

Role of Fluorocarbon Surfactant in the Preparation of Polytetrafluoroethylene-modified Polyacrylate Emulsion

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ABSTRACT: Role of fluorocarbon surfactant in the preparation of polytetrafluoroethylene-modified polyacrylate emulsion is investigated. The fluorocarbon surfactant has an efficient preemulsification to polytetrafluoroethylene (PTFE) powder. It enables PTFE powder to be introduced into the copolymer of *n*-butyl acrylate, *n*-methyl methacrylate, *n*-styrene, and α -methacrylic acid. Thereby, stable PTFE-modified polyacrylate emulsion can be formed. The effects of fluorocarbon surfactant on the surface tension, particle size and particle size distribution of the emulsion, as well as the relation between fluorocarbon surfactant and the amount of PTFE powder are fully investigated. The particle size and

the surface tension of emulsion strongly depend on the fluorocarbon surfactant concentration in the reaction system. The particle size distribution becomes narrower and the stability of the emulsion is improved with the increasing of the fluorocarbon surfactant concentration. According to the experiments, a possible mechanism of fluorocarbon surfactant in polymerization is proposed. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 2138–2145, 2007

Key words: polytetrafluoroethylene; fluorocarbon surfactant; preemulsion; polytetrafluoroethylene-modified; surface tension; contact angle

INTRODUCTION

Fluorine-containing polymers have been applied in various fields, such as textiles,^{1,2} leather,^{3,4} wood,⁵ stone,^{6,7} optical fibers,^{8,9} and paper industry.¹⁰ In recent years, many investigators have been attracted by the applications of fluorine-containing polymers, especially fluorine-containing acrylate polymers in emulsion. Until now, there are four main pathways to prepare the fluorine-containing acrylate polymers: (1) to prepare block or graft fluorine-containing acrylate copolymers^{11–13}; (2) to synthesize the fluorine-containing acrylate polymer with special particle configuration, such as core-shell structure and interpenetrating polymer network (IPN) construction^{14–16}; (3) to blend fluorine-containing acrylate polymers and fluorine-free acrylate polymers^{17,18}; (4) to copolymerize fluorine-containing monomers and acrylate monomers randomly.¹⁹ However, these approaches have some disadvantages, such as rigorous reaction conditions, high price of the fluorinated monomers and

the use of toxic or noxious monomers in the process of manufacture, which limits extensive application of the fluorine-containing polymers. Therefore, it is significant for us to find a new method that is simple, environment-friendly, and economical for the preparation of fluorine-containing acrylate polymers.

It is well known that PTFE has a number of interesting and remarkable properties, including low dielectric constant, water and oil repellency, high chemical and thermal stabilities, and self-cleaning property due to its low surface energy and high chemical energy of C–F bond.^{20,21} However, PTFE powder is usually used as the filling mixed directly with polymers in fluorine-containing coatings.²² In that, a phase separation will happen owing to the large difference in surface tension between PTFE and polymer.

To resolve the poor compatibility between PTFE and polyacrylate, PTFE powder is preemulsified with fluorocarbon surfactant in water and dispersed under high shear stirring, and then the preemulsified PTFE is used in the acrylate copolymerization. In previous work, we have successfully synthesized PTFE-modified polyacrylate emulsions by *n*-butyl acrylate (BA), *n*-methyl methacrylate (MMA), *n*-styrene (St), and α -methacrylic acid (MAA), and have studied the properties of the emulsions and their

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films.^{23,24} Fluorocarbon surfactant plays a crucial role in the preparation of PTFE-modified polyacrylate emulsion. In this article, we investigated the emulsification ability of fluorocarbon surfactant to PTFE in the emulsion and the effect of the amount of the fluorocarbon surfactant on the particle size distribution and stability of emulsion. In addition, a possible mechanism of fluorocarbon surfactant in polymerization based on experiments is proposed. The resulting PTFE-modified polyacrylate emulsions could be applied in fluorine-containing coatings, adhesives, optical and synthetic polymeric materials.

EXPERIMENTAL

Materials

n-Methyl methacrylate (MMA), *n*-styrene (St), *n*-butyl acrylate (BA), α -methacrylic acid (MAA) (Sigma-Aldrich, Shanghai, China) were distilled and stored at normal temperature (15–20°C). Sodium dodecyl sulfate (SDS) and polyoxyethylene octyl phenol ether (OP) (Beijing Chemical Reagent Company, China) used as the surfactants without further purification are of reagent grade. Ammonium persulfate (APS) and sodium bicarbonate (NaHCO₃) are of reagent grade. Fluorocarbon surfactant (C₁₀F₁₉OC₆H₄SO₃Na, FC6201) was obtained from Shanghai 3F New Materials Co. Ltd. of China used as the surfactants without further purification. Polytetrafluoroethylene (PTFE) (2 μ m) power (Shanghai 3F New Materials, China) was used as functional reagent, and the water used was distilled followed by deionization.

Preparation of the PTFE-modified polyacrylate emulsion

Table I gives the recipe to synthesize the emulsion of PTFE-modified polyacrylate. The process is as follows:

Preemulsion stage

PTFE powder and fluorocarbon surfactant FC6201 (Part I of Table I) were mixed into beaker containing 40 mL water. The mixture was stirred under high shear stirring (14,000–15,000 rpm) with high-speed dispersor, and dispersed simultaneously by ultrasonicator for 1 h at normal temperature to produce a PTFE preemulsion.

Seeding polymerization stage

PTFE preemulsion was charged into a 500 mL four-neck flask with reflux condenser, nitrogen inlet and dropping funnels. Subsequently, the deionized water

TABLE I
Recipe for the Synthesis of PTFE-modified Polyacrylate Emulsion with a Semi-continuous Emulsion Polymerization Process

No.	Feed name	Weight (g)
I	PTFE powder	6.0
	FC6201	2.4 (3.55 mM) ^a
	Deionized water	40.0
II	Deionized water	70.0
	SDS	0.6
	OP	0.8
III	MMA	20.0
	BA	36.0
	St	10.0
	MAA	2.0
IV	APS	0.6 (2.63 mM) ^a
	NaHCO ₃	0.6
	Deionized water	30.0

BA : MMA : St : MA (W/W) = 18 : 10 : 5 : 1; the ratio can be adjusted according to the desired T_g ; the monomer mixture and initiator were fed respectively at constant feed rates.

^aConcentrations based on aqueous phase.

containing mixed emulsifiers SDS and OP-10 (Part II of Table I) and about one-tenth of the mixed monomers (Part III of Table I) were added into the flask. Nitrogen gas was continuously bubbled into the system with the stirring at about 400 rpm in the entire experiment. When the temperature was 50–60°C, about 20% of initiator with concentration 0.5–1.0% was fed into the flask, and then the temperature was raised to 60–70°C and kept until the mixture in the flask appeared white with blue.

Feed stage

Emulsion was prepared by using an optimized semi-starved feed procedure. The temperature first was kept at 70–75°C with an appropriate dropping rate (without many circulation monomers) until initiator and the residual monomers were completely added into the seed emulsion. Then the temperature was elevated to 80–85°C and maintained it for about 1 h. Thereafter the emulsion was cooled to room temperature and filtered through glass wool to remove the coagulum. Finally the pH was adjusted to 7.0–8.0 with ammonia.

Characterization

Surface tension was determined with JZHY-180 interfacial tensometer (Chengde Testing Machine, Hebei, China) by ring detachment method at 23°C. Appropriate fluorocarbon surfactant solutions and PTFE-modified polyacrylate emulsions were prepared and measured after 24 h.

Contact angles were measured by the sessile drop method at room temperature using a JC2000C2

contact angle goniometer (Shanghai Zhongchen Powereach Company, China). Deionized water and solution of fluorocarbon surfactant with different concentrations were dropped respectively, on the surface of the latex films and PTFE sheets with a micro syringe in atmosphere. More than 10 contact angles were averaged to get a reliable value for each sample.

The particle sizes and their distribution of the fluorine-containing emulsions were measured by dynamic light scattering with a Malven zetasizer 3000 HSA particle sizer.

FTIR spectra were recorded with Nicolet Instruments Research Series 5PC Fourier Transform Infrared spectrometer. For all the samples, KBr pellets were prepared and measured in the range from 4000 to 400 cm^{-1} .

Scanning electron microscopy (SEM) micrographs were taken with SHIMADZU SSX-550. Samples were prepared in the following manner. Preemulsion of PTFE powder and PTFE-modified polyacrylate emulsions were diluted with deionized water, dropped onto silicon wafer and dried at room temperature. Pictures were taken at voltage of 15.0 kV.

Transmission electron microscopy (TEM) micrographs were obtained using a JEM-2000 EX transmission microscope at an accelerating voltage of 200 kV. The samples were prepared by wetting either a carbon-coated or a Formvar-coated grid with a small drop of the dilute latex solution. Upon drying, it was stained with a small drop of 2% phosphotungstic acid (PTA) for 30 min and dried at room temperature before analysis.

RESULTS AND DISCUSSION

Role of fluorocarbon surfactant in aqueous solution and emulsion

A series of solutions are prepared by dissolving different amount of fluorocarbon surfactant in deionized water both in the presence and absence of PTFE powder, and measured after 24 h. Figure 1(a) represents the relation between surface tension and fluorocarbon surfactant concentration both in the presence and absence of PTFE. The surface tension decreases with the increasing of the fluorocarbon surfactant concentration in both systems. As PTFE is introduced into the fluorocarbon surfactant solution, the slope of the curve is different from that in the absence of PTFE. It can be seen that the value of surface tension in the presence of PTFE is higher than that in the absence of PTFE. The reason is that a part of fluorocarbon surfactant molecules are adsorbed at the interface between PTFE and water, which leads to the decreasing of fluorocarbon surfactant molecules adsorbed at the interface between water and air.

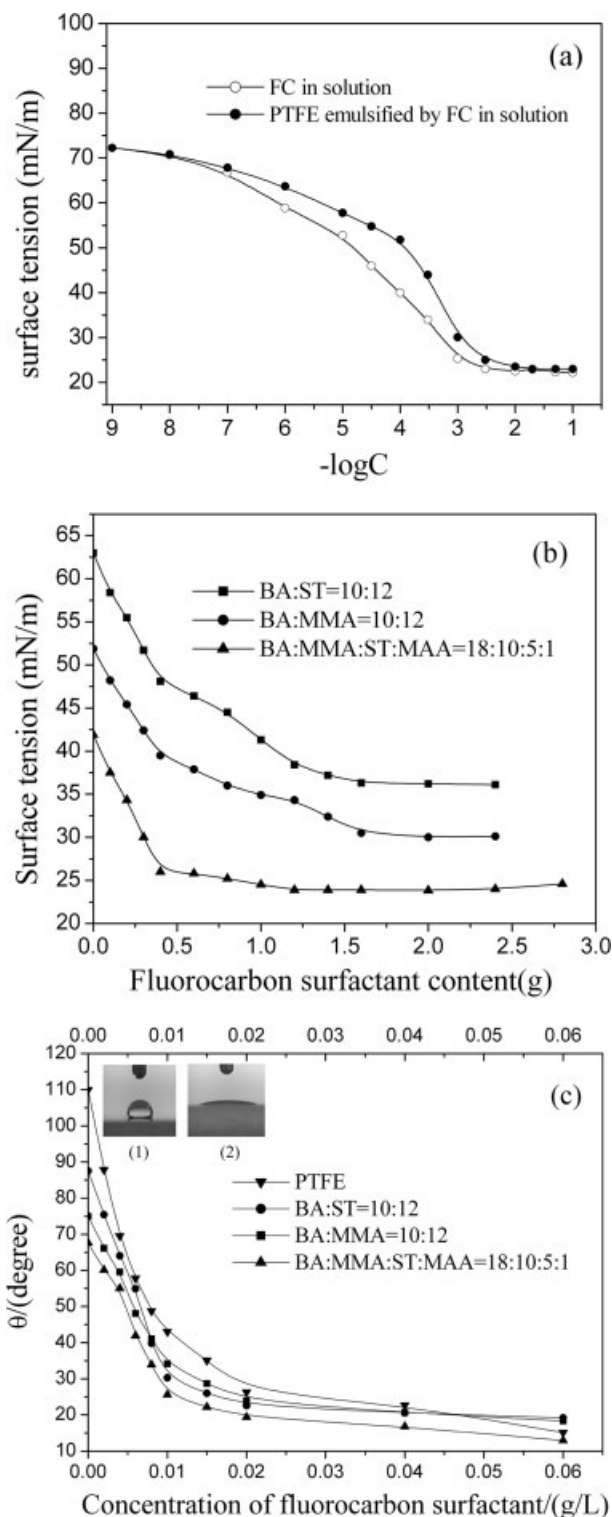


Figure 1 (a) Surface tension as a function of fluorocarbon surfactant concentration in the absence and in the presence of PTFE: (○) without PTFE; (●) with 0.5 g PTFE. (b) Surface tension as functions of fluorocarbon surfactant concentration in different emulsions. (c) Static contact angles on different polymers as functions of fluorocarbon surfactant concentration, (1) static contact angle of water on PTFE, (2) static contact angle of the fluorocarbon surfactant solution with 0.01 g/L on PTFE.

As shown in Figure 1(a), when the concentration of fluorocarbon surfactant is above 1.5 wt % ($-\log C = 2.82$), the surface tension both level off. It indicates that the surface of PTFE particles is covered sufficiently by fluorocarbon surfactant molecules.

To determine the effect of fluorocarbon surfactant concentration on surface tension of emulsions, the mixed monomers ratios 10 : 12 ($W_{BA} : W_{St}$) in System 1, 10 : 12 ($W_{BA} : W_{MMA}$) in System 2, and 18 : 10 : 5 : 1 ($W_{BA} : W_{MMA} : W_{St} : W_{MAA}$) in System 3 are selected. Figure 1(b) shows the effect of fluorocarbon surfactant concentration on the surface tension of emulsions in different systems. The surface tension values of the three systems are different because of the different monomer ratios. However, the change tendencies of the surface tension are the same for the three systems. Namely, with the addition of fluorocarbon surfactant, the surface tension falls quickly and then levels off. The decrease of surface tension minimizes the difference of interfacial tension between PTFE and polyacrylate.

Figure 1(c) shows the contact angles of the fluorocarbon surfactant solution with different concentration on PTFE sheet and the latex films with different MMA, BA, and ST contents. The contact angles decrease quickly and then level off with the increasing of fluorocarbon surfactant concentration. The contact angles are very small when the concentration of fluorocarbon surfactant is above 0.01 g/L [Fig. 1(c)]. The small contact angles reveal that the fluorocarbon surfactant has a strong surface wetting capability to PTFE sheet and polymer films with different MMA, BA, and ST contents.

Consequently, it is possible that PTFE particle is introduced into polyacrylate copolymer in the presence of fluorocarbon surfactant. To obtain stable emulsion, monomer ratio of BA : MMA : St : MAA is selected as 18 : 10 : 5 : 1(w/w) [System 3 in Fig. 1(b)] in the following experiments.

Select of the optimal ratio of PTFE to fluorocarbon surfactant

Under above condition, the optimal ratio of PTFE to fluorocarbon surfactant is selected in the following experiments. First, the ratio of PTFE powder to fluorocarbon surfactant is changed from 0 to 5.8. As shown in Figure 2(a), when the ratio of PTFE powder to fluorocarbon surfactant is less than 2.5, the change of surface tension isn't obvious with the increase of the ratio. In this stage, PTFE powder can be enwrapped adequately by fluorocarbon surfactant, and the system is stable. However, with further raise of the ratio, the surface tension increased rapidly from 23.9 to 27.5 mN/m. It can be explained that when the PTFE powder can not be enwrapped

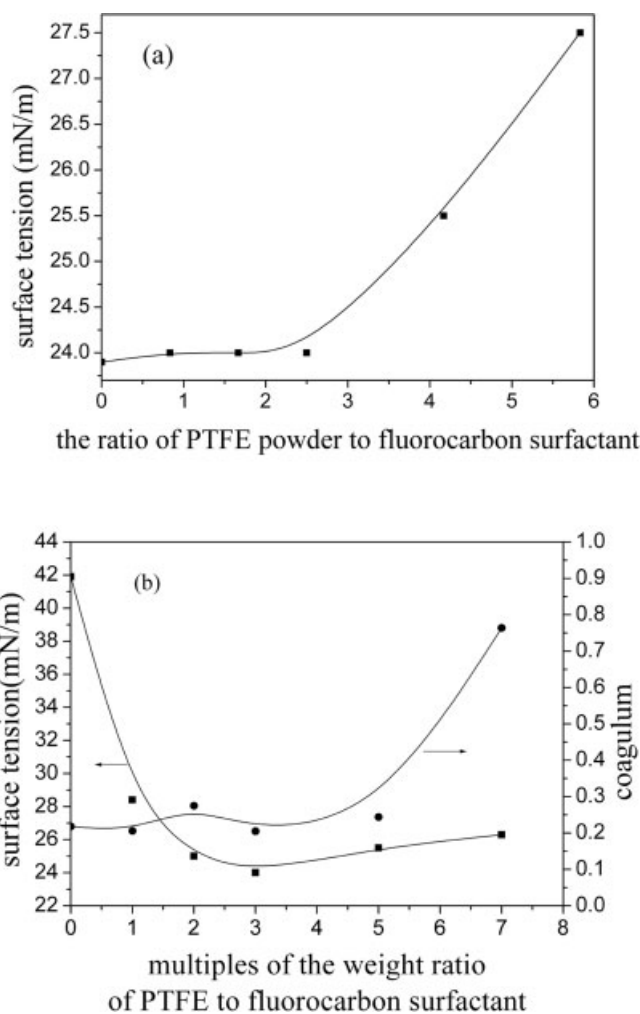


Figure 2 Effect of the weight ratio of PTFE to fluorocarbon surfactant on the surface tension, in which fluorocarbon surfactant content is fixed (a), effect of PTFE and fluorocarbon surfactant content on surface tension (■) and coagulum (●), in which the weight ratio of PTFE powder to fluorocarbon surfactant is a constant (b). The monomers ratio of System 3 in Figure 1 (a) was selected as these experiments.

adequately by fluorocarbon surfactant, the coagulum generates and adsorbs a part of fluorocarbon surfactant in the emulsion, which results in the increase of surface tension.

The further experiment results are shown in Figure 2(b). The weight ratio of PTFE powder to fluorocarbon surfactant is fixed as 1.0 : 0.4, and then their total content is changed gradually from 0 to 9.8 g. With the increasing of total content from 0 to 4.2 g, the surface tension decreased sharply from 42 to 23.9 mN/m. However, the surface tension of emulsion rises from 23.9 to 26.3 mN/m while the total content further increases from 4.2 to 9.8 g. When their total content is 4.2 g (3 g PTFE and 1.2 g fluorocarbon surfactant), both the surface tension and the coagulum show the minimum value.

Hence, it is concluded that the optimal ratio of PTFE to fluorocarbon surfactant should be below 2.5 [Fig. 2(a)], and the amount of PTFE and fluorocarbon surfactant should be about 3.0 g and 1.2 g [Fig. 2(b)], respectively.

Effect of fluorocarbon surfactant concentration on particle size and particle size distribution of the emulsion

The effect of fluorocarbon surfactant concentration in emulsions [System 3 in the Fig. 1(b)] on the particle size and particle size distribution of emulsions in the absence of PTFE is shown in Figure 3(a–c). It can be seen that the average particle size decreases with the increasing of fluorocarbon surfactant concentration from 0 wt % to 1.1 wt %. Usually, the increasing of the surfactant concentration can raise the number of micelles, which results in the decrease of particle size. However, too much fluorocarbon surfactant could break the double electric layers around each latex particle, and even lead to aggregation among latex particles.²⁵ Consequently, the average particle size and particle size distribution of emulsion increase with increment of fluorocarbon surfactant. The effect of different ratio of PTFE to fluorocarbon surfactant in latices [System in the Fig. 2(a)] on latex particle size is also investigated. As shown in Figure 3(d,e), with the increasing of the weight ratio, the average latex particle size increases. When the weight ratio is about 2.5, the distribution of particle size is narrow and the average particle size is 152.1 nm. At this ratio, PTFE powder has been emulsified and enwrapped adequately by fluorocarbon surfactant, so the reaction system becomes stable, and the distribution of particle size is homogeneous. Further increase the ratio, the PTFE content is beyond the emulsification ability of fluorocarbon surfactant, which results in the formation of larger latex particles. Consequently, the particle size increases and particle size distribution broadens obviously. It is concluded that, if the ratio of PTFE powder to fluorocarbon surfactant is appropriate, the system will be stable, the particle size will be homogeneous and particle size distribution will be narrow.

Comparing of FTIR spectra

Figure 4 shows the FTIR spectra of PTFE powder, polyacrylate emulsion and PTFE-modified polyacrylate emulsion. In the polyacrylate emulsion spectrum [Fig. 4(b)], the absorption peak at about 3400 cm^{-1} is due to the O–H stretching vibration. The characteristic peaks of C–H ($-\text{CH}_2$, $-\text{CH}_3$) and C=O groups originating from BA, MMA and MAA are shown at $2800\text{--}3000\text{ cm}^{-1}$ and 1700 cm^{-1} , respectively. The peaks at $1550\text{--}1350\text{ cm}^{-1}$ due to deforma-

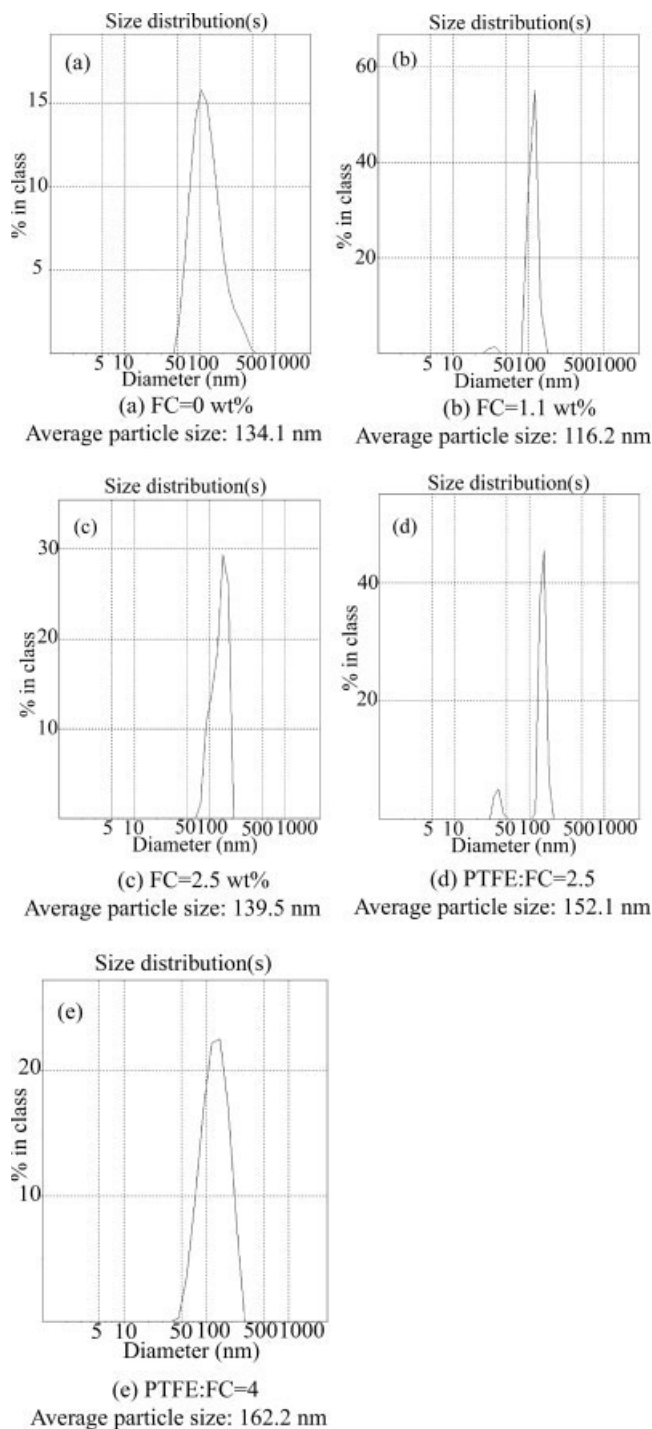


Figure 3 Effects of fluorocarbon surfactant content on particle size and size distribution of the emulsions in the absence of PTFE (a)–(c), effects of weight ratio between PTFE and fluorocarbon surfactant on particle size and size distribution of emulsions (d), (e).

tion vibration of C–H and O–H are identified. Compared with the polyacrylate spectrum [Fig. 4(b)], the PTFE-modified polyacrylate spectrum [Fig. 4(c)] shows many differences between 1000 and 1300 cm^{-1} . The peak at 1243 cm^{-1} is the bending

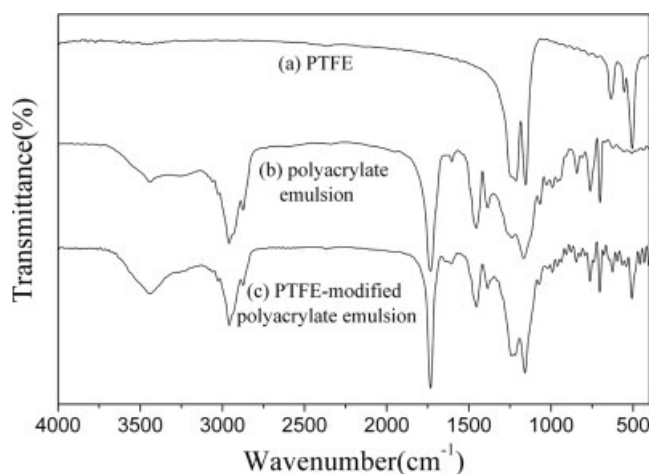


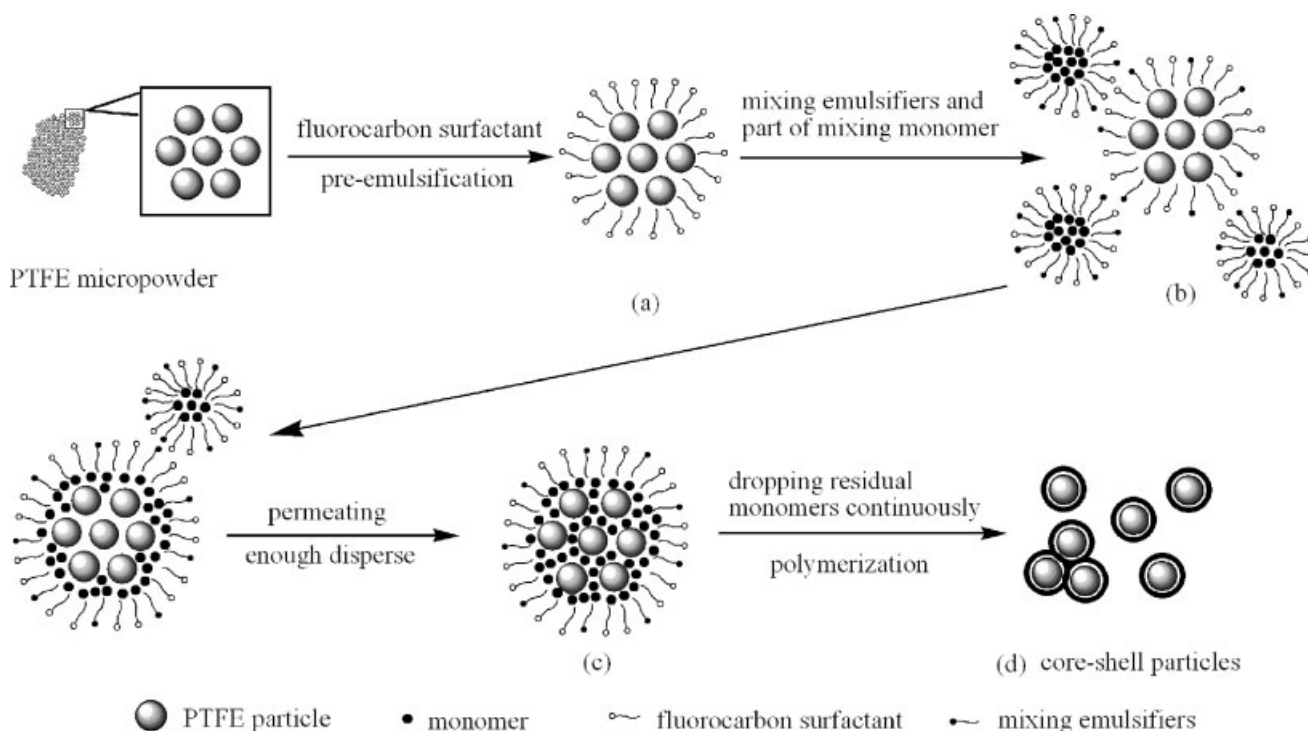
Figure 4 FTIR spectra of PTFE powder (a), polyacrylate emulsion (b) and PTFE-modified polyacrylate emulsion (c).

vibration of CF_2 groups, the peaks at 1217 cm^{-1} , 1158 cm^{-1} are attributed to the stretching vibration and deformation vibration of CF_2 groups, which result from PTFE. The absorption peaks at $470\text{--}670\text{ cm}^{-1}$ attribute to the deformation vibration of the CF_2 groups correspond to PTFE, which does not appear in Figure 4(b). Consequently, based on the stability of the PTFE-modified polyacrylate emulsion and the FTIR study, we can confirm that it is able to obtain the PTFE-modified polyacrylate emulsion in the presence of fluorocarbon surfactant.

Role of fluorocarbon surfactant in emulsion polymerization

According to experiments, a possible role mechanism of fluorocarbon surfactant in polymerization is proposed in Scheme 1. The process of PTFE powder preemulsified by fluorocarbon surfactant (FC6201) in water is completed under high shear stirring and dispersed simultaneously by ultrasonicator. As shown in Figure 5(a), PTFE particles exist as the PTFE nanoparticles aggregate before high-shear stirring. Then the PTFE powder (PTFE nanoparticles aggregate) is emulsified and dispersed into individual PTFE nanoparticles under high-shear stirring. The PTFE micelles [Scheme 1(a)] are formed in the semitransparent solution. Thereafter the solution including emulsifiers (SDS and OP) and a part of mixed acrylate monomers are added to the PTFE preemulsion. After sufficient dispersing, the micelles with similar surfactants surface layer of PTFE and mixed monomers are formed [Scheme 1(b)], which improves their compatibility. Therefore, the mixed monomers are able to permeate and disperse in the voids of the PTFE nanoparticles aggregate in the micelles [Scheme 1(c)]. Subsequently, the latex particles containing core/shell structures [Scheme 1(d)] are obtained by dropping initiator and remainder mixed monomers under monomer-starved polymerization condition.

The PTFE nanoparticles aggregate (average particle size $2\text{ }\mu\text{m}$) and voids existed among adjacent



Scheme 1 Proposed mechanism about the role of fluorocarbon surfactant in PTFE-modified polyacrylate emulsion polymerization.

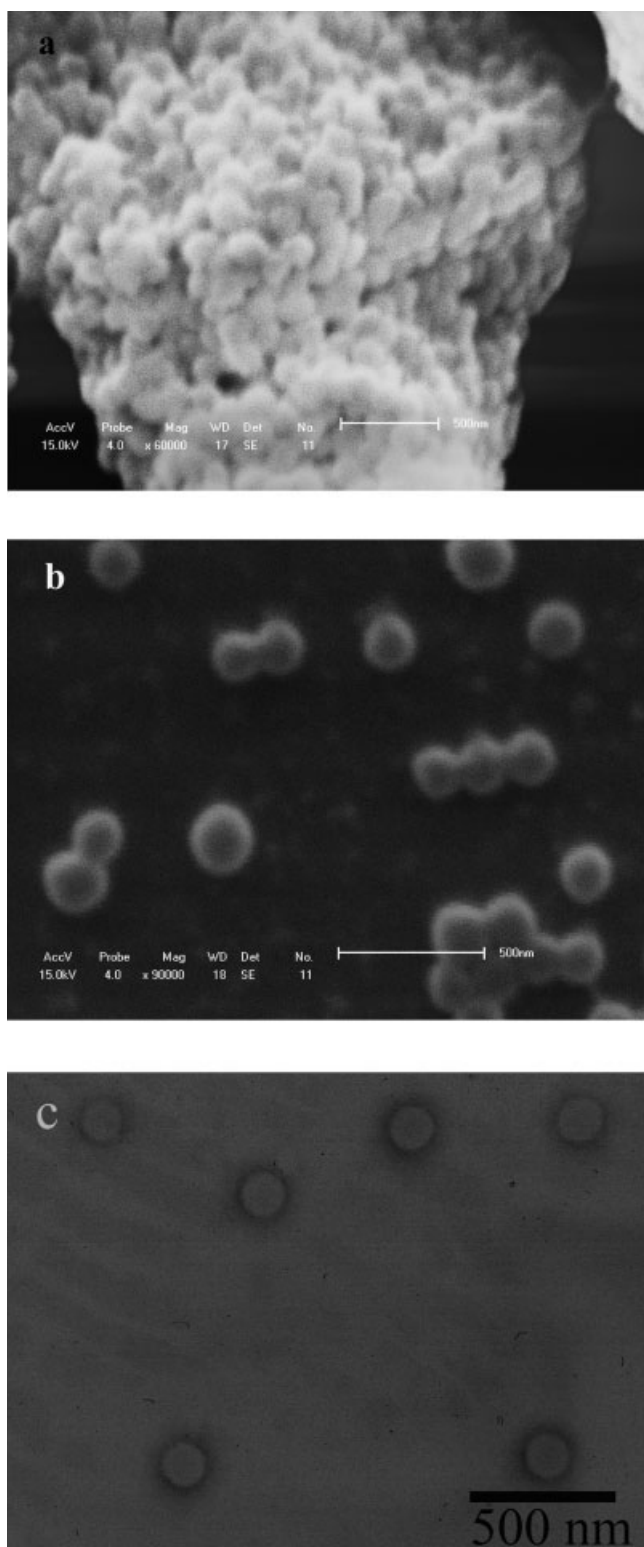


Figure 5 SEM micrographs of PTFE powder (a), SEM micrographs of PTFE-modified polyacrylate latex particles (b), TEM micrographs of PTFE-modified polyacrylate latex particles (c).

PTFE nanoparticles aggregate have been proved by the SEM micrograph [Fig. 5(a)]. Fluorocarbon surfactant can be adsorbed on the surface of PTFE because

fluorocarbon branches in fluorocarbon surfactant have similar chemical structure to the surface fluorocarbon chains in PTFE.²⁶ The voids will favor the absorbance of fluorocarbon surfactant on the surface of PTFE particles. However, the fluorocarbon surfactant preemulsified to PTFE is only adsorbed at the PTFE/water interface, because the high crystallinity of PTFE makes it difficult to be swollen.²⁷ The core/shell structure particles shown in Figure 5(c) prove that the polyacrylate has covered the PTFE particles, which confirm the proposed mechanism.

Preemulsification of PTFE plays an important role in the process of the experiment. If PTFE isn't preemulsified enough, the system would be unstable during the emulsion polymerization. The immiscibility among PTFE powder, monomers and water is attributed to their large surface tension differences, which makes it difficult to prepare the PTFE-modified polyacrylate emulsion. The result of the experiment reveals that the quantity of the coagulum is decreased in the presence of sufficient fluorocarbon surfactant during the emulsion polymerization. The reason is that fluorocarbon surfactant can reduce the surface tension difference among PTFE powder, acrylate monomers and water, which can improve their miscibility. On the other hand, it is necessary that the solution be stirred under high shear stirring and ultrasonic dispersing, which can transfer quickly fluorocarbon surfactant to interface by convection and form a new surface layer of fluorocarbon surfactant. In conclusion, the preemulsification of PTFE powder by fluorocarbon surfactant is crucial for preparation of the PTFE-modified polyacrylate emulsion.

CONCLUSIONS

The fluorocarbon surfactant can preemulsify PTFE powder efficiently and minimizes the surface tension difference between copolymer and PTFE. These functions of the fluorocarbon surfactant enable PTFE preemulsified to enter BA/MMA/St/MAA copolymer and resolve the poor miscibility and dispersibility between PTFE and polyacrylate. A kind of stable PTFE-modified polyacrylate emulsion is obtained. It has been demonstrated that the final particle size and particle size distribution of fluorine-containing emulsion can be controlled by changing the weight ratio of PTFE to fluorocarbon surfactant in the reaction system. Additionally, a mechanism about the role of fluorocarbon surfactant in the polymerization of PTFE modified polyacrylate is proposed and analyzed. FTIR, SEM, and TEM micrographs not only confirm PTFE is introduced into the copolymer but also prove the proposed mechanism. The

PTFE-modified polyacrylate emulsion resolved the poor miscibility of PTFE with polyacrylate.

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