

Preparation and Characterization of Green Acrylic Latex Modified with Fluorinated and Crosslinking Monomers

LIJUN CHEN, XIN ZHANG AND DAWEI CHEN

School of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310032, China

ABSTRACT

The environmental friendly polyacrylate latex was prepared by semi-continuous seeded emulsion polymerization of butyl acrylate (BA), methyl methacrylate (MMA), hexafluorobutyl methacrylate (HFMA) and hydroxy propyl methacrylate (HPMA), which was initiated with potassium persulfate (KPS) and emulsified with the novel mixed surfactants of sodium dodecyl benzene sulfonate (SDBS) and myristyl hydroxypropyl sulpho betaine (betaine). The structure of the latex was confirmed by Fourier transform infrared spectroscopy (FTIR). The particle size of the latex was measured by Zetatrac dynamic light scattering detector. The properties of latex film were tested by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), contact angle (CA) and DSC. The stability of the latex was improved.

Key words : Modification, Acrylic polymer latex, Preparation, Characterization

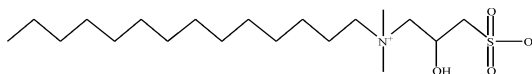
1. INTRODUCTION

Acrylate emulsion had been widely used in application of emulsion polymerization, it had excellent film form property and its film had good oil resistivity, cohesiveness, corrosion resistance and so on. Nevertheless, the bad water resistance, cold-proof and heat-proof property of the latex film confined its adhibition^[1,2]. Fluorinated acrylate emulsion had good

adhesion and film forming of acrylate emulsion. The strong electronegativity and lower polarization of fluorine gave polymer oleophobicity, hydrophobic, anti-fouling, radiation resistance and excellent electrical insulation properties^[3,4]. Thus, we used it to overcome some shortcoming of conventional acrylate emulsion and improve its performance. HPMA was also introduced into this system. A

kind of acrylates containing active hydroxyl can be synthesized by copolymerization of HPMA and other acrylic monomers, which are also applied in acrylate crosslinking agent as crosslinking monomer. It can give latex film hardness, scrub resistance and high temperature resistance^[5, 6].

Nowadays, the combination of anion emulsifiers and nonionic emulsifiers was widely used in emulsion polymerization, the charge effect of anion emulsifiers and space steric hindrance effect of nonionic emulsifiers were considered to stabilize latex particle, such as SDBS and OP-10, but the emulsifier of alkyl phenol was hard to be degraded and was toxic for people and environment, and according to the requirement of sustainable development strategy and improvement of people's environmental awareness, environmental emulsifier had attracted many researchers' attention. Betaine, is renewable easily biodegradable amphoteric surfactant with low toxicity, low irritation to skin and eye, the superior properties such as good surface activity in a wide scope of pH value, chemical resistance, good emulsibility, dispersibility and antistatic property.



Most of conventional surfactants system can be replaced by this kind of green emulsifier which simultaneously has anion and cation group and can mix with most emulsifier system. The unique properties of betaine such as its neutrality, good solubility in water, methanol and ethanol and excellent formulation character of anion decided its wide application in many areas^[7-9]. In addition, the surfactant of

betaine has excellent resistance to hard water. But the report in the acrylate emulsion polymerization was rarely mentioned. This work synthesized a kind of novel acrylate polymer latex when amphoteric surfactant betaine and anionic surfactant SDBS were used as emulsifier. Hexafluorobutyl methacrylate (HFMA) and hydroxy propyl methacrylate (HPMA) were used as modified monomer. The objective is to replace most of the non-biodegradable conventional surfactants with this kind of green surfactant. The influence of emulsifier on emulsion performance, influence of functional monomer on hydrophobicity of latex film is studied. The mechanical stability and ionic stability of the latex was also measured.

2. EXPERIMENTAL

2.1 Materials

MMA and BA, which were analytically pure, were purchased from Shanghai Chemical Reagents Supply Procurement of Five Chemical Plants (China) and were distilled under reduced pressure prior to polymerization. HFMA, which was industrial grade, was obtained from Harbin Xeogia Fluorinesilicon Material Co Ltd (China). HPMA, which was bought from Shanghai Aladdin Biochemical Technology Co Ltd. Betaine, which was the industrial grade, was a gift from Henan Titaning Chemical Technology Co Ltd. SDBS, which was chemically pure, was provided by Shanghai Yingpeng Chemical Reagent Co Ltd (China). KPS, which was chemically pure, was obtained from Shanghai United Initiators Co Ltd (China). The water used in the experiment was de-ionized.

2.2 Preparation of polyacrylate latex

Firstly, all of the emulsifiers and moderate amount of de-ionized water were added into a 250 ml four-neck flask, which equipped with reflux condenser, mechanical stirrer and dropping funnels under the condition of agitation. The solvent in the reactor was

heated to 80 °C. The 10wt% of the initiator and 10wt% of mixed monomers, which composed of MMA, BA, HFMA and HPMA, were dripped into the reactor slowly within the range of 15 min to 20 min via two different dropping funnels at the same time. The reaction was maintained for another 15 min than the seeded emulsion was obtained. Secondly, the rest of the residual monomer and the KPS aqueous solution were fed into the reactor under starved-feed addition simultaneously within the range of 3.0 h to 4.0 h by two dropping funnels. After completion of addition, the temperature was kept at 90 °C for another 40 min. Finally, the emulsion in the reactor was cooled and

TABLE 1. Recipe for preparing emulsion

Ingredients	Amount/g	Ingredients	Amount/g
BA	13.35	KPS	0.18
MMA	13.35	SDBS	0.68
HFMA	2.4	Betaine	0.45
HPMA	0.9	De-ionized water	70

filtered. Thus, the acrylic polymer latex was obtained. A typical recipe for the emulsion polymerization was shown in Table 1

2.3 Characterizations

The chemical structures of the latex films were analyzed by Fourier transform infrared (FTIR) spectrometric analyzer (Thermo Nicolet infrared AVATAR370, USA). The differential scanning calorimetry (DSC Q100, USA) was applied to determine the glass transition temperature (Tg) of the film of the latex. The hydrodynamic particle size of the latex was determined by Zetatrac dynamic light scattering detector (Malvern Zetasizer Nano S90, UK) at 25 °C. The mechanical stability of the latex was tested by the centrifugal machine with the rotation speed of 3000 r/min for 30 min. The calcium ion stability of the latex was tested with 16 ml of the latex and 4 ml of the CaCl₂ whose concentration was 5 wt%. Conversion percentage was calculated according to the following equation:

$$X\% = \left(\frac{W_3 - W_1}{W_2} \right) \times (W_A - W_B) / W_C \times 100\%;$$

where X was the conversion ratio; W₁ was the weight of the glass-surface vessel; W₂ was the weight of the latex; W₃ was the weight of the glass-surface vessel and latex, which was dried by vacuum drying oven under 80 °C; W_A was the weight of total inventory rating; W_B was the weight of non-volatile ingredients in the recipe. W_C was the weight of all monomer in the recipe. Coagulation rate of the reaction was calculated according to the following equation:

$$Y\% = \frac{M_1}{M_2} \times 100\%;$$

where Y was the gel percentage, M₁ was the weight of coagulum, which was collected through stirrer and flask walls and was dried out by vacuum drying oven; M₂ was the weight of the total monomer in the recipe. Water absorption of film was calculated according to the following equation: w_i(%) = (m₁ - m₀)/m₀ × 100%; where w_i was the water absorption, m₁ and m₀ were the mass of wet film and dry film, respectively.

3. RESULT AND DISCUSSION

3.1 FTIR and DSC analysis of the film

FTIR of the film of the acrylic polymer latex was given in Figure 1. In Figure 1, the absorption peak at 3400 cm⁻¹ was the characteristic stretching vibration of -OH in the HPMA, 2956 cm⁻¹, 2930 cm⁻¹ and 2874 cm⁻¹ were the characteristic stretching peaks of C-H, and 1727 cm⁻¹ was stretching vibration of C=O, and 1451 cm⁻¹ was bending vibration peak of -CH₂-, and 1385 cm⁻¹ was the flexural vibration peak of C-H in CH₃, 1144 cm⁻¹ was the stretching peak of C-H. From the spectrum, there was no C=C absorption peak detected in the range of 1500 cm⁻¹ to 1700 cm⁻¹, this confirmed that all the monomers had taken part in the copolymerization reaction and the latex had been prepared successfully.

DSC of the film of the acrylic polymer latex was given in Figure 2. It was clearly that the latex film had only one glass transition

temperature ($T_g=13.8^\circ\text{C}$), this mean there was no homopolymerization in the copolymer system, that is, various monomer copolymerized a kind of irregular copolymer, formed a homogeneous system.

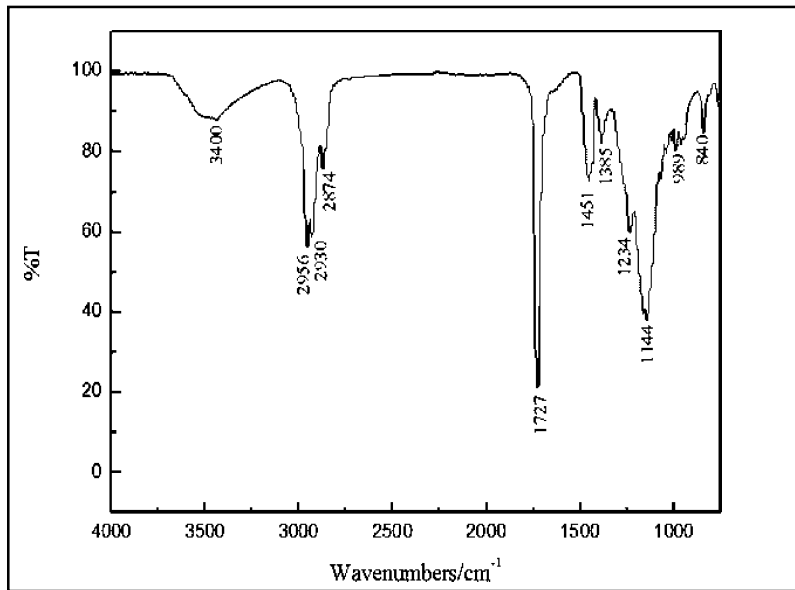


Fig.1. FTIR of film

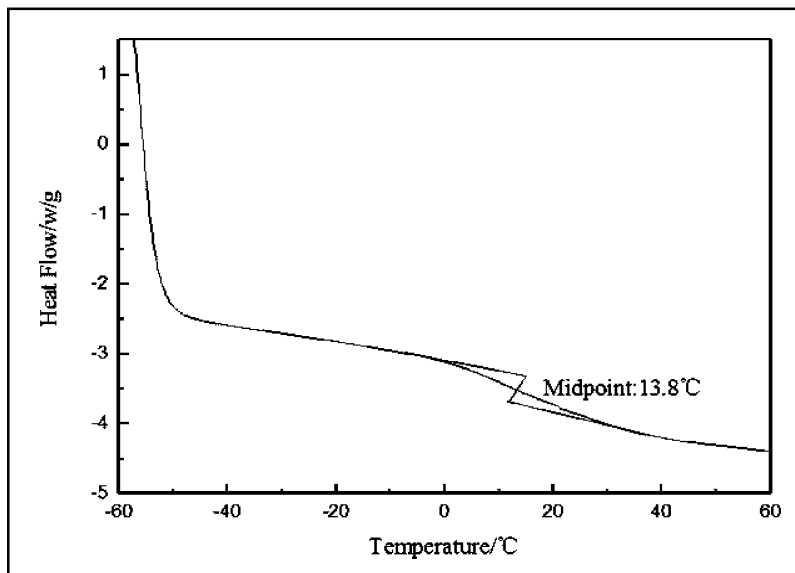


Fig. 2. DSC of film

3.2 Influence of amount of emulsifier on particle size of latex

The effect of amount of emulsifier on average particle size of the latex was given in Figure 3. It can be seen that the average particle size decreased with the increase of amount of emulsifier, this situation probably caused by the mechanism of micelle nucleation. Emulsifier firstly formed monomolecular particle, then with the increase of emulsifier, the concentration of

emulsifier reached critical micelle concentration (CMC), after the formation of micelle, when monomer was added into the mixture solution of water and emulsifier, dispersive monomer was encircled by micelle under stirring, lipophilic group of micelles were attracted into surface of monomer and the hydrophilic segment contact with water, the interaction increased the solubility and stability of monomer. Thus, the particle of latex decreased.

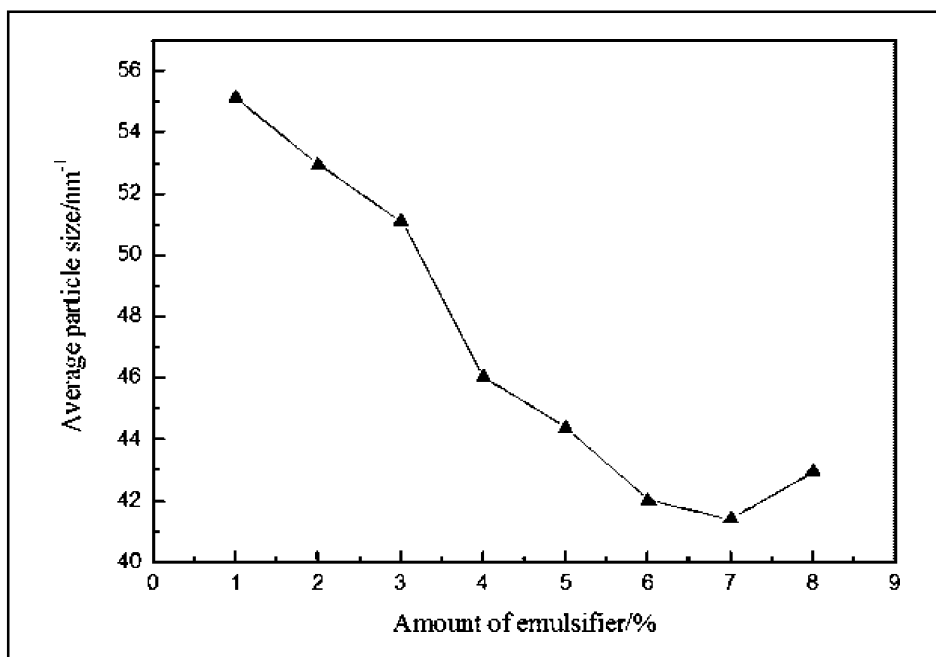


Fig. 3. Effect of amount of emulsifier on average particle size

3.3 Effect of amount and mass ratio of emulsifier on properties of latex

The effect of amount of emulsifier on latex's properties was given in Table 2, which showed that the conversion rate was increased when the amount of emulsifier was in the range of 1% to 3%, which was related to its mechanism

of micelle nucleation. When we increased the dosage of emulsifier until reached the CMC of emulsifier, micelle would appear and increase, it provided more reaction place for monomer, this improved the conversion rate. The coagulation rate was highest under the 1% amount of emulsifier, then dropped and

TABLE 2. Effect of amount of emulsifier on properties of latex

Amount of emulsifier/%	Conversion percentage/%	Coagulation percentage/%	Appearance of emulsion	Mechanical stability
1	97.41	0.046	●	√
2	98.50	0.006	●	√
3	99.37	0.014	●	√
4	96.57	0.013	●	√
5	97.04	0.011	●	√
6	98.79	0.005	●	√
7	97.02	0.010	●	√
8	98.87	0.012	●	√

Notes: ● means that the appearance of the latex is translucent with blue light.

√ stands for the good stability of latex.

TABLE 3. Effect of the mass ratio of emulsifier on properties of latex

Mass ratio of Betaine to SDBS	3:1	2:1	1:1	1:2	1:3
Conversion percentage	98.29	95.25	96.25	99.17	99.12
Coagulation percentage	0.016	0.006	0.010	0.014	0.010
Mechanical stability	√	√	√	√	√
Storage stability	√	√	√	√	√

Notes : √ stands for the good stability of latex.

contained stable basically. This can be explained that the reaction zone was not enough when the amount of emulsifier was 1%, and the whole system was unstable, thus causing more gel. We can also know that the emulsion had well mechanical stability and the appearance of emulsion was white and blue. From the above analysis and considering environmental protection, 3% amount of emulsifier was chose. Table 3 told us that the

monomer had high conversion percentage and low coagulation rate relatively when the mass ratio of betaine to SDBS was 1:3, so this proportion was chose.

3.4 Effect of amount of initiator on conversion percentage and coagulation percentage

Effect of amount of initiator on conversion rate and gel rate was shown in Figure 4. The

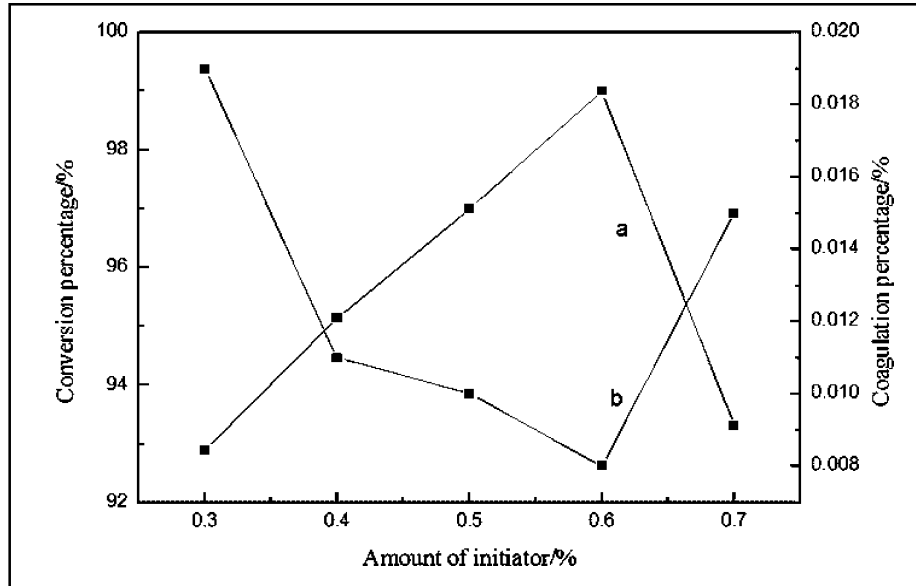


Fig. 4. Effect of amount of initiator on conversion rate and gel rate (a: conversion percentage curve; b: coagulation percentage curve)

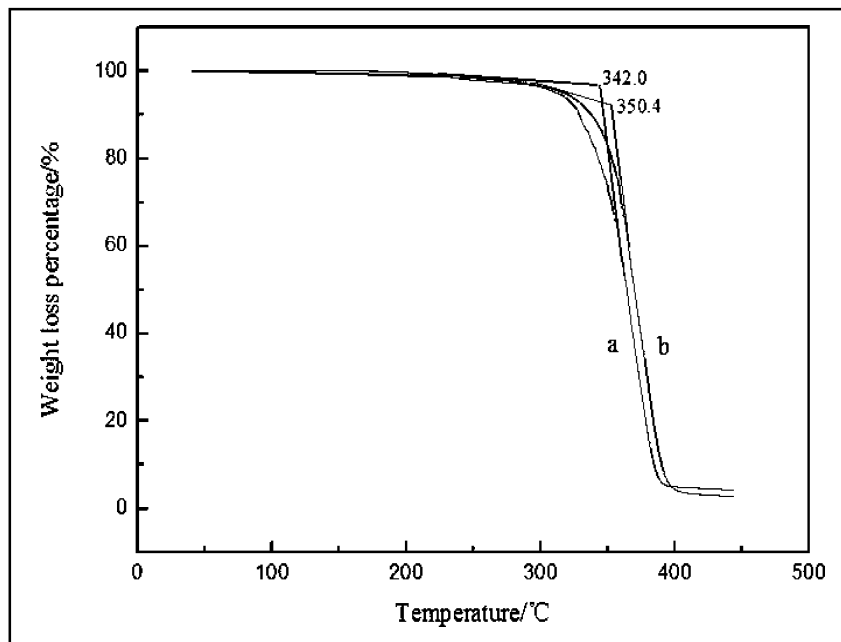


Fig. 5. TGA of film (a: acrylate copolymer; b: modified acrylate copolymer)

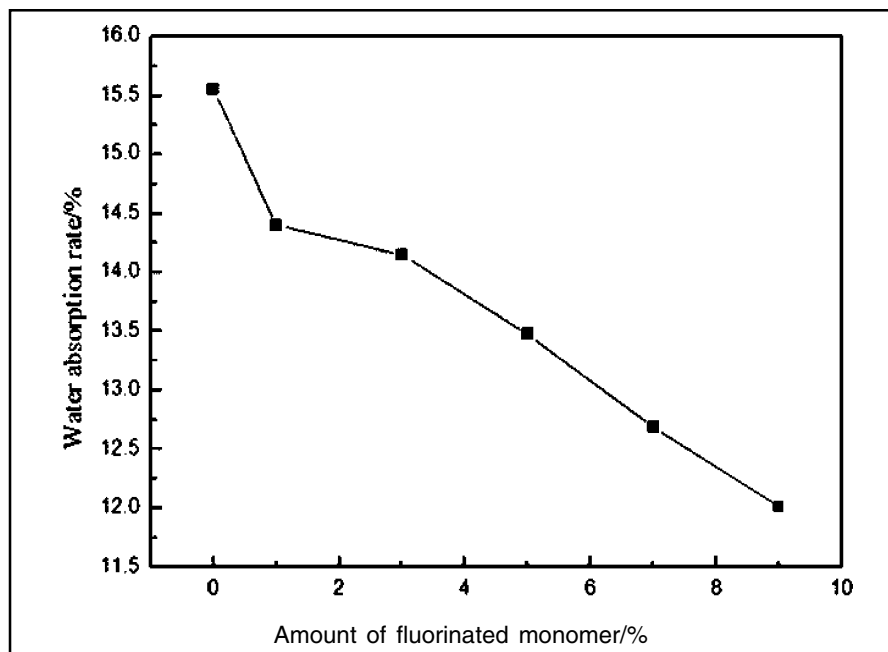


Fig. 6. Influence of amount of fluorinated monomer on water absorption of film

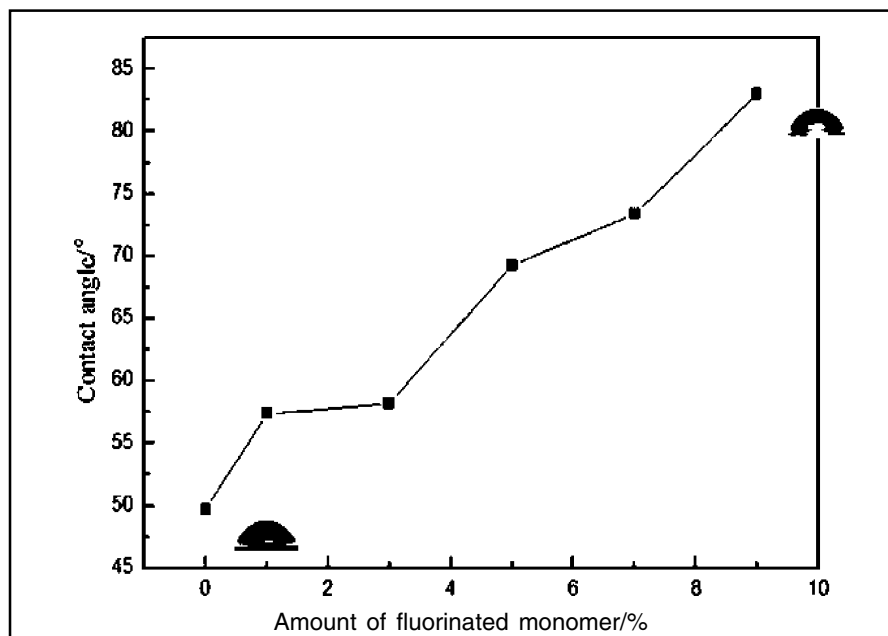


Fig. 7. Influence of amount of fluorinated monomer on CA

conversion rate was increased whereas the gel rate was decreased when the amount of initiator was less than 0.6%, this may be that the increased initiator created more free radical to trigger the reaction of monomer; it also formed a more stable system, so the conversion rate was raised. The reaction speed was too fast to contain a stable system and the reaction heat was difficult to emit when the amount of initiator was excessive. Thus, 0.6% was suitable dosage of initiator in this work.

3.5 TGA of films

Thermo-gravimetric analysis (TGA) was used to investigate the thermal stability of the film, which was given in Figure 5. It can be seen that the modified polyacrylate latex had 8 °C higher temperature than that of unmodified polyacrylate latex, which may be caused by the combined effect of the high bond energy of C-F in the fluorinated monomer and netted and interlaced structure of latex film introduced by HPMA.

3.6 Water absorption and contact angle

Influence of amount of the fluorinated monomer on water absorption and contact angles of latex film were presented in Figure 6 and Figure 7, respectively. The water absorption rate was decreased with increase of amount of fluorinated monomer, the relation of contact angle and amount of monomer had opposite trend. This may be attributed to the excellent hydrophobicity of the C–F bond; the fluorinated groups migrated to the surface and decreased the interfacial energy, especially at high temperature circumstances^[10-12], which improved the water resistance of the latex film.

4. CONCLUSIONS

The environment friendly modified acrylic latex was prepared successfully via semi-continuous seeded emulsion polymerization of BA, MMA, HFMA and HPMA in water phase initiated with KPS and emulsified with SDBS and betaine. The optimum conditions of preparing the green fluorinated polyacrylate latex were optimized and the results were as follows: the amount of emulsifiers was 3%; mass ratio of betaine to SDBS was 1:1, the amount of the initiator was 0.6%. The mass ratio of BA to MMA was 1:1; the amount of HFMA was 8% and the amount of HPMA was 3%. In this case, the conversion was high and the polymerization stability was good. In addition, the water resistance and thermal properties of the latex films were improved significantly in comparison with the film of the unmodified latex.

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