

PREPARATION OF NOVAL PERFLUORINATED ACRYLATE COPOLYMER EMULSION CONTAINING NANO-TiO₂ AND ITS APPLICATION ON COTTON FABRICS

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Abstract: The emulsion of copolymer (6-F-n-butyl methacrylate, methyl methacrylate and butyl methacrylate) (CSPA) was prepared using FK-300B and cetyltrimethylammonium bromide as the emulsifier; ammonium persulfate (APS) as initiator. Fourier transfer infrared (FTIR) analysis revealed that the copolymers consist of above three monomers. CSPA had the excellent water-oil repellent performance when the molar ratio of FMA, MMA and BMA was about 1:1:1, the molar ratio of initiator to monomer was about 0.5%, the weight ratio of emulsifier to monomer was about 10%. The particle size of CSPA with cationic charges was mainly in the range of 20nm-110nm.

KEYWORDS: CATIONIC, SHORT-CHAIN PERFLUORINATED ACRYLATE COPOLYMER, WATER-OIL REPELLENT PERFORMANCE, COTTON FABRICS

1. Introduction

Water-oil repellent agent which can greatly reduce the substrate's surface energy has been widely applied in textile, garment and carpet [1]. Fluorchemicals have been known to exhibit both water and oil repellency since the late 1950s and 1960s, nowadays varieties of water-oil repellent agent are available in the market [2-3].

The traditional perfluoroalkyl-based water-oil repellent agent was mainly used perfluoro-n-octyl sulfonic acid as functional monomer, which had an excellent water-oil repellent performance for its long branched-chain fluoroalkyl. However, due to its high bioaccumulation and toxicity, the copolymer which consisted of perfluoro-n-octyl sulfonic acid was abandoned to produce and apply in some developed country [4-7]. Short branched-chain perfluoroalkyl-based water-oil repellent finishing agent has good biodegradability and can be used as alternatives, which have attracted more and more people's attention [8, 9]. Hayakawa Y. et al [10] synthesized a novel polymethacrylate using fluoroalkyl heterocyclic as comonomer. Monika J. et al [11] synthesized β -fluoroalkyl acrylates from fluoroacetic esters via three-step and the prepared copolymers show an excellent water and oil repellent performance.

In this paper, we used the FMA, MMA and BMA as the comonomers and prepared cationic water-oil repellent agent (CSPA), the effects of the molar ratio of comonomer, the amount of emulsifier and initiator on properties of CSPA was investigated.

2. Preconditions and means for resolving the problem

2.1 Materials

6-F-n-butyl methacrylate (FMA, analytical grade), methyl methacrylate (MMA, analytical grade) and butyl methacrylate (BMA, analytical grade) were provided by Shanghai Lingfeng Chemical Reagent Co. Ltd., china, and the structure of FMA is shown in Fig.1. Cetyltrimethylammonium bromide (analytical grade), MgCl₂ and ammonium persulfate (APS, analytical grade) were purchased from Guoyao Chemical Reagent Co. Ltd., china. FK-300B was provided by DuPont Co. Ltd. BX-300 was used as crosslinker which purchased from Guangdong Benda printing Co. Ltd., china. Cotton fabrics (the desized, scoured, bleached and mercerized plain weave 40 x 40 cotton weighted 141g/m²).

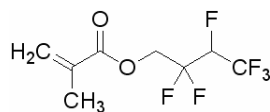


Fig.1 Chemical structure of FMA

2.2. Preparation of CSPA

The synthesis of CSPA was outlined in scheme 2. The copolymerization was performed in 250mL four-necked kettle equipped with mechanical stirrer, thermometer, reflux condenser and inlet system of nitrogen. Carefully measured reagents of FMA, MMA, BMA, distilled water, FK-300B and cetyltrimethylammonium bromide was charged into the kettle followed by stirring at 180r/min for 15min under 50 to get the pre-emulsion. 4/5 of the total pre-emulsion was removed from the kettle and then put into a drip funnel. 1/5 of the total pre-emulsion was heated to 78 and then stirred at 250r/min for 30min, the left pre-emulsion were slowly dropped into the kettle within 30 min and kept temperature at 78°C for 6 hours.

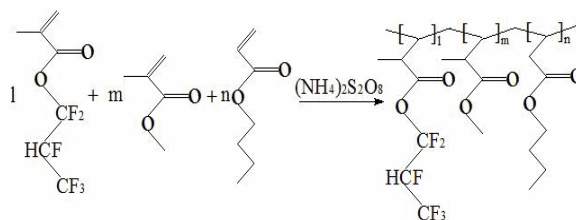


Fig.2 Copolymerization

2.3. Cotton fabric finishing

Cotton fabric samples were first immersed in an aqueous solution containing CSPA 80g/L, BX-300 8g/L and MgCl₂ 0.5g/L at pH 9.0-10.0 and then padded through two dips and two nips to reach a wet pickup of 70-80%. The samples were first dried at 80 for 3min and then cured at 160 for 3min. The contact angle was obtained by Wilhelmy method at 25 using KrÜs interface tension meter (KrÜs GmbH, Hamberg, Germany).

2.4. Characterization

The CSPA was demulsification with methanol, and then washed by methanol for 3 times to obtain the copolymer. The FTIR spectra of copolymer (in KBr pellet) were recorded on a Nicolet Nexus 560 FTIR spectrometer (Thermo Electron Corporation, American). The particle size distribution and its zeta potentials were measured by Nano-ZS90 (Malvern Instruments Ltd., UK). The relative absorbance (R) was calculated according to the reference [12].

The intrinsic viscosity of copolymer was measured with Ubbelohde viscometer (temperature 25°C, acetone as the solvent). Contact angles of water on pigments were measured with Drop Shape Analysis System DSA100 (Krüss Company, German).

Pigment powder was pressed with a pressing machine to form a slice. The contact angles of water with different pH value on the slice were recorded. Three replicates on each sample were made to give an average value. Oil Repellency was measured according to AATCC Test Method 100.

3. Results and discussion

3.1. Effect of molar ratio of monomer

3.1.1. Amount of FMA

Tab.1 Effect of amount of FMA on water-oil repellent performance^a

Molar ratio of FMA/(MMA+BMA)	Water contact angle/°	Oil repellent rating/Grade
0.1	121.2	2
0.3	125.9	3
0.5	132.4	4
0.7	133.7	4
0.9	133.5	4

^aNote: the molar ratio of MMA/BMA was equal to 1:1, molar ratio of APS/ monomer was equal to 0.5% and weight ratio of emulsifier / monomer was equal to 10%.

Tab.1 showed that the water-oil repellent performance of finishing fabrics increased with an increase of amount of FMA in CSPA, and almost unchanged when the molar ratio of FMA/(MMA+BMA) was about 0.5. It was known that C-F in FMA is the main functional groups which can attribute to improve the water-oil repellent performance. Therefore, the water-oil repellent performance of finishing fabrics would be increased with an increase of amount of FMA. However, when the amount of FMA reached to 0.5, almost all the fabric surface was occupied by C-F groups. That was to say, C-F groups on the fabric surface would not increase any more, resulting in that the water-oil repellent of finishing fabrics was no longer increasing as the FMA dosage increased.

3.1.2. Amount of MMA

Tab.2 Effect of amount of MMA on water-oil repellent performance^a

Molar ratio of MMA/BMA	Water contact angle /°	Oil repellent rating/Grade
0.2	126.7	3
0.5	129.4	4
1.0	132.4	4
1.5	128.7	3
2.0	127.2	3

^aNote: the molar ratio of FMA/(BMA+MMA) was equal to 0.5, molar ratio of APS/ monomer was equal to 0.5% and weight ratio of emulsifier / monomer was equal to 10%.

Tab.2 showed that the CSPA could greatly improve the water-oil repellent performance of finishing fabrics when the molar ratio of FMA/ (BMA+MMA) was equal to 0.50, and MMA/BMA was about 1.0. As it was known that molar ratio of MMA/BMA

could determine the glass transition temperature of the CSPA, when the amount of MMA was small, the glass transition temperature of CSPA was low, the formed film would be easily destroyed by rubbing strength. However, when amount of MMA was high enough, the formed film on fabric surface would become brittle, the adhesion between copolymer and the fabrics decreased, thus also led to a poor water-oil repellent performance.

3.2. Effect of amount of emulsifier

Tab.3 Effect of amount of emulsifier on water-oil repellent performance^a

Weight ratio of emulsifier / monomer /%	Water contact angle /°	Oil repellent rating/Grade
4	112.5	3
8	124.7	4
10	132.4	4
12	129.8	3
20	124.3	3

^aNote: the molar ratio of FMA/(BMA+MMA) was equal to 0.5, MMA/BMA was equal to 1.0, molar ratio of APS/ monomer was equal to 0.5%.

Tab.3 showed that the water-oil repellent performance was more close to the amount of emulsifier, when the amount of emulsifier was small, the emulsion was not stable and some copolymer was deposited, thus led to a poor water-oil repellent performance. On the other hand, when the amount of emulsifier was high enough, some emulsifier would not absorb on the latex particles and then form micelles, which could greatly reduce the wetting energy, resulting in poor water-oil repellent performance too.

3.3. Effect of amount of APS

Tab.4 Effect of amount of APS on water-oil repellent performance^a

Molar ratio of APS/ monomer/%	[η](dl/g)	Water contact angle/°	Oil repellent rating/Grade
0.25	11.16	130.4	4
0.5	9.84	132.4	4
0.75	8.60	124.6	3
1.00	7.25	117.8	2

^aNote: the molar ratio of FMA/(BMA+MMA) was equal to 0.5, MMA/BMA was equal to 1.0 and weight ratio of emulsifier / monomer was equal to 10%.

As can be seen in Tab.4 the intrinsic viscosity decreased gradually as the amount of APS increased, when the amount of APS was equal to 0.5%, it seemed that the water-oil repellent performance of the fabrics which treated with CSPA reached to its maximum. When the amount of APS increased, the number molecular weight of the copolymer decreased which led to poor film-forming, therefore, the water-oil repellent performance reduced with an increase of APS.

Based on the above experimental, the optimal conditions for preparation of CSPA were that the molar ratio of FMA, MMA and BMA was 1:1:1, the molar ratio of APS to monomers was equal to 0.5%, the weight ratio of emulsifier to monomers was equal to 10%. The following emulsion was prepared under these conditions.

3.4. Characterization and performance

3.4.1. FT-IR

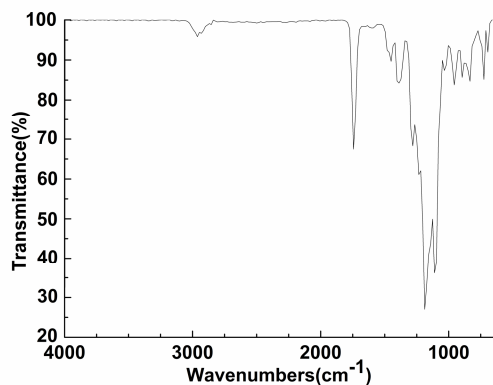


Fig.3 FTIR spectra of copolymer

The synthesized copolymers were characterized by Fourier transfer infrared (FTIR) analysis. The FTIR spectra were shown in Fig. 3. As seen from the figure, the characteristic absorptions of CF_2 (1104cm^{-1} and 1185cm^{-1}), $\text{C}=\text{O}$ (1742cm^{-1}), CH_2 and CH (2960cm^{-1} and 1384cm^{-1}) and stretching vibration of $\text{C}-\text{O}$ (1288cm^{-1}) were clearly visible. This confirmed that the acrylic monomers had been polymerized.

3.4.2. Particle size and zeta potentials distribution

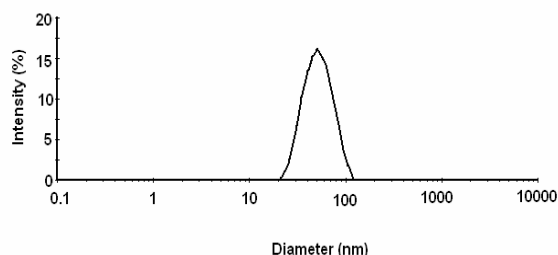


Fig.4 Particle size distribution of CSPA

Fig. 4 showed the particle size distribution curve of CSPA, and the sizes were in the range of 20-110nm, the average size of the particle was about 50 nm, which indicate that the latex was uniformly distributed into aqueous media.

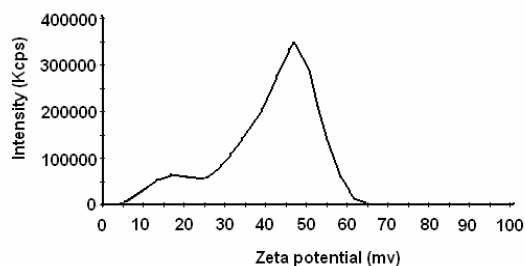


Fig.5 Zeta potentials distribution of latex

Figure 5 showed that the latex had some positive charges on its surface, its average zeta potentials was about 34.21mV. It was known that the electric repulsive forces would produce when the latex with the same charges, the more amounts of charges on the particle surface, the higher stability of the CSPA was. In addition, compared with the negative charges on the latex, the latex with positive charges would be more easily absorbed onto the cotton fabrics.

3.4.3. Stability

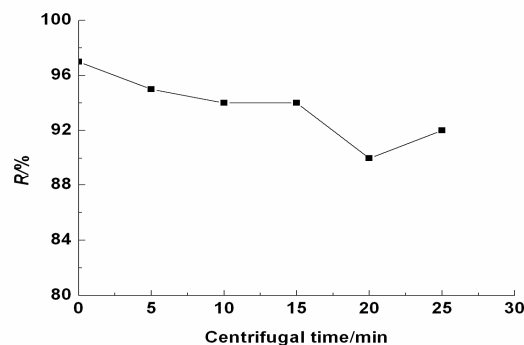


Fig.6 Centrifugal stability of CSPA

Fig.6 showed that the relative absorbance decreased with the centrifugal time increasing, and changed small when centrifugal time was above 15min. According to Stokes' law ($v = [2(\rho - \rho_0) r^2 / 9\eta] \cdot g$). The large particle in CSPA would be deposited first under the centrifugal forces, thus leading to relative absorbance decreasing. Fig.6 also told us that CSPA had excellent centrifugal stability.

4. Conclusion

The optimal conditions for preparation of CSPA were that the molar ratio of FMA, MMA and BMA was 1:1:1, the molar ratio of initiator to monomers was equal to 0.5%; the weight ratio of emulsifier to monomers was equal to 10%. Under these conditions, the prepared CSPA with small particles had an excellent stability.

5. References

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