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SHORT COMMUNICATION

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Preparation and properties of polytetrafluoroethylene-modified polyacrylate via emulsion polymerization

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Abstract One method of preparation of polytetrafluoroethylene(PFTE)-modified polyacrylate emulsion has been studied. Through pre-emulsion technology, PTFE powder could be dispersed by high speed shearing with high-speed dispersor. PFTE-modified polyacrylate has been prepared by in situ copolymerization of *n*-butyl acrylate, *n*-methyl methacrylate, *n*-styrene, and α-methacrylic acid in the presence of seed particles of dispersed PTFE by semi-starved addition method. The properties of the emulsion under various polymerization conditions were investigated. The morphology of the latex particles with about 180 nm were observed by scanning electron microscopy (SEM). It was shown that the particles with linear PTFE/core–polyacrylate/shell could eventually be dispersed homogeneously. TG showed that the heat-stability was improved obviously.

Keywords Polytetrafluoroethylene (PTFE) · PTFE-modified · Polyacrylate · Miscibility · Emulsion polymerization

Introduction

In recent years, the studies on fluorine-containing acrylate have received much attention. Fluorine resin can be prepared with fluorine-containing ethers and alkenes monomers based on copolymerization under special conditions [1–5]. However, at normal temperature and normal pressure, fluorine-containing ethers and alkenes monomers are poisonous gases and are hard to store. Fluorine-containing emulsion prepared by fluorine-containing acrylate comonomers have also been reported [6–9], but the cost is very high. As we all know, PTFE have heat resistance, inertness and low coefficient of friction because it is composed of C–F bond with high chemical energy [10, 11]. So studies on the application of PTFE have attracted many researchers. Lots of researches have been done on PTFE-modified polymer properties [12–16]. But PTFE is usually used as the padding of the fluorine-contained coatings [17]. However, phase separation will happen if an amount of PTFE is mixed directly with polymer. There are few reports that PTFE powder is used in emulsion polymerization. The reason is that micro-sized PTFE particles are not miscible and dispersed well with polyacrylate [18]. In this paper, in order to resolve the difficulty of phase separation, PTFE powder was emulsified and dispersed with fluorine-carbon surfactant by high-speed stir.

PTFE-modified polyacrylate emulsion was prepared by copolymerization of acrylate comonomers in aqueous medium composed of anionic, nonionic, fluorine-carbon surfactants, and the particles of PTFE. It has simple preparation technology, low cost, low forming membrane temperature, and no pollution. Properties of emulsion under various polymerization conditions, such as varying monomers ratio, different composite surfactant component, temperature, amount of PTFE, were investigated and optimized. The

PTFE/core–polyacrylate/shell nanoparticles could eventually be dispersed homogeneously observed by scanning electron microscopy (SEM) and the excellent qualities were examined. PTFE-modified polyacrylate emulsion can be used in fluorine contained coatings, synthetic polymeric materials, and adhesives.

Experimental

Materials

n-Butyl acrylate (BA), *n*-methyl methacrylate (MMA), *n*-styrene (St), α-methacrylic acid (MA), were distilled and stored at 15°C. Sodium dodecyl sulfate (SDS), dodecyl polyoxy ethylene (OP-10) and fluorocarbon surfactant ($C_{10}F_{19}OC_6H_4SO_3Na$) (FC6201) were of reagent grade used as the surfactants without further purification. Ammonium persulfate (APS) was of reagent grade. PTFE powder (2 μm) made in Shanghai of China was used as functional reagent. The water used was distilled following deionization.

Emulsion polymerization of PTFE-modified polyacrylate

Table 1 gives the recipe to synthesize the emulsion of PTFE-modified polyacrylate. These were carried out as follows.

Pre-emulsion stage

Polytetrafluoroethylene powder and fluorine–carbon surfactant (6201) were dispersed under the stirring speed of 15,000 rmp for 25–30 min with high-speed dispersor at normal temperature.

Seeding polymerization stage

Pre-emulsion PTFE were added to a four-necked jacketed glass reactor (500 ml) fitted with a reflux condenser, a nitrogen gas inlet tube. The distilled water containing SDS, OP-10, and $NaHCO_3$ was added to the reactor. The appropriate masses of the mixing monomers were then added to constant-press dropping funnel with the target solids content (wt%) of the desired latex (e.g., 33% solids content requires 16 g of BA, 9 g of MMA, 4 g of St, 1 g of MA and 3 g of PTFE in 67 ml of water). The stirring speed was 500 rmp for the following experiments.

When the temperature was ramped to 50–60°C, about 10% (wt%) of the mixed monomers and 20% of the initiator with concentration 1.5% (39 ml) were fed into the reactor. The temperature was kept between 60 and 70°C until the mixture in the reactor appeared blue fluorescence.

Feed stage

Emulsion was prepared using an optimized semi-starved feed procedure. The appropriate dropping rate was kept without much circulation between 70 and 75°C until the monomers and initiator were completely added. Then the temperature was increased and kept between 80 and 85°C for 1 h. The latex was then cooled to room temperature and filtered through glass wool to remove coagulum. Finally the pH was adjusted to 6–7 with thick ammonia.

Results and discussion

Optimal reaction conditions

The polymerization reaction conditions of pure polyacrylate and benzene acrylate emulsion have already been studied for many years [18–23]. In this paper, the optimized reaction conditions such as monomers ratio, composite surfactant component, and temperature, were investigated under the condition of 8.8% (ratio of PTFE/acrylate monomers) PTFE-contained emulsion, also content of PTFE.

Effect of the monomers ratio

The properties of appearance, rigidity, adhesive force of the emulsion film were investigated under different monomer ratios of (10–20):(5–20):(0–10):1 (w/w) BA/MMA/St/MA and 8.8% PTFE. From Table 2, it can be seen the adhesion force increased slightly and rigidity decreased gradually with the increase of the BA content. However, with the increasing of St or MMA content, the adhesion force decrease slightly, while rigidity increase gradually. In order to obtain the suitable adhesion force and high rigidity, we select monomer ratio 18:10:5:1 (w/w) as in the following experiments.

Effect of composite surfactants component

Emulsion containing a ratio of BA:MMA:ST:-MA:PTFE of 18:10:5:1:3 (w/w) with a wide range of surfactants amount were polymerized at 70–80°C. Fluorocarbon emulsifier (FC6201) is used to disperse PTFE in pre-emulsion stage with a 0.4:1 FC6201/PTFE ratio. The average particle size and ratio of water absorption are strongly affected by the surfactant amount. The particle size was analyzed by Malvern Zetasizer 3000HSA. The results were shown in Table 3. The average latex size decreases with increasing

Table 1 Recipe for the synthesis of acrylate copolymer emulsion with a semicontinuous emulsion polymerization process

Pre-emulsion stage		Seed stage		Feed stage	
Ingredient	Amount (g)	Ingredient	Amount (g)	Ingredient	Amount (g)
PTFE powder	6	BA	3.6	BA	32.4
		MMA	2.0	MMA	18
$NaHCO_3$	0.2	St	1	St	9
				MA	2
FC6201[c]	2.4 (3.55 mM)[a]	APS	0.12 (0.526 mM)[a]	APS	0.48
Composite emulsifiers[b]	1.3				0.1
DI water	101				39

BA:MMA:S:MAt(W/W) = 18:10:5:1; the monomer mixture and initiator were fed separately at constant feed rates

[a] Concentrations based on aqueous phase

[b] ω OP-10 : ω SDS = 0.4:0.3

[c] $C_{10}F_{19}OC_6H_4SO_3Na$

Table 2 Effect of the monomers ratio

m(BA):m(MMA):m(St):m(MA)	Appearance of emulsion film	Rigidity	Adhesion force (grade)
10:10:5:1	Mass chap	–	–
15:10:5:1	Translucent	0.660	2
18:10:5:1	Translucent	0.625	1
20:10:5:1	Translucent	0.610	1
18:5:5:1	Translucent	0.600	1
18:15:5:1	Translucent	0.670	1
18:20:5:1	Translucent	0.701	2
18:10:0:1	Translucent and tacky	0.360	1
18:10:10:1	Mass chap	–	–

Table 3 Effect of the surfactants concentration on the fluorine-containing latex average size[a]

NO.	[OP-10]:[ABS] (w/w, g)	$\bar{d}$ (nm)[b]	Gel content[c] (%)	Centrifugal stability[d] (gel content %)	Ratio of absorbing water (%)
1	0.1:0.2	471	20	23	10
2	0.2:0.3	221	3	5	14
3	0.3:0.3	200	0.8	1	17
4	0.3:0.5	150	0.1	0	26
5	0.5:0.3	186	0.2	0	24
6	0.5:0.5	136	0.4	0	32

[a] The concentrated emulsion was prepared at 70–80°C.

[b] $\bar{d}$ means the number-average diameter of the latex particles

[c] Gel was formed during the period of synthesis

[d] Gel was formed after centrifugation

surfactant amount because larger surface areas between the continuous and dispersed phases protected by the absorbed surfactant become possible as the surfactant amount increases.

One can also see that the amount of gel decreased with increasing surfactant amount. From Table 3, when the ratio of [OP-10]:[ABS] amount is 0.1:0.2(w/w, g), 20% gel content is formed. At relatively low surfactant amount, the repulsion between the surfaces of the latex particles, which ensures the stability of the emulsion, is relatively small because the surface is not completely covered with surfactant, so gel is formed. When the ratio of [OP-10]:[ABS] amount is 0.3:0.5, only 0.1% gel content is formed because the surface can be completely covered with surfactant molecules. However, the ratio of absorbing water of latex film increased with increasing amount of surfactant. Therefore, the optimum the ratio of monomers: OP-10: SDS is (18:10:5:1):(0.3–05):(0.3–0.4) (w/w).

Effect of reaction temperature

Under the above polymerization conditions, the effect of the reaction temperature on the emulsion property was studied in Table 3. Conversion rate was examined by gravimetric method. From Table 3, we can conclude that the polymerization would not carry out well if the temperature is above 85°C or below 65°C. This can be explained as follows. Below 65°C, the APS initiator decomposes slowly; conversion rate of the monomers is low. Above 85°C, APS initiator decomposes quickly and induce overfull free radicals, which make monomers polymerize quickly. The polymerization in this system becomes unstable and gel was formed. In order to

Table 4 Effect of reaction temperature on the conversion of monomers

t(°C)	Gel content	Emulsion appearance	Conversion of monomers (%)	Centrifugal stability of the emulsion
55–65	None	Blue fluorescence, milk white	< 85	Stable
65–75	None	Blue fluorescence, milk white	85–95	Stable
75–85	None	Milk white	> 95	Stable
85–90	Trifle	Milk white	> 95	Gel formed

decrease the formation of gel and obtain high conversion rate, three different temperature periods are chosen in the experiment. Between 60 and 70°C, forming nucleus stage of PTFE-modified polyacrylate needs 1.5–2 h. During the period of monomers feed, the temperature is kept at 70–80°C. When the monomers and initiator are completely added, the temperature is increased and kept at 80–85°C for 1 h to obtain high conversion of monomers (Table 4).

Effect of the amount of PTFE7

Under the above conditions, the emulsion containing 0–13% (0–8.84 g) PTFE/polyacrylate ratio was synthesized at 70–85°C. The effect of the amount of PTFE on emulsion properties was investigated. The surface tension of the emulsion was determined by ring detachment method. The results are seen in Fig. 1.

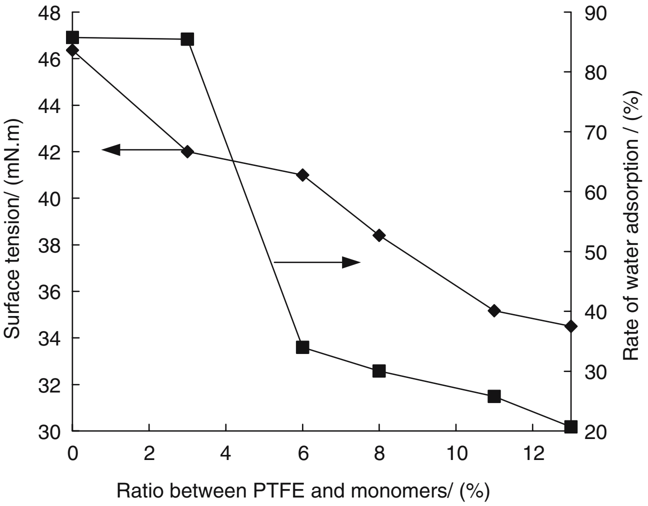

Fig. 1 Effect of the ratio of PTPFE/polyacrylate monomers on the surface tension and water endurance

From Fig. 1, it is clear that surface tension of the emulsion decreases gradually with the increasing of PTFE amount. After the ratio of PTFE and polyacrylate reaches 11% (7.48 g PTFE), the change trend of surface tension is mild. On the other hand, with increase ratio, especially in the range of 2–8% (1.36–5.44 g PTFE amount), the rate of absorption of water decreases quickly. This can be considered to be as a result of the increase of the hydrophobic PTFE on the surface of the latex membrane. However, above 8% ratio, the trend of the rate of water absorption decreased slowly. One possible explanation is that water endurance of the latex membrane is killed because of phase separation of PTFE with polyacrylate. Another reason is that the PTFE particles are probably tended to coagulate with polyacrylate. Therefore, the 6–11% (4.08–7.48 g amount PTFE) PTFE/acrylate monomers ratio is selected.

Comparing the properties of PTFE-modified latex film

The emulsion of pure polyacrylate and 8.8% (ratio PTFE/acrylate) PTFE modified were prepared under the above-optimum condition. The properties of the latex and film were investigated in Table 5.

From Table 5, the minimum formation temperature (MFT) of the PTFE-modified emulsion is lower than that of the polyacrylate emulsion. Both the surface tension and the viscosity decrease obviously. The stability of temperature and pH of the emulsion modified by PTFE is better than that of polyacrylate. The appearance of polyacrylate latex film is even, transparent, while the appearance of PTFE-modified polyacrylate latex film is even, translucent. The endure rinse times of PTFE-modified is more than 3,000. Ratio of absorbing water is 12% lower than that of pure polyacrylate. The ability of water resistance is improved obviously. It can be concluded based on the literature that, when latex film is formed, PTFE will move to the

Table 5 Compare of the emulsion properties

Item	Pure acrylate emulsion	PTFE-modified acrylate emulsion
Appearance	Blue fluorescence, milky fluid	Blue fluorescence, milky fluid
Solids content/%	31	32
MFT/°C	8	4
Surface force/mN m^{-1}	46	33
Viscosity /mP s	2.1	1.7
Stability of Ca^{2+}/5%$CaCl_2$ aq 5:1	Lots of gel	Stable
High temperature stability/60°C 48 h	Little gel	Stable
Low temperature stability/5°C, 48 h	Stable	Stable
Endure rinse times	1,500	3,000
Ratio of water absorption/%	40	28

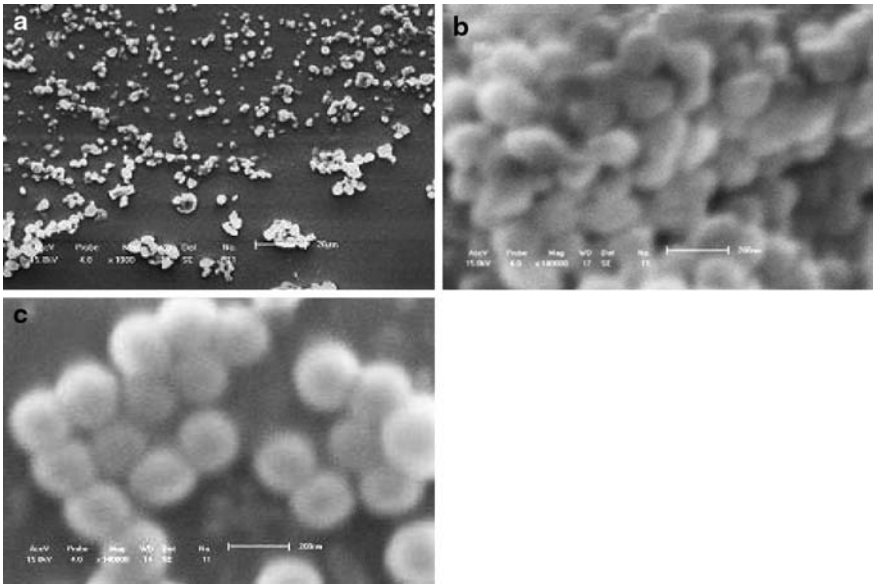

Fig. 2 SEM photographs of PTFE powder (**a**), PTFE powder emulsified with FC6201 through pre-emulsion technology (**b**) and 8.8% (PTFE/polyacrylate ratio) PTFE-modified polyacrylate particle (**c**)

outside of the membrane layer because of its low surface energy [24]. Thus PTFE-modified polyacrylate emulsion and film have attractive properties of temperature stability and water resistance.

SEM

The micrographs of particles of the PTFE powder, PTFE powder emulsified by FC6201, and 8.8% (ratio of PTFE/acrylate) PTFE-modified polyacrylate emulsion diluted 50 times with distilled water were observed with SEM.

Figure 2 shows the SEM micrograph of the PTFE powder particles (a) with 500 times, and PTFE powder emulsified by FC6201 (b), PTFE-modified polyacrylate composite nanoparticles (c) with 25,000 times. From (a), the PTFE powder particle is inhomogeneous micron-sized. However, (b) shows that the particles of PTFE latex are globe and anomalous oblong nanometer-sized affected by the addition of fluorine–carbon emulsifier, as described in the literature [25]. From (c), we can observe that the surface of PTFE-modified latex membrane is very smooth and latex particles are full globe. This indicates that the PTFE powder has been changed from micron-sized particles into nanometer-sized latex particles by pre-emulsion, and the latex particles of PTFE have changed from anomalous oblong to full globe through emulsion polymerization. It can be concluded that the pre-emulsified technology can make PTFE powder disperse well, and the comonomers polymerized around of the particles of smashed PTFE which can make particle figure from anomalous oblong to full globe by semi-starved addition method. The morphology of linear PTFE/core–polyacrylate/shell is thermodynamically stable, which has been proved in the literature [26].

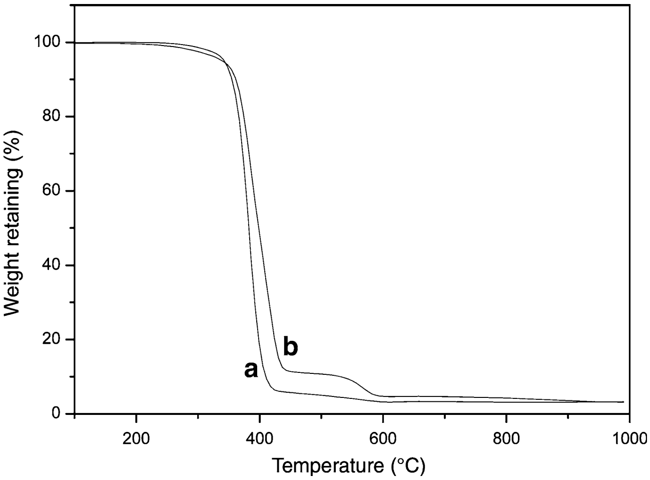

Fig. 3 The relationship between weight retaining and temperature of pure polyacrylate (**a**) and 8.8% ratio (w PTFE/polyacrylate) PTFE-modified polyacrylate (**b**)

Hot stability of PTFE-modified polyacrylate

Pure polyacrylate and 8.8% (ratio PTFE/acrylate) (6 g w) PTFE-modified polyacrylate were determined by thermogravimetry (TG) under vacuum condition. Results are seen in Fig. 3.

Figure 3 shows the relationship between weight retaining and temperature of pure polyacrylate (a) and 8.8% PTFE-modified polyacrylate (b). From Fig. 3, it is clear that weight retaining of 8.8% PTFE modified is higher than that of pure polyacrylate after 340°C. Pure polyacrylate loses weight most rapidly at 360°C, while modified polyacrylate at 370°C. Lost weight temperature increases 10°C. Furthermore, it is also obtained that weight retaining of 8.8% PTFE-modified polyacrylate is

60% and increases 27% compared with pure polyacrylate at 390°C. Namely, hot endurance of PTFE modified has been obviously improved . It can be concluded that F–C bond of PTFE with strong bond energy has improved decomposition temperature of polyacrylate. An additional possible reason is hydrogen bond of fluorine atom and hydrogen. Thus, the interaction can increase the heat-stability of polyacrylate. Therefore, it is an available way to improve heat-stability of polyacrylate through blend of the polyacrylate and PTFE at molecular level.

Conclusion

In the paper, the method of preparation of PTFE-modified polyacrylate emulsion has been studied. Although, PTFE powder is an inertia polymer with micron-sized, it can be dispersed by pre-emulsion technology and changed into nanometer-sized particle used in the modification of polyacrylate emulsion. Polymerization conditions of PTFE-modified polyacrylate were optimized. By comparing the properties of pure polyacrylate and PTFE modified, we concluded that composite particle film can offer the advantage properties of PTFE. SEM shows linear PTFE/core–polyacrylate/shell could eventually be dispersed homogeneously. On the other hand, TG shows that it is a possible available way to improve heat-stability of polyacrylate through blend of the polyacrylate and PTFE.

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