

# Study on Synthesis and Application of Short Chain Fluorinated Acrylate Water and Oil Repellent Finishing Agent Emulsion

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## Abstract

With bis-(2,2,3,3,4,4,5,5-octafluoropentyloxy) acrylate (OFAE) and octafluoropentyl acrylate (OFAC) as comonomers, a short chain fluorinated acrylate water and oil repellent finishing agent emulsion was synthesized by miniemulsion polymerization. The best synthesis process of acrylic miniemulsion with short fluorine chain was explored by single factor analysis method: the molar ratio of OFAE and OFAC was 2:1, the mass ratio of emulsifier and auxiliary emulsifier was 7:1, the mass ratio of cationic emulsifier and nonionic emulsifier was 2:1 and the polymerization temperature was 65 °C. The FT-IR spectrum showed that the fluorinated acrylate participated in the polymerization and the polymerization was complete. The XPS energy spectrum showed that there were C, O and F elements on the surface of the latex film. The TG-DTG analysis and particle size distribution showed that the emulsion of the short chain fluorinated acrylate water and oil repellent finishing agent had good thermal stability and uniform particle size distribution; The changes of cotton fabric before and after finishing were analyzed by SEM and static contact angle CA..

## Keywords

Fluorinated Acrylate Polymer; Miniemulsion Polymerization; Water and Oil Repellent Finishing.

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## 1. Introduction

Fluorine-containing finishing agent [1] is a finishing agent based on perfluoro or polyfluoroalkyl compounds (also known as fluorocarbons). Perfluoro or polyfluoroalkyl compounds refer to chemicals in which all or part of the hydrogen atoms in the carbon chain of the compound molecule are replaced by fluorine atoms to form a fluorocarbon chain structure. Fluorine-containing textile finishing agents are widely used in actual production and life because there are a large number of C-F bonds in the fluorine-containing chain segment, and the -CF<sub>3</sub> group has a very small surface tension, which can minimize the surface free energy and critical surface tension of the fabric [2], and can endow the fabric with excellent water and oil resistance, stain resistance and washing resistance. Especially in textile dyeing and finishing industry [3].

Fluorinated acrylate polymers are the main components of fluorinated water and oil repellent finishing agents in the market at present, but perfluorooctane sulfonyl compounds (PFOS) and perfluorooctanoic acid compounds (PFOA) will be produced in the process of oxidative degradation of long carbon chain fluorinated acrylate polymers ( $-C_nF_{2n+1}$ ,  $n \geq 8$ ). PFOS/PFOA have bioaccumulation and long-distance migration in the natural environment, are difficult to degrade, have the possibility of inducing cell canceration, and bring potential harm to human health and the natural environment [4]. Since 2006, Europe has imposed strict restrictions on the market input and use of such products. At present, many countries have completely banned the use of fluorinated polymers with 8C and above [5][6]. According to the report of 3m Company [7], perfluorocarboxylic

acids or sulfonylates with perfluoroalkyl carbon chain length  $\leq 4$  are not bioaccumulative. In addition, many studies have also shown that fluorine-containing derivatives with perfluorocarbon chain length  $\leq 6$  are basically not harmful to the environment[8],[9],[10]. Due to the use of non-perfluoroalkyl groups (such as  $-C_3F_6H$ ) as short fluorocarbon chains, the existence of some carbon-hydrogen bonds after surface treatment leads to a sharp increase in surface energy, which makes it difficult to obtain ideal water and oil repellency [11],[12]. Therefore, it has become a research hotspot in the textile industry and textile chemicals manufacturing industry to find and develop substitutes for long carbon chain fluorinated acrylate polymers ( $-C_nF_{2n+1}$ ,  $n \geq 8$ ).

## 2. Experimental

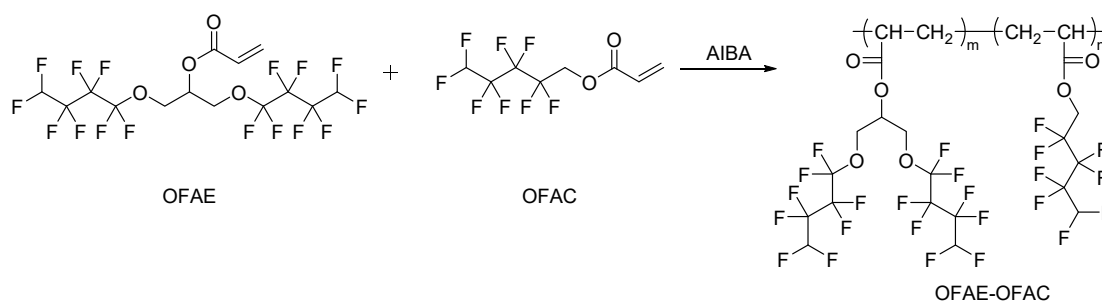
### 2.1 Materials, Reagents and Instruments

Materials: 10 cm  $\times$  10 cm (warp  $\times$  weft) pretreated cotton fabric

Reagents: Bis (2,2,3,3,4,4,5,5-octafluoropentyloxy) acrylate (OFAE): self-made; octafluoropentyl acrylate (OFAC), self-made; 2,2'-azobisisobutyramidine dihydrochloride (AIBA), 98%+, Shanghai Titan Technology Co., Ltd.; Lauryl alcohol polyoxyethylene ether (Brij L4), analytically pure, Sigma Aldrizzi (Shanghai) Trading Co., Ltd.; cetyl trimethyl ammonium bromide (CTAB), 99%, Shanghai Titan Technology Co., Ltd.; paraffin oil, analytically pure, Shanghai Titan Technology Co.

Instruments: Photochemical contact angle meter, C602 customized version, Keno Industrial Co., Ltd., USA; Fourier transform infrared meter, Frontier Near/Mid-IR Std, Thermo Scientific Co., USA; heavy analyzer, Q500 type, TA Instrument Co; X-ray Photoelectron Spectrometer, Thermo Nexsa, Thermo Fisher Scientific Co., Ltd.; Scanning Electron Microscope SEM, Thermo Quattro S, Thermo Fisher Scientific Co., Ltd.; Laser Particle Sizer, Litesizer 500, Anton Paar (Shanghai) Trading Company.

### 2.2 Synthesis of Short Chain Fluorinated Acrylate Water and Oil Repellent Finishing Agent Emulsion



**Fig 1.** Miniemulsion polymerization scheme

#### 2.2.1 Pre-emulsification

Cetyl trimethyl ammonium bromide (CTAB)(0.3552g) and lauryl alcohol polyoxyethylene ether (Brij L4)(0.1776 g) were dissolved in a certain volume of deionized water, stirred and dissolved in a water bath at 50 °C. Bis (2,2,3,3,4,4,5,5-octafluoropentyloxy) acrylate (OFAE) (3.5823 g, 6 mmol) and octafluoropentyl acrylate (OFAC)(0.8584 g, 3 mmol) are mixed and then transferred into a mixed solution of an emulsifier and a coemulsifier Dodecyl Mercaptan(0.1382 g). After stirring for 15 min in a water bath at 50 °C, the monomer pre-emulsion was prepared by high-speed stirring and homogenization for 15 min at the speed of 15000 r/min under the action of a high-speed shear dispersion emulsifying machine.

#### 2.2.2 Miniemulsion Polymerization

The monomer pre-emulsion prepared by pre-emulsification was transferred to a three-necked flask equipped with a thermometer, a condenser tube, mechanical stirring, and nitrogen protection, slowly heated to the polymerization temperature of 65 °C, and after 30 min of heat preservation, the water-soluble initiator 0.1332 g of azobisisobutyramidine hydrochloride AIBA aqueous solution (1.6 g/L)

was added completely within one hour. After the dropwise addition, the polymerization was continued at 65 °C for 12 h. The solution after the reaction is cooled to room temperature and filtered, and the obtained filtrate is the aqueous short-chain fluorine-containing acrylate water-repellent and oil-repellent finishing agent.

### 2.2.3 Finishing Process of Cotton Fabric

Cotton fabrics to be finished were immersed in different concentrations (30 g/L, 30 min) of water-borne short-chain fluorinated acrylate water and oil repellent finishing agent for several minutes, followed by M-dipping and N-rolling (rolling pick-up 80%), pre-drying 90 °C, 3 min), baking (160 °C, 3 min), after soaping with a soaping agent, washing the residual reagent on the surface of the cotton fabric with deionized water, drying at low temperature, placing the cotton fabric in a drying oven, cooling, and testing the contact angle.

## 2.3 Structure Characterization and Performance Test of Short Chain Fluorinated Acrylate Water and Oil Repellent Finishing Agent

### 2.3.1 FT-IR Characterization

The copolymer latex films were characterized by Fourier transform infrared spectroscopy (FT-IR) in the attenuated total reflection (ATR) mode in the range of 600 ~ 4 000 cm<sup>-1</sup>.

### 2.3.2 X-ray Photoelectron Spectroscopy (XPS)

X-ray electron spectroscopy (XPS) was used to analyze the elements and their contents in the copolymer latex film. The excitation source was AlK $\alpha$  ray ( $h\nu = 1486.6\text{eV}$ ), the working voltage was 12.5kV, the filament current was 6ma, and the signals were accumulated for 10 cycles.

### 2.3.3 Emulsion Particle Size Distribution Test

Take 1-2 drops of the filtered copolymer emulsion into a cuvette, dilute it with deionized water to the measurable range of the laser particle size analyzer at 25 °C with Litesizer 500 laser particle size analyzer, and determine the particle size distribution of the emulsion.

### 2.3.4 Latex Film Thermogravimetric Analysis and Derivative Thermogravimetry (TG-DTG) Test

5 mg of the prepared latex film was measured with a thermogravimetric analyzer under N<sub>2</sub> flow, the initial temperature was 30 °C, and the temperature was raised to 600 °C at a heating rate of 10 °C/min.

## 2.4 Application Characterization and Performance Test of Short Chain Fluorinated Acrylate Water and Oil Repellent Finishing Agent

### 2.4.1 Fabric SEM Test

The original cotton fabric and the water and oil repellent finished cotton fabric were put on the conductive tape respectively, and the surface of the fabric was sprayed with gold (spraying time was 40s). The surface morphology of the fabric was observed by scanning electron microscope (SEM) with scanning times of 200, 2000, 20000 and working voltage of 5 K V.

### 2.4.2 Static Contact Angle Test

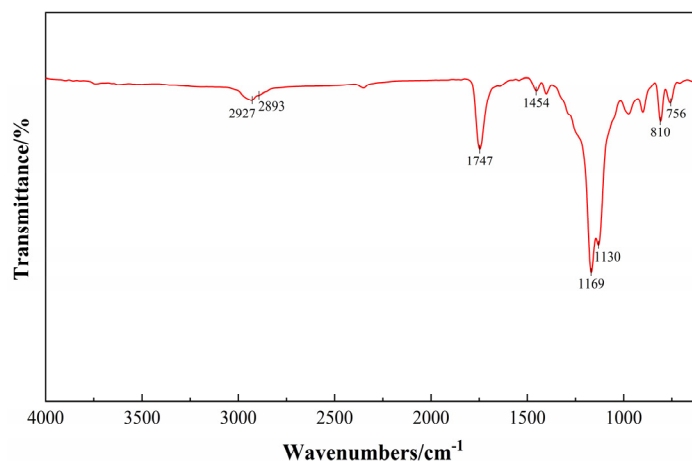
The contact angle of cotton fabric to water and oil (paraffin oil, hexadecane) is used to measure the effect of water and oil repellency. The static contact angle of cotton fabric was tested by an optical contact angle measuring instrument, and 2  $\mu\text{L}$  deionized water and 5  $\mu\text{L}$  oil (paraffin oil and n-hexadecane) were dropped on the surface of the fabric respectively, and the test began after 30 s. Measure 3 times at different positions of the same sample, and take the average value.

## 2.5 Structure and Properties of Short Chain Fluorinated Acrylate Emulsion as Water and Oil Repellent Finishing Agent

### 2.5.1 Copolymer Structure Analysis

#### 2.5.1.1 Latex Film FT-IR Characterization

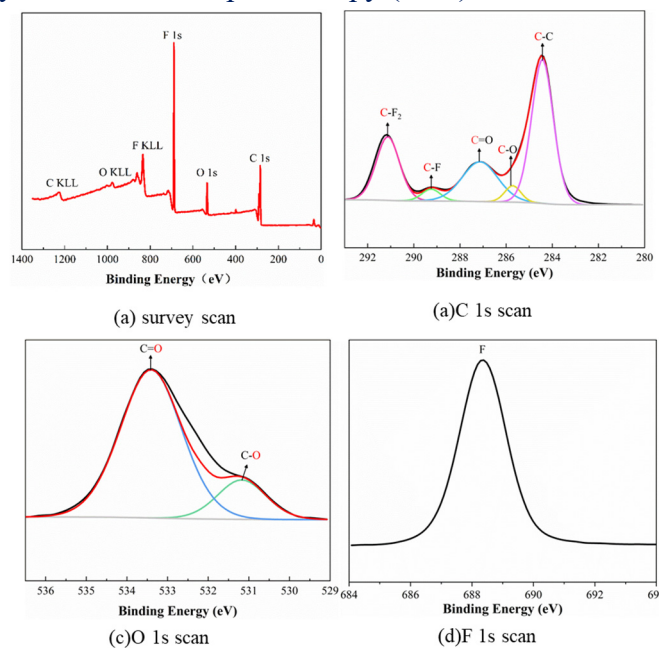
The infrared spectrum of the polymer short-chain fluorine-containing acrylate water-and oil-repellent finishing agent is shown in fig. 2



**Fig 2.** Latex film Fourier attenuation total reflection infrared spectroscopy

It can be seen from the figure 2 that the wave number at  $2927\text{ cm}^{-1}$  and  $1454\text{ cm}^{-1}$  is the characteristic absorption peak of symmetric stretching vibration and in-plane bending vibration of methylene  $-\text{CH}_2-$  on the main carbon chain of the polymer, and the wave number at  $2893\text{ cm}^{-1}$  is the characteristic absorption peak of out-of-plane rocking vibration of methine  $-\text{CH}-$  on the main carbon chain. The long and narrow peak at  $1747\text{ cm}^{-1}$  is the characteristic absorption peak of the stretching vibration of the ester carbonyl group  $\text{C}=\text{O}$ , the  $\text{C}-\text{O}-\text{C}$  stretching vibration absorption peak of the ester carbonyl group at  $1169\text{ cm}^{-1}$ , and the characteristic absorption peak of  $\text{CF}_2-$  at  $1130\text{ cm}^{-1}$  and  $810\text{ cm}^{-1}$ ; The carbon-carbon double bond  $\text{C}=\text{C}$  has no obvious characteristic absorption peak of stretching vibration at  $1640\text{ cm}^{-1}$ . In summary, it can be preliminarily judged that the fluorine-containing monomer has successfully synthesized the water-based short-chain fluorine-containing acrylate water-and oil-repellent finishing agent

#### 2.5.1.2 Latex Film X-ray Photoelectron Spectroscopy (XPS) Characterization



**Fig 3.** XPS survey scan(a), C1s scan(b), O1s scan(c) and F1s scan(d) spectra of polymer latex film

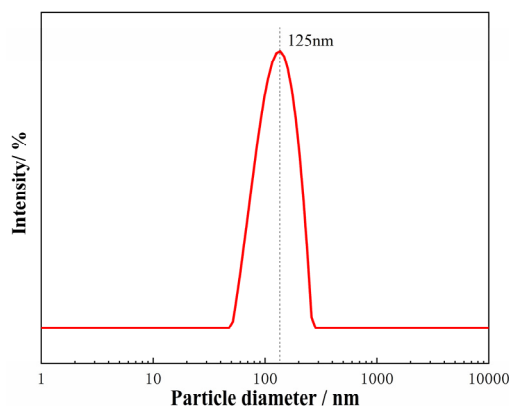
The composition of the chemical elements on the surface of the emulsion film was analyzed by using an XPS tester, and the results are shown in the figure.3 According to the peak positions, it can be determined that there are C 1s, O 1s and F 1s elements on the surface of the fluorine-containing

acrylate polymer emulsion film, and their chemical shifts are around 284 eV, 532 eV and 688 eV, respectively. And that content of F element on the surface of the emulsion film can reach 29.47% shows in Table 1, which is high. This indicates that the fluorine-containing groups with low surface energy in the copolymer move to the film-air interface during the film formation process, and a large number of fluorine elements gather in the outermost layer of the copolymer film. According to the different connecting groups of C, O and F, the corresponding chemical shifts are also different. According to the binding energy and the peak separation method, it is known that C has five different chemical environments, while the chemical environments of the two O in the ester group are different, forming two peaks with similar shapes, and the chemical environment of F is similar, so it shows a single peak distribution.

**Table 1.** Types and contents of elements in latex film

Atomic species	C	O	F
Atomic content/%	61.11	9.42	29.47

### 2.5.1.3 Particle Size Distribution of Short Chain Fluorinated Acrylate Water and Oil Repellent Finishing Agent Emulsion

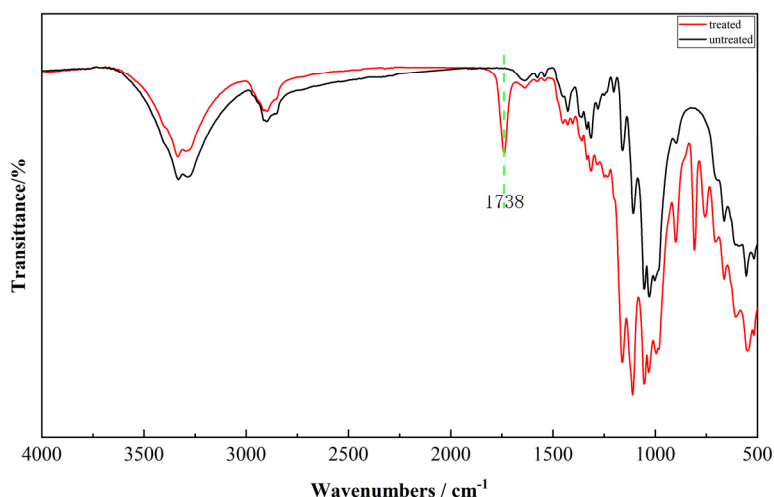


**Fig 4.** Particle Size Distribution of Emulsion of Short Chain Fluorinated Acrylate Water and Oil Repellent Finishing Agent

It can be seen from Fig. 4 that the particle size distribution of the copolymer emulsion is below 300 nm, the peak value is near 125 nm, the PDI is 0.25, the particle size distribution area is compact, and it is in a monomodal state, indicating that the emulsion is evenly distributed and has good stability.

### 2.5.2 Performance Analysis of Finished Cotton Fabric

#### 2.5.2.1 FT-IR Characterization

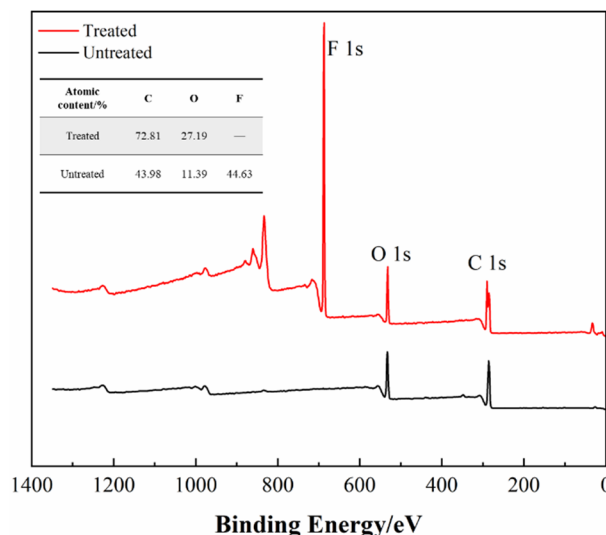


**Fig 5.** FT-IR spectrum of cotton fabric before and after finishing



Fig. 5 is the infrared spectrum of the cotton fabric before and after finishing. New characteristic absorption peaks appeared on the surface of the cotton fabric finished with the short-chain fluorinated acrylate water and oil repellent finishing agent, in which the stretching vibration peak of C=O in the acrylate polymer was at  $1738\text{ cm}^{-1}$ , indicating that the short-chain fluorinated acrylate water and oil repellent finishing agent had successfully reacted with the cotton fabric.

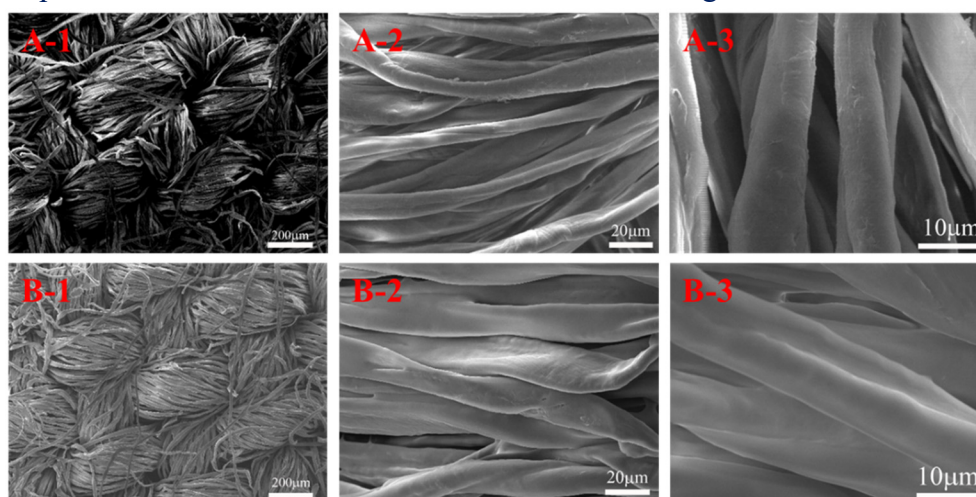
#### 2.5.2.2 XPS Full Spectrum Characterization



**Fig 6.** XPS full spectrum of cotton fabric before and after finishing

Fig. 6 shows that the comparison of the XPS elements of the cotton fabric before and after finishing. The unfinished cotton fabric only contains C and O elements, while the surface of the finished cotton fabric contains C, O and F elements, and the chemical shift peak values are 532 eV, 284.8 eV and 688 eV respectively. Compared with the unfinished cotton fabric, F element is added. And that content of F element is as high as 44.63%. It is proved that the fluoropolymer is successfully applied to the surface of the cotton fiber.

#### 2.5.2.3 SEM Spectrum of Cotton Fabric Before and After Finishing Characterization



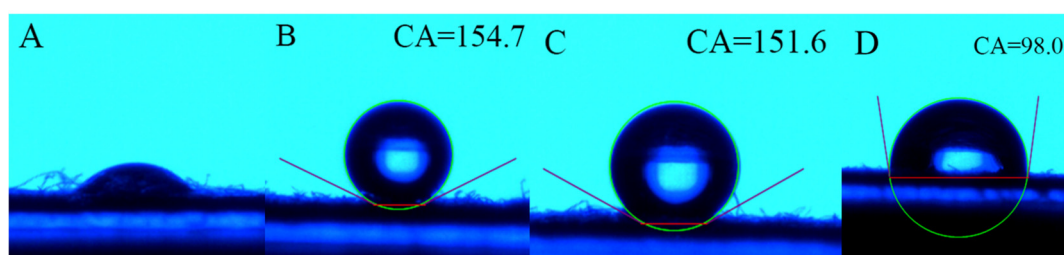
**Fig 7.** SEM spectrum of cotton fabric before and after finishing: A-1, A-2 and A-3 are before finishing, and B-1, B-2 and B-3 are after finishing, with scanning multiples of 100, 1000 and 3000 times

Fig. 7 is the SEM spectrum of the cotton fabrics before and after finishing, showing the unfinished cotton fabrics of A-1, A-2 and A-3 magnified by 100, 1000 and 3000 times respectively, and the finished cotton fabrics of B-1, B-2 and B-3 magnified by 100, 1000 and 3000 times respectively. By comparing the surface morphology of the cotton fabric before and after finishing, it is found that the surface of the unfinished cotton fabric is rough and the cotton fiber has obvious wrinkles. The fiber

surface of the finished cotton fabric becomes smooth and flat, which indicates that the fluorinated copolymer forms a uniform hydrophobic film on the surface of the cotton fabric after finishing, and the fiber is wrapped up. The fluoroalkyl side chain of the short-chain fluorinated acrylate water and oil repellent finish reduces the surface tension of the finished cotton fabric, and has good water repellency.

#### 2.5.2.4 Contact Angle Comparison of Cotton Fabric Before and after Finishing

The C602 optical contact angle meter was used to measure the water static contact angle and the secondary oil static contact angle of the cotton fabric before and after finishing with aqueous short chain fluorinated acrylate water and oil repellent finishing agent. As shown in Fig. 8, A indicates that the cotton fabric before finishing is not water and oil repellent, B and C indicate that the water static contact angle after finishing is  $154.7^\circ$  and  $151.6^\circ$ , and D indicates that the contact angle after finishing to Hexadecane is  $98^\circ$ , which can be applied to actual water and oil repellent activities.



**Fig 8.** Water static contact angle and oil contact angle of cotton fabric before and after finishing: A is water contact angle before finishing, B and C are water contact angles after finishing, and D is Hexadecane contact angle

### 3. Conclusion

The optimal synthesis process of short chain fluorinated acrylate miniemulsion was obtained as follows: the amount of emulsifier was 4% of monomer mass, the mass ratio of compound emulsifier CTAB to Brij L4 was 2:1, and the mass ratio of emulsifier to coemulsifier was 7:1. OFAE: OFAC = 2:1 (mol/mol), the dosage of initiator AIBA was 1.5% of the total monomer mass, the polymerization temperature was  $65^\circ\text{C}$ , and the reaction time was 12h. Under the process conditions, the contact angle of the cotton fabric to water is  $150.8^\circ$ . the water contact angle of the cotton fabric finished by the short chain fluorinated acrylate miniemulsion is  $154.7^\circ$ , and the contact angle of the cotton fabric finished by the short chain fluorinated acrylate miniemulsion to Hexadecane is  $98^\circ$ .

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