

Preparation and surface properties of UV curable fluorinated pure acrylic based waterborne polyurethane coatings

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Abstract A series of fluorinated pure acrylic based waterborne polyurethane (FPAU) were synthesized by free radical polymerization, which structures were characterized by Fourier transform infrared spectroscopy (FT-IR) and ^1H nuclear magnetic resonance (^1H NMR). The surface properties of the cured FPAU films were measured by X-ray photoelectron spectroscopy (XPS) analysis and contact angle (CA) analysis. The results showed that the water and bromonaphthalene contact angle increased and surface free energy decreased with fluorinated acrylate monomer addition.

Keywords: UV curable, Waterborne, Polyurethane, Fluorinated

Introduction

UV curable technology was called the 5E technology for its environmental friendliness and prominent performance. Waterborne coatings using ultraviolet (UV)-curing technology have gained increasing interest because they can decrease air pollution, reduce risk of fires, improve aspects of occupational health and safety, lower energy consumption, and have high curing speed^[1-3].

Polyurethane (PU) is a high performance polymer material due to its unique properties, including excellent abrasion resistance, flexibility, hardness, chemical resistance, solvent resistance, light stability, and weatherability^[4-5].

Acrylic polymers with fluorine-containing 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. Therefore, fluorine-containing acrylate copolymers have attracted more and more attention from many investigators for their unique properties and wide-ranging applications^[6-10].

Combination of PU with fluorinated acrylate polymer is expected to be effective to increase the performances of the resulting materials. In recent years, a lot of investigations have been conducted the fluorine-containing polyurethane acrylic hybrid latexes due to their special surface property, good adhesion to matrices, excellent flexibility, high thermal stability, good chemical resistance and high weatherability environmental friendly properties^[11-12].

In this article, a series of UV curable fluorinated pure acrylic based waterborne polyurethane were synthesized. The structures were characterized by Fourier transform infrared (FT-IR) spectrometry and ^1H nuclear magnetic resonance (^1H NMR). The surface properties of the cured FPAU films were measured by X-ray photoelectron spectroscopy (XPS) analysis and contact angle (CA) analysis.

Experiment

Materials

Isophorone diisocyanate (IPDI) is of industrial grade and supplied by Bayer Chemicals, Inc. 2-hydroethylacrylate (HEA) was purchased from Shanghai Beihe chemical reagent factory and distilled before use. Triethylamine (TEA) is of analytical grade and purchased from Tiansheng chemical reagent factory. methyl methacrylate (MMA), butyl acrylate(BA), and acrylic acid(AA), are of CP grade and purchased from Xilong chemical reagent factory. α - α' -azoic-isobutyronitrile (AIBN) was used as an initiator and purchased from the Qingxi Reagent Co., Shanghai, China. Di-n-butyltindilaurate (DBTDL) was used as a catalyst and was purchased from the First Reagent Co., Shanghai, China. p-Hydroxyanisole MEHQ was used as a inhibitor and was purchased from Aladdin reagent Co., Shanghai, China. 2,2,3,4,4,4-Hexafluorobutyl acrylate(BFA-6), 1H,1H,7H-Dodecafluoroheptyl acrylate acrylate(BFA-12), 1H,1H,7H-Dodecafluoroheptyl methacrylate methacrylate(MBFA-12), and 1H,1H,2H,2H-perfluorooctyl methacrylate(MBFA-13) are of Reagent Grade, purchased from Harbin Xuejia fluorine silicone Co.,LTD, Xylene, Butyl acetate, and acetone are of CP grade and purchased from Xilong chemical reagent factory.

2-Hydroxy-2-methyl-1-phenyl-1-propanone (Darocur 1173, supplied by Ciba-Geigy, Switzerland) was used as a photoinitiator for UV curing.

Fluorinated polyacrylate (FPA) prepolymer synthesis

An appropriate amount of Xylene, Butyl acetate, and 80 wt% AIBN was added to a 250 mL flask and stir the mixture till complete dissolution at room temperature and then, it was heated up till 80 °C. Subsequently, an appropriate amount of acrylate monomer (MMA, BA, HEA and AA) and fluorine-containing acrylate (BFA-6, BFA-12, MBFA-12 and MBFA-13) were drop wise to the flask, kept the polymerizations temperature for 4 h. Adding the remaining 20wt% AIBN, immediately, then the reaction was maintained for another 3 h. finally the resultant was cooled to room temperature and the products was purified by petroleum ether.

Fluorinated pure acrylic based waterborne polyurethane synthesis

A 250 ml round-bottomed, four-necked flask was fitted with a mechanical stirrer, thermometer, condenser, and a dropping funnel. IPDI was put into a reactor with DBTDL as catalyst and MEHQ as a inhibitor ,the HEA was drop wise to the flask, where the reaction was carried out at 0 °C in a ice-bath . the temperature was raised to 45 °C after finishing to adding the monomer, the reaction was maintained for another 4 h. And then, an appropriate amount of purified PAF was added according to content the –OH, here the temperature was risen to 50 °C ,and the reaction continued for another 12 h. The reaction scheme of FPUA is shown in Scheme 2.

Neutralization and dispersion of the FPAU

After the reaction mixture temperature was dropped to 35 °C , the carboxylic acid groups were neutralized by the addition of TEA with acetone as a solvent, and the degree of neutralization was 100%. The mixture was stirred for further 30 min. Then, the prepolymer was dispersed by adding distilled water to the prepolymer solution which was stirred vigorously. The addition rate was controlled carefully using a tubing pump with a calibrated flow rate. Finally, the temperature was risen to 60 °C to remove acetone under vacuum.

Measurement

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. Samples were prepared by coating the solution onto KBr pellet.

^1H NMR data were obtained with Nuclear Magnetic Resonance Spectrometer- Bruker 400MHZ AdvanceIII (Bruker Company, Germany).

X-ray photoelectron spectroscopy (XPS) was employed to characterize the surface composition of the copolymer films. The XPS experiments were carried out on a VG Scientific ESCALab220i-XLS system with an AlK α X-ray source (1253.6 eV). The X-ray gun was operated at a power of 300 W. The chamber pressure during analysis was about 3×10^{-9} Torr. All spectra were calibrated by the C1s peak of the C–C bond at 284.6 eV.

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 bromonaphthalene.

Results and discussion

Synthesis and Characterization

The fluorinated pure acrylic based waterborne polyurethane (FPAU) was prepared by three steps. First a series of the fluorinated polyacrylate(FPA) were synthesized by free radical polymerization technique, as illustrated as Fig.1. And the formulations of FPA are listed in Table 1. Second the fluorinated pure acrylic based waterborne polyurethane was synthesized, as illustrated as Fig.2. Finally, the polyurethane were neutralized and dispersion.

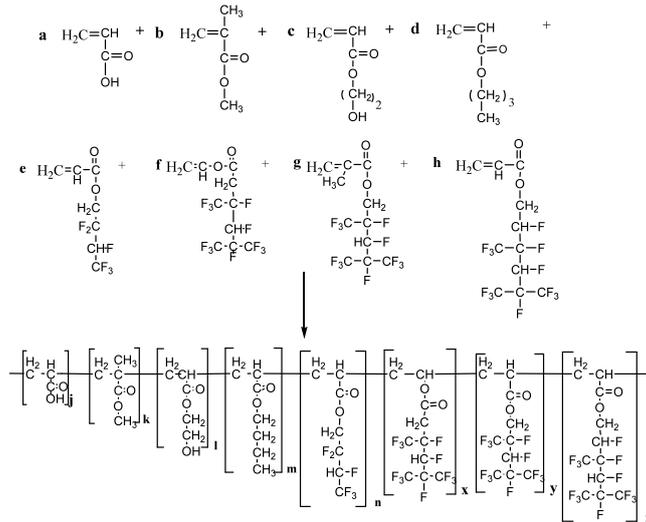


Fig.1 The reaction scheme of PAF

Table.1 Raw materials composition of FPA

| sample | FPA | | | | |
|--------|--------------------|-------|--------|---------|---------|
| | MMA:BA:HEA:AA | BFA-6 | BFA-12 | MBFA-12 | MBFA-13 |
| A1* | 30:30:30:10 | × | × | × | × |
| A2* | 28.8:28.8:28.8:9.6 | × | × | × | 4 |
| A3* | 28.2:28.2:28.2:9.4 | × | × | × | 6 |
| A4* | 27.6:27.6:27.6:9.2 | × | × | × | 8 |
| A5* | 27:27:27:9 | × | × | × | 10 |
| B1* | 30:30:30:10 | × | × | × | × |
| B2* | 28.2:28.2:28.2:9.4 | 6 | × | × | × |
| B3* | 28.2:28.2:28.2:9.4 | × | 6 | × | × |
| B4* | 28.2:28.2:28.2:9.4 | × | × | 6 | × |
| B5* | 28.2:28.2:28.2:9.4 | × | × | × | 6 |

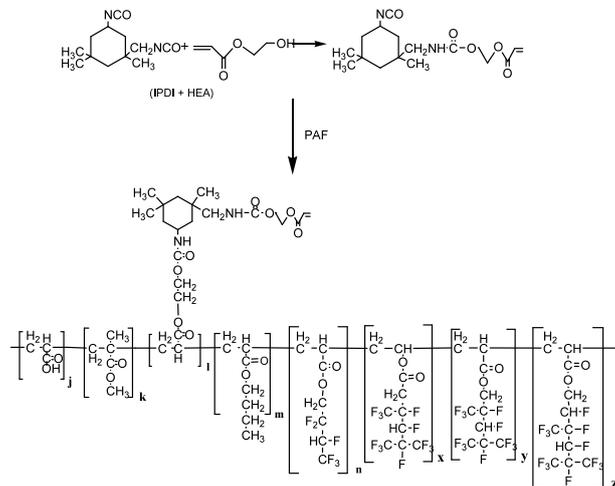


Fig. 2 The reaction scheme of FPAU

Fig.3 shows the FT-IR spectra of FPA and FPAU polymer. It can be seen that the characteristic absorption bands at 2,960 and 1,731 cm^{-1} indicate the stretching of $-\text{CH}_2$ asymmetric stretching and C=O stretching vibration, respectively. And a combination of rocking and wagging vibration of $-\text{CF}_3$ groups at 656 and 701 cm^{-1} in the fingerprint region, are all detected in the FPA and FPUA spectra. In the spectrum of FPAU, the peak of stretching vibrations of isocyanate groups at 2240 cm^{-1} can not find and the peaks of amide and double bond at 1,536 cm^{-1} , 810 cm^{-1} respectively can be find, which indicate the synthesis was successfully.

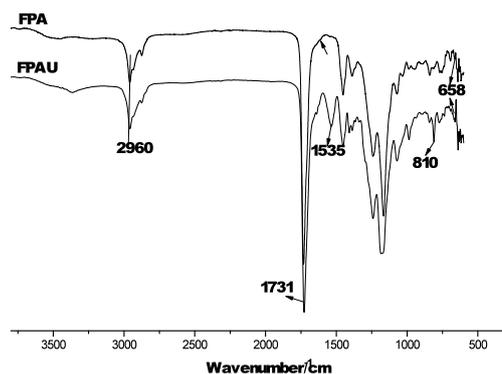


Fig.3 FTIR spectra of FPA and FPAU

Fig. 4 shows the ^1H NMR spectra of FPA and FPAU. For FPA spectra, no peaks appeared at 6.5-5.5ppm, peaks at 4.8 ppm were designated to the splitting of $-\text{CHF}$, which confirms that FA monomer has been introduced into the hybrid polymer. For FPAU spectra, the Protons peak of acrylic ester double bonds was observed, while the Protons peak of FPA was retained. The results were consistent with the FT-IR spectra.

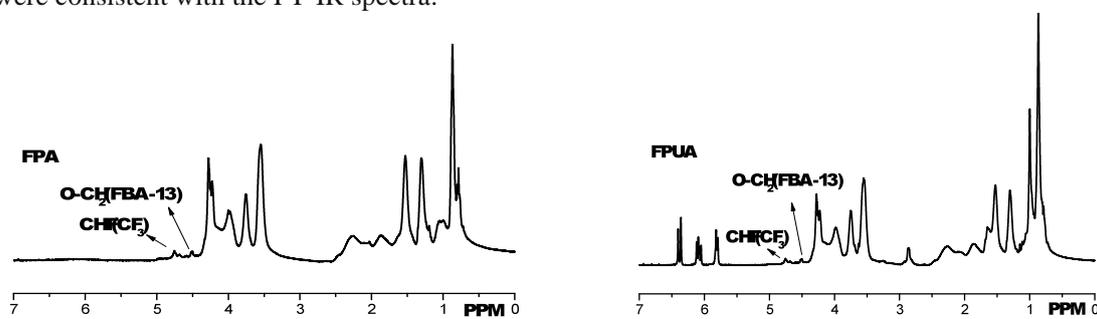
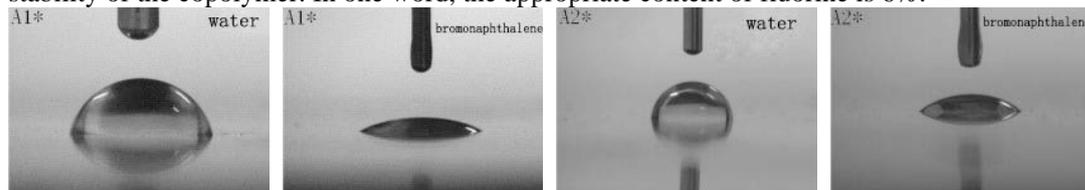


Fig.4 ^1H NMR spectra of FPA and FPAU

The surface properties of the cured films

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 surface properties of the films are conducted by determination of the contact angle existing on the surface of the polymers. We chose water and bromonaphthalene as the wetting liquids. The contact angle was affected by a series of factors.

The effect of fluorine content on water and bromonaphthalene contact angle of different films are showed in Fig. 5, the surface energy are listed in Table 2 in detail. The result showed that, when the content of FBA-13 increased to 6%, the water contact angle and bromonaphthalene contact angle increased, and the surface energy of the film decreased rapidly. As the hydrophobic monomer of fluorine aggregated easily, lead to a low surface energy. With the fluorine content was increased further, the contact angle of film to water and film to bromonaphthalene don't change much, for the gathering of the fluorine reached saturation. Furthermore the strong hydrophobic of fluorine is difficult to copolymerization with acrylate, which will lower the stability of the copolymer. In one word, the appropriate content of fluorine is 6%.



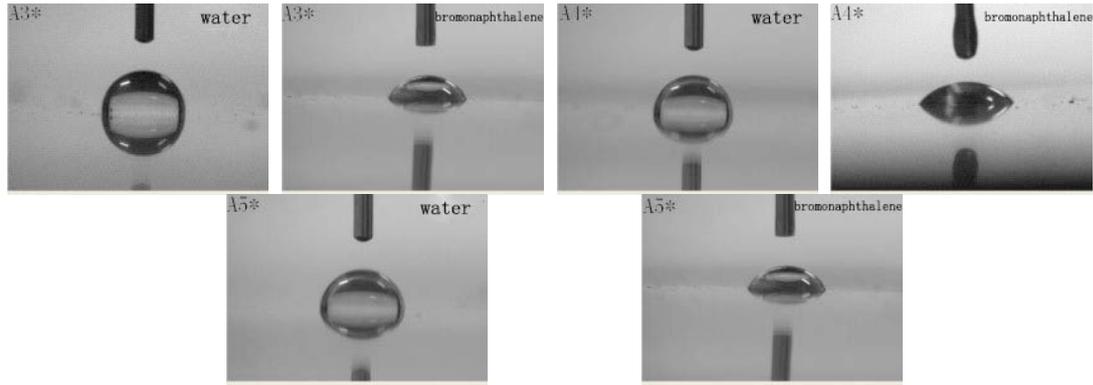


Fig.5 Effect of fluorinated content on water and bromonaphthalene contact angle of different films

Table.2 Effect of fluorinated content on surface free energy of different films

| sample | MBA-13 [%] | W-CA [°] | B-CA [°] | surface free energy [mJ/m ²] | Solid dispersion Force [mJ/m ²] | Solid polarity force [mJ/m ²] |
|--------|------------|----------|----------|--|---|---|
| A1* | 0 | 78.4 | 28.1 | 43.549 | 39.498 | 4.052 |
| A2* | 4 | 92.4 | 40.3 | 35.715 | 34.643 | 1.072 |
| A3* | 6 | 107.6 | 57.6 | 31.312 | 26.300 | 0.041 |
| A4* | 8 | 103.4 | 59.7 | 25.637 | 25.239 | 0.398 |
| A5* | 10 | 102.1 | 62.3 | 24.615 | 23.925 | 0.690 |

W-CA water contact angle

B-CA bromonaphthalene contact angle

The water and bromonaphthalene contact angle and the surface energy of different films with different length of fluorine-carbon chain are listed in Table 3. The results showed that the contact angle of water and bromonaphthalene increasing with the increasing of fluorine-carbon chain length, whereas the surface energy decreasing. When the length of fluorine-carbon chain is 3, the film to water and bromonaphthalene contact angle is 85.5° and 36.4°, respectively. As it reaches to 7, the contact angles increase to 107.6° and 57.6°, respectively. For the fluorine aggregated easily during the film formation, longer the length of fluorine-carbon chain is, more the aggregate would be, result in excellent hydrophobicity of the film and low surface energy. Moreover, the shield effect to polar groups is better as the length of fluorine-carbon chain increase.

Table.3 Effect of length of fluorine-carbon chain on surface free energy of different films

| sample | length of fluorine-carbon chain | W-CA ¹ [°] | B-CA ² [°] | surface free energy [mJ/m ²] | Solid dispersion Force [mJ/m ²] | Solid polarity force [mJ/m ²] |
|--------|---------------------------------|-----------------------|-----------------------|--|---|---|
| B1* | 0 | 78.4 | 28.1 | 43.549 | 39.498 | 4.052 |
| B2* | 3 | 85.5 | 36.4 | 38.745 | 36.323 | 2.423 |
| B3* | 6 | 98.2 | 47.5 | 31.811 | 31.305 | 0.507 |
| B4* | 6 | 100.3 | 48.1 | 31.312 | 31.016 | 0.297 |
| B5* | 7 | 107.6 | 57.6 | 26.341 | 26.300 | 0.041 |

¹W-CA water contact angle

²B-CA bromonaphthalene contact angle

The FPUA films were annealed at the temperature of 120°C for 2h and 4h respectively, to investigate the effect of heat treating on water and bromonaphthalene contact angle of different films.

Table.4 Effect of heat treating on surface free energy of different films

| Treating time | B2* | | | B3* | | | B5* | | |
|---------------|----------|----------|-------------------------------------|-----------------------|-----------------------|-------------------------------------|----------|----------|-------------------------------------|
| | W-CA [°] | B-CA [°] | surface energy [mJ/m ²] | W-CA ¹ [°] | B-CA ² [°] | surface energy [mJ/m ²] | W-CA [°] | B-CA [°] | surface energy [mJ/m ²] |
| 0h | 85.5 | 36.4 | 38.745 | 98.2 | 47.5 | 31.811 | 107.6 | 57.6 | 26.341 |
| 2h | 90.2 | 38.5 | 36.841 | 107.4 | 55.8 | 27.233 | 122.3 | 70.5 | 8.166 |
| 4h | 90.7 | 38.7 | 36.662 | 108.3 | 56.4 | 26.916 | 124.1 | 71.2 | 6.349 |

¹W-CA water contact angle

²B-CA bromonaphthalene contact angle

The results show that the contact angle of the film after annealing at high temperature is increased obviously than that of the films at room temperature, and exhibited good surface property. 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.

XPS analysis

The XPS analysis gives some insight into the chemical composition of the surface of fluorine-containing PUA film. In this article, film-glass interface, film-air interface and film-air interface after heat treating 2h was investigated, and the results are shown in Fig. 6. The survey spectra reveal the characteristic signal of carbon (C1s at 285.60 eV), nitrogen (N1s at 397.9eV), oxygen (O1s at 533.61 eV), and fluorine (F1s at 684.9 eV). In the C1s spectrum (Fig. 4b), the peaks are attributed to the aliphatic carbon atoms (C1s at 284.60 eV), the ester atoms (C1s at 285.56 eV), and the carbon atoms of $-CF$ (C1s at 289.02 eV) and $-CF_3$ (C1s at 293.70 eV) groups, respectively. It is well known that the fluorine-containing group of copolymers has a tendency to migrate to the film-air interface and occupy it during the forming film of latex, which can effectively decrease the surface free energy of the latex film.

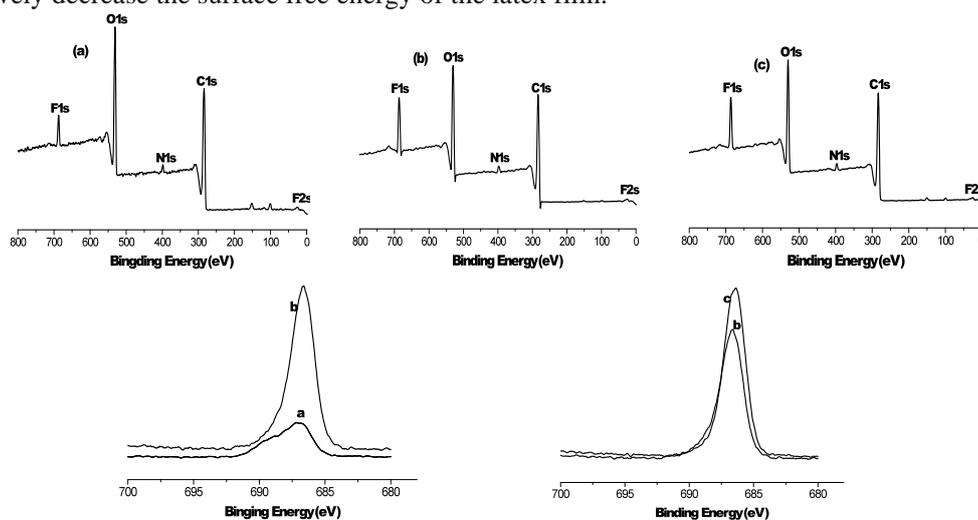


Fig.6 XPS spectrum (F1s) of films

Table.5 Atomic composition for the surface of films

| Surface | F1s (%) | C1s (%) | O1s (%) | N1s (%) |
|---|---------|---------|---------|---------|
| Film-glass interface (a) | 5.18 | 60.52 | 32.51 | 1.78 |
| Air-film interface (b) | 12.35 | 56.83 | 28.45 | 2.37 |
| Air-film interface after heat treating 2h (c) | 15.17 | 54.58 | 28.28 | 1.97 |

The XPS test result shows that the wt% of fluorine in the Air-film interface is 12.35%, much higher than that in the film-glass interface 5.18 %, while the content of fluorine in the film-air interface after heat treating 2h even higher, which further indicates that the fluorine aggregated easily near the film surface, while heat treatment which accelerate the movement of fluorine chain segment migrate to the film surface, result in the enhance of the fluorine aggregated.

Conclusions

A series of FPUA were successfully synthesized. With increasing the content of FBA-13, the water and bromonaphthalene contact angle of the cured films increase and the surface energy decreases, and appropriate content is 6%. The contact angle of water and bromonaphthalene increasing with the increasing of fluorine-carbon chain length, whereas the surface energy decreasing. The XPS results indicate that the fluorine chain segment migrates to the film surface, and heat treatment can accelerate the movement.

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