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Preparation and characterization of a novel fluorinated acrylate resin

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ABSTRACT

The novel fluorinated acrylate resin was successfully prepared by solution polymerization of 2-(perfluoro-(1,1-bis-isopropyl)-2-propenyl)oxyethyl methacrylate (POMA) with butyl acrylate (BA), methyl methacrylate (MMA) and methacrylic acid (MAA) initiated by AIBN in the co-solvents of ethyl acetate, butyl alcohol and toluene. POMA was synthesized from the intermediate perfluoro nonene and 2-hydroxyethyl methacrylate as the staring reactants. Films of the novel fluorinated acrylate resin were prepared by coating the resin directly on the clean glass sheet and allowed to dry at room temperature. The characteristics of the film such as hydrophobicity, glass transition temperature and thermal stability were characterized with the contact angle, differential scanning calorimetry and thermo-gravimetric analysis respectively. The structure of the novel fluorinated acrylate resin was investigated by Fourier transform infrared (FTIR) spectrometry. The influences of the fluorine content on the performance of the acrylate resin were studied. Results show that the hydrophobicity, chemical resistance, glass transition temperature and thermal stability of the acrylate resin are improved when the fluorinated monomer is introduced to copolymerize with other monomers. However, the hydrophobicity of the fluorinated acrylate resin is improved slightly via annealing.

1. Introduction

It is well known that the fluorine-containing polymers are widely used in material science owing to their unique properties including high thermal, chemical, aging and weather resistance; low dielectric constants, refractive index, surface energy and flammability; excellent inertness to solvents, hydrocarbons, acids, alkalis and moisture adsorption as well as interesting oil and water repellency due to the low polarizability and the strong electronegativity of the fluorine atom [1–7]. Among the fluoropolymers, the popularity of fluorinated acrylic polymers is increasing as components for high-performance paint and varnish in the textile, paper, leather, construction, automotive and aerospace industries, optics and microelectronics. There are a number of papers concerning their preparation and properties, most of which fluorinated acrylic emulsions have been prepared via different emulsion polymerization technologies [8–18]. However, the constituent of the fluorinated acrylate latex, which is prepared via emulsion polymerization, is complex. It is difficult to remove the residual emulsifiers in the resin, which have a negative effect on the integral properties of the resin. For example, the contact angle of the film is small because of the hydrophilic emulsifiers. The fluorinated acrylate resin, which is prepared via solution polymerization, is seldom reported. In the present paper, using the intermediate perfluoro nonene and 2-hydroxyethyl methacrylate as the staring reactants, we would like to report the convenient method to synthesize a new fluorinated acrylate resin by the solution polymerization technique (see Scheme 1).

2. Results and discussion

2.1. FTIR spectrum and F-NMR

Fig. 1 shows the FTIR spectra of the fluorinated acrylate resin which was synthesized via solution polymerization. 2960 cm^{-1} and 2875 cm^{-1}were the characteristic stretching peaks of C–H (CH_3, CH_2), 1201 cm^{-1} was stretching vibration of C–O–C in MMA, 1727 cm^{-1} was stretching vibration of C=O, 1457 cm^{-1} was distortion vibration of –COO–, 1238 cm^{-1} and 696 cm^{-1} were the stretching vibration and wagging vibrations of C–F bonds respectively. 1638 cm^{-1} was the characteristic absorption peak of C=C which was linked with C–F bond and had relatively high stability and was much weaker in comparison with the strength of absorption peak of conventional double bond. FTIR spectrum of resin shows that four kinds of BA, MMA and MAA and POMA all took part in the copolymerization reaction and fluorinated acrylate resin was prepared. Fig. 2 is the ^{19}F NMR of the fluorinated acrylate resin. It shows the following spectral data.

^{19}F NMR ($CDCl_3$, δ in ppm): −56.2(3F, CF_3), −69.5(6F, $CF(CF_3)_2$), −71.8(6F, $CF(CF_3)_2$), −166.8(F, $CF(CF_3)_2$), −168.8(F, $CF(CF_3)_2$). The above data also confirm that POMA has participated in the copolymerization.

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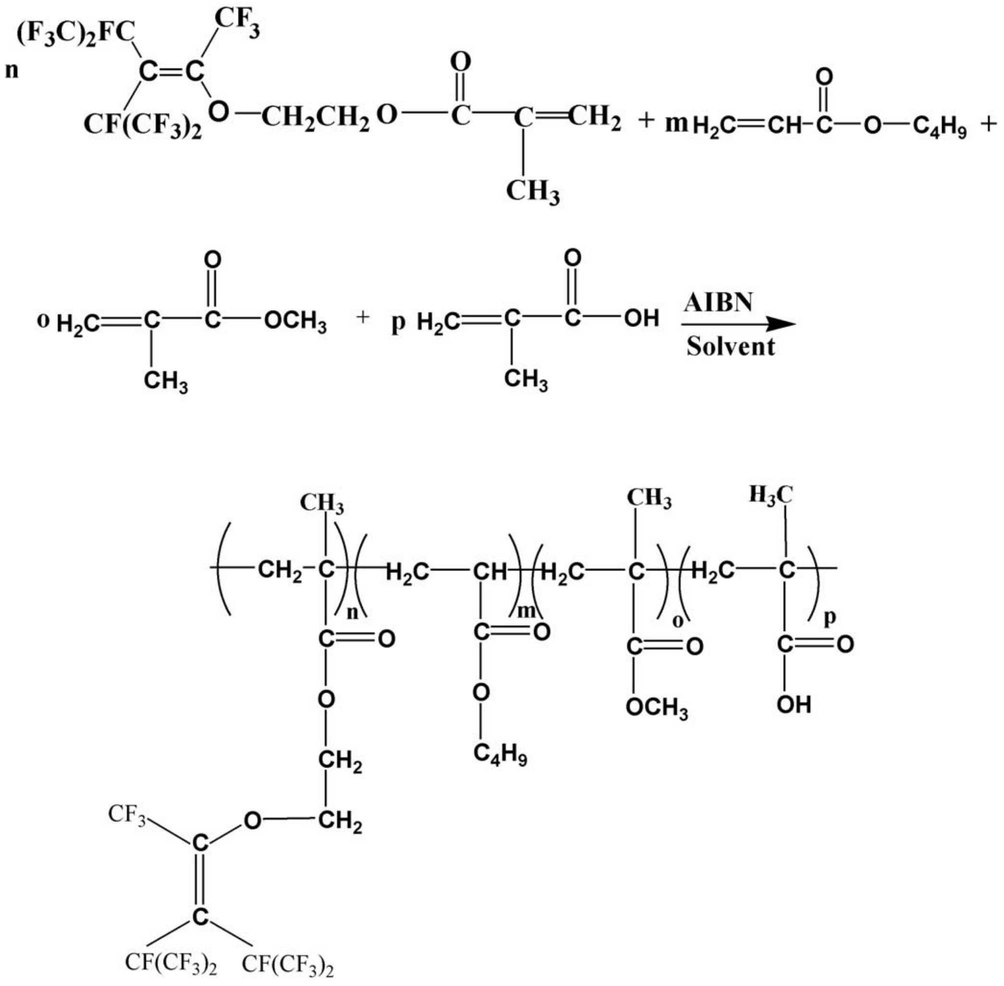


Scheme 1. Synthesis pathway of the fluorinated acrylate resin.

2.2. Measurement of contact angle

Contact angle is a typical property to understand the surface energy of materials. The hydrophobic property of a polymeric material can be estimated in terms of contact angle measurement by depositing a water drop or n-hexadecane drop on the surface of film and the value of contact angle depends on the chemical compositions of film surface [19,20]. The higher the wetting resistance of film surface, the higher contact angle is. Because the fluorinated polymers have good hydrophobic property and fluorine atom tends to locate on the film surface during the film formation. It is expected that introducing more fluorinated monomers into a single polymer can increase the hydrophobic property of polymer. The contact angles of the fluorinated acrylate resin with various fluorine contents are shown in Fig. 3. One can see that when the fluorinated monomers are introduced into the polymer chains, the films of fluorinated acrylate resin show higher contact angle compared with the acrylate resin without fluorine as expected. In addition, in the case of fixing the content of other monomer, the contact angles of the fluorinated acrylate resin films are increased with the increase in hydrophobic fluorine content. The increase of the contact angle is caused by the fact that the fluorinated groups have the tendency to migrate toward interface and preferentially locate at the interface to minimize the interfacial energy. The lower the surface energy is, the larger the contact angle. In this study, the contact angles of the fluorinated acrylate resin with water are more than 90°. Generally, if a surface contact angle of a substance with water is more than 90°, it means hydrophobic. Oil tends to be spread on the surface of substance, due to the fact that the contact angle to oil is smaller than that of water [21]. In addition, the typical pictures are taken and shown in Figs. 4 and 5 during the course of testing the contact angle. The relationship between the water contact angle and time is shown in Fig. 6. It is found that the water contact angle is decreased slightly with the increase of time, which also confirms that the copolymer has good hydrophobicity.

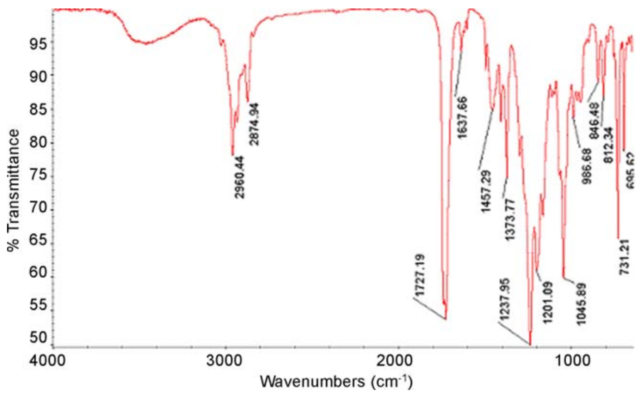


Fig. 1. FTIR spectrum of the fluorinated acrylate resin.

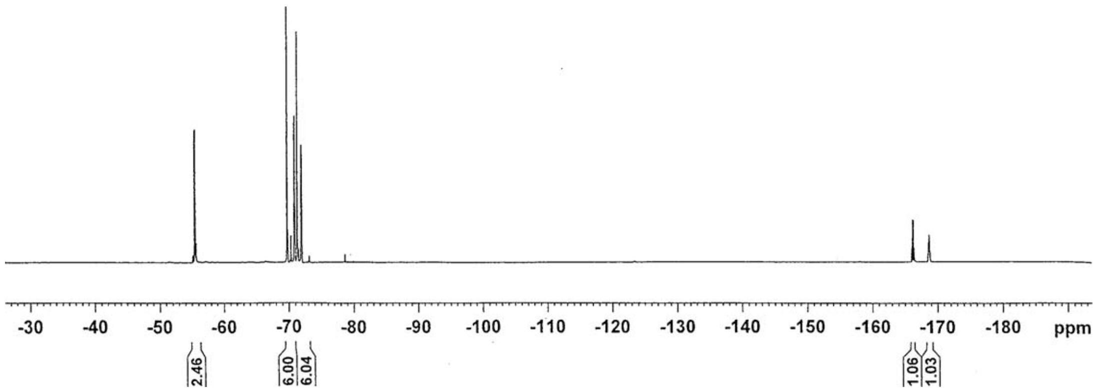


Fig. 2. ^{19}F NMR of the fluorinated acrylate resin.

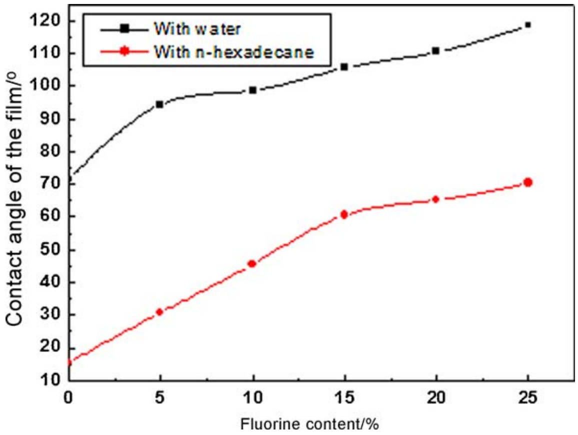


Fig. 3. Influence of the fluorine content on the contact angle of the film.

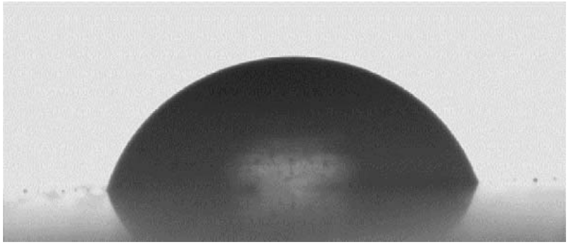


Fig. 4. Contact angle between acrylate film and water (contact angle = 71.5°).

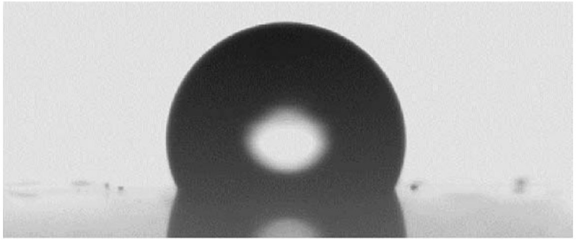


Fig. 5. Contact angle between fluorinated acrylate film and water (contact angle = 118.4°).

2.3. Tests of chemical resistance

The glass slides coated with polymer film were immersed into a solution of 5% H_2SO_4 and a solution of 5% NaOH at room temperature for 24 h, respectively. Then, the glass slides were washed with distilled water, and dried under atmosphere. The contact angle of polymer film was examined and shown in Table 1. The results indicate that the contact angle has not changed obviously, implying the excellent chemical resistance of polymer film. The fluorinated acrylate resin has the excellent chemical resistance, which is attributed to the unique feature of the fluorine atom. The fluorine atom has the highest electronegativity and very small atomic radius. And the bond energy of C–F is biggest among covalent bond in the organic compound. The long side chain of C–F bond makes the fluorinated moieties accede to the outermost layer because of its low surface energy. The fundamental chain of C–C is enclosed with fluorine atom intensively and the spiral structure is formed to protect C–C against impacting when the fluorine atom is combined with the fundamental chain of C–C in the resin molecule. Although the fluorinated acrylate resin possesses hydrophilic segments, such as carboxy groups, they are covered or shielded with C–F bonds, which are oriented to the surface of the film. Furthermore, in Table 3, it can be seen that the added amount of the MAA is fewer than that of other monomers. Thus, the film of the fluorinated acrylate resin is not immersed and damaged by chemical mediator. Furthermore, higher fluorine content in the fluorinated acrylate resin is, and better the chemical resistance of the film is.

2.4. Annealing

A physical treatment of annealing at 80 °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

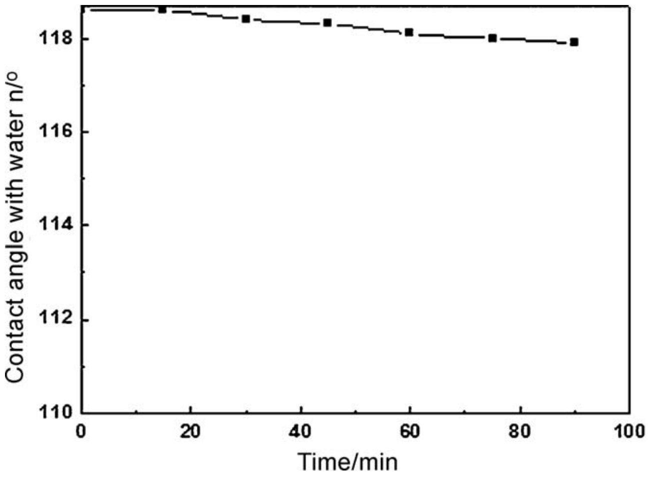


Fig. 6. Relationship between the water contact angle and time.

Table 1
Contact angle of the fluorinated acrylated resin treated with chemical mediator.

Fluorine content/%	Contact angle of the film/°					
	With water			With n-hexadecane		
	1	2	3	1	2	3
0	71.5	58.7	57.6	15.4	13.2	12.8
5	94.3	92.4	91.7	30.8	29.5	29.1
10	98.7	97.5	96.8	45.6	44.8	44.5
15	105.6	105.2	104.1	60.5	59.8	59.6
20	110.4	109.8	108.3	65.2	64.6	64.3
25	118.6	118.2	117.8	70.3	69.8	69.5

1, Before treatment; 2, Treated with 5% H_2SO_4; 3, Treated with 5% NaOH.

Table 2
Contact angle of the fluorinated acrylated resin before and after annealing.

Fluorine content/%	Contact angle of the film/°			
	With water		With n-hexadecane	
	Before annealing	After annealing	Before annealing	After annealing
0	71.5	71.8	15.4	15.6
5	94.3	95.2	30.8	31.2
10	98.7	99.3	45.6	45.7
15	105.6	106.3	60.5	60.8
20	110.4	111.2	65.2	65.6
25	118.6	118.9	70.3	70.5

polymer film before and after annealing is shown in Table 2. From Table 2, it can be seen that there were no visible increments of contact angles for all tested films. This phenomenon can be explained by the following fact. The solvents in the fluorinated acrylated resin volatilized quickly and more perfluoroalkyl groups had been oriented to the polymer–air interface during the course of the film-forming of the fluorinated acrylate resin without annealing. Annealing can arrange perfluoroalkyl groups to be more regularly oriented to the polymer–air interface; this had less effect on the contact angle of the film of the fluorinated, which is different from that of the fluorinated acrylate emulsion. In that case, annealing had a great effect on the contact angle of the film of the fluorinated acrylate emulsion because the water in the fluorinated acrylate emulsion volatilized slowly during the course of during the course of the film-forming of the fluorinated acrylate emulsion without annealing.

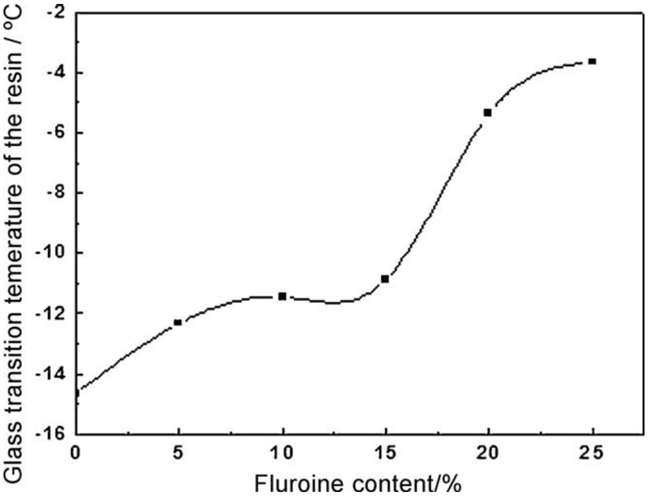


Fig. 7. Influence of the fluorine content on the glass transition temperature of the resin.

2.5. *Glass transition temperature of the fluorinated acrylate resin*

The glass transition temperature of the fluorinated acrylate resin can be preliminarily estimated from FOX equation:

$$\frac{1}{t_g} = \frac{m_1}{t_{g1}} + \frac{m_2}{t_{g2}} + \ldots + \frac{m_i}{t_{gi}} \tag{1}$$

where m_i is the mass fraction of copolymerized monomer; t_{gi} is the value of glass transition temperature of homopolymer. The determination of the glass transition temperature is related to other components of polymer, the tested method and instrument, and the velocity of raised temperature. However, FOX equation neglects the influence of relative molecular mass of polymer on the glass transition temperature. Therefore, there is some difference between the theoretical value and the measured value of the glass transition temperature [22]. Fig. 7 shows that the glass transition temperature of the fluorinated acrylate resin is increased with the increase in fluorine content in the monomers. This phenomenon can be explained by the fact the carbon chains of POMA is the same with the ones of 2-hydroxyethyl methacrylate, whose hydrogen on the double bond is not replaced by other groups although the hydrogen on the hydroxyl group in 2-hydroxyethyl methacrylate is replaced by perfluoro nonene group. The glass transition temperature of the homopolymer of POMA is higher than the one of the homopolymer of BA (soft monomer) because 2-hydroxyethyl methacrylate is the hard monomer. The added amount of MMA is constant. For two kinds of copolymerized monomer, e.g. POMA and BA, FOX equation can be turned into

$$\frac{1}{t_g} = \frac{m_1}{t_{g1}} + \frac{m_2}{t_{g2}} \tag{2}$$

where m_1 is the mass fraction of POMA; m_2 is the mass fraction of BA; t_{g1} is the glass transition temperature POMA homopolymer; t_{g2} is the glass transition temperature of homopolymer BA. The following equation can be obtained via differentiating Eq. (2):

$$\frac{dt_g}{dm_1} = \left(\frac{1}{t_{g2}} - \frac{1}{t_{g1}}\right) \cdot t_g^2 \tag{3}$$

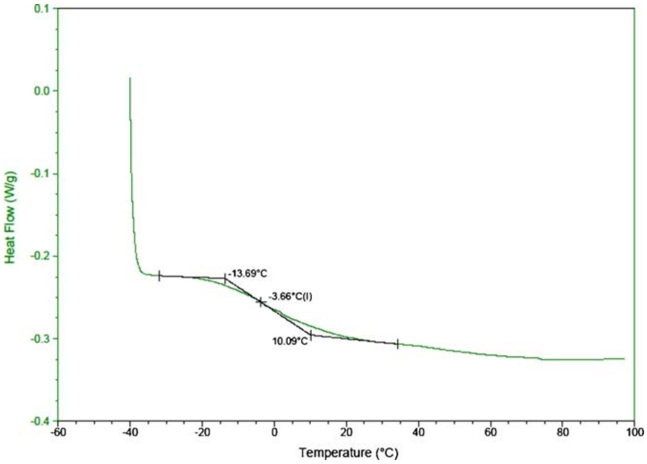


Fig. 8. Glass transition temperature of the resin when fluorine content was 25%.

In Eq. (3), t_{g2} is smaller than t_{g1}, so $1/t_{g2}$ is more than $1/t_{g1}$, and dt_g/dm_1 is positive, i.e. t_g of polymer increases with the increase of the amount of POMA. Besides, in Fig. 8, it can be seen that the fluorinated acrylate resin has only one glass transition temperature, which shows that the resin is a kind of random copolymer and the consistency among the chain segment is fairly good.

2.6. Thermal stability of the film

Thermo-gravimetric analysis (TGA) was used to investigate the thermal stability of the fluorinated acrylate resin was given in Fig. 9, which was performed under the N_2 atmosphere. The TGA curve in Fig. 9 showed that the initial temperature of the lost weight was $T_{ia}(139.6\ ^\circ\mathrm{C}) < T_{ib}(149.3\ ^\circ\mathrm{C}) < T_{ic}(165.9\ ^\circ\mathrm{C})$, which was attributed to the low bond energy of C=C linked with C–F bond (seen in Fig. 1). The temperature of rapid lost weight for all the films was around 360 °C, which was corresponding to the depolymerization of carbon chain. Finally the complete decomposition temperature of the films was $T_{cc}(416.9\ ^\circ\mathrm{C}) < T_{ca}(436.4\ ^\circ\mathrm{C}) < T_{cb}(454.3\ ^\circ\mathrm{C})$. In view of the complete decomposition temperature of the films, it can be seen that the complete decomposition temperature increased clearly with the increase of the fluorine content, which indicated that the thermal stability of resin film was improved with the increment of fluorine content. It is caused by the fact that the fluorine groups were introduced into the molecule of the polymer through solution polymerization, the perfluoroalkyl groups containing C–F bond with high bond energy can shield and protect the non-fluorinated segment beneath them.

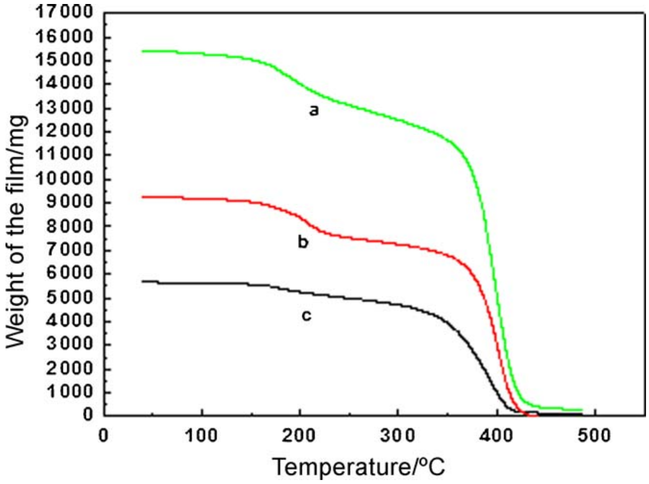


Fig. 9. TGA curves of (fluorinated) acrylate resin (a) fluorinated acrylate resin (fluorine content was 5%); (b) fluorinated acrylate resin (fluorine content was 10%); (c) unmodified acrylate resin.

3. Conclusions

In conclusion, a novel fluorinated acrylate resin was prepared via solution polymerization technology. That is, using BA, MMA, MAA and POMA as the copolymerized monomers, and the mixtures of ethyl acetate, butanol, and toluene as solvent, and AIBN as the initiator to create a hydrophobic surface and raise the performance of the acrylate resin via solution polymerization. The hydrophobicity, chemical resistance, glass transition temperature and thermal stability of the acrylate resin are improved when the fluorine monomer is introduced to copolymerize with other monomers. However, the hydrophobicity of the fluorinated acrylate resin is improved slightly via annealing.

4. Experimental

4.1. Materials

Butyl acrylate (BA), methyl methacrylate (MMA), methacrylic acid (MAA), which were chemically pure grade, were obtained from Wulian Chemical Plant, Shanghai, China. They were purified further by distilled water under reduced pressure prior to use. Ethyl acetate and butanol, which were analytically pure grade, were purchased from Shuanglin Chemical Reagent Company, Hangzhou, China. Toluene, which was analytically pure grade, obtained from Juhua Reagent Co., Ltd., Quzhou, China. 2,2,-Azo-bis-iso-butyronitrile (AIBN), which was chemically pure grade, was purchased from Shanghai No. 4 Reagent & H.v. Chemical Co., Ltd., Shanghai, China. 2-(perfluoro-(1,1-bis-isopropyl)-2-propenyl)oxyethyl methacrylate (POMA)* was prepared in our laboratory. The prepared method was based on our previous research results.

4.2. Synthesis of fluorinated monomer POMA

2-Hydroxyethyl methacrylate and triethylamine were introduced into a three-necked flask with the stirrer. N,N-dimethylformamide (DMF) was then added into the flask and the stirrer was agitated for 5 min. Perfluoro nonene was added dropwise within 3 h at room temperature. The reaction continued for 4 h after perfluoro nonene was dripped completely. The resulting mixture was dissolved in 2.5% HCl solution to separate the mixture. The lower

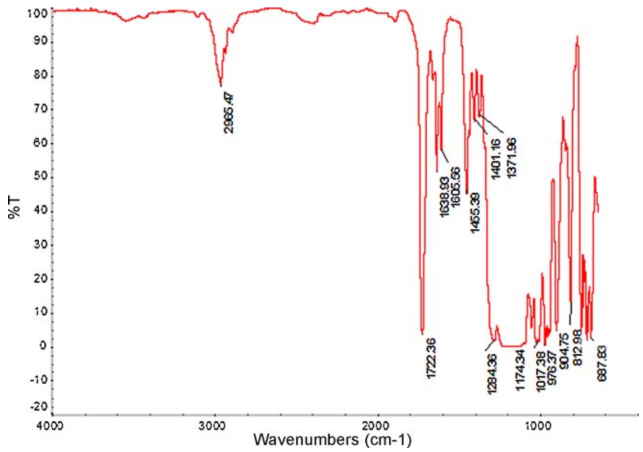


Fig. 10. FTIR spectrum of POMA.

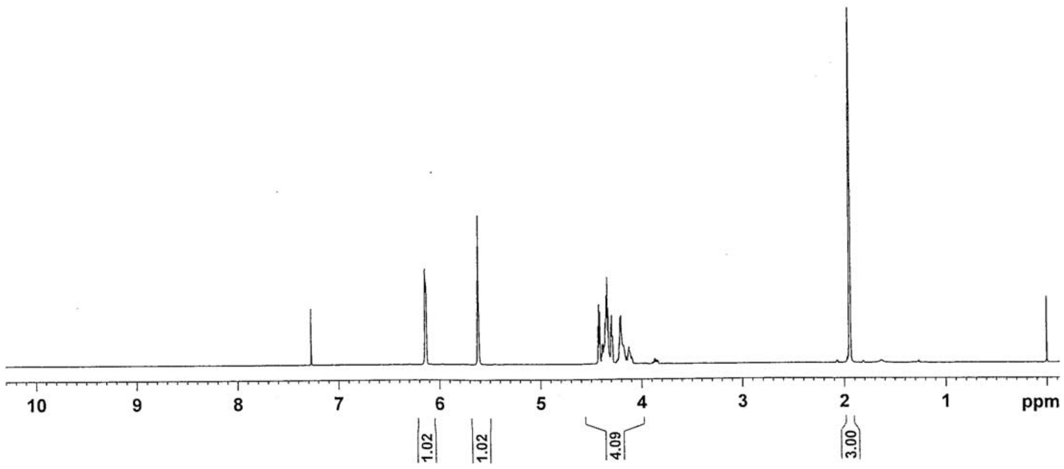
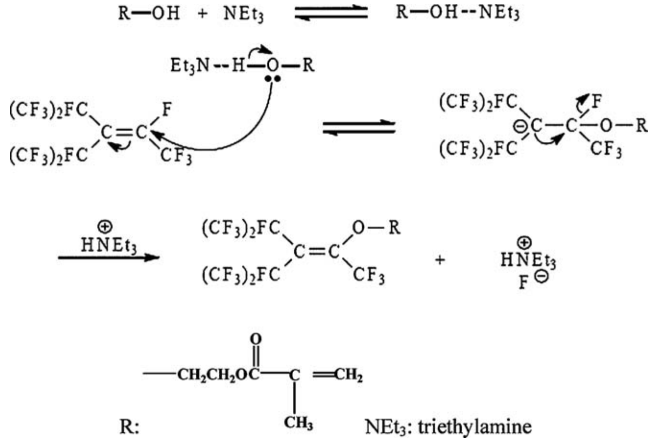


Fig. 11. ^{1}H NMR of POMA.



Scheme 2. Plausible reaction mechanism of synthesizing POMA.

liquid was washed with 5% HCl solution and then with the distilled water. The obtained liquid was dried with Na_2SO_4. Thus, POMA was obtained for next solution polymerization. FTIR spectrum of POMA was shown in Fig. 10. 2965 cm^{-1} was the characteristic stretching peak of –CH_3, 1722 cm^{-1} was stretching vibration of C=O, 1639 cm^{-1} and 813 cm^{-1}was the characteristic stretching peaks of C=C bond, which was linked with F atom. 1605 cm^{-1} was the characteristic stretching peaks of C=C bond, which was linked with H atom. 1455 cm^{-1} was distortion vibration of –COO–, 1284 cm^{-1} and 1174 cm^{-1}were the characteristic stretching peaks of C–F bond, 1174 cm^{-1} was the characteristic stretching peak of C–O–C, 976 cm^{-1} was the deformation vibration of –CH_2. Fig. 11 was the ^{1}H NMR of POMA. It showed the following spectral data.

^{1}H NMR($CDCl_3$, δ in ppm): 6.1 (1H, CH_2), 5.6(1H, CH_2), 4.4–4.1(4H, CH_2–CH_2), 1.9(3H, CH_3). Both Figs. 10 and 11 certified that POMA had been prepared. The plausible reaction mechanism of synthesizing POMA is shown in Scheme 2.

4.3. Preparation of the fluorinated acrylate resin

The fluorinated acrylate resin was prepared by the solution polymerization technique. The moderate amount of solvent was added into the reactor which was equipped with two dropping funnels and a condenser under the condition of the agitation. The solvent in the reactor was heated to 80 °C. The initiator solution and the mixed monomers were dripped into the reactor simultaneously and slowly within 4 h. The reaction continued about 30 min when the initiator and the mixed monomers were dripped completely. Thus, the fluorinated acrylate resin was obtained. A series of fluorinated acrylate resins has been synthesized with the same solid content, while the fluorine content in mixed monomers was different such as 0, 5, 10 15, 20 and 25% of fluorine. The prepared recipe, the conversion of the mixed monomers, the molecular weight of the fluorinated acrylate resin and its distribution were given in Table 3.

Table 3
Recipes for the synthesis of fluorinated acrylate resin.

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
Mixed monomers						
BA (g)	20.01	20.01	20 .03	20.00	20.00	20.00
MMA (g)	10.04	10.02	10.21	10.02	10.06	10.02
MAA (g)	2.07	2.01	2.02	2.11	2.05	2.14
POMA (g)	0	1.69	3.56	5.72	8.01	10.04
Mixed solvent						
Ethyl acetate (g)	27.00	28.04	30.66	31.50	34.14	35.25
Butanol (g)	13.51	14.01	15.05	15.72	17.00	17.52
Toluene (g)	13.51	14.03	15.04	15.72	17.25	17.65
Initiator (g)						
AIBN	0.95	0.94	0.94	0.92	0.90	0.93
Conversion (wt %)	98.35	98.26	98.54	97.46	97.25	98.53
$\bar{M}_n$	45220	47850	49540	53850	56740	59640
$\bar{M}_W/\bar{M}_n$	3.28	3.35	3.46	3.53	3.56	3.58

4.4. Characterization

The structure of composite emulsion was characterized by Fourier infrared spectrometric analyzer (Thermo Nicolet AVATAR370, USA). General thermal analyzer (STA449C, Germany) was used to analyze the thermal stability of the fluorinated acrylate emulsion. The raised temperature was in the range from 30 °C to 500 °C. The velocity of the raised temperature was 10 °C/min. The differential scanning calorimetry (DSC Q100, USA) was applied to determine the glass transition temperature (T_g) of the fluorinated acrylate emulsion. The raised temperature was in the range from −40 °C to 100 °C. The velocity of the raised temperature was 10 °C/min. The contact angles between film and water or oil (i.e. n-hexadecane) were determined with the DataPhysics contact angle meter (OCA-20, Germany) at room temperature. The molecular weight of the resin and its distribution are determined by gel permeation chromatography (PL-GPC50, Polymer Laboratories, USA), which is calibrated with standard polystyrene by using THF as eluant. ^{1}H NMR and ^{19}F NMR spectra were recorded with Bruker AVANCE III 500 MHz (Switzerland) spectrometer. $CDCl_3$ was used as internal reference for chemical shift of ^{1}H and ^{19}F. The purification method of the fluorinated acrylate resin was that the coated film on the glass with the resin is dried for 5 h at 50 °C in the oven. In the case, the solvents and un-reacted monomers were removed completely.

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