Synthesis of *Bis*(1H, 1H, 2H, 2H-perfluoro-octyl)methylenesuccinate Copolymers and Their Application on Cotton Fabrics

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ABSTRACT: *Bis*(1H, 1H, 2H, 2H-perfluoro-octyl)methylenesuccinate (FOM)/ethyl acrylate (EA)/methyl methacrylate (MMA) copolymer (FOME) latexes, FOM/butyl acrylate (BA)/MMA copolymer (FOMB) latexes, and FOM/octyl acrylate (OA)/MMA copolymer (FOMO) latexes were synthesized by continuous emulsion polymerization. Solution polymerization was also carried out to prepare FOMB. The influences of fluorine content and curing conditions on the surface properties of polymer films were discussed. The water and oil repellency of cotton fabrics treated with the FOM copolymers was better than that of conventional poly(fluoroalkyl acrylate)s containing the same fluorinated chain. The polymer films or the treated fabrics were characterized by Fourier transform infrared, scanning electron microscope, atomic force microscopy, thermogravimetric analysis, x-ray photoelectron spectrometry, and wide angle x-ray diffraction. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Fluorine containing chemicals are closely related to human live,[1,2] and fluorinated acrylate are extensively used in fabrics finishing industry, electronic industry, and national defense.[3-6] Poly(fluoroalkyl acrylate)s with long fluoroalkyl (Rf) groups have excellent water and oil repellency. The addition of a small amount of fluorinated monomer can increase the surfaces repellency for both water and oil significantly.[7] However, fluoroalkyl acrylates with long carbon chain length may cause a series of problems such as bioaccumulation and environmental damage.[8,9] The polymers with perfluorocarbon chains more than seven carbon will be withdrawn from the market.[10] Research effort is now under way to develop environment friendly materials such as polymers with short perfluorocarbon to replace the traditional reagents.[11]

Conventional poly(fluoroalkyl acrylate)s with short fluoroalkyl (Rf) groups are easy degradable but poor water and oil repellent. However, it was reported that the Rf groups being present in closely packed clusters of two or more Rf groups could decrease surface energy and crystallinity, while increase the water, thermal stability, flame, and oxidation retardancy.[12,13] *Bis*(1H, 1H, 2H, 2H-perfluoro-octyl)methylenesuccinate (FOM) contains two adjacent fluorinate segments, and the structure

might be benefit for lowing surface energy of its polymer. Recently, though plenty of copolymers of fluorinated-free methylenesuccinate have been reported and widely used in industry, little work has been done to investigate the preparation and the properties of bi-fluorinated methylenesuccinate copolymers. Because itaconates show lower tendency toward homopolymerization, the early researches were mainly focused on the synthesis of alternating copolymers with electron-donating monomers as comonomers, such as vinyl ethers, vinyl esters, styrenes, and α-olefins.[14]

Solution polymerization and emulsion polymerization are usually adopted to obtain fluoric-containing acrylate polymers. Fluoroacrylate copolymer prepared by radical initiated solution polymerization is easy conductive and is easier to purify from raw products.[13] The solution product could be used for coating of glasses without curing and is a possible way to be concerned.[15] On the other hand, emulsion polymerization is extensively used for fluorinated acrylate copolymer,[16-18] to exclude environmentally hazardous organic solvents. Emulsion polymerization is suitable for incorporation of functional compounds (especially hydrophobic substances) into polymer particles. Emulsions are aqueous dispersions of relatively stable and small oil droplets, and they are favorable for the finishing of fabrics.[19,20]
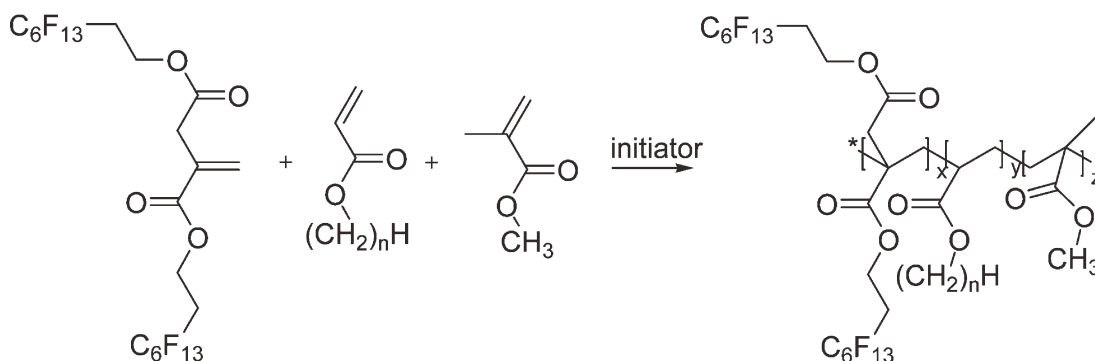
Scheme 1. Polymerization of fluorinated monomers. (*x* was determined by fluorine contained in copolymer. Copolymer FOME: $n = 2$, $y/z = 3/1$, emulsion polymerization; Copolymer FOMB: $n = 4$, $y/z = 2.34/1$, emulsion polymerization or solution polymerization; Copolymer FOMO: $n = 8$, $y/z = 1.63/1$, emulsion polymerization.)

In this manuscript, methylenesuccinate with short fluoroalkyl (Rf) groups was synthesized. Continuous emulsion polymerization was used to prepare various copolymers. FOM/EA/MMA copolymer (FOME) latexes, FOM/BA/MMA copolymer (FOMB) latexes, and FOM/OA/MMA copolymer (FOMO) latexes were synthesized with FOM as functional monomer, methyl methacrylate (MMA) as "hard" monomer, and ethyl acrylate (EA) or butyl acrylate (BA) or octyl acrylate (OA) as "soft" monomer, respectively. To investigate the differences between solution polymer and emulsion polymer, solution polymerization was also proceeded to prepare FOMB solution. The influences of fluorine content and curing conditions on the surface properties of polymer films were discussed. The water and oil repellency of the copolymers used as textile finishing agent on cotton fabrics were investigated. The water and oil repellency of the FOM copolymers was compared with 1H, 1H, 2H, 2H-perfluoro-octyl acrylate (FOA) copolymers and 1H, 1H, 2H, 2H-fluorodecyl acrylate (FDA) copolymers, respectively. Further, surface morphologies of the copolymer films were obtained by atomic force microscopy (AFM), and the properties of the copolymers were investigated by contact angle (CA), thermogravimetric analysis (TGA), and wide angle x-ray diffraction (WAXD). Surface chemical composition of fabrics coated with FOM copolymers was also investigated by x-ray photoelectron spectrometry (XPS) measurement.

EXPERIMENTAL

Materials

Sodium lauryl sulfate, span-80, isopropyl alcohol, analytical pure were obtained from Shanghai Reagent Factory, Shanghai, China. Ammonium persulfate (AP), 2,2-azo-*bis*-isobutyronitrile (AIBN), itaconic acid, *p*-toluene sulfonic acid, hydroquinone, toluene, silica gel, ethyl ether, ethyl acetate, MMA, EA, BA, OA, analytical pure were obtained from Aladdin Reagent Company, Shanghai, China. All the above reagents were used without further purification. 1H, 1H, 2H, 2H-perfluoro-1-octanol, FOA and FDA were obtained from XEOGIA Fluorine-Silicon Chemical Company, Harbin, China. They were distilled to use. The water used in this experiment was distilled followed by deionization.

Measurement

Fourier transform infrared (FTIR) spectra were recorded on Thermo Electron Corporation Nicolet 5700 FTIR spectrometer,

using KBr pellets and films. The particle size was recorded on an LS800 particle sizer. The surface morphology of the treated cotton fabrics was obtained from a scanning electron microscope (SEM) (HITACHI S-4700). Water repellency was measured according to AATCC 193-2005 test method and examined by measuring the contact angle, respectively. Oil repellency was tested according to AATCC 118-2002 test method. The contact angles for water drops ($\sim 3 \ \mu$L) were recorded on a contact angle meter (Dataphysics Co. OCA40 Micro) at 25°C in air. Thermal property was tested on DTA-TG thermal analyzer (Diamond TG/DTA 5700, American Perkin EImer Company). AFM image was obtained by an atomic force microscope (MultiMode V, Veeco). XPS measurement for cotton fabrics coated with fluorinated copolymers was carried out on an X-ray Photoelectron Spectrometer (XSAM800, Kratos, UK) with Al Kα as X-ray source. The depth and area of the measurement as well as detection angle were 5 nm, 400 μm^2 and 45°, respectively. WAXD patterns of polymers were obtained from X-ray polycrystalline diffraction instrument (X'Pert-Pro MPD).

Preparation of FOM

FOM was prepared by the esterification of itaconic acid (13.01 g, 0.10 mol) with 1H, 1H, 2H, 2H-perfluoro-1-octanol (72.82 g, 0.20 mol). The objective monomer was obtained by using *p*-toluene sulfonic acid (1.52 g) as catalyst, hydroquinone (0.96 g) as the anti-polymerizing agent, toluene (150 mL) as solvent and water carrying agent. The objective product was isolated by column chromatography (ethyl ether : ethyl acetate = 3 : 1). Oil, yield 85%; FTIR (KBr) *v*: 3001.9, 1750.7, 1726.8, 1642.2, 1330.3, 1317.9, 1269.7, 1217.2, 1157.8, 1096.2, 1048.6, 734.8. ^{1}H-NMR (CDCl$_3$, 400 MHz) δ: 6.377 (*m*, 1 H), 5.804 (*m*, 1 H), 4.449 (*t*, $J = 7.8$ Hz, 2 H), 4.377 (*t*, $J = 7.8$ Hz, 2 H), 3.359 (*m*, 2 H), 2.559 (*t*, $J = 7.5$ Hz, 2 H), 2.521 (*t*, $J = 8.1$ Hz, 2 H).

Polymerization

The copolymerization was carried out as the outline in Scheme 1.

Continuous Emulsion Polymerization. A mixture of MMA, acrylate, FOM, Span-80, and sodium lauryl sulfate was pre-emulsified on an emulsification instrument. EA, BA, and OA were used as "soft" monomers, respectively. Mass ratio of MMA
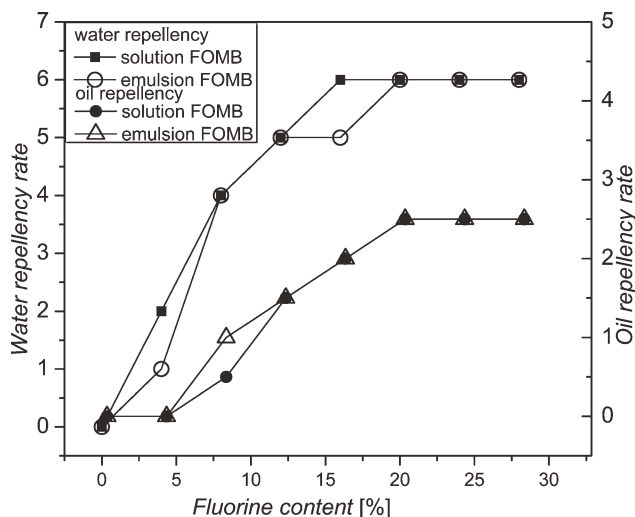
Figure 1. Effect of fluorine content of copolymer on the water and oil repellency.

and "soft monomer" was 1 : 3. The flask was stirred and heated to 70°C under a nitrogen atmosphere. A solution of AP dissolved in distilled water was then dripped into the mixture within 1 hr. The polymerization was kept for 3 hr at the temperature of 70°C. Finally, copolymer emulsion (FOME, FOMB, or FOMO) was obtained. Conventional fluorinated acrylates (FOA or FDA) copolymers were prepared with the same method.

Semicontinuous Solution Polymerization. Monomers were polymerized in isopropyl alcohol using AIBN as initiator. The mixed monomers (MMA, BA, FOM) and 1/2 amount of AIBN soluted in isopropyl alcohol was heated at 70°C under a nitrogen atmosphere. Residual AIBN soluted in isopropyl alcohol was then dripped into the mixture within 1 hr. The polymerization was kept for 3 hr at the temperature of 70°C. Mass ratio of MMA and BA was 1 : 3. Finally, copolymer solution FOMB was obtained.

Treatment of Cotton Fabrics with Fluorinate Copolymers
The desized, scoured, bleached twill weave cotton 133 $\times$ 72 2/1, weighed 128 (g/m^2) fabric samples were immersed in an aqueous solution of obtained copolymers, and then padded through two dips and two nips with a wet pick-up of 100%. Finally, the samples were dried at 110°C for 3 min and cured at a certain temperature for certain time.

To obtain an optimum process and investigate the impact of fluorine concentration, curing temperature, and curing time on the surface properties of fluorinated copolymers, cotton fabrics were treated by copolymers FOMB (copolymer solution or copolymer latexes) with various fluorinate content (5%–30%), and cured at different temperatures (120°C–180°C) or for different time (30–180 s).

RESULTS AND DISCUSSION

Effect of Fluorine Content of Copolymer on the Water and Oil Repellency
The surface energy depends on the chemical composition of the material. Fluorine atoms arranged on the surface of the
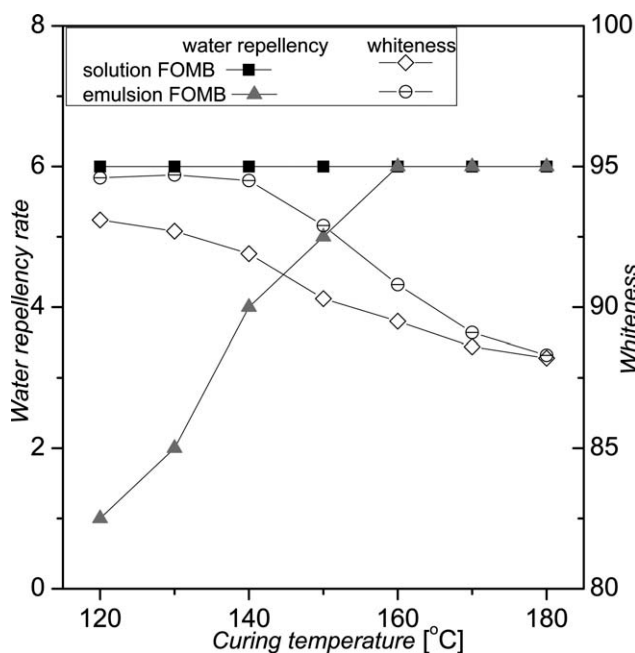
polymers have played an important role in lowering the surface energy. The fluorine content of polymer will affect the properties of water repellent and oil repellent. The more perfluoroalkyl groups uniformly organized on the surface, the better surface property is obtained. As expected, the wettability of the films depended on the fluorinated monomer concentration. Figure 1 shows that the water and oil repellency was improved with the increment of fluorine content of FOMB. Increment of water and oil repellency indicated the enrichment of fluorinated chains at the polymer surface. At the higher fluorine content, the tendency became weak, it seemed that a dense accumulation of fluorinate groups at the air–polymer surface had formed and the fluorinate groups' enrichment had reached a maximal value. In such situation, to increase fluorine content of the polymer will have little effect on surface properties of the copolymers.

The Effect of Curing Temperature and Curing Time on Fabric Properties
The curing treatment affects the movement of copolymer chains remarkably.[21,22] The heat treatment will make a significant impact on the aggregation of fluorine. Figures 2 and 3 show how the curing temperature and time affected the surface properties of the copolymers. These results indicated the relationship between temperature and self-organization of fluorinated side chain on the film surfaces formed by the emulsion copolymer and solution copolymers. It could be expected that the migration of the fluorinate unit onto polymer surface will be very slow. Figure 2 indicated that the water and oil properties of the emulsion polymer increased rapidly with the prolonging curing time at the same curing temperature. The phenomenon suggested the aggregation of fluorinate unit onto the air-polymer surface increased gradually and finally reached a maximal value. Under higher temperature, flexibility of the polymer chains
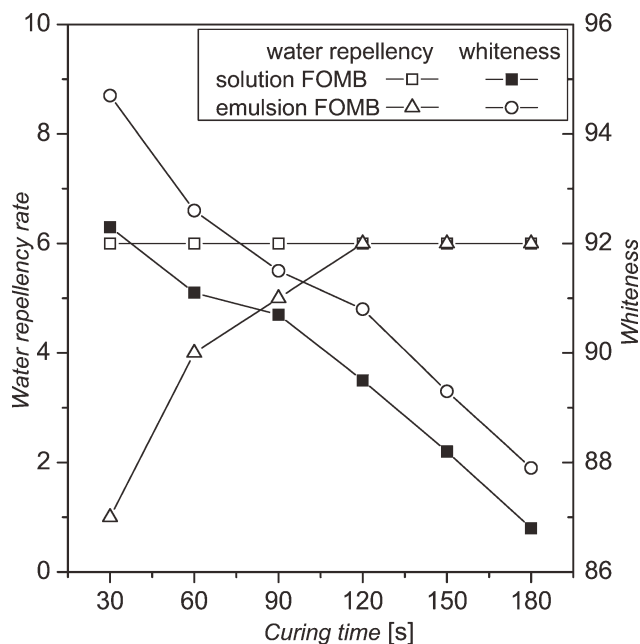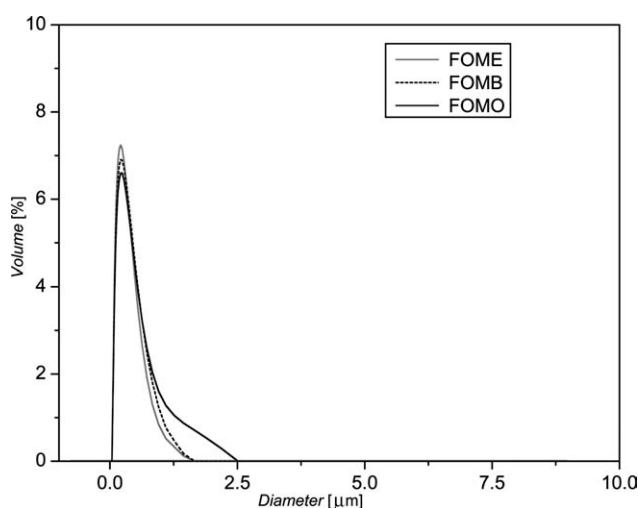

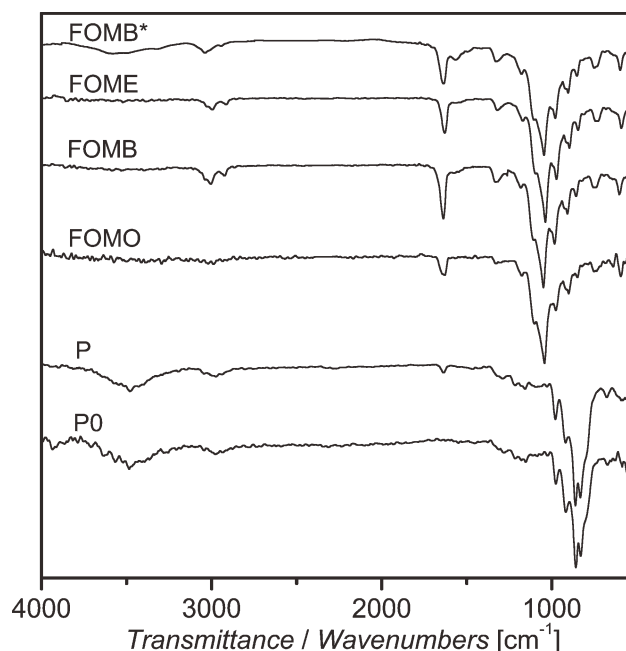**Figure 2.** Effect of curing time on the properties of fabrics.

Figure 3. Effect of curing temperature on the properties of fabrics.

Figure 5. FTIR spectra of the copolymer films and fabrics. (* Prepared by solution polymerization; P: cotton fabrics treated with FOM copolymer; P0: untreated cotton fabrics.)

would increase. As it is known that fluorinated groups have relatively low surface energy, and they have strong tendency to spread to the surface.[23,24] Figure 3 suggested that the migration of fluorinate units was much faster at higher curing temperature, and it took less time to reach maximal surface excess value. However, as regarding to the whiteness of cotton fabrics, it was unfavorable to expose the fabrics either in high temperature or for a long time. It was different for solution polymer that heat treatment had little effect on the surface activities of the polymer. The water and oil repellency of solution polymer had little change after curing. It could be inferred that fluorinate group in solution polymers migrated preferentially toward air-film interface during the film formation to minimize the interfacial energy.

Figure 4. Particle size distribution of latexes.

Particle Size of Latexes

The particle size distribution by the volume content (%) of different size of particles in fluorine contained latexes was shown in Figure 4. The designed latexes with similar particle size distribution were formed. The average size of the latex particles was 0.15–0.2 μm, in which 90% distributed between 0.035 and 1.259 μm. It was well in accordance with the color of the emulsions (white with blue light).

FTIR Spectra of FOM Copolymers and the Fabrics Treated with FOM Copolymer

Figure 5 shows FTIR spectra of solution copolymer FOMB, emulsion copolymers (FOME, FOMB, and FOMO), untreated cotton fabrics (P0) and treated cotton fabrics (P). The absence of C=C characteristic stretching vibrations around 1640 cm^{-1} confirmed the monomers had mostly been polymerized. The spectra of the polymers shown strong C—F absorption bands at 1100–1300 cm^{-1}, the stretching vibration absorption of 1100–1240 cm^{-1} overlapped with the stretching vibration absorption of ester groups at 1250 cm^{-1}, the absorption at 1288 cm^{-1} was attributed to CF$_3$ groups. Intense absorption band at 1730–1760 cm^{-1} arose from C=O stretch modes. Curve P was sharper than curve P0 at about 1700 and 1300 cm^{-1}, what was resulted from the characteristic stretching vibration absorption of C=O bond and characteristic absorption bands of C—F in fluorinate copolymer. It could be inferred that the polymer had been attached onto the fibers.

Scanning Electron Microscopy

The surface morphologies of cotton fibers were investigated by SEM. The typical top views of the untreated cotton fabric and treated cotton fabric were shown in Figure 6(A–C). The native cotton fiber presented a comparatively smooth surface. A coat of resin was observed on the treated fiber surface. It indicated
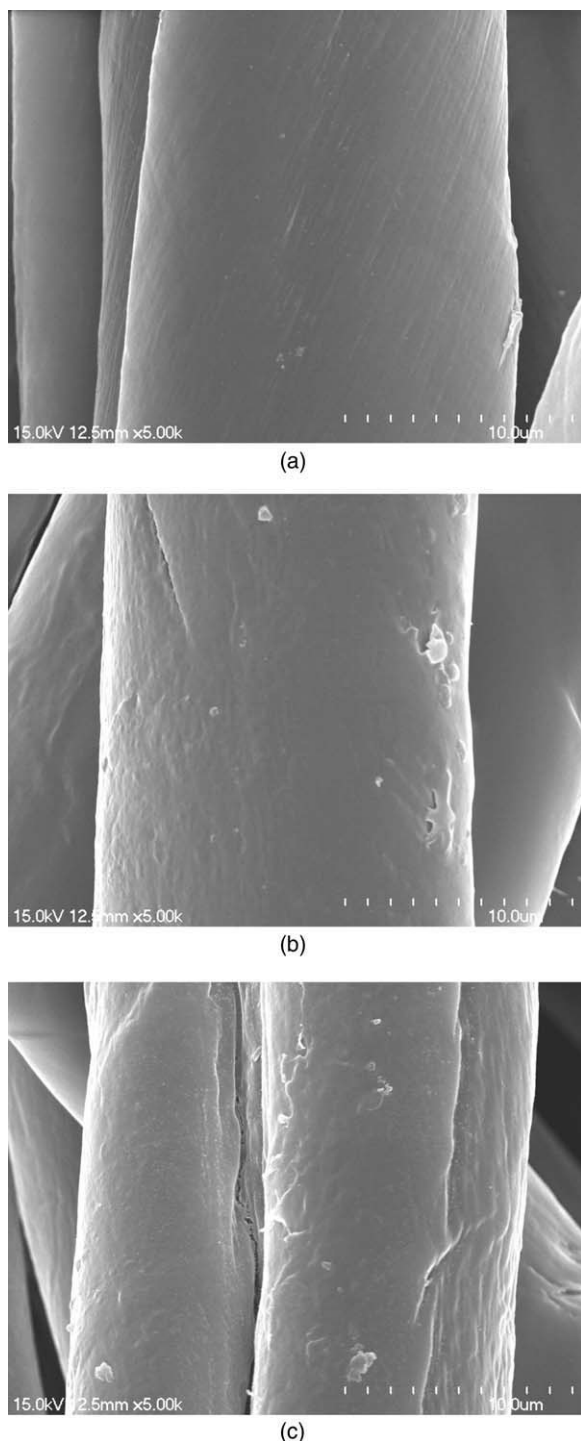
Figure 6. SEM of cotton: (A) untreated cotton; (B) cotton treated with FOM copolymer emulsion; (C) cotton treated with FOM copolymer solution.

that the fluorinated copolymers had good film forming property and a dense fluorinated copolymer film had formed.

Atomic Force Microscopy

The nanoscale structure of the polymer surface was observed by AFM. The micro or nanoscale roughness has been proven to be another effect upon the generation of super hydrophobic prop-

erty. The microscopy image (Figure 7) shown that the air-surface of the polymer film was not absolutely smooth, with visible aggregates of characteristic sizes 30–150 nm on the surface. The micro-scale roughness might contribute to high contact angle of water droplets on the surface.[25-27]

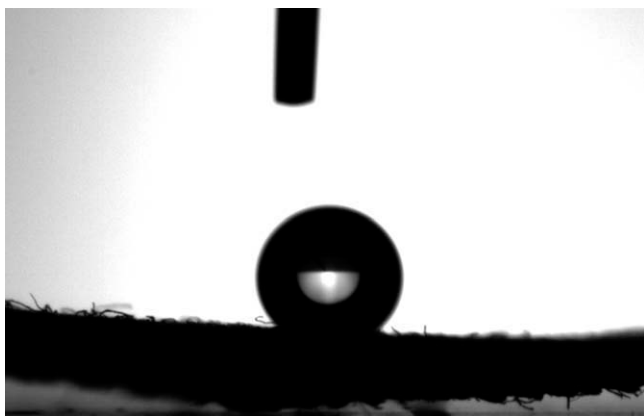### Water and Oil Repellency

Water and oil repellency of the cotton fabrics treated with solution polymer and emulsion polymers were examined. Contact angle measurement was used to study the water repellent property of finished textile, and the drop-test was also employed for further investigation of water proofing property. Photo of water drop on fabrics coated with FOMO was shown in Figure 8. The results were compared with that of conventional poly(fluorinated)acrylates and summarized in Table I. Fabrics treated with solution copolymer FOMB showed similar water and oil repellency to emulsion copolymer FOMB. Among all cotton fabrics treated with FOM copolymers, cotton fabric treated with FOMO shown the highest water and oil repellency. It showed that the hydrophobic and oleophobic properties increased with the increment of carbon chain length in fluorine-free acrylate. The results reflected that longer carbon chain acrylate had better synergetic effect with fluoro-component,[11,28] and resulted in lower surface free energy of homologous fluorinated polyacrylate.

FDA copolymers show well water repellent property while FOA copolymers have relatively poor water repellency. However, FDA copolymers are not environmental friendly. The tendency of aggregation and self-alignment of Rf groups are important to control their surface properties.[29] The adjacent groups might be beneficial to the aggregation and self-alignment of Rf groups on the polymer surface. Just as expect, methylenesuccinate copolymers
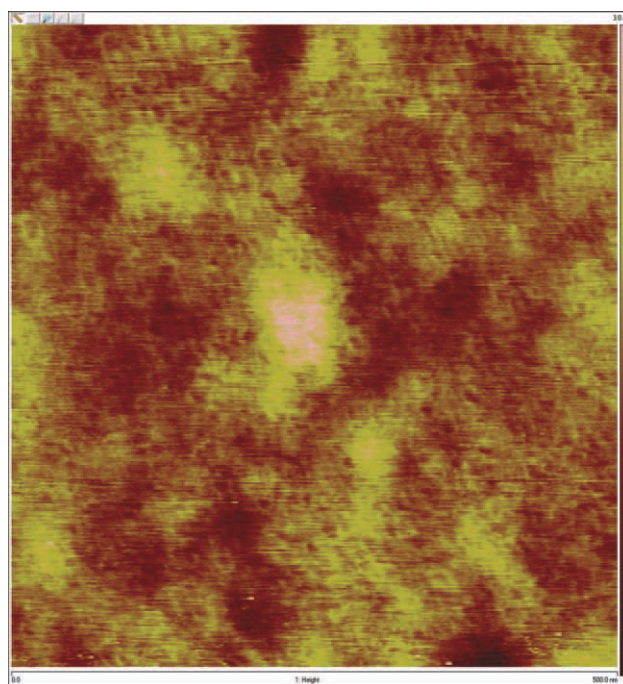
Figure 7. AFM image of the surface based on FOM copolymer: size 5 μm × 5 μm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

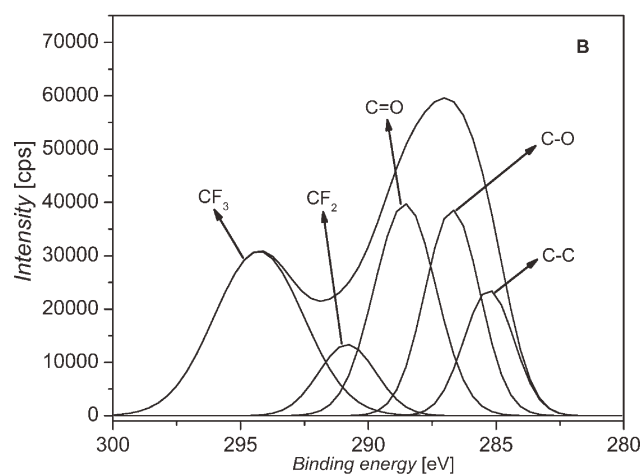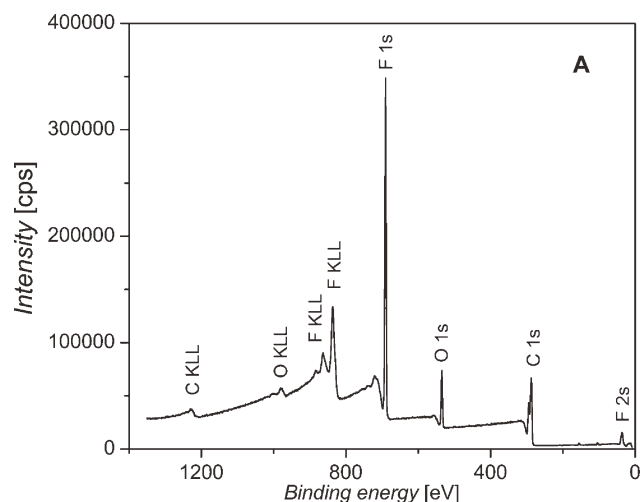**Figure 8.** Image of water drop on fabrics treated with copolymer FOMO.

containing two adjacent short fluorinate esters segments polymers provided better water and oil repellency than acrylate copolymers containing the same fluorinate groups. The water repellency rate of FOM copolymer was slightly lower than corresponding FDA copolymer, but the oil repellency was much better than FDA copolymer. It is possible for FOM copolymers to replace the conventional poly(fluoroalkyl acrylate)s with long Rf groups.

Surface Chemical Composition of FOM Copolymers-Coated Fabrics

The analytic results of XPS measurement were shown in Figure 9(A,B). C 1s, O 1s, F 1s, and F 2s peaks appeared at around 288, 533, 690, and 33 eV, respectively. The high resolution XPS spectrum of C 1s was fitted with five subpeaks having equal width corresponding to CF_3 at 293.6 eV, CF_2 at 291.8 eV, C=O at 288.4 eV, C—O at 286.1 eV, C—C at 284.8 eV.[30] The atomic concentration of i element (Ci) was calculated using eq. (1).

$$C_i = \frac{I_i/\text{ASF}_i}{\sum\limits_{j} I_j/\text{ASF}_j}$$

Figure 9. XPS spectra of the cotton fabrics surface coated with FOMO: (A) wide scan survey spectrum for all elements; (B) High resolution spectrum for C 1s signals.

Here, the ASF values of C 1s, O 1s, and F 1s are 0.25, 0.66, and 1.00, respectively. The calculated atom concentration of F in the outmost surface coated with FOMO was 47.9%, significantly

higher than the atom concentration in bulk of FOMO (F%, 16%). The result had confirmed the surface enrichment of fluorinated segments. The concentration of F for the outmost

Table I. Water and Oil Repellency of Cotton Fabrics Coated with Fluorinate Copolymers

Sample	Functional monomer	"Soft" monomer	Water contact angle (°)	Water repellency rate	Oil repellency rate
Untreated	–	–	0	0	0
FOMB[a]	FOM	BA	139	6	2.5
FOME	FOM	EA	138	5	2
FOMB	FOM	BA	143	6	2.5
FOMO	FOM	OA	141	9	4.5
FOAE	FOA	EA	135	5	0
FOAB	FOA	BA	136	5	0
FOAO	FOA	OA	138	7	1
FDAB	FDA	BA	147	7	0.5
FDAO	FDA	OA	145	10	2.5

[a]Prepared by solution copolymerization.
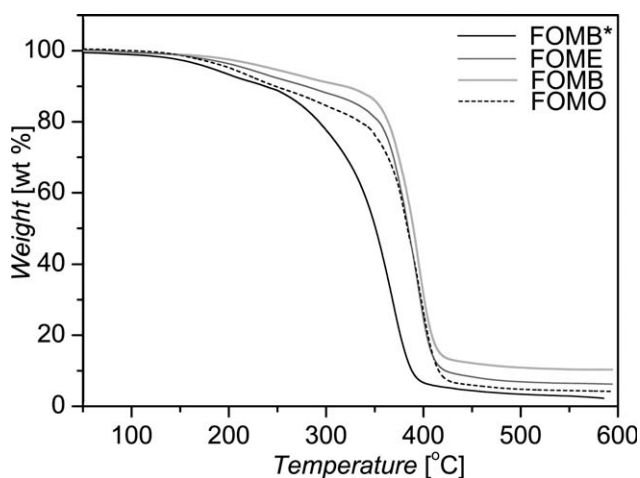
Figure 10. TGA curves of FOM copolymers. (*Prepared by solution polymerization).

Figure 11. WAXD patterns of copolymers. (*Prepared by solution copolymerization).
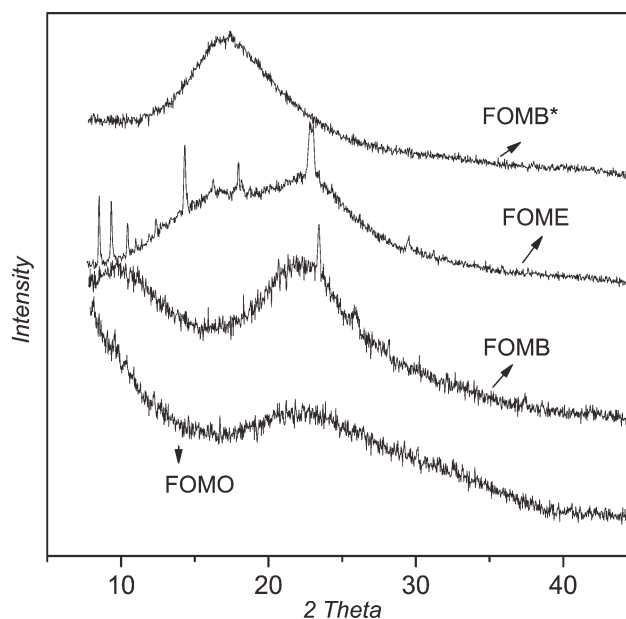
surface of FOMB-coated cotton fabric was also investigated, which was 31.02%. The better water and oil repellency of FOMO might be ascribed to the higher concentration of F in the outmost surface of FOMO-coated fabric, which means the enrichment of fluorine segments on the surface plays an important role in achieving high water and oil repellency.

Thermal Property

Thermal properties of polymers were studied by thermogravimetric analysis (TGA). Some TGA curves are presented in Figure 10. The decomposition of all polymers occurred between two main temperatures, thermal degradation characteristics of FOM copolymers were also displayed in Table II. In a comparison of the thermal stabilities, temperatures corresponding to a weight loss of 5%, 10%, 50%, and 85% to the initial weight were obtained from TGA. Copolymers were stable until 175–200°C. Above, they underwent decomposition in two stages. The solution polymer film seemed to be less thermal stable than emulsion polymer film. It began to decompose quickly at about 250°C, whereas the emulsion polymer samples began the main decomposition at 350°C.

XRD

XRD was performed to further investigate crystallization information of FOM copolymers. The dispersion peak in XRD curve of solution copolymer FOMB (Figure 11) was at ∼ 15°, whereas it was at ∼ 22° for curves of emulsion FOM copolymers. Except some small diffraction peak in curve of FOME, no obvious

diffraction peak was observed in the XRD spectrum of fluorinated copolymers. It confirmed that fluorinated copolymers have no crystal at room temperature.

CONCLUSION

A series of FOM copolymers were synthesized by continuous emulsion polymerization and semi-continuous solution polymerization, respectively. The average size of the latex particles prepared by emulsion polymerization was 0.15–0.2 μm. Atomic force microscopy show that the air-surface of the polymer film was not absolutely smooth, with visible aggregates of characteristic sizes 30–150 nm on the surface. The solution copolymer film seemed to be less thermal stable than emulsion polymer film. It began to decompose quickly at ∼ 250°C, while the emulsion copolymer samples began the main decomposition at 350°C. XRD result confirmed that fluorinate copolymers had no crystal at room temperature.

The water and oil repellency was improved with the increment of fluorine content of the polymer. But at the higher fluorine content, the tendency became weak. The water and oil properties of the emulsion polymer increased rapidly with the prolonging curing time at the same curing temperature or with the

Table II. Thermal Degradation Characteristics of FOM Copolymers

Sample	T5 (%)[a]	T10 (%)[a]	T50 (%)[a]	T85 (%)[a]	T_{max} (Δm)[b]	Δm[c]
FOMB[d]	195	249	358	390	369 (61.9%)	97.0%
FOME	213	274	383	408	392 (65.0%)	93.9%
FOMB	244	319	389	417	394 (57.8%)	89.6%
FOMO	197	242	382	408	395 (67.3%)	96.1%

[a]Temperature corresponding to a weight loss of 5%, 10%, 50%, and 85% to the initial weight, [b]Temperature corresponding to the temperature where the decomposition rate was maximum, [c]Weight loss at 550°C, [d]Prepared by solution polymerization.

increment of temperature at the same time, and finally reached a maximal value. However, it was different for solution polymer that heat treatment had little effect on the surface activities of the polymer. The water and oil repellency of solution polymer had little change after curing. FOM copolymers provided better water and oil repellency than corresponding FOA copolymers. The water repellency rate of FOM copolymer was slightly lower than FDA copolymer, but the oil repellency was much better than FDA copolymer. The hydrophobic and oleophobic properties increased with the increment of carbon chain length in fluorine-free acrylate. XPS results indicated the surface enrichment of fluorinated segments in FOMO was more significant than that of FOMB, and it might have some relationship to the better water and oil repellency of FOMO.

ACKNOWLEDGMENTS

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