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ORIGINAL PAPER

Synthesis and properties of cationic polyurethane-fluorinated acrylic hybrid latexes by emulsifier-free emulsion polymerization and the solvent-free method

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Abstract A series of cationic polyurethane-fluorinated acrylic hybrid latex (PUFA) have been synthesized by solvent-free method. In the method, vinyl monomers acted as dilution agent and the polyurethane (PU) having quaternary ammonium groups acted as macromolecular emulsifier without using any other solvent and surfactant. The structure and properties of PUFA were characterized by Fourier transform infrared spectroscopy (FT-IR), F^{19} nuclear magnetic resonance (F^{19} NMR), particle size distribution (PSD) analysis, transmission electron microscopy (TEM), contact angle (CA), surface free energy analysis, scanning electron microscope (SEM) equipped with energy dispersive X-ray spectrometry (EDS), and thermogravimetric (TG) analysis. The FT-IR, F^{19} NMR, and EDS confirmed that the FA monomer had been introduced into the chain of the PUFA hybrid polymer. The PSD analysis indicated the particles of PUFA were smaller than corresponding pure PU dispersion and narrower in particle size distribution. The CA and surface free energy analysis proved the PUFA hybrid latex film with fluorine possessed higher contact angle and lower surface free energy in contrast with the film without fluorine. The FPUA films exhibited good surface property which could be enhanced at higher annealing temperature. The EDS of PUFA confirmed the fluorine enrichment on the surface of PUFA. TG analysis suggested the PUFA hybrid latex film had a better thermal stability than pure PU.

Keywords Polyurethane · Fluorinated acrylate · Emulsifier-free emulsion polymerization · Surface property · Thermal stability

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Introduction

Waterborne polyurethanes (PU) are known to be environment-friendly materials with good adhesion, elasticity, and chemical resistance [1–8]. However, some properties of waterborne polyurethane such as water resistance and weather resistance need to be improved further. Anionic PU dispersions are often encountered in the literature and there are only few reports on cationic PU dispersions [9, 10]. Cationic PU dispersions show very high adhesion to various ionic substrates, especially anionic substrates such as leather and glass.

Fluorinated polymers are known to have many useful and desirable features such as unique surface/optical properties and high resistances to thermal, chemical, and weather attack owing to the low polarizability and the strong electronegativity of fluorine atom [11–13]. Acrylic polymers with fluorine-containing groups or perfluoroalkyl groups, in particular, can provide the material with low surface energies and the acrylic groups ensure that the polymers can adhere well to various substrates [14–16]. Therefore, they have been used progressively in a wide range of applications [17–19], e.g. surface coatings for textile, paper, leather, and walls of buildings.

Combination of PU with fluorinated acrylate polymer is expected to be effective to increase the performances of the resulting materials. It combines some virtues of polyurethane and fluorinated acrylate polymer, such as high thermal stability, good chemical resistance (to acids, bases, and solvents), low water absorptivity and attractive surface properties, excellent resistance to ultraviolet radiation and nuclear radiation, excellent flexibility, good wearability, and high weatherability [20–22]. However, there have been not many reports in the open literature about the preparation and the properties of these hybrid materials, especially for cationic polyurethane-fluorinated acrylate hybrid latex.

In this article, we prepared the cationic PUFA hybrid emulsion by emulsifier-free emulsion polymerization and the solvent-free method in a three step process. The first step was the preparation of the polyurethanes prepolymer, in this step the vinyl monomer mixture was added in order to reduce the high viscosity of reactive system instead of organic solvent. The second step involved neutralization of the PU prepolymer and dispersion in water. The last step was the emulsion polymerization of the vinyl monomers added in the first step under emulsifier-free conditions. In the present study, the resulting emulsifier-free PUFA hybrid latex particles were characterized by Fourier transform infrared (FT-IR) spectrometry, F^{19} nuclear magnetic resonance (F^{19} NMR), particle size distribution (PSD) analysis, contact angle (CA), surface free energy analysis, scanning electron microscope (SEM) equipped with energy dispersive X-ray spectrometry (EDS), and thermogravimetry (TG) analysis. The emphasis was put on the structure and property contrast of PU and PUFA as well as the effect of FA content on PUFA hybrid polymers.

Experimental part

Materials

Polytetramethylene ether glycol (PTMG, $M_n = 1{,}000$ g/mol) was dried at 60 °C under vacuum before use, isophorone diisocyanate (IPDI), *N*-methyldiethanolamine (MDEA), trimethylolpropane (TMP), acetic acid (HAc), dibutyltin dilaurate (DBTDL), and the water soluble initiator 2,2′-azobis[2-methylpropionamidine] dihydrochloride (AIBA), are of analytical grade and used without further purification. Styrene (St) and n-butyl acrylate (n-BA) are analytical grade and cleaned before use. The perfluoroalkyl acrylate (FA) used in current study is a mixture of $CH_2{=}CHCOOCH_2CH_2(CF_2)_nCF_3$ with different n ($n = 6$–8) which was kindly supplied from CHINA Fluoro Technology CO., LTD. FA was stirred over CaH_2 overnight at 40 °C, then distilled under reduced pressure.

Preparation of cationic polyurethane-fluorinated acrylate hybrid latexes

Polyurethane prepolymer synthesis

Polyurethane prepolymers (shown by Fig. 1a) based on IPDI, PTMG1000, MDEA, and TMP were prepared with MDEA as cationic chain extender, TMP as crosslinker, the mixture vinyl monomers of St, BA, and FA as diluting agent instead of solvent, and DBTDL as catalyst, where the mole ratio of –NCO in IPDI to –OH in PTMG, MDEA, and TMP is 1.16, the catalyst content is 0.4 wt%. Briefly, a 500 ml round-bottomed, four-necked flask was fitted with a mechanical stirrer, thermometer, condenser, and a dropping funnel. IPDI, PTMG1000, MDEA, and TMP as a solution in mixture monomers of St, BA, and FA were put into a reactor with DBTDL as catalyst. Condensation reaction was carried out at 80 °C in a water bath under a nitrogen atmosphere for 2 h. Here, St, BA, and FA were used as a

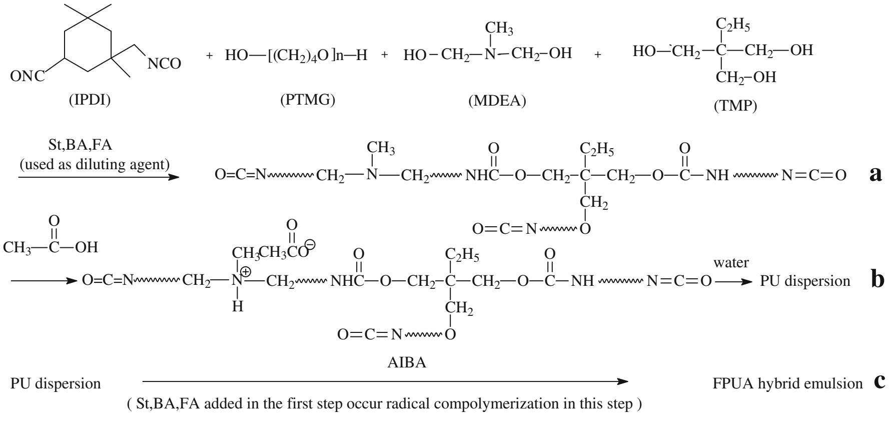

Fig. 1 **a** Preparation of PU prepolymer, **b** neutralization and dispersion of the prepolymer, and **c** radical emulsion polymerization

solvent and served to lower the viscosity of the reaction medium but would later be used as monomers in subsequent emulsion polymerizations.

Neutralization and dispersion of the prepolymer

After the polyurethane prepolymer temperature dropped to 40 °C, the tertiary amine groups were neutralized by the addition of acetic acid (shown by Fig. 1b), and the degree of neutralization was 100%. The mixture was stirred for further 30 min to ensure the reaction was completed. Then, the prepolymer was dispersed by adding distilled water (DI water) to the prepolymer solution which was stirred vigorously. The addition rate was controlled carefully using a tubing pump with a calibrated flow rate.

Radical emulsion polymerization

When AIBA was added into the dispersion, the vinyl monomers swollen in PU dispersion were initiated (shown by Fig. 1c). Waterborne PU acted as macromolecular emulsifier without using any other surfactant. The aqueous solution of AIBA was dropped into the vessel at 80 °C within 2 h. After the addition, the polymerization was kept at 80 °C for 4 h. After completing copolymerization, hybrid latex of PUFA was obtained. Table 1 presents the recipes of the PU, PUA (w (FA) = 0%) and PUFA latexes.

Characterization of latex particles and films

Fourier transform infrared (FT-IR) spectra were recorded on a VETOR-2 Fourier Transform Infrared Spectrometer (Bruker Company, Germany) in the range from 4,000 to 400 cm^{-1} in transmission. The PU and PUFA polymer dissolved in tetrahydrofuran. Samples were prepared by coating the solution onto KBr pellet. F^{19}NMR data were obtained with Nuclear Magnetic Resonance Spectrometer-Bruker 400MHZ AdvanceIII (Bruker Company, Germany).

The particle size and its distribution of the synthesized latex were measured by Nano-ZS particle sizer (Malvern Instruments Company, UK). Samples were diluted with distilled water into an appropriate concentration as indicated by the instrument.

Transmission electron microscopy (TEM) micrographs of the PUFA particles were taken with H-600 transmission electron microscope (Hitachi Company, Japan) with an acceleration voltage of 200 kV. The sample was stained with 2% phosphotungstic acid (PTA) solution.

Contact angles (CA) were measured by the sessile drop method at room temperature, using a JC2000A contact angle goniometer (Shanghai Zhong Chen Powereach Co., China). Static contact angles were obtained from liquid droplets on the surface of latex films. Typically, three drops of the liquid were placed on the surface of the latex films and three readings of contact angles were taken for each drop. The average of nine readings was used as the final contact angle of each sample. Wetting liquids used for contact measurements were water and diiodomethane, as suggested by Owens and Wendt [23]. Total surface free energies (γ) and

Table 1 Recipes of the PU, PUA, and PUFA latexes

	PU	PUA w(FA) = 0%	PUFA5 w(FA) = 5%	PUFA10 w(FA) = 10%	PUFA15 w(FA) = 15%	PUFA20 w(FA) = 20%	PUFA25 w(FA) = 25%	PUFA30 w(FA) = 30%
St/g	7.50	7.50	6.75	6.00	5.25	4.50	3.75	2.50
BA/g	7.50	7.50	6.75	6.00	5.25	4.50	3.75	2.50
FA/g	0.00	0.00	1.50	3.00	4.50	6.00	7.50	10.00
IPDI/g	7.60	7.60	7.60	7.60	7.60	7.60	7.60	7.60
PTMG/g	4.60	4.60	4.60	4.60	4.60	4.60	4.60	4.60
MDEA/g	2.78	2.78	2.78	2.78	2.78	2.78	2.78	2.78
TMP/g	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12
HAc/g	1.83	1.83	1.83	1.83	1.83	1.83	1.83	1.83
AIBA/g	0.00	0.15	0.15	0.15	0.15	0.15	0.15	0.15
DI water/g	60.50	116.00	116.00	116.00	116.00	116.00	116.00	116.00

Note: keeping $R = 1.16$, 18.52 wt% of MDEA on PU monomers, 0.8 wt% of TMP on PU monomers, 1.5 wt% AIBA on total vinyl monomers. The total amount of vinyl monomers to PU monomers ratio was kept at 50:50 by weight throughout. The total solid content of PU, PUA, and FPUA latex were all kept at 20% by weight their polar (γ_p) and dispersion (γ_d) components were calculated by extended Fowkes' equation [24].

$$\gamma_L(1 + \cos\theta) = 2(\gamma_{Ld}\gamma_{Sd})^{1/2} + 2(\gamma_{Sp}\gamma_{Lp})^{1/2} \qquad (1)$$

where γ_L is the surface tension of wetting liquid and γ_{Ld} and γ_{Lp} are the dispersive and polar components, respectively. γ_{Sd} and γ_{Sp} for the latex films could be calculated by substituting values for water and diiodomethane into Eq. 1 and solving the corresponding set of simultaneous equations. The total surface energy γ_S is the summation of γ_{Sd} and γ_{Sp}. The γ_L, γ_{Ld}, and γ_{Lp} for water are 72.8, 21.8, and 51.0 mJ/m^2 and for diiodomethane are 50.8, 49.5, and 1.3 mJ/m^2, respectively. Samples were prepared by coating from a total solid content of 5 wt% hybrid latexes onto cleaned glass substrates. The films were dried at room temperature and then annealed at 30 °C for 24 h, or 120 °C for 4 h, respectively.

Morphology and composition of the hybrid latex film were characterized by using JSM-6460 scanning electron microscope (Jeol, Japan) equipped with energy dispersive spectrometry (EDS) (Oxford Instruments, UK). Samples were gold coated and observed using an accelerating voltage of 20 kV.

Thermogravimetry (TG) analysis was performed on a Q500 thermogravimeter (TA Instruments Company, USA) under the nitrogen atmosphere at a heating rate of 10 °C min^{-1} from 30 to 550 °C.

Results and discussion

Fourier transform infrared spectroscopy and F^{19} nuclear magnetic resonance

Figure 2a shows the FT-IR spectrum of polyurethane (PU) and polyurethane-fluorinated acrylate hybrid (PUFA) polymer. In these two spectra, the characteristic absorption bands at 3,320 and 2,946 cm^{-1} indicate the stretching of hydrogen bonding of N–H band and –CH$_2$ asymmetric stretching, respectively. The bands at

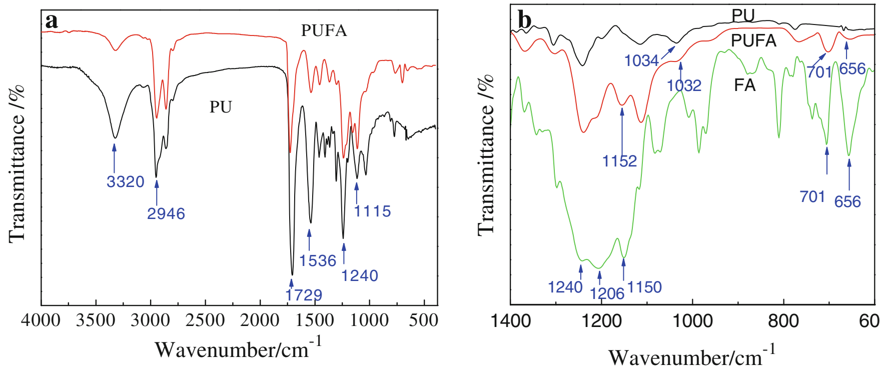

Fig. 2 FT-IR spectrum of PU and PUFA: **a** the whole spectrum of PU and PUFA; **b** the partial spectrum of PU, PUFA and FA

1,729 cm^{-1} (amide I, νC=O), 1,536 cm^{-1} (amide II, δN–H and νC–N), 1,240 cm^{-1} (amide III, νC–N and δN–H), and 1,115 cm^{-1} (antisymmetric νC–O–C) confirm the formation of urethane group. Figure 2b shows the partial spectrum of PU, PUFA, and FA. The stretching vibrations of $–CF_2$ groups at 1,150 cm^{-1}, $–CF_3$ groups at 1240, 1206 cm^{-1}, and a combination of rocking and wagging vibration of $–CF_3$ groups at 656 and 701 cm^{-1} in the fingerprint region, are all detected in the FA and PUFA spectrum in Fig. 2b. But for PU spectra, the stretching vibrations of $–CF_2$ groups at 1,152 cm^{-1} and the wagging vibration of $–CF_3$ groups at 701 cm^{-1} in PUFA disappear obviously. At the same time compared with PU in Fig. 2b, the flexing vibration peaks of O=C–O–C at 1,034 cm^{-1} are much weaker in PUFA, and shift to low wave number by 2 cm^{-1}. This can be explained as follows. Electron cloud of ester group could be attracted by fluorine atom of fluorine carbon chains, which results in the weak interaction between them [25]. Thus, FT-IR spectrum reveal that FA monomer can be introduced into the latex as desired.

F^{19}NMR (Fig. 3) for the PUFA shows four different peaks remarkably [a: −80.7 ppm ($–CF_3$); b: −113.63 ppm ($–CF_2–CF_3$); d: −126.21 ppm ($–CH_2CF_2–$); c: −121.5 to −123.6 ppm (others $–CF_2–$)]. F^{19}NMR also confirms that FA monomer has been introduced into the hybrid polymer.

Latex particle size and morphology

Figure 4 shows the particle size distributions of PU, PUA, and PUFA25 latexes. As seen from Fig. 4, the average particle size of PU (a) and PUA (b) is 72.78 and 64.70 nm, respectively. The hybrid latex particle size decreases in comparison with the corresponding PU dispersion. This can be explained as followed. When PU propolymer was dispersed in water, the hydrophobic acrylic monomer used as diluting agent assembled in the inner of PU particles. When the radical initiator was added into the dispersion, the acrylic monomers swollen in PU dispersion were initiated. As the density of acrylic polymer is bigger than the corresponding acrylic monomers, the volume of the acrylic polymer would shrink, so the hybrid latex

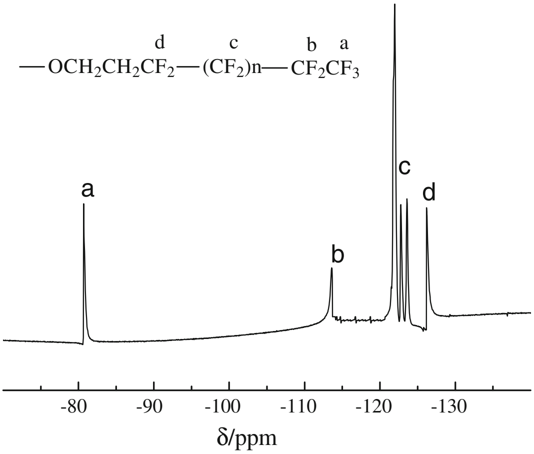

Fig. 3 F^{19}NMR spectra of PUFA

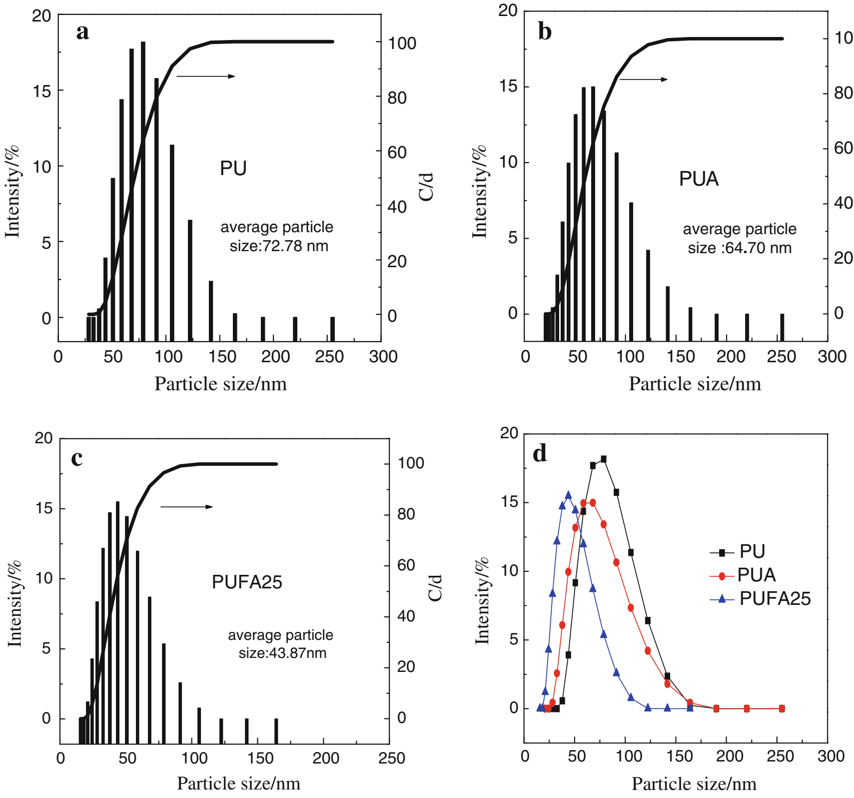

Fig. 4 Particle distribution of polymer emulsions. **a** PU; **b** PUA; **c** PUFA25; **d** the comparison of PU, PUA, and PUFA25

particle size decreases. A second reason maybe is that the newly grown hybrid particles are more hydrophobic than the swollen particles before polymerization of the acrylic monomers and expel water from the particles.

Compared with PUA (b) (0 wt% content of FA), the particle size of PUFA25 (c) (25 wt% content of FA) decreases. This result maybe attributed to the density of FA monomer is bigger than the other vinyl monomers. The more FA content, the smaller the swollen PU particles size. But, the study finds when the FA content increases to 30 wt%, the particle size of PUFA increases. As FA is hydrophobic monomer, overmany monomer could destroy the stability of hybrid dispersion. It clearly indicates in Fig. 4d that the PUA and PUFA hybrid latexes particle size is smaller than PU and narrower in particle size distribution.

The morphology of PUFA25 emulsion particles enlarged 50,000 and 100,000 times, respectively, was observed by TEM in Fig. 5. The particle is spherical and the average particle size is mainly about 20–50 nm, a few of PUFA25 particle size can reach 70–80 nm. The observed emulsion size is consistent with the results measured by particle size distribution analysis (shown in Fig. 4c). As the polyurethane prepolymer could act as macromolecular emulsifier for its hydrophilic

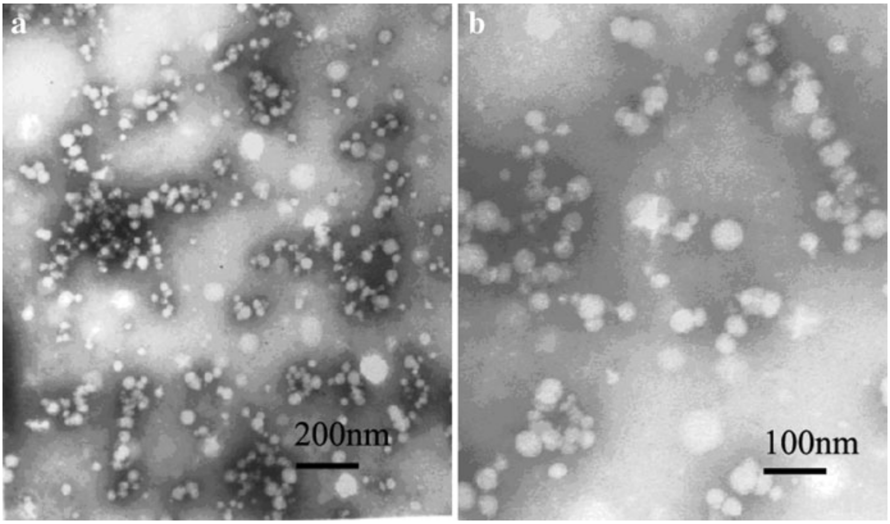

Fig. 5 TEM photograph of PUFA25 **a** 50,000×; **b** 100,000×

quaternary ammonium groups, the hydrophobic acrylic monomer could migrate into the polyurethane particle adequately before the radical polymerization to achieve the homogeneous particle size. It may be concluded that the outer component is more polyurethane while the inner component is more hydrophobic fluorinated polyacrylate. From Fig. 5b, we can see that the smaller particles have a tendency to aggregate.

According to the results of PSD analysis and TEM mentioned above, it could be concluded that the hybrid particles have been successfully obtained by emulsifier-free emulsion polymerization.

Surface properties

The contact angle

Surface properties of polymers are usually governed by the structure and chemical composition of the outermost surface layer and, thus, are quite different from the bulk properties. Preliminary investigations of the hybrid polymers' surface properties were conducted by determination of the contact angle existing on the surface of the polymers. We chose water and diiodomethane as the wetting liquids. The contact angles of PUA and PUFA5 hybrid film treated at 30 °C are showed in Fig. 6.

The water and diiodomethane contact angle of the air-side surface of the latex film without fluorine namely PUA treated at 30 °C is 83.30° and 34.50°, respectively, while the corresponding contact angle of the PUFA5 latex film with 5 wt% FA is 102.67°and 86.50°, indicating the wetting-resistant property of the film is evidently enhanced even with a very small amount of FA. Since fluorine atom has extremely low surface free energy and self-aggregated property, this property causes

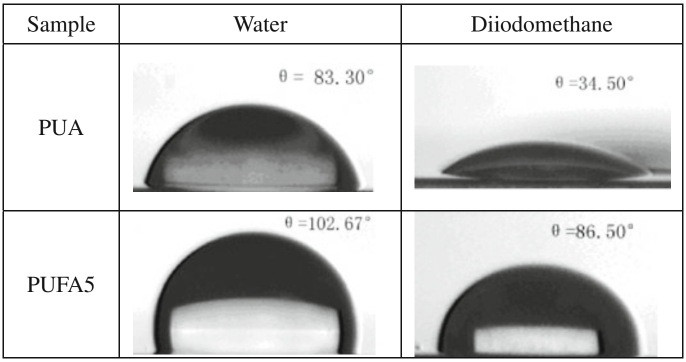

Fig. 6 The contact angles of PUA and FPUA films annealed at 30 °C

Table 2 The contact angles of PUA and PUFA films annealed at 30 and 120 °C

Samples	FA content/%	Water/deg 30 °C	Diiodomethane/deg 30 °C	Water/deg 120 °C	Diiodomethane/deg 120 °C
PUA	0	83.30	34.50	90.67	37.00
PUFA5	5	102.67	86.50	103.75	84.00
PUFA10	10	96.00	83.75	104.00	86.00
PUFA15	15	101.00	83.00	106.00	86.00
PUFA20	20	95.33	82.25	106.00	87.00
PUFA25	25	86.67	81.33	111.00	86.80
PUFA30	30	90.60	80.80	116.00	88.00

the fluorinated segment to be absorbed and oriented to the surface of the systems so as to increase the contact angles.

The contact angles of water and diiodomethane on the latex films annealed at 30 and 120 °C with different amount of FA are listed in Table 2. There is an interesting case in the Table 2 that the contact angles of PUFA treating at 30 °C do not always increase with an increase in FA content of hybrid polymer. This concludes that fluorine content maybe not always the dominating parameter determining the surface property since other physical factors such as the cross-linking density, phase separation phenomena, glass transition temperature, and the degree of fluorine group arrangement order in the surface may play major roles. The heat treatment affects the polymer chains movement remarkably, so the heat treatment will make an impact on the segregation of fluorinate units dramatically. Table 2 shows that the contact angles of water and diiodomethane for hybrid polymer surface increase with increasing annealing temperature.

The surface free energy

From the contact angles of water and diiodomethane, the surface free energies of the films were calculated. Tables 3 and 4 show the surface free energy of the PUFA films annealed at 30 and 120 °C, respectively. The surface free energy of the film with fluorine is much lower than that of the films without fluorine. Since perfluoroalkyl groups with low surface tension are introduced into polymer chains, the surface energy of the latex film is greatly lessened and latex film cannot be wetted easily.

Table 4 also shows that the surface free energy of the latex films containing FA diminishes after annealing at high temperature. The FA content influences the surface free energy of films treating at 30 °C in a irregular way. However, The FA content influences the surface free energy of films treating at 120 °C in a regular way that the higher the FA content, the lower the surface free energy. This behavior maybe attributed to the special properties of the F atoms because the fluoroalkyl groups prefer to migrate to the air/polymer interface and occupy the outermost surface at high annealing temperature. At the same time, the structure of the outermost layer shows a more regular arrangement of perfluoroalkyl groups most of which are perpendicularly oriented to the air side at higher heat treating temperature.

Surface analysis of PUFA hybrid emulsion films

Fluorine element can be observed directly in Fig. 7 which also confirmed FA monomer has been introduced into the hybrid polymer. By analyzing the EDS of the film–air interface of PUFA15 hybrid film, we have obtained the element content of the surface of the latex film (Table 5). Carbon content is a little higher than the

Table 3 The surface free energy of PUA and PUFA films annealed at 30 °C

Temperature	30 °C						
	PUA	PUFA5	PUFA10	PUFA15	PUFA20	PUFA25	PUFA30
θH_2O/deg.	83.30	102.67	96.00	101.00	95.33	86.67	90.60
θCH_2I_2/deg.	34.50	86.50	83.75	83.00	82.25	81.33	80.80
γ_d/mJ/m^2	40.12	12.70	13.32	14.31	14.02	13.46	14.21
γ_p/mJ/m^2	2.40	2.72	4.74	2.72	4.73	8.97	6.65
γ/mJ/m^2	42.52	15.42	18.06	17.03	18.75	22.43	20.86

Table 4 The surface free energy of PUA and PUFA films annealed at 120 °C

Temperature	120 °C						
	PUA	PUFA5	PUFA10	PUFA15	PUFA20	PUFA25	PUFA30
θH_2O/deg	90.67	103.75	104.00	106.00	106.00	111.00	116.00
θCH_2I_2/deg	37.00	84.00	86.00	86.00	87.00	87.00	88.00
γ_d/mJ/m^2	40.32	14.11	13.10	13.33	12.82	13.37	13.40
γ_p/mJ/m^2	0.79	2.04	2.24	1.70	1.82	0.77	0.22
γ/mJ/m^2	41.11	16.15	15.34	15.03	14.64	14.14	13.62

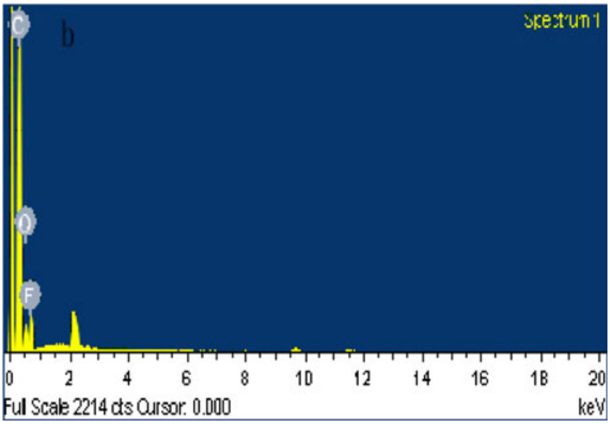

Fig. 7 EDS of the film–air interface of PUFA15 hybrid film

Table 5 Element content of the air–film interface of PUFA15 hybrid film

Element	Determined weight (%)	Theoretical weight (%)
C	68.65	61.29–61.50
O	15.27	16.68–16.88
F	16.08	8.83–9.32
N	0.00	4.10

theoretical weight average in the bulk. Oxygen content is almost the same as the average. The fluorine content in the air–film interface is 16.08%, almost twice higher than the average (8.83–9.32%). The nitrogen element does not exist in the air–film interface of PUFA15 hybrid film. It is concluded that fluorine-containing group of copolymers has the tendency to extend into the air–film interface and occupy the air–film interface during the forming film of latex, and the urethane groups are buried in the inner of the hybrid polymer film, which can effectively decrease the surface free energy of the latex film. This result is consistent with the result suggested by the contact angles and surface free energy analysis.

Thermal stability

The thermogravimetric curves of PU, PUA, and PUFA films are shown in Fig. 8. The thermal decomposition data are given in the form of thermal indexes T_5, T_{30}, and T_{50} (i.e., the temperatures corresponding to 5, 30, and 50%) of weight loss in Table 6. It can be seen from Table 6 that the 5% weight loss of the pure PU and PUA is 195 and 234 °C, respectively. At 50% weight loss, the TGA trace of PUA shows more than 60 °C shift toward higher temperature compared with the pure PU (from 321 to 382 °C). Both Fig. 8 and Table 6 show that hybrid PUA and FPUA are more stable than pure PU, indicating a synergistic effect of PU and acrylate polymer.

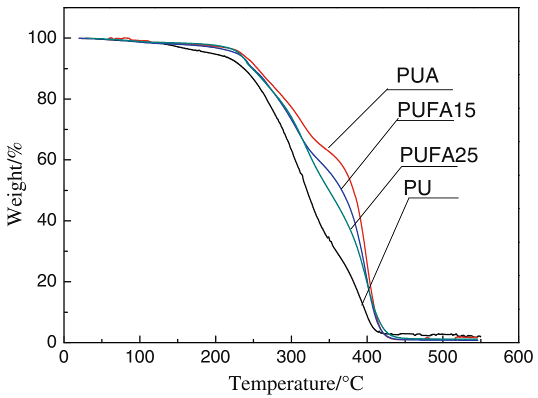

Fig. 8 The TGA curves of the latex films of PU, PUA, and PUFA

Table 6 The temperature of thermal lost weight of the latex film of PU, PUA, and FPUA

Sample	T_5/°C	T_{30}/°C	T_{50}/°C
PU	195	289	321
PUA	234	320	382
PUFA15	228	307	367
PUFA25	231	309	350

However, if we compare the stability of PUA, PUFA15, and PUFA25 from Fig. 8 and Table 6, we note a decrease of the thermo-oxidative stability with the increase of FA content. Namely, hybrid resins show the stability trend as PUA > PUFA15 > PUFA25. The thermal stabilization usually brought by fluorine is not observed here. It maybe can be explained as followed. Since the total amount of vinyl monomers (St, BA, and FA) keeps constant in the hybrid polymer recipe. As the content of FA increases, the content of St which has benzene ring in its structure decreases. The introduction of fluorine acrylate monomer in the polymeric system, which could be considered as a fragile part comparing to benzene ring introduced by St, is probably at the origin of the premature degradation of PUFA with higher FA content [18].

Conclusions

A series of PUFA have been synthesized by emulsifier-free emulsion polymerization and the solvent-free method. FT-IR, F^{19} NMR, and EDS of PUFA confirmed the FA monomer has been introduced into the chain of hybrid polymer. The PU emulsion particle size was around 72.78 nm. The PUA and PUFA hybrid emulsion particle size were smaller than PU and narrower in particle size distribution and there was a trend that the particle size of PUFA decreased with the FA content increase. TEM indicated the PUFA particle was spherical and liable to aggregate. The obtained hybrid latex films with fluorine proved to possess higher contact angle and lower surface free energy than the films without fluorine. The contact angle increased and the surface free energy decreased regularly with the increase of FA content when the films were annealed at higher temperature such as 120 °C. The element content of the surface of the latex film analyzed by EDS indicated that the fluorinated group aggregated in the film surface while the polyurethane was buried in the inner of the film during the forming film of hybrid latex. All of the PUFA with different FA content had more thermal stability than PU. However, the thermal stability of PUFA decreased with the increase of FA content in hybrid polymer because of the decrease of St content in hybrid polymer simultaneously.

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