

Synthesis, Film Morphology, and Performance of Cationic Fluorinated Polyacrylate Emulsion with Core-Shell Structure

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ABSTRACT: A novel cationic fluorinated polyacrylate emulsion (CFBDH) was prepared by polymerization of dodecafluoroheptyl methacrylate (DFMA) with butyl acrylate (BA), dimethylaminoethyl methacrylate (DM), and 2-hydroxypropyl acrylate (HpA) via seeded emulsion polymerization. Chemical structure, particle morphology, glass transition temperature, and thermal property of resultant CFBDH were characterized by FTIR, ¹H-NMR, TEM, DSC, and TGA, respectively. The as-synthesized product was utilized to treat the clean glass sheet and cotton fabric substrates, then morphology, components, hydrophobicity, and other performances of films on those substrates were investigated by SEM, AFM, XPS, and contact angle meter, etc. Results show that the target product possesses anticipative structure and its latex particles have uniform spherical core-shell structure with an average diameter of 126 nm. The core-shell CFBDH latex film thus has two T_g and its

thermal property has been improved due to the introduction of fluorine-containing acrylate monomer. The CFBDH film on cotton fabric surface seems to be smooth compared to the blank by SEM. However, the CFBDH film on silicon-wafer is inhomogeneous and has many low or high peaks. At 2 nm data scale and in 1 μm^2 scanning field, the root mean square roughness of CFBDH film reaches to 0.205 nm. XPS analysis indicates the perfluoroalkyl groups have the tendency to enrich at the film-air interface. In addition, CFBDH can provide good hydrophobicity for the treated fabric and do not influence whiteness of the treated fabric indeed. However it will make the treated fabric slightly stiff at high doses. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 2376–2383, 2012

Key words: morphology; core-shell polymers; atomic force microscopy; fluoropolymers; latices

INTRODUCTION

Because of the low polarizability and the strong electronegativity of the fluorine atom,^{1–3} fluorine-containing polymers possess high thermal, chemical, aging, and weather resistance; low dielectric constants, refractive index, surface energy, and flammability; excellent inertness to solvents, hydrocarbons, acids, alkalis and moisture adsorption as well as interesting oil and water repellency. Consequently, it has been widely used in the field of coatings, fabric finish, leather, and packing.^{4–6} The research on the development of more effective and more environmentally friendly fluorinated polymer products is the main-

stream in the field of modern fluorinated materials all the time. Therefore, many researchers still devote themselves to investigating and developing the fluorinated polymeric latex with low volatile organic compounds (VOC) and zero VOC. Fluorinated polyacrylate emulsions are born with special surface property, good adhesion to matrices and especially environmental protection value, thus they have attracted increasing attention of many investigators.

Up to date, fluorinated acrylate polymers emulsions with various structures, such as graft,⁷ random,⁸ hybrid nanocomposites,⁹ and core-shell,^{4,10–12} can be synthesized by conventional emulsion polymerization, suspension-emulsion combined polymerization, mini emulsion polymerization, seeded emulsion polymerization, and other synthetic polymerization techniques. Core-shell fluorinated polyacrylate latex synthesized via seeded emulsion polymerization was particularly attractive as a result of their typical advantage in film formation compared with general emulsion, especially the latex consisting of fluorine-free acrylic core and fluorine-containing acrylic shell. During the film-forming process, the fluorine-

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containing acrylic shell preferentially migrated to the surface and endowed the materials with excellent surface properties. In contrast, fluorine-free acrylic core assembled in the bulk and provided the materials with good adhesion towards substrate.

Anionic fluorinated acrylic polymers emulsions with core-shell structure are often reported in literatures;^{4,10–14} however, little work has been focused on the preparation and the film morphology of the cationic fluorinated acrylic latexes with core-shell structure, which show very high adhesion to different ionic substrates, especially anionic substrates such as textile, paper, leather, and glass. So in this article, we fabricated a novel cationic fluorinated polyacrylate emulsion (CFBDH) with core-shell structure through seeded emulsion polymerization of DFMA, BA, DM, and HpA and then utilized Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance spectrum (¹H-NMR), transmission electron microscopy (TEM), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), contact angle (CA), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM), etc., to investigate the structures and morphology of the emulsion and its films.

EXPERIMENTAL

Materials

Butyl acrylate (BA), dimethylaminoethyl methacrylate (DM), 2-hydroxypropyl acrylate (HpA) were purchased from Shanghai Chemical Auxiliary, China, and used as received. Dodecafluoroheptyl methacrylate (DFMA) was supplied by Harbin XEO-GIA Fluorine-Silicon Chemical, China and used as received. The initiator ammonium persulfate (APS) was purchased from Shanxi Baohua Technology, China and used without further purification. The mixed emulsifier systems were composed of octadecyl trimethyl ammonium chloride (1831) and alkyl alcohol polyoxyethylene ether (AEO-9), which were both purchased commercially and used as received.

Silicon wafers, kindly provided by Songjiang Silicon Material, Shanghai, China, were cleaned and dried based on our previous works.^{15,16} A cotton fabric with a density of 133 × 72 (the counts of warp × fill yarns, 10 cm × 10 cm) was purchased from Huarun textile manufacture company, Shaanxi, China. Prior to finishing treatment, a piece of cotton fabric was successively ultrasonicated using deionized water and acetone at 25°C for 30 min, respectively, then dried at 100°C for 5 min. This process was to remove the slurry and contaminants on the fiber/fabric substrates.

Preparation of core-shell CFBDH latex

The core-shell DFMA/BA/DM/HpA latex was synthesized by seeded emulsion polymerization. All the

polymerization steps were conducted under the protection of nitrogen gas in a 250-mL four-neck flask equipped with reflux condenser, mechanical stirrer, dropping funnel, and a nitrogen inlet. The first step was to obtain the seed latex. Ten grams BA and 1 g DM were pre-emulsified at 50°C for 0.5 h in the flask containing 80 g deionized water and 1.35 g mixed emulsifiers of 1831 and AEO-9 (at weight ratio of 1831/AEO-9 = 1 : 2). When the flask was heated to 80°C, 0.055 g of initiator (APS) was added to prepare the seed latex for 0.5 h. The second step was to synthesize the core-shell copolymer as follows. The mixture monomers of 5 g BA, 10 g DFMA, 0.5 g DM, and 0.5 g HpA, and 0.08 g APS were added drop-by-drop during 3–4 h. After the addition of all these materials, the reaction temperature was held at 85°C for another 0.5 h. The latex was obtained eventually by adjusting its pH value to 3–4 with NaHCO₃ solution at room temperature. Meanwhile, fluorine-free polyacrylate emulsion was also synthesized by copolymerization of BA, DM, and HpA according to the aforesaid procedure and noted as CBDH.

Application of the CFBDH latex on glass and cotton fabric substrates

CFBDH was dissolved with deionized water to form a 0.03 wt % or certain concentration polyacrylate aqueous solution. A prepared silicon wafer or a sheet of cotton fabric was impregnated into the above CFBDH solution and kept for several seconds, then dried at 80°C for 5 min and cured at 170°C for 3 min. Finally, the samples were kept in a desiccator to balance for 24 h. According to the substrates used, samples were noted as CFBDH/Sil (for the silicon wafer substrate), CFBDH/cotton (for the cotton fiber/fabric substrate), respectively.

Characterization of the CFBDH latex and its film

FTIR spectra of samples were recorded between 4000 and 500 cm⁻¹ on a Bruker VECTOR-22 spectrophotometer using KBr pellet technique.

¹H-NMR analysis was performed with INOVA-400 spectrometer using CDCl₃ as solvent and tetramethylsilane (TMS) as an internal standard.

The particle size and its distribution of the CFBDH latex were measured by Nano-ZS particle sizer (Malvern Instruments Company, UK). Transmission electron microscopy (TEM) micrographs of the CFBDH particles were taken with H-600 transmission electron microscope (Hitachi Company, Japan) with an acceleration voltage of 200 kV. The samples were stained with 2% phosphotungstic acid (PTA) solution.

The glass transition temperature (T_g) of polymer samples was measured by a NETZCH DSC-200. The

scanning rate was 10°C/min from -80°C to 100°C under nitrogen atmosphere. Thermogravimetry analysis (TGA) was performed on a Q500 thermogravimeter (TA Instruments Company, USA) under the nitrogen atmosphere at a heating rate of 10°C/min from 30 to 800°C.

The surface morphology of the cotton fibers/textiles or silicon wafer treated by CFBDH were observed by SEM and AFM. SEM measurement were carried out on S-570 scanning electron microscope (Hitachi) after the fiber/fabrics were coated with gold in a vacuum, the morphologic photographs were taken at magnification of 1500 and 5000 times. AFM images were obtained with a Nanoscope IIIA AFM (Digital Instruments, USA) in tapping mode. All the scanning was performed at 22°C and in air of relative humidity of 48%.

The surface chemical compositions of the treated textiles were analyzed by XPS instruments. XPS analysis were performed on a Physical Electronics Model 5700 X-ray photoelectron spectrometer (PHI) equipped with monochromatic Al K α source (150W, 15KV, KE = 1486.6 eV). The nominal photoelectron take-off angle was 30°, and the vacuum degree of analysis chamber was 6.7×10^{-8} Pa. In the XPS measurement, the deviation of the binding energy was corrected by the C1s photoelectron emission signal occurring at 284.8 eV due to hydrocarbon contamination on the sample surface.

Static contact angles (CAs) of water on the air-exposed film surface were performed by the sessile drop method on a JC2000A contact angle goniometer (Shanghai Zhong Chen Powereach, China) at 20°C. The injection volume of liquid was 5 μ L and the average of five readings was used as the final contact angle of each sample.

Bending rigidity (BR) and whiteness of the treated fabrics by CFBDH were measured with a Kawabata Evaluation System (KES) instrument and an YQ-Z-48B fluorescent whiteness tester, respectively.

RESULTS AND DISCUSSION

Structure characterization of the polymers

Figure 1 demonstrated FTIR spectra obtained from fluorine-free polyacrylate latex CBDH [Fig. 1(a)], fluorinated polyacrylate latex CFBDH [Fig. 1(b)] and the monomer DFMA [Fig. 1(c)]. All of the three spectra exhibited the characteristic stretching and distortion vibration peaks of C-H (CH₃) at 2965 cm⁻¹ and 1459 cm⁻¹, stretching vibration of C=O at 1738 cm⁻¹, asymmetrical and symmetrical stretching vibration of C-O at 1245 cm⁻¹ and 1171 cm⁻¹, respectively. The absorption at 1641 cm⁻¹ and 888 cm⁻¹ in Figure 1(c) should be attributed to the characteristic of C=C bonds of DFMA.¹⁴ However,

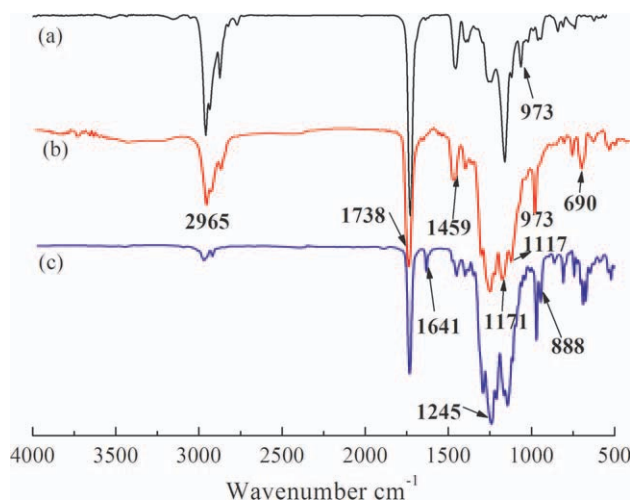


Figure 1 FT-IR of (a) CBDH, (b) CFBDH and (c) monomer DFMA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

there were neither of the above two absorption peaks in Figure 1(b), which indicated C=C bonds of DFMA participated in polymerization.

It was also shown that the outline of fluorine-containing latex CFBDH was similar to that of polyacrylate latex CBDH in Figure 1(a) and (b). The absorption at 973 cm⁻¹ was characteristic of BA. However, the stretching vibration of -CF₂ and -CF₃ groups at about 1289–1100 cm⁻¹ and asymmetrical stretching vibration of C-O at 1245 cm⁻¹ overlapped each other,^{9,17–19} which resulted in broadening of absorption peaks at 1245–1100 cm⁻¹ compared with that of CBDH. Furthermore, strong signal at 1117 cm⁻¹ and weak absorption band at 690 cm⁻¹ should be assigned to the stretching vibration of -CF₂ and -CF₃ groups and the wagging vibration of CF₂ groups, respectively.^{17–19}

Figure 2 was ¹H-NMR spectrum of the CFBDH. The typical δ_{H} of O-CH₂ and CFH in DFMA were found at 4.55 ppm (*h*H) and 5.54 ppm (*i*H).⁴ Peaks at δ 0.92 ppm (*a*H), δ 1.2 ~ 1.8 ppm (*b*H, *c*H, *e*H, *f*H) and δ 3.64 ppm (*d*H) belonged to the δ_{H} of O-CH₂CH₂CH₂CH₃ in BA and the δ_{H} of main chain, respectively. Peaks at δ 4.02 ppm (*s*H) and δ 3.43 ppm (*l*H) were assigned to the δ_{H} of O-CH₂ in DM and the δ_{H} of -OH in HpA. In one word, both FT-IR spectrum and ¹H-NMR spectrum indicated that the monomers were polymerized together through seeded emulsion polymerization. The deduced chemical structure was also presented in Figure 2.

Morphology and size of the CFBDH particles

Particle size distribution (PSD) and zeta potential graph of the CFBDH emulsions were shown in Figures 3 and 4, respectively. As seen from Figure 3,

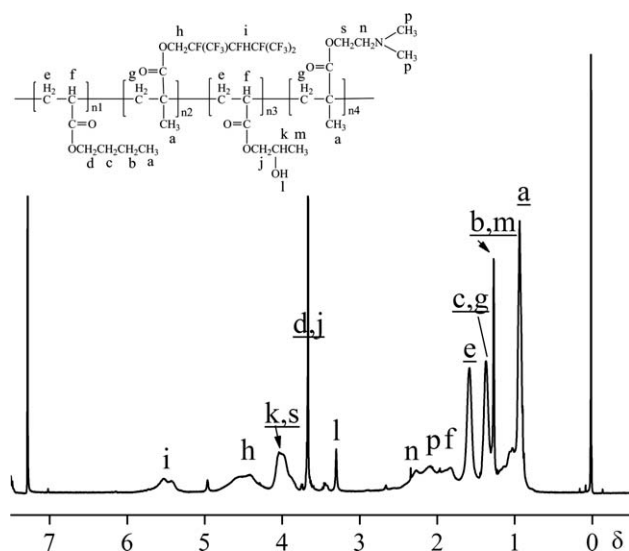


Figure 2 ^1H -NMR spectrum of CFBDH.

PSD of the CFBDH is about 30–500 nm and the average particle size is 126 nm. Besides, the zeta potential of the CFBDH latexes is +21.16 mV from Figure 4, which demonstrates that the latexes particles possess positive charges and this will improve not only stability of the latexes but adhesion of the latex particles to anionic matrices such as textile, paper, leather, and glass.

TEM photographs of CFBDH were presented in Figure 5. It can be seen from Figure 5 that the latex particles exist with clear and uniform spherical core-shell structure due to the difference of electron penetrability to the core phase and the shell phase. The light and dark regions in the particles correspond to the polyacrylate core phase and the fluorinated polyacrylate shell phase, respectively.^{4,12} The particles are uniform spheres with the average diameter of

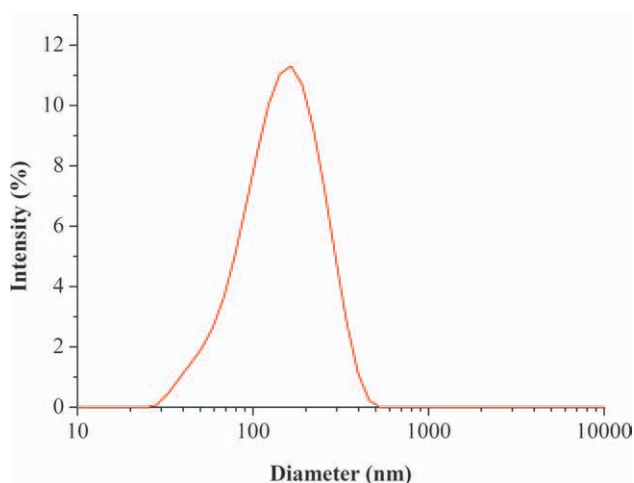


Figure 3 Particle size distribution of CFBDH emulsions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

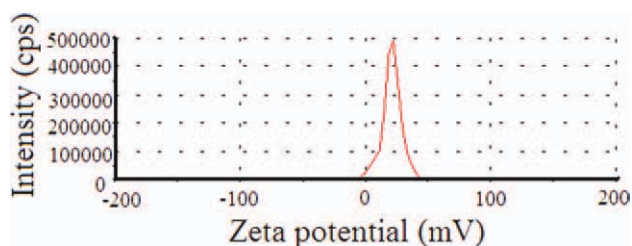


Figure 4 Zeta potential graph of the CFBDH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

about 120 nm, which is consistent with the results measured by PSD analysis (shown in Fig. 3).

Thermal properties of the CFBDH film

To investigate thermal properties of the CFBDH film, DSC, and TGA were implemented in this article and shown independently in Figures 6 and 7. Two glass transition temperatures (T_g), i.e., -39.2°C and 29.6°C , can be seen from Figure 6, which represent T_g of the core phase and the shell phase, respectively. The DSC result accounts for that the core-shell structure is formed, which is in accordance with the core-shell structure of the latex particles shown in TEM photographs.

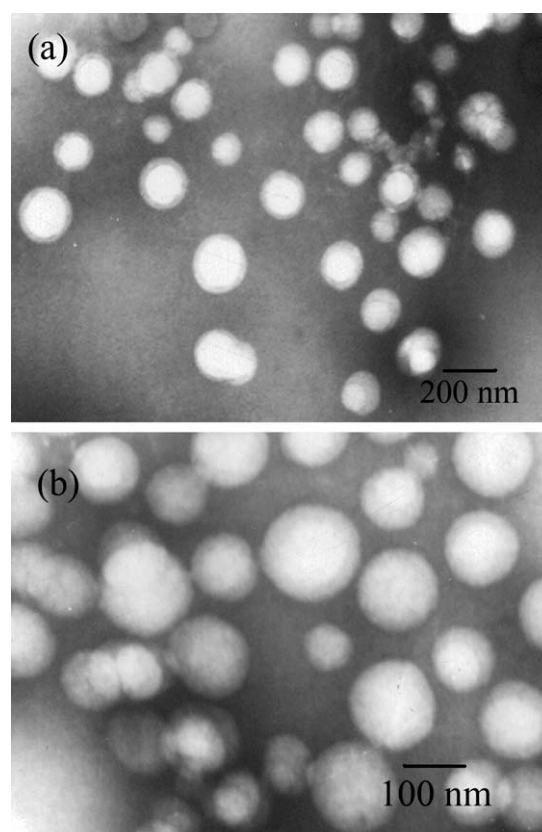


Figure 5 TEM photographs of the CFBDH: (a) $\times 100,000$ and (b) $\times 200,000$.

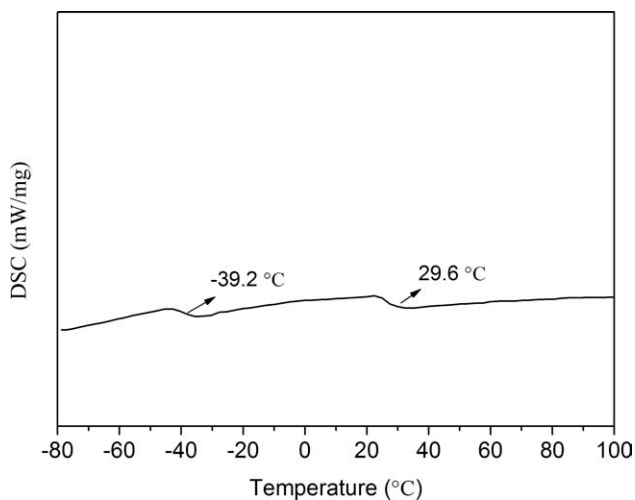


Figure 6 DSC thermograms of the CFBDH.

Meanwhile, it can be seen from the TGA curves that the initial and complete decomposing temperatures of fluorine-free polyacrylate emulsion film,

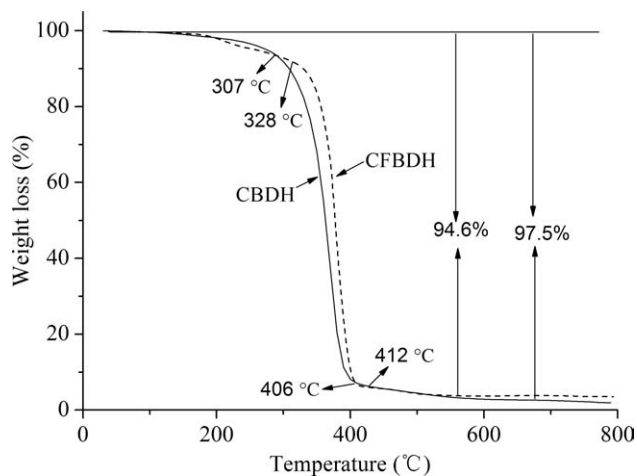


Figure 7 TGA curves of the CBDH and the CFBDH.

CBDH, are 307°C and 406°C, respectively. Whereas the decomposition of fluorinated polyacrylate emulsion film begins at 328°C and ends at 412°C,

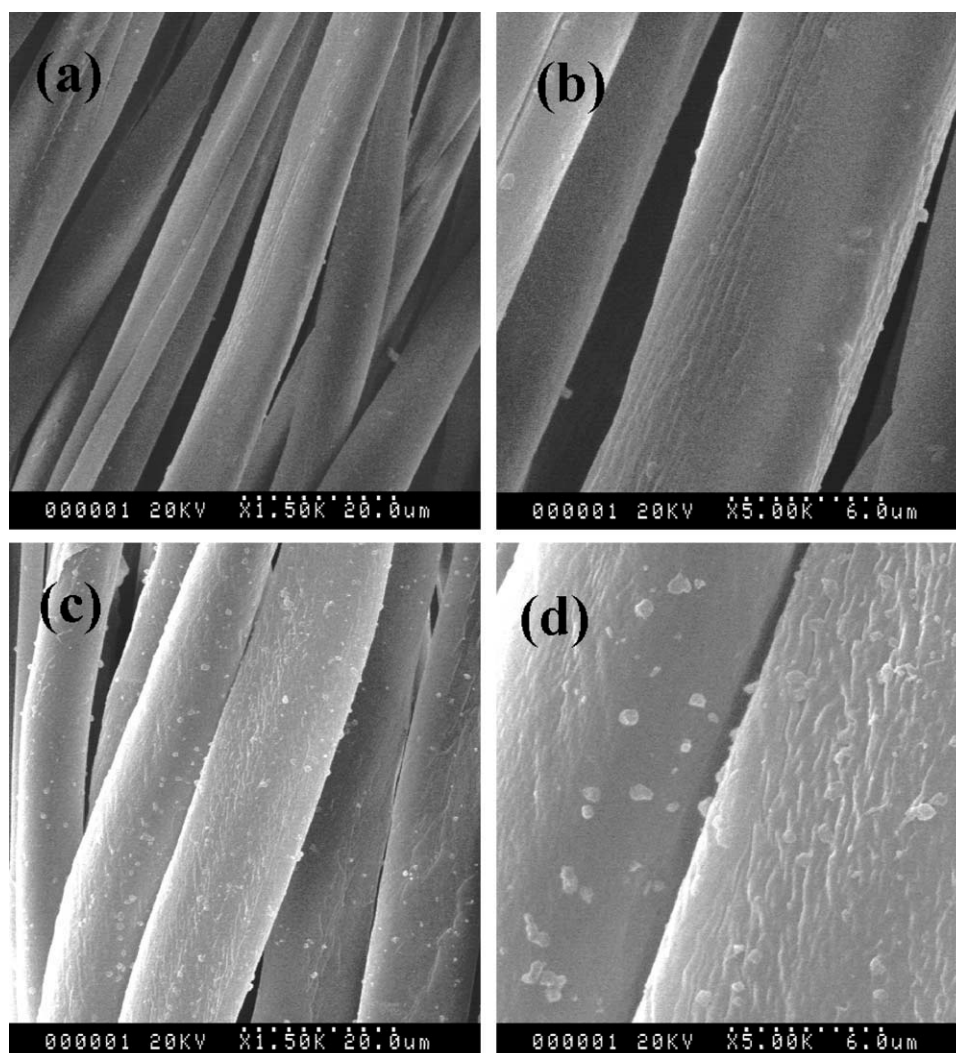


Figure 8 SEM photographs of treated pure cotton fabrics by CFBDH (a) ($\times 1500$), (b) ($\times 5000$), and untreated ones (c) ($\times 1500$), (d) ($\times 5000$).

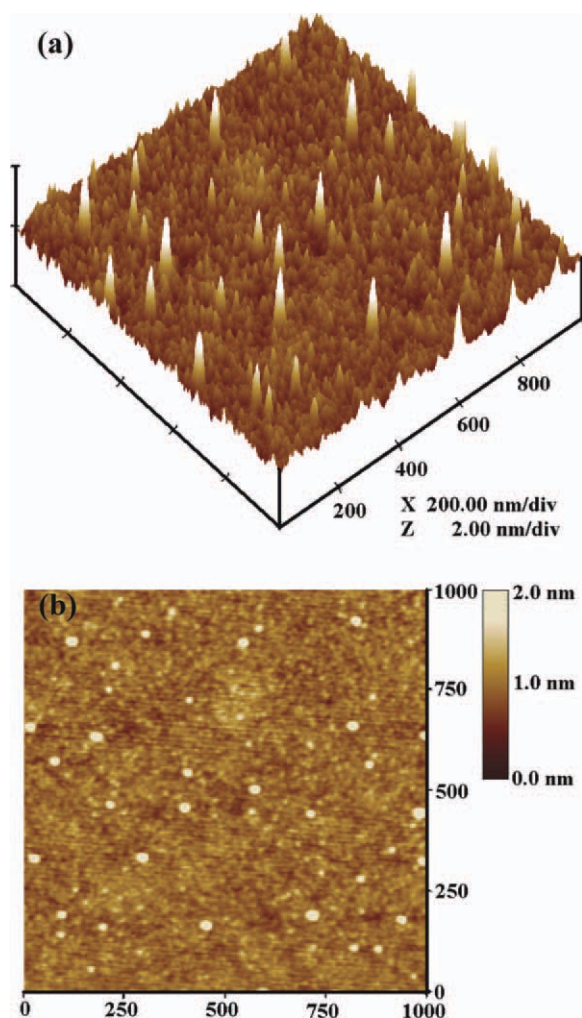


Figure 9 AFM images of CFBDH film with a R_q of 0.205 nm. (a) Three dimensional and (b) Height image. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

indicating thermal stability of the latex films is enhanced due to the introduction of DFMA. This phenomenon could be illustrated that through seeded emulsion polymerization, fluorine containing acrylate monomer could be anchored in the shell of the latex particles and the perfluoroalkyl groups containing C–F bonds has high bond energy. Thus thermal stability of the copolymer is improved.¹²

Film morphology of the CFBDH on substrates

It is well known that properties or application performances of a polymer depend largely on its structure or morphology on substrates. Thus exploration of its morphology on substrates is of great importance. Fluorinated polyacrylates possess low-surface tensile strength. This property makes them outspread easily and adsorbed onto the surface of hydrophilic matrix (e.g., fabric), forming films of molecular dimensions. As such films sheath the

fibers, more or less modified morphology of the treated fibers should be observed in experiments. Thus from observation of the treated fiber surface, we can get information about morphology of fluorinated polyacrylate on the fiber substrate. Figure 8 presented a series of SEM photographs of pure cotton fabrics/fibers treated or untreated by CFBDH. Figure 8 clearly shows that relatively smooth surfaces are visualized on the treated fibers at the magnification of 5000 times (the observation rule = 6.0 μm), in comparison with the untreated fibers. The photographs demonstrate that a fluorinated polyacrylate resin film has been coated on the treated fiber surfaces. And a majority of the grooves have disappeared on the treated fiber surface or become shallower; moreover the edges of some fiber surface look blunt and smoother. However, SEM cannot

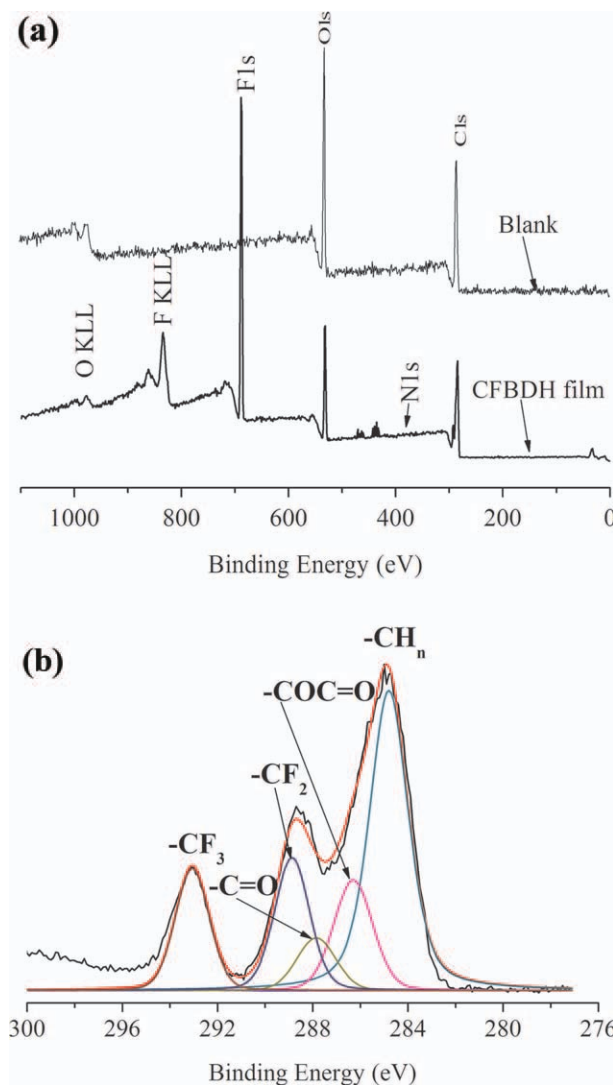


Figure 10 XPS spectra of the CFBDH film: (a) on cotton surface (b) C1s signals with 30° take-off angle. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE I
Element Content of the CFBDH Film-Air Surface on the Cotton Fabric

	Element content (%)				Ratio of F/C
	F1s	O1s	N1s	C1s	
Theoretical value	45.6	11.38	0.268	39.4	1.157
Experimental value	59.29	20.95	0.078	19.67	3.014

reveal a clear micro-morphology or the precise structure of the CFBDH film on the fiber surface, and hence the more powerful instrument is needed.

AFM is a newly developed instrument which is widely used for detecting the morphology of polymer films on a nanometer scale.²⁰ Since natural fabrics or fibers are easily misshapen during AFM observation, a polished and rigid silicon wafer is usually replaced as substrate to research film morphology and microstructures of functional polymer.^{15,21–23} Therefore, the precise morphology of the CFBDH film on the silicon-wafer matrix was studied by AFM in this work and the result was shown in Figure 9. It is distinctly discovered that when the observation rule decreases to 2 nm, the macroscopic relative smooth CFBDH film substantially exhibits an inhomogeneous structure on the silicon surface. There are some higher bright peaks resulting from fluoroalkyl groups and many lower dark peaks belonging to the softer nonfluorinated acrylate^{19,24} in its three-dimensional topography (Fig. 9). And in 1 μm^2 scanning field, the average roughness of CFBDH film (expressed by the root mean square roughness, Rq.) reaches 0.205 nm. This is the results of phase separation of the fluoroalkyl segments.²⁵ Basically, the interaction between acrylate polymers and the polar silicon-wafer substrate is smaller than that between F-containing groups and silicon surface, and it is easier for fluoro-containing segments to erect on a silicon surface than acrylate polymers. So in the annealing process the fluoroalkyl groups preferred to migrate to the air/polymer interface and occupy the outmost surface.¹⁹

XPS analysis of the CFBDH film

The XPS analysis gave some insight into the chemical compositions of the film-air interface of core-shell fluorinated acrylic emulsion film on cotton surface and the results were shown in Figure 10 and Table I. The survey spectrum seen in Figure 10(a) reveal the strong characteristic signal of carbon, oxygen (O1s at 532.0 and 533.5 eV) and fluorine (F1s at 688.4 and 691.0 eV) as well as a weak nitrogen (N1s at 399.4 eV) signal as expected. In the C1s spectrum, shown in Figure 10(b), it is resolved into five Gaussian curve-fitted peaks: $-\text{CF}_3$ around 293.1 eV, $-\text{CF}-$ around 288.9 eV, $-\text{C}=\text{O}$ around 287.9 eV, $-\text{C}-\text{O}-\text{C}=\text{O}$ around 286.3 eV, and hydrocarbon ($-\text{CH}_n$; $n = 0-3$) around 284.8 eV, from high to low binding energy. These peak assignments agreed well with the reported values.^{25,26} Quantitative evaluation of the spectrum was carried out by determining the areas of C1s, O1s, N1s, and F1s peaks and multiplying them by the appropriate sensitivity factors. The theoretical atomic compositions were calculated from knowledge of the acrylic polymer recipe. The results, presented in Table I, are given as atomic percentages and compared with the calculation values. The observed contents of fluorine, oxygen, and ratio of F/C are more than those in the theoretical values; however, contents of nitrogen and carbon are fewer than those in the theoretical values, which imply that the outmost layer of the dried film is composed of mainly perfluorooctyl groups and some ester groups.²⁷ As a result of hydrophilicity and cationic charge of nitrogen-containing acrylate segment, it is susceptible to be absorbed onto the anionic cotton substrate. Then this leads to decrease of the nitrogen content at the interface of air-film. In a word, XPS analysis indicates the perfluoroalkyl groups have the tendency to enrich at the film-air interface, which are consistent with aforesaid AFM morphology of the CFBDH film.

Application performance of the CFBDH

Morphology will affect the performance of a functional polymer. Fluorinated polyacrylate latex has

TABLE II
Performance of the Cotton Fabric Treated by the CFBDH

Dose of the CFBDH latex (g/100g H ₂ O)	WCA (°)	Static absorbing time (h)	Grade of oil repellent	Whiteness (°)	BR (mN)	
					w	f
0	0	<1 s	0	85.42	189	101
0.3	128.2	1.2	1	85.44	185	104
0.6	131.8	3.5	3	85.36	183	103
0.8	132.3	>6	5	84.68	195	108
1	134.2	>6	6	84.4	197	110
1.2	134.3	>6	6	85.24	206	117
1.5	134.2	>6	6	84.5	220	123
2	134.2	>6	6	84.92	228	125

WCA, water contact angles; BR, bending rigidity; w, wrap; f, fill.

favorable film-forming ability, low surface free energy property which is often used as water and oil repellent finish to treat textile.^{28,29} When the non-homogenous, phase-separated film morphology of core-shell CFBDH aggregates and sheathes on the cotton surface, the surface and mechanical properties of the treated fabrics will be changed. Hence, the performance of the cotton fabrics treated or untreated with CFBDH was determined and shown in Table II.

As expected, along with the increase of the CFBDH dose to 1.0 g, the hydrophobicity of the treated fabrics, such as WCA, static absorbing time and grade of oil repellent, gradually attains the best values, which should be originated from the equilibrium of absorption and rearrangement of perfluoroalkyl groups on the cotton surface. The whiteness of the treated fabrics changed little; however, bending rigidity of the treated fabrics will increase compared to the blank while dose of the CFBDH latex is more than 0.8 g in 100 g aqueous solution. And this result implies that hand feel of the treated fabrics by great dose of the CFBDH latex will change stiff, which is also accordant with T_g of the CFBDH shell phase, 29.6°C, exceeding the ambient temperature.

CONCLUSIONS

A novel cationic core-shell fluorinated polyacrylate emulsion (CFBDH) has been successfully synthesized via seeded emulsion polymerization. TEM observation demonstrates it possesses uniform spherical core-shell structure with an average diameter of 126 nm. DSC and TGA analyses illustrate that the CFBDH has two T_g and its thermal stability is thus enhanced by introduction of fluorine-containing monomer.

SEM and AFM detections demonstrate that CFBDH is a good film-forming material. Although the macroscopic CFBDH/Cotton film seems to be smooth in appearance, the microscopic morphology of the CFBDH/Sil film is inhomogeneous and exists in a phase-separated state in fact. In addition, CFBDH can provide good hydrophobicity, such as WCA, static absorbing time and grade of oil repellent for the treated fabric and do not influence whiteness of the treated fabric. However, it will make the treated fabric slightly stiff at high doses.

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