement instrument (KRUSS DSA 30).

3. Results and discussion

The synthesis reactions are shown in Scheme 1. The produced fatty acids were directly employed in synthesis of acid chlorides, which were then reacted with trifluoroethanol or tetrafluoropropanol to produce the vegetable oil-based fluorinated esters. These vegetable oil-based fluorinated esters were copolymerized



Scheme 1.

with styrene. The fluorocarbon copolymers, that is, vegetable oil-based fluorocarbon water repellent agents were employed in fabric treatments.

3.1. FT-IR analysis

Figs. 1 and 2 show typical FT-IR spectra of vegetable oils (soybean oil and linseed oil), sodium soap, corresponding fatty acids and fatty acid chlorides. The changes of peak positions reflect the different structures formed during the reactions. In Figs. 1 and 2, the position of C═O band changed dramatically, suggesting that structural changes occurred. The carbonyl band of soybean oil and linseed oil appears at 1746 cm^{-1} in (a) but moved to 1710 cm^{-1} in (c) when it was converted to fatty acid, and then shifted to 1800 cm^{-1} in (d), the formation of fatty acid chlorides. The band at 1563 cm^{-1} in Fig. 1(b) attributes to the presence of COO^{-}, the characteristic peak of sodium soap. The FT-IR spectra of four different fatty acid fluorinated esters are shown in Fig. 3. The C═O band in (e1) now moved to 1760 cm^{-1}, suggesting that the fatty acid

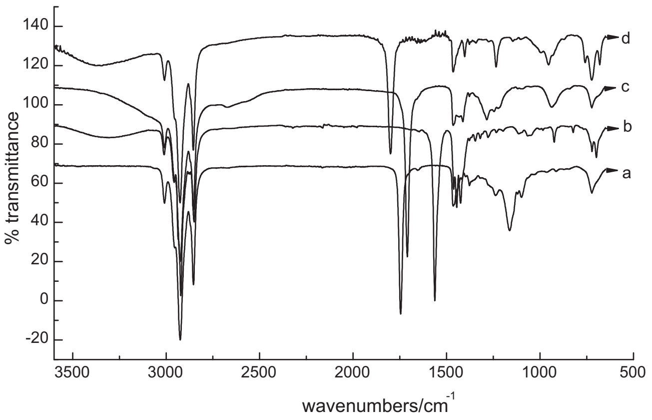


Fig. 1. FT-IR spectra of (a) soybean oil, (b) sodium soap, (c) fatty acid, and (d) fatty acid chloride.

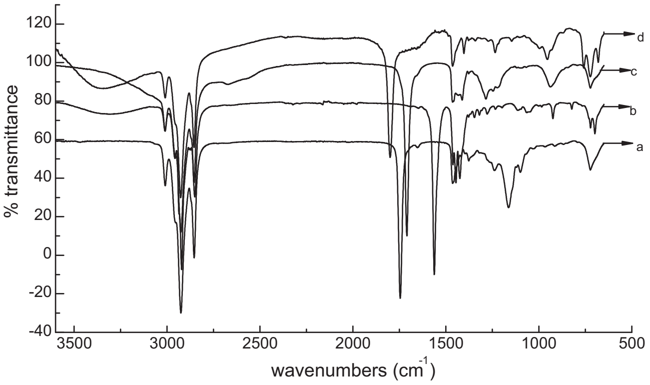


Fig. 2. FT-IR spectra of (a) linseed oil, (b) sodium soap, (c) fatty acid, and (d) fatty acid chloride.

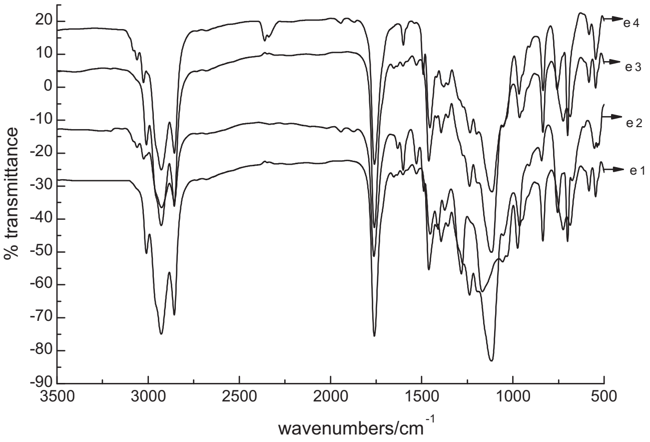


Fig. 3. FT-IR spectra of (e1) STE, (e2) SFE, (e3) LTE, and (e4) LFE.

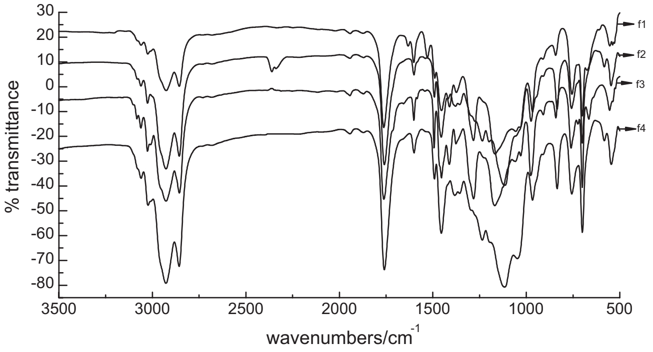


Fig. 4. FT-IR spectra of (f1) STP, (f2) SFP, (f3) LTP, and (f4) LFP.

chloride has reacted with 2,2,2-trifluoro ethanol to form an ester. Strong absorbance around 1168 cm^{-1} and 1285 cm^{-1} also indicated that the fluoroalkyl alcohols have reacted with acryl chloride to form new esters. Hydroxyl groups have a stretching vibration at 3200–2500 cm^{-1}, a main characteristic peak of carboxylic acid. Also, out-of-plane vibration of OH appears at 938 cm^{-1} in (c). The peaks at around 3009 cm^{-1} in Fig. 1(a)–(d), and 3005 cm^{-1} in (e1) of Fig. 3 confirm the presence of unsaturated carbons (C=C), while the bands at ~2900 cm^{-1} can be assigned to CH stretches of the CH_3 and CH_2 groups. The peaks around 720 cm^{-1} represents the $-(CH)_2$, indicating the presence of long chain alkyl groups.

Fig. 4 shows the FT-IR spectra of copolymerized products of the oil based fluorocarbon esters with styrene. The new bands at 1602 cm^{-1} and 1488 cm^{-1} in (f1), the main characteristic peaks of benzene ring, indicate the existence of styrene in the fluorocarbon copolymers.

3.2. NMR analysis

^{19}F NMR spectra of tetrafluoropropyl and fatty acid tetrafluoropropyl esters (from soybean oil and linseed oil respectively) were measured, revealing peaks at 73.5 ppm (3F, CF_3CH_2OH) in trifluoroethyl, 73.5 ppm (3F, CF_3CH_2O-) in trifluoroethyl ester soybean oil, and 76.9 ppm (3F, CF_3CH_2O-) in trifluoroethyl ester linseed oil (Li, Hanson, & Larock, 2001). Other representative peaks appeared at 128.2 ppm (2F, CF_2H-), 140.9 ppm (2F, $-CF_2-$) in tetrafluoropropyl, at 125.3 ppm (2F, $CF_2H-(CF_2CH_2O-)$), 128 ppm (2F, CF_2H-), 139.4 ppm (2F, $-CF_2-(C\ H_2O-)$), 140.9 ppm (2F, $-CF_2-$) in tetrafluoropropyl ester from soybean oil, at 125.3 ppm (2F, $CF_2H-(CF_2C\ H_2O-)$), 127.9 ppm (2F, CF_2H-), 139.4 ppm (2F, $-CF_2-(CH_2O-)$), 140.8 ppm (2F, $-CF_2-$) in tetrafluoropropyl ester from linseed oil. The ^{19}F results are consistent with the agent structures as proposed. The peaks at 128 ppm (2F, CF_2H-), 140.9 ppm (2F, $-CF_2-$) in tetrafluoropropyl ester from soybean oil, at 127.9 ppm (2F, CF_2H-), 140.8 ppm (2F, $-CF_2-$) in tetrafluoropropyl ester from linseed oil indicate existence of a small portion of tetrafluoropropanol in the esters.

3.3. Water repellency assessment

3.3.1. Effect of concentration on water repellency

Table 1 shows the water repellency performance of the cotton fabrics treated with four different kinds of the agents in different concentrations. The finished cotton fabric showed distinct water repellency compared with those unfinished cotton fabrics. It can be seen that the water contact angles of the cotton fabrics treated with the esters increased as the concentration of the agents increased in the finishing baths. However, the contact angle decreased a little when the concentration of the water repellency agent surpassed 60 g/L. The linseed oil-based fluorocarbon water repellent agents provided the higher contact angle on cotton fabrics than the soybean oil-based fluorocarbon water repellent agents under the same conditions. The vegetable oil-based water repellent agents from trifluoroethanol performed better than that from tetrafluoropropanol.

The time of water disappearance on the cotton fabrics treated with the soybean oil-based fluorocarbon agents was measured, and the linseed oil-based fluorocarbon water repellent agents showed similar phenomenon as the water contact angles. With increasing concentrations of the agents, the time of water disappearance presented ascendant trend until the finishing concentration of 80 g/L and declined a little when the concentration was above 80 g/L. Similarly, the linseed oil-based fluorocarbon water repellent agents provided better water repellency on the cotton fabrics than the soybean oil-based fluorocarbon water repellent agents under the same conditions, while water repellent agents from trifluoroethanol performed better than that from tetrafluoropropy.

The whiteness and breaking strength of cotton fabrics finished with the water repellency agents decreased in comparison with that of the unfinished fabrics. The concentration of the agents showed more adverse effect on the whiteness than the breaking strength of the fabrics. Higher concentration provided better water repellency, however, more harmful effects to whiteness and breaking strength of the products. The optimized conditions for each modified vegetable oil should be further explored. Overall, the linseed oil-based water repellent agents gave better water repellency than soybean oil based ones, while the ones from trifluoroethanol did better than that from tetrafluoropropy.

3.3.2. Effect of curing temperature on water repellency

The effect of curing temperature on water repellency of the cotton fabrics finished with different agents is shown in Table 2. The water contact angles of cotton fabrics treated with the soybean oil-based fluorocarbon water repellent agents and the linseed oil-based fluorocarbon water repellent agents increased with the curing temperature until 170 °C, then declined a little above 170 °C, indicating that too high temperature could cause damage to the fabrics and surface water repellent structures formed on the fabrics.

The time of water disappearance on the finished cotton fabrics showed the best water repellency at 180 °C for vegetable oil-based fluorocarbon water repellent agents. When the curing temperature surpassed 180 °C, there was no obvious change based on the time of water disappearance.

The whiteness of cotton fabrics treated with modified vegetable oils decreased compared with that of the unfinished fabrics. At the same curing temperature, the whiteness of the fabrics finished with the soybean oil-based fluorocarbon water repellent agents was higher than that finished with the linseed oil-based fluorocarbon water repellent agents. When cured under the same temperature, the whiteness of the fabrics finished with the water repellent agents from tetrafluoropropy declined less than that from trifluoroethanol.

There is no obvious decrease in breaking strength of cotton fabrics finished with all water repellency agents at the curing temperature under 170 °C. The substantial downtrend of breaking strength of the finished cotton fabrics appeared when the curing temperature exceeded 170 °C.

3.3.3. Effect of predrying time on water repellency

The fabrics were padded with the water repellent agents and then dried in a preliminary process (predrying) at 100 °C. The contact angle increased initially with prolonging the predrying time from 1 to 4 min, however, decreased or had no obvious change once the drying time exceeded 4 min. For the cotton fabrics treated with LTP and LFP, the contact angle reached the maximum value at predrying time of 3 min, the difference is that the former changed a

Table 1
Effects of concentration of different water repellent agents on water repellency.

Water repellent agents	Concentration (g/L)	Contact angle (°)	Time for water disappearance (s)	Whiteness[a]	Breaking strength (N)[b]
STP	20	141	240	77.3	310.7
	40	137.3	783	76.4	327.5
	60	141.7	1207	76.4	308.4
	80	135.3	1249	72.6	302.8
	100	136.3	1240	73	303.7
SFP	20	138.2	1860	77	218.6
	40	140.6	1740	76.1	235.7
	60	141.3	1870	74.2	234.4
	80	138.6	1895	73.5	243.9
	100	138.9	1797	73	245.5
LTP	20	139.3	5130	76.3	366.8
	40	139.9	5238	75.3	320.6
	60	141.5	6430	72.8	321.7
	80	141.3	6710	69.7	311.8
	100	140.6	6700	68.4	304.8
LFP	20	135	393	76.95	314.2
	40	137	805	76.65	305.8
	60	143	7180	73.35	307.7
	80	143	11,340	72.55	304.4
	100	141	10,310	70.6	305.4

[a] The whiteness of unfinished of cotton fabric is 80.0.
[b] The breaking strength of unfinished of cotton fabric is 329 N.

Table 2
Effects of curing temperature of different water repellent agents on water repellency.

Water repellent agents	Curing temperature (°C)	Contact angle (°)	Time for water disappearance (s)	Whiteness[a]	Breaking strength (N)[b]
STP	150	138.8	240	75.4	304.6
	160	139.6	783	76.2	324.3
	170	140.1	1207	76.2	315.6
	180	137.6	1249	74.5	257.9
	190	136	1240	73.4	256.2
SFP	150	141.9	1860	75.8	258.6
	160	141.2	1740	76.1	236.9
	170	142.4	1870	76	264.9
	180	142.4	1895	75.3	263.9
	190	139.2	1797	73.6	259.6
LTP	150	139.4	5130	72	387.5
	160	142.2	5238	71	361.6
	170	143.6	6430	71.3	344.9
	180	140.7	6710	69.3	261.2
	190	138.3	6700	65.9	242.9
LFP	150	138.31	393	74.45	244.3
	160	140.18	805	74.25	226.3
	170	141.44	7180	74.45	273
	180	139.72	11,340	73.95	227
	190	136.4	10,310	70.5	236

[a] The whiteness of unfinished of cotton fabric is 80.0.
[b] The breaking strength of unfinished of cotton fabric is 329 N.

little and the latter decreased a lot. The cotton fabrics treated with STP and SFP showed the highest contact angle at a predrying time of 4 min.

The time for water disappearance on the samples finished with the modified linseed oil was the longest when predrying time was 3 min. The SFP and STP provided the longest time for water disappearance at 5 min and 4 min of predrying time, respectively.

The whiteness of samples finished with different water repellent agents decreased in comparison with that of the unfinished fabrics. With the increase of predrying time, the whiteness did not change significantly. Under the same condition, the whiteness of the fabrics finished with the soybean oil-based fluorocarbon water repellent agents were better than that of the one finished with the linseed oil-based fluorocarbon water repellent agents.

The breaking strength of the cotton fabrics treated with different water repellency agents decreased compared with the unfinished samples. With the predrying time prolonged from 1 to 5 min, the breaking strength increased at first and then decreased a little, which partly due to the formation of a polymer film on surfaces of the fabrics.

In the whole aspect, the optimum predrying time is different among the fabrics finished with different polymers. The longer the predrying time, the better the water repellency However, too long predrying time (above 5 min) could bring harmful effects to the breaking strength.

3.4. *Durability of water repellency ability*

The durability of water repellency of the finished cotton fabrics is shown in Figs. 5 and 6. The cotton fabric were immersed into 2 g/L soap solution, rotated at 40 °C for 10 min, and rinsed for 2 min with tap water, then dried at room temperature. This was a cycle

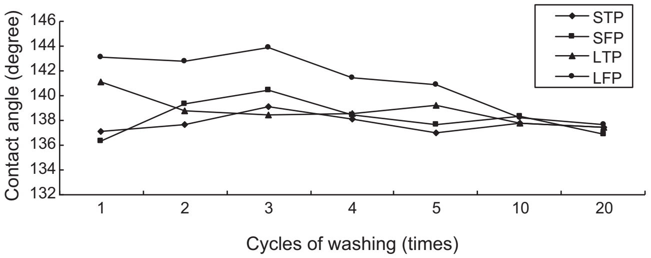


Fig. 5. Durability of water repellency of finished cotton fabric measured with water contact angle.

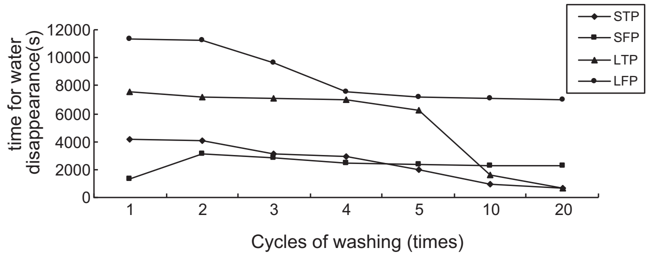


Fig. 6. Durability of water repellency of finished cotton fabric measured with time for water disappearance on fabrics.

of washing. The cycle was repeated up to 10 cycles of washing. The contact angle and the time for water disappearance on the finished fabrics were tested after washing for different cycles.

The contact angle decreased substantially along with increase of the cycles of washing. After 10 cycles of washing, the contact angle remained about 138° and kept at 136° even after 20 cycles of washing, indicating good washing durability of the water repellency of the finished cotton fabrics.

The tendency of the time for water disappearance is shown in Fig. 6, which is almost the same as that of contact angle. The time for the water disappearance on the fabrics treated with SFP and LFP decreased initially and showed no obvious change above 3 cycles of washing. The fabrics treated with the STP and LTP showed shortened water disappearance time, which was further decreased suddenly after 10 cycles of washing. Overall, the LFP provided the highest water contact angle, the best durability of water repellency on the fabrics.

4. Conclusions

New vegetable oil based fluorocarbon agents were synthesized from reacting fatty acids hydrolyzed from soybean oil and linseed oil with 2,2,2-trifluoroethanol and 2,2,3,3-tetrafluoropropanol. Then agents were copolymerized with styrene to form FT-IR and NMR identified that the vegetable oil-based fluorocarbon water repellent agents were produced.

The finishing conditions of fabric with different vegetable derivatives were investigated to find out the optimum concentration, curing temperature and predrying time in terms of water contact angle and time for water disappearance on fabrics, and whiteness and breaking strength of the fabrics as indicators. The results showed that these oil derivatives could provide desired water repellency but also have adverse effects on fabric whiteness and breaking strength. The LFP provided the best water repellency and favorable durability of water repellency among all modified vegetable oils. After 20 cycles of washing, the contact angle of the treated samples remained about 137°.

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