

Synthesis and Characterization of Fluoropolymer Modified Polyacrylate in Emulsion Polymerization

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ABSTRACT: A novel method to produce fluorine-containing polyacrylate emulsion is presented. It is prepared by the copolymerization of *n*-methyl methacrylate, *n*-styrene, *n*-butyl acrylate, and α -methacrylic acid in the presence of swollen particles of PTFE. The structure and properties of the polymers are characterized by GPC, PSD, SEM, and XPS. The number-average molar mass (M_n) 51,332, and the polydispersity 5.8688 are obtained. The mean diameter of latex particles is 300nm. Scanning electron microscopy reveals that particles of the emulsion are well dispersed. Meanwhile,

the F_{1s} content of the surface on the latex membrane is 8.99%. It is shown that the method of mixing micron and nanometer-sized particles should be made the next step of research. It is also proved that inertia polymers can be used in emulsion property modification. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 558–562, 2006

Key words: emulsion polymerization; fluoropolymer; modified; polyacrylate; XPS

INTRODUCTION

In recent years fluorine-containing polymers used in coatings have received much attention for their attractive properties of hot-stability, hydrophobic/oleophobic ability,¹ and low surface energy.^{2,3} Studies on water-borne fluorine resin emulsion have attracted many researchers. Much research has been done on the preparation of fluorine-containing ether monomer modified polyacrylate based on copolymerization under special conditions.^{4–8} However, at normal temperature and normal pressure, fluorine-containing olefin monomers are poisonous gases, which has hindered the industrial scale-up of fluorine-containing emulsion polymerization. Fluorine-containing emulsion prepared by fluorine-containing acrylate comonomers has also been reported,^{9–15} but the cost is high. Many people have synthesized fluorine-containing polymer modified polyacrylate through different synthesis technologies.^{16–20} In recent years PTFE is mostly used as padding of the coatings.²¹ Nevertheless, to our knowledge, PTFE powder modified polyacrylate emulsion has not been reported so far. In this study, we have used PTFE as the functional reagent that modified polyacrylate.

In this study, fluorine-containing polyacrylate emulsion was prepared by copolymerization of acrylate monomers in aqueous medium composed of

ionic, nonionic, fluorine-carbon surfactant, and the swollen particles of PTFE. It has simple preparation technology, low cost, low forming membrane temperature, and no pollution. The number-average mole mass (M_n), the weight-average molecular mole mass (M_w), and the polydispersity were measured by GPC. The mean diameter and distribution of the latex particles were measured by a granularity distribution apparatus. The figure of the composite nanoparticles was observed by scanning electron microscopy (SEM). We found that polyacrylate is miscible with PTFE at the molecular level.

Polymerization mechanism

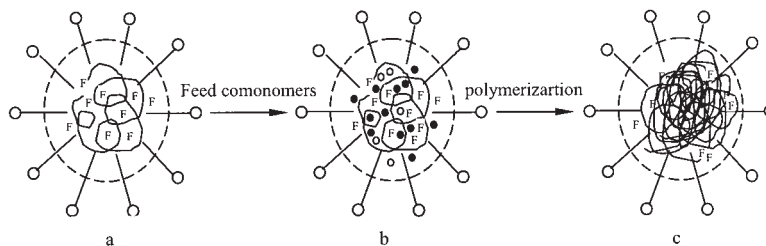
The polymerization mechanism can be seen in Scheme 1. PTFE powder is pre-emulsified and swollen by fluorine-carbon surfactant (6201). The fluoropolymer micelles are formed (a), and then acrylate monomers are added continuously to helical long carbon chain conformation of swollen PTFE through the semistarvation dripping method (b). Meanwhile, a reaction of copolymerization is carried out among the mixing monomers. As a result, linear PTFE entangles with a part of polyacrylate at the molecular level in the swollen micelles (c), which can increase the miscibility of PTFE with polyacrylate.

EXPERIMENTAL

Materials

n-Methyl methacrylate(MMA), *n*-styrene (St), α -methacrylic acid (MA), and *n*-butyl acrylate (BA) were dis-

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Scheme 1 Sketch map of feed emulsion polymerization. \circ and \bullet are comonomers; (a) swollen PTFE micelles, (b) monomers diffuse into swollen micelles, and (c) nucleation latex particle.

tilled and stored at 15°C. Sodium dodecyl sulfate (SDS), dodecyl polyoxy ethylene (op-10), and fluorine-carbon surfactant ($C_{10}F_{19}OC_6H_4SO_3Na$) (6201) were of reagent grade and used as the surfactants without further purification. Ammonium persulfate was of reagent grade. Polytetrafluoroethylene (PTFE) ($2\mu m$) power made in Shanghai of China was used as the functional reagent. The water used was distilled following deionization.

Emulsion polymerization of PTFE modified polyacrylate

Table I gives the recipe to synthesize emulsion of the PTFE modified polyacrylate. This were carried out as follows. During the first pre-emulsion process, PTFE powder and fluorine-carbon surfactant (6201) were dispersed under the stirring speed of 15,000rpm for 25 ~ 30 min with a high speed disperser at normal temperature, then were added to a four-necked jacketed glass reactor (500mL) fitted with a reflux condenser, a nitrogen gas inlet tube, and a polytetrafluoroethylene stir. Then the purified water containing ABS, OP-10, and $NaHCO_3$ was added to the reactor. The appropriate masses of the mixing monomers were then added to a constant-pressure dropping funnel to reach the solids content (wt %) of the desired latex (e.g., 32% solids content requires 32g of BA, 18g of MMA, 8g of St, 2g

of α -MA, and 6g of PTFE in 143mL of water). The stirring speed was 500rpm for the following experiments. The second period of the polymerization was the seeding stage. Heat and agitation were applied by an appropriate thermostat-stirring apparatus until the temperature was ramped to 50 ~ 60°C, and then 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°C ~ 70°C until the mixture in the reactor appeared as blue fluorescence.

During the third period, the emulsion was prepared using an optimized semistarved feed procedure. The appropriate dropping rate was kept without much circulation between 70 ~ 75°C until the monomers and initiator were completely added. Then the temperature was increased and kept between 80–85°C for 1h. 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

Average molar mass and polydispersity of PTFE modified polyacrylate

The membrane of pure polyacrylate and 3 and 5% (wt %) PTFE modified polyacrylate content were, respec-

TABLE I
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
$NaHCO_3$	0.2	MMA	2.0	MMA	18
Fluorocarbon surfactant 6201 ^c	2.4 (3.55 mM) ^a	St	1	St	9
Composite emulsifiers ^b	1.3	APS	0.12 (0.526mM) ^a	MA	2
DI water	101			APS	0.48
					0.1
					39

BA : MMA : S : MA (W/W) = 18 : 0 : 5 : 1; the ratio can be adjusted according to the desired T_g ; the monomer mixture and initiator were fed separately at constant feed rates.

^a Concentrations based on aqueous phase.

^b ω (OP-10) : ω (ABS) = 0.4 : 0.3.

^c $C_{10}F_{19}OC_6H_4SO_3Na$.

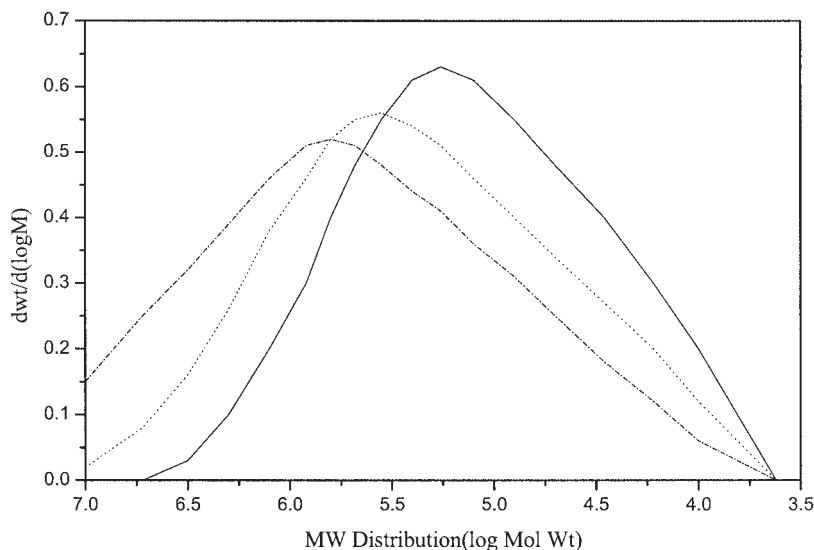


Figure 1 GPC traces for the PTFE modified polyacrylate prepared by emulsion polymerization: 0% PTFE modified (Dash Dot), 3% PTFE modified (Dot), and 5% PTFE modified (Solid).

tively, dissolved in tetrahydrofuran (3mg/mL). Their average molar mass and polydispersity were determined by an American 410 Water GPC. The results can be seen in Figure 1.

Figure 1 shows that low molecular mole mass and narrow molecular mole mass distributions of PTFE modified polyacrylates are obtained; and the more PTFE content increases, the more Mn, Wn, and polydispersity decrease.

One possible explanation for the above changes relating to the mechanism of emulsion polymerization is

suggested. In the micelles without PTFE, monomers and free-radicals have more chances to meet and terminate each other than in the PTFE-containing swollen micelles. So polymers with different polymerization degrees lead to a wide distribution of the mole mass.

When PTFE is added to acrylate, the polymerization environment will be different from acrylate emulsion without PTFE. Under semistarvation conditions, some monomers and free radicals diffuse into swollen PTFE latex particles; others diffuse into polyacrylate latex particles. Helical long carbon chain conformations of PTFE block the increases of chains. Therefore, the average mole mass decreases distinctly. PTFE entangles with polyacrylate, which can decrease their phase separation.

Mean diameter and distribution of the latex particles

Particle size distribution (PSD) of pure polyacrylate and PTFE modified polyacrylate was analyzed by a

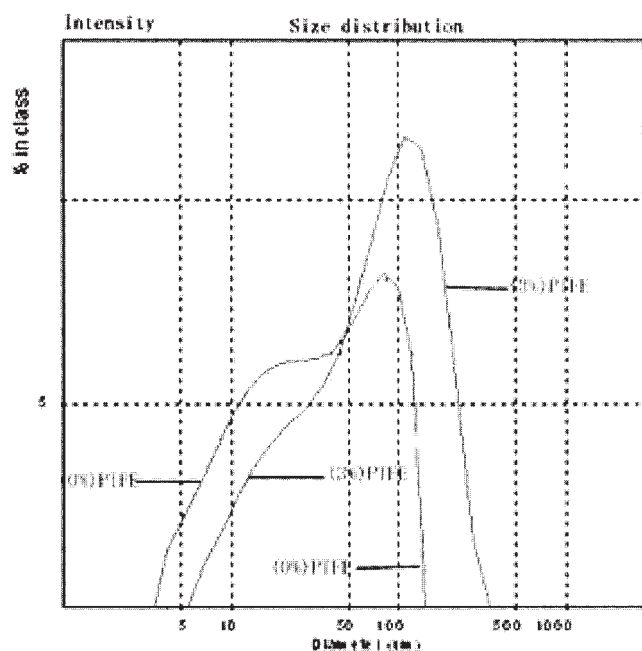


Figure 2 Distribution of latex particles of the 0% PTFE modified polyacrylate and 3% PTFE modified.

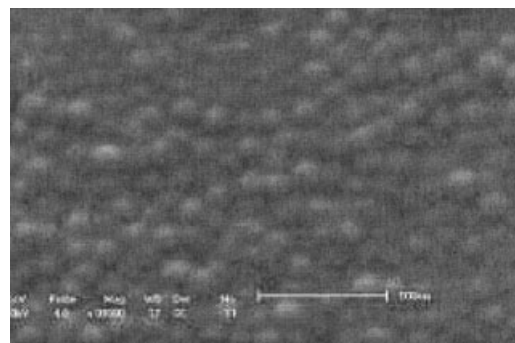


Figure 3 SEM micrograph of PTFE modified polyacrylate composite nanoparticles.

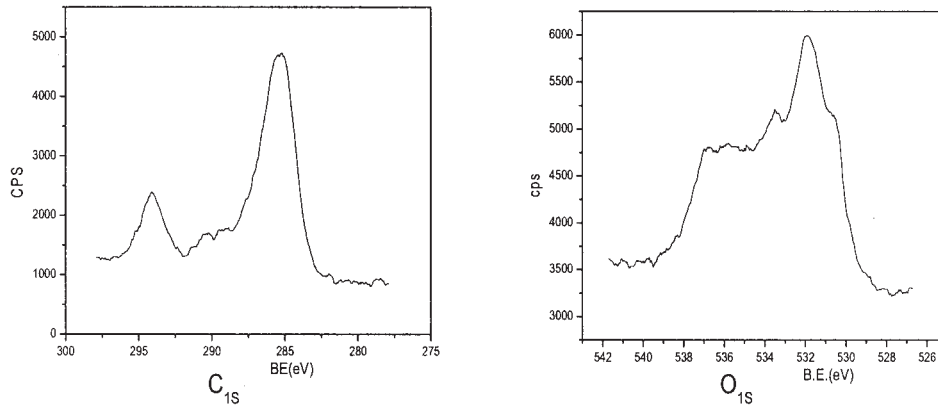


Figure 4 C_{1s} and O_{1s} XPS spectrum charts of the pure polyacrylate latex membrane prepared by emulsion polymerization.

Malvern Zetasizer 3000HSA. The results can be seen in Figure 2. Mean diameter of the latex particles without PTFE is 50nm, in which 70% distributed between 10nm and 100nm. Mean diameter of 3% PTFE modified latex particles is 300nm, in which 80% distributed between 200nm and 400nm. A SEM micrograph of the surface of 3% PTFE modified polyacrylate is shown in Figure 3. From Figure 3, we can also observe that the

surface of the 3% PTFE modified latex membrane is very smooth, and the size of latex particles is nanometer because PTFE powder has been swollen and broken into pieces by pre-emulsified technology. Some of the comonomers diffuse and polymerize in the particles of PTFE. Thus, polyacrylate and PTFE can entangle with each other, which could reduce phase separation between polyacrylate and PTFE.

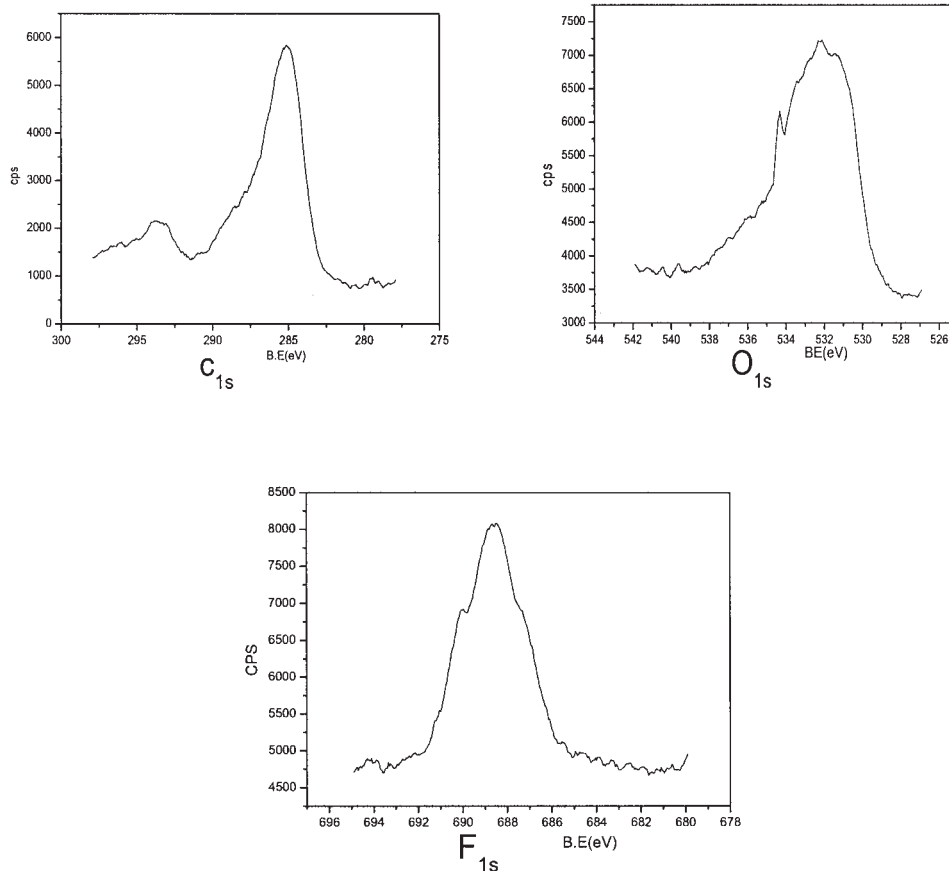


Figure 5 C_{1s} , O_{1s} , and F_{1s} XPS spectrum charts of the latex membrane modified by PTFE prepared by emulsion polymerization.

TABLE II
Element Content of Surface on the Polyacrylate and PTFE Modified Polyacrylate

Item	Element	Peak area	Sensitivity factor	Determined (%)	Theoretical (%)
Polyacrylate	C _{1S}	15430	0.25	75.08	73.82
	O _{1S}	13516	0.66	24.92	26.18
Polyacrylate modified by fluoropolymer	C _{1S}	20605	0.25	69.28	69.09
	O _{1S}	17066	0.66	21.73	23.69
	F _{1S}	10697	1.0	8.99	7.22

Surface chemistry composition of the PTFE modified polyacrylate

Figures 4 and 5 show the XPS survey spectra of pure polyacrylate latex membrane and 3% PTFE modified, respectively. For pure polyacrylate, the characteristic signals for carbon (C_{1S} at 285eV) and oxygen (O_{1S} at 532eV, 533eV, and 536eV) are detected. For PTFE modified polyacrylate, the characteristic signal for fluorine (F_{1S} at 688eV) is detected, besides carbon and oxygen. However, the carbon signal at 285eV is noticeably stronger than pure polyacrylate for the additional carbon atoms in PTFE. Oxygen signal at 536eV almost disappears because of the weak interaction between the oxygen atom of polyacrylate and the fluorine atom of PTFE.

By analysis of the XPS spectrum, we have obtained the element content of the surface on the latex membrane (Table II). From the Table, the values of the C_{1S} and O_{1S} content on the surface of pure polyacrylate are higher than those of PTFE modified polyacrylate. In addition, the value of O_{1S} content on the surface of the PTFE modified polymer is less than the theoretical one, whereas the value of F_{1S} content on the surface is obviously more than the theoretical one. It can be concluded that PTFE moves outside of the membrane layer for its low surface energy when the emulsion forms membrane. Thus, PTFE modified polyacrylate membrane has attractive properties of hot-stability and chemical stability. Properties of the fluoropolymer modified polyacrylate will be discussed in another article.

CONCLUSIONS

PTFE modified polyacrylate is prepared by copolymerization of acrylate monomers in aqueous medium composed of ionic, nonionic, fluorine-carbon surfactant, and the swollen particles of PTFE. The molecular weight distribution becomes narrower and narrower with the increasing quantity of PTFE. Furthermore, SEM and the particle distribution show that average sizes of the latex particles are in the level of nanometers and the surface of the modified PTFE latex membrane is very smooth. Thus, polyacrylate is miscible

with PTFE at the molecular level. Through analysis of the surface chemistry constitution by XPS, it can be concluded that PTFE has a trend of moving outside of the membrane layer for its low surface energy when the emulsion forms membrane, and we can find that interaction exists between PTFE chains and polyacrylate chains. It is also shown that the method of mixing micron and nanometer sized particles can be made the next step of research. Therefore, it is proved that inertia polymers can be used in emulsion property modification.

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