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Synthesis and characterization of a novel fluorine-containing polymer emulsion with core/shell structure

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Abstract

A novel fluorine-containing polymer emulsion **4** with core/shell structure was synthesized in water phase by a two-stage emulsion polymerization technique using monomer **3** (i.e., 2-methacryloyloxyethyl perfluorooctanoate (MAEF)) reacting with the monomers such as butyl acrylate (BA), acrylic acid (AA) and styrene (ST). The monomer **3** was synthesized from the intermediate **2** (pentadecafluoro-octanoyl chloride) reacting with β-hydroxyethyl methacrylate (HEMA). Polymer film were prepared by coating emulsion **4** directly on a cleaned glass plate and allowed to dry at room temperature. Moreover, the characteristics of polymer film such as hydrophobicity, chemical resistance, surface composition, thermal stability, emulsion particle morphology, as well as the film-forming property were also studied.

Keywords: Fluorine-containing polymer emulsion; Hydrophobicity; Chemical resistance; Surface composition; Thermal stability; Emulsion particle morphology

1. Introduction

It is well known that the fluorine-containing polymers are widely used in material science owing to their extremely low surface energy. There are a number of papers concerning their preparation and properties [1–6], in which the plasma treatment, grafting reaction, sol–gel technique, self-assemble technique, living polymerization, and solution polymerization have been discussed in detail [7].

In the present paper, using the intermediate **2** (pentadecafluoro-octanoyl chloride) [8,9] and β-hydroxyethyl methacrylate (HEMA) as the starting reactants we reported a convenient method to synthesize a new fluorine-containing polymer emulsion with core/shell structure in water phase by a two-stage emulsion polymerization technique (see Scheme 1).

2. Results and discussion

2.1. Measurement of contact angle

Contact angle is a typical property to understand the surface energy of materials. Based on the Fowkers' equation [10], the relationship between the total surface free energies (γ), polar (γ^{p}) and dispersion component (γ^{d}) can be expressed as $\gamma = \gamma^{d} + \gamma^{p}$.

Along with the equation of Owers and Wendt [11], it may be rewritten as follows: $\gamma_{LV}(l + \cos\theta c) = 2(\gamma^{d}_{SV}\gamma^{d}_{LV})^{1/2} + 2(\gamma^{p}_{SV}\gamma^{p}_{LV})^{1/2}$, where p and d stand for the polar and the dispersion component, respectively; θc is a contact angle; γ_{SV} and γ_{LV} are the interfacial tensions at the solid–vapor and liquid–vapor interfaces, respectively. By examining the contact angles on a solid surface with two kinds of liquids whose polar and dispersion components are known, the total surface free energy of a solid and its components can be calculated. According to this calculation we have gotten the value of γ_{SV} to be 15.31 mN/m ($\gamma^{d}_{SV} = 13.44\,\mathrm{mN/m}$ and $\gamma^{p}_{SV} = 1.87\,\mathrm{mN/m}$) for a polymer film containing 12% fluorine, implying that the surface energy of the proposed polymer film is lower than one of polytetrafluoroethylene (PTFE: $\gamma_{SV} = 18.4$ mN/m). That is, a hydrophobic and oleophobic polymer film was obtained.

The lower the surface energy is, the larger the contact angle. Generally, if a surface contact angle of a substance with water was more than 90°, it means hydrophobic. Oil tends to be spread on the surface of substance, due to their contact angle smaller than water [12]. In this study, polymer film were prepared by coating emulsion **4** directly on a cleaned glass plate (7.5 cm × 2.5 cm) and allowed to dry at room temperature. After that, a 0.05 mL of doubly distilled water and *n*-

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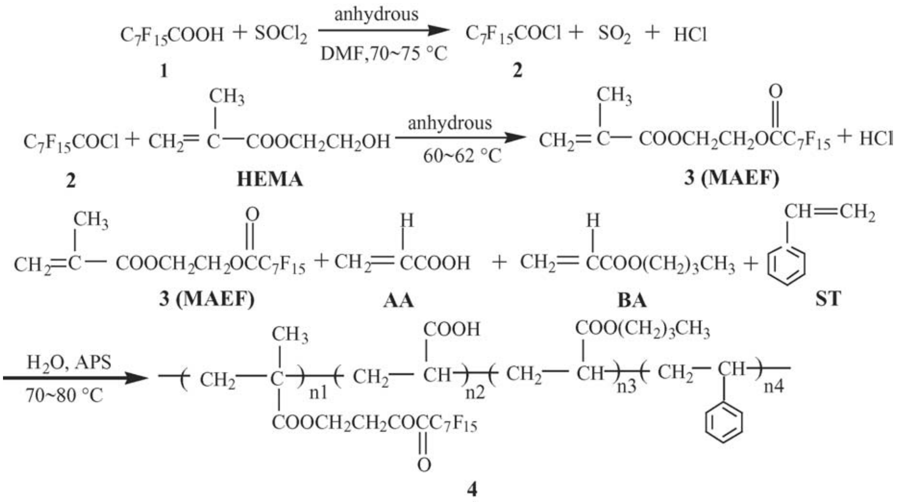

Scheme 1.

hexadecane from a syringe was dropped carefully onto the glass slides coated with the film. The contact angles of water (θ_{water}) and *n*-hexadecane (θ_{oil}) were read out by a contact angle meter at 20 ± 2 °C shown in Table 1.

2.2. Tests of chemical resistance

The glass slides coated with polymer film were immersed into a solution of 10% H_2SO_4 and a solution of 8% NaOH under room temperature for 24 h, respectively. Then, washing the glass slides with distilled water, and drying under atmosphere, the contact angle of polymer film was examined shown in Table 1. The results indicate that the contact angle has not changed obviously, implying the excellent chemical resistance of polymer film.

2.3. Annealing

A physical treatment of annealing at 110 °C for 1 h was accepted to modify the arrangement of perfluoroalkyl groups at the polymer–air interface. A comparison of contact angle of the polymer film before and after annealing was shown in Table 2, there were visible increments of contact angles for all tested films. The results were in accordance with the reported result [13].

2.4. Stability of emulsions

The stability of polymer emulsion was tested under the following conditions: room temperature for 3 months; 80 °C or −10 °C for 1 h; or putting it into a centrifugal separator (1000 rpm) for 5 min. No emulsion breaking could be observed in all of the tests, implying the proposed emulsion has an excellent stability.

Table 1
Contact angle of the proposed polymer film

Polymer film	% Fluorine in polymer	θ_{oil} (°) (*n*-hexadecane)	θ_{water} (°)		
			Before treatment	After 10% H_2SO_4	After 8% NaOH
1	8	58	98	94	91
2	12	64	107	103	98
3	18	69	116	109	99
4	0	37	78	45	40

Table 2
Contact angle of the proposed polymer film before and after annealing

Polymer film	% Fluorine in the polymer	θ_{water} (°)	
		Before annealing	After annealing
1	8	98	102
2	12	107	113
3	18	116	120
4	0	68	69

2.5. X-ray photoelectron spectroscopy (XPS)

Surface composition and concentration of some elements in the outermost layer of sample were examined by XPS, using Cls 285.00 ev as standard and resulting in analysis depth of 5–40 Å. Elemental compositions (atomic percentage) of polymer film (18% fluorine in polymer film as showing in Table 1) were: C1sb 1.405%, Clsa 0.694%, C1s 59.551%, O 20.299%, F 18.05%. C1s and F1s of polymer film XPS spectra were given in

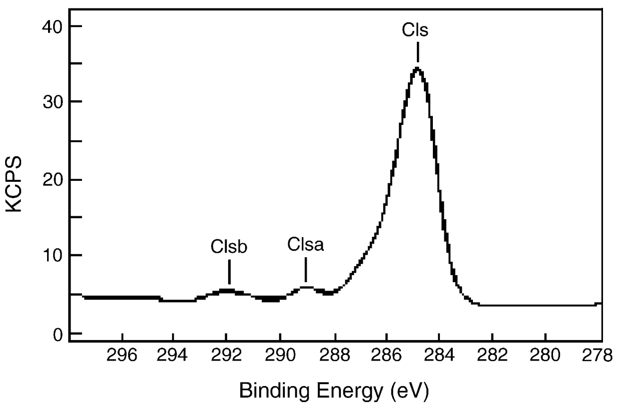

Fig. 1. XPS spectra of C1s of polymer film.

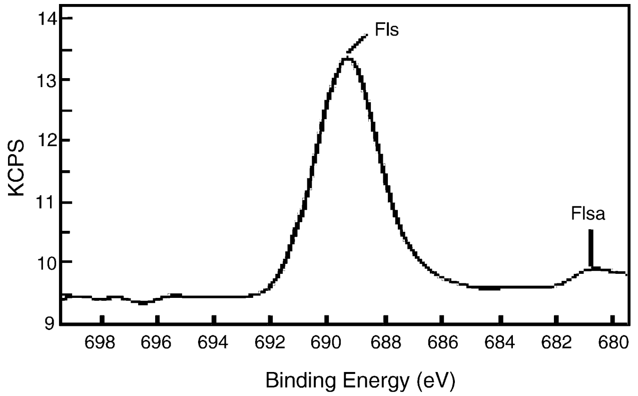

Fig. 2. XPS spectra of F1s of polymer film.

Fig. 1 and Fig. 2, respectively. The C1s peak showed three main components corresponding to aliphatic α-carbon atoms and $-CF_2$ and $-CF_3$ contributions. There were two binding energy at 689.24 and 680.77 eV in Fls XPS spectra, which were attributed to $-CF_2$ and $-CF_3$. These above results have further proved the polymer film with good hydrophobicity, oleophobicity and chemical resistance, which come from the arrangement of perfluoroalkyl groups at the polymer film surface.

2.6. Thermal stability of polymer film

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of polymer film were given in Fig. 3, which were performed under the N_2 atmosphere at a heating rate of 10 °C/min from 25 to 800 °C. The TGA curve in Fig. 3 showed that the lost weight at 259.1 °C corresponding to dehydration of carboxyl on polymer chain; the rapid weight lost occurred at 348 °C; this was attributed to the depolymerization of carbon chain; finally, the complete decomposition was at 602 °C. The DSC curve in Fig. 3 showed a glass transition (Tg) at 237.3 °C. Fig. 4 represented a derivative thermo gravimetric (DTG) trace showing a mild decomposition and a strong decomposition at temperature from 150 to 250 °C and 300 to 420 °C, respectively, which agreed that the polymer film have good thermal stability.

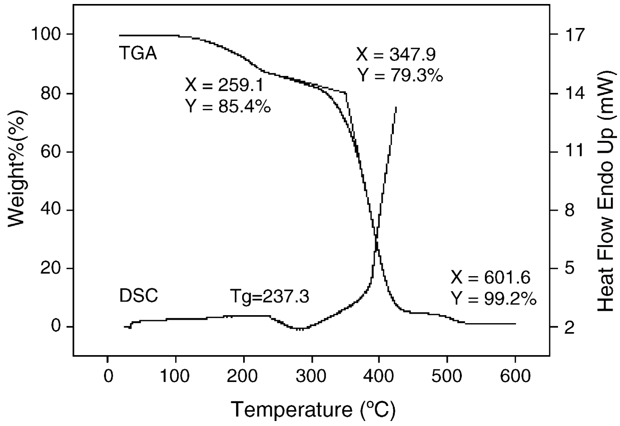

Fig. 3. TGA and DSC of the polymer film.

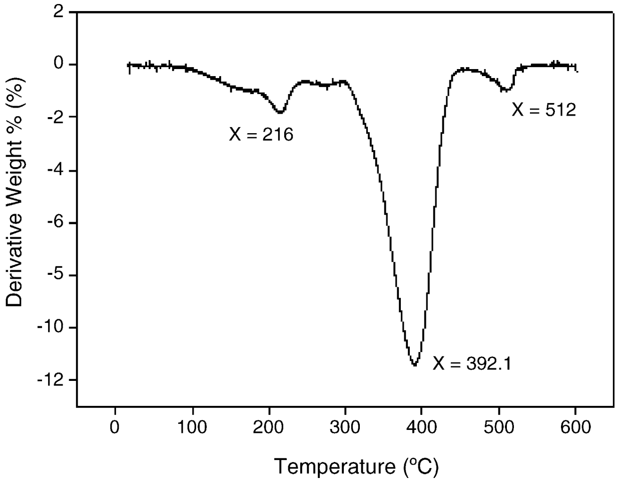

Fig. 4. DTG of the polymer film.

2.7. Particle morphology

The morphology of polymer emulsion containing 18% fluorine was observed by transmission electron microscopy

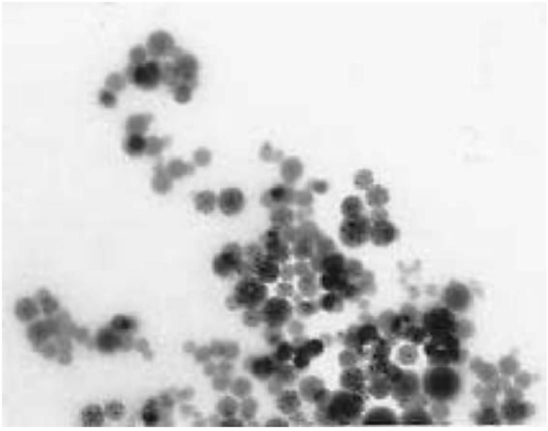

Fig. 5. TEM photograph of polymer emulsion (18% F).

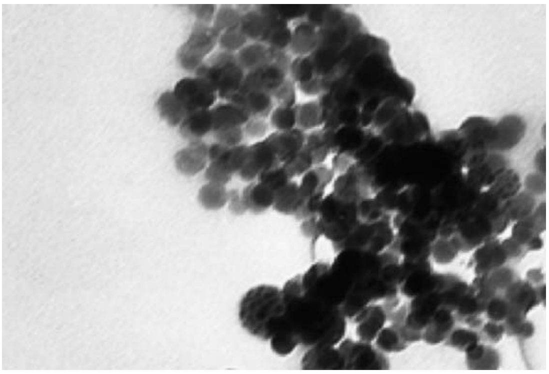

Fig. 6. TEM photograph of polymer emulsion (without fluorine).

(TEM) showing in Fig. 5. It can be seen that the diameter of particle was about onry 45 nm (magnifying power was 48,000), polymer particle had clear core/shell structure and polymer micro spheres were spherical, stable and uniform, so the polymer film was completely smooth and transparent. TEM photographs of another kind of polymer emulsion (containing 8 and 12% of fluorine) were similar to Fig. 5. The morphology of non-fluorine polymer emulsion (i.e., no fluorine in polymer emulsion) was observed by TEM showing in Fig. 6. As can be seen, the polymer particles were not stable and uniform, appearing the conglutination. Thus, the polymer film was not completely clear and smooth.

3. Conclusions

In conclusion, a novel fluorine-containing polymer emulsion with core/shell structure was prepared in water phase through a two-stage emulsion polymerization method. That is, using a nonfluorine monomer as core, and the fluorine-containing monomer as shell, to create a hydrophobic and oleophobic surface and raise the efficiency of fluorine compared with other particle structures such as random copolymer or latex blending [14]. The final product is a clear, cobrless polymer film coating, indicating the presence of nanophases as shown by TEM. The fluoropolymer latex has not pollution in surrounding. The surface of polymer film was found to have an excellent hydrophobicity and oleophobicity. At the same time, the outstanding thermal stability, chemical resistance and good film-forming properties were also tested.

4. Experimental details

4.1. Materials

Pentadecafluoro-octanoic acid (PFOA) was obtained from Chemical Reagent Company, Nanjing, China. Thionyl chloride, dimethyl formamede (DMF), ammonium persulfate ($(NH_4)_2S_2O_8$, APS) and sodium hydrogen carbonate ($NaHCO_3$) were used as initiator and buffering agent, respectively, which were used as received. β-Hydroxyethyl methacrylate, butyl methacrylate, styrene, acrylic acid were purchased from Chemical Reagent Company, Tianjin, China, which were purified further by distilled under reduced pressure prior to use. Sodium dodecylsulfare (SDS) and *p*-octyl polyethylene glycol phenyl ether (OP) were obtained from Chemical Reagent Company, Beijing, China. Distilled water was used in polymerization. However, for the contact angle measurement, the doubly distilled water ($\gamma_{LV} = 72.8$ mNAn at 20°C, $\gamma_{LV}^{d} = 22.1\,\mathrm{mN/n}$, $\gamma_{LV}^{p} = 50.7\,\mathrm{mN/m}$) must be used. The *n*-hexadecane (Germany) has a surface tension of 26.0 mN/m at 20°C. ($\gamma_{LV}^{d} = 26.0\,\mathrm{mN/m}$, $\gamma_{LV}^{p} = 0\,\mathrm{mN/m}$).

4.2. Instruments

The IR spectra of products were measured on a Digilab FTS3000 FTrR spectrometer. Elemental analysis was tested on a PE2400CHN. Contact angle measurements were performed with Japan CA-A instrument. XPS spectra were recorded using a VG SCIENTIAESCA210 spectrometer, equipped with double Mg anode X-ray source ($h\nu = 1253.6$ ev). TG/DTG and DSC were recorded by means of a Perkin Elmer PE7 series instrument, in the temperature range from 25° to 800°C with a heating rate of 10°C/min.

4.3. Synthesis of **2** (pentadecafluoro-octanoyl chloride)

In this study, a convenient method was described for the preparation of Pentadecafluoro-octanoyl chloride with high yield (97.1%) from pentadecafluoro-octanoic acid and thionyl chloride by using DMF as catafyst. A mixture containing 10 g (0.024 mol) of pentadecafluoro-octanoic acid 1.7 g (0.014 mol) of thionyl chloride and 0.5 mL of DMF were placed into a three-necked flask with a magnetic stirrer, a reflux condenser and a thermometer. The reaction solutbn was kept at 70–75°C for 2 h. The resulting product consisted of a yellow liquid upper layer and a white liquid lower layer. The aqueous phase (i.e., lower layer) was first separated, and then, distilled under reduced pressure to remove the thionyl chbride. Finally, 10.07 g of clear liquid were obtained, that is compound **2**. FTIR spectrum of Compound **2** was shown in Fig. 7 (curve b). The characteristic peak at 1802 cm^{-1} was attributed to caibonyl stretching, the appearances of C–F stretching band of compound **2** at 1250, 1215 and 1149 cm^{-1} were also observed, respectively. These results are in good agreement with the data published [15]. Elemental analysis results are listed below: Calcd for $C_8F_{15}OC1$: C, 19.42. Found: C, 19.38.

4.4. Synthesis of fluorinated monomer **3** (MAEF)

A 5.2 g (0.04 mol) of HEMA was introduced into a three-necked flask with a magnetic stirrer and a reflux condenser, 17.3 g (0.04 mol) of **2** were added drop wise within 2 h at room temperature. The mixture were heated on an oil bath and stirred at 60–62°C for additional 11 h. The resulting mixture was

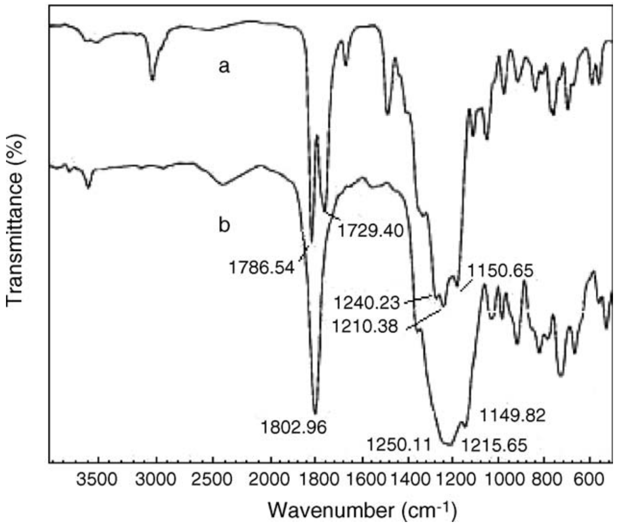

Fig. 7. FTIR spectrum of monomer **3** (a) and compound **2** (b).

dissolved in diethyl ether anhydrous followed by adding 5% NaOH solution. After phase separation of the mixture the intermediate (i.e., monomer **3**) was extracted in the ester layer, and then, washed with distilled water to pH 7–8. After separating, the organic phase was distilled under reduced pressure to remove diethyl ether, getting 15.8 g monomer **3** (yield 75.2%), they need not be dried further for next emulsion polymerization. FTIR spectrum of monomer **3** was shown in Fig. 7 (curve a). The absorption band at 1786 cm^{-1} was attributed to caibonyl stretching in the CF_2–COO–CH group; the absorption band at 1729 cm^{-1} was attributed to carbonyl stretching in the C–COO–CH_2 group; the appearances of C–F stretching band of **2** at 1240, 1210 and 1150 cm^{-1} were observed, respectively. These results are in good consistent with the data reported by Gu et.al. [16]. Efemental analysis results: Calcd for $C_{14}H_9F_{15}O_4$: C, 31.94; H, 1.71. Found: C, 31.88, H, 1.69.

4.5. Preparation of core/shell latex particle *4*

The core/shell particles were prepared by a two-stage emulsion polymerization. That is, the poly (*n*-butyl acrylate-co-styrene) core was polymerized by a conventional batch emulsion polymerization (in first stage), and then, the poly (MAEF-co-BA-co-ST-co-AA) shell was introduced by semi-continuous addition of monomers (in second stage) in the same reactor. The surface free energy of film can be reduced further by this way. Owing to the method simpler, coatings' cost can be decreased, too. A typical procedure was below.

For the synthesis of poly (*n*-butyl acrylate -co-styrene) core, 40 g of water, 0.6 g of surfacatant (SDS/OP) and 0.1 g of $NaHCO_3$ were added to the reactor. After purging nitrogen gas for 20 min, this mixture solution was heated with stirring up to 70 °C, followed by adding dropwise ASP solution (0.15 g of ASP dissolved in 5 g of water) and monomers (1 g of ST and 0.5 g of BA) from each inlet separately within 30 min. At that time, the polymerization temperature will be up to 75 °C. And then, the shell monomer mixture (9.75 g of ST, 12.25 g of BA, 0.5 g of AA and 7.5 g of MAEF) were added dropwise within 2 h and heated at 78 °C for additional 2 h. Cooling down to 50 °C in atmosphere, using ammonia water to adjust the pH 7–8. The target, an emulsion containing high fluorine with core/shell structure was obtained.

A series of polymer emulsions has been synthesized with the same constitution of core, while the fluorine content in polymer emulsbn was different such as 0, 8, 12 and 18% of fluorine. As canbe seen from Tables 1 and 2, the more the fluorine content in polymer emulsion is, the better the chemical resistance, hydrophobicity and oleophobicity for the polymer film.

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