

Synthesis and Characterization of Crosslinking Waterborne Fluorinated Polyurethane-Acrylate with Core-Shell Structure

Qiaoli Luo, Yiding Shen, Peizhi Li, Chen Wang, Zhifang Zhao

Key Laboratory of Auxiliary Chemistry & Technology for Chemical Industry of Ministry of Education, School of Chemistry and Chemical Engineering, Shaanxi University of Science & Technology, Xi'an 710021, People's Republic China
Correspondence to: Q. Luo (E-mail: 18049660655@163.com)

ABSTRACT: Crosslinking core-shell emulsions of waterborne fluorinated polyurethane-acrylate (WFPUA) were successfully synthesized using a solvent-free method. The crosslinkers of diacetone acrylamide and adipic dihydrazide were introduced into the WFPUA emulsions. The physical properties of hybrid emulsions such as the average particle size, stability, and viscosity were characterized. The core-shell of crosslinking WFPUA emulsion synthesized in this study was observed by transmission electron microscopy. Then, the results of Fourier transform infrared spectroscopy, atomic force microscopy, and X-ray photoelectron spectroscopy indicated that the fluorinated monomer (FA) had been polymerized into the crosslinking waterborne polyurethane-acrylate polymer, and the fluorinated groups have evident enrichment on the film-air surface with the increase of FA content. At the same time, the thermal properties, water repellent/antifouling properties, and mechanical properties were measured. Moreover, the thermal properties and the elongation are raised but tensile stress and shore hardness are decreased with the increase of FA content. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2014, 131, 40970.

KEYWORDS: crosslinking; emulsion polymerization; functionalization of polymers; polyurethanes; properties and characterization

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INTRODUCTION

Waterborne polyurethane-acrylate (WPUA) has the advantages of both polyurethane (PU) and polyacrylate (PA) that has been widely developed mainly because of its good processability, such as excellent mechanical properties and environment friendliness. In recent years, classic applications of these materials contain wood finishes, textiles, adhesives, coatings, metals, and leather finishing.^{1–5} However, WPUA has the drawbacks of weak water-resistance, relatively low mechanical and limited outdoor durability which be compared with solvent-based polyurethane-acrylate.⁶

Fluorinated polyurethane-acrylate is a new class of functional materials. It has many practical and desirable features such as unique properties and high resistance (to acids, bases, and solvents) and weather attack, owing to the polarizability and electronegativity of the fluorinated atoms. Fluorinated polyurethane-acrylate combines some virtues of PU, PA, and fluorinated polymers, such as high thermal stability, active surface performance, and good water-resistance.^{7–13} However, the main drawbacks are the relatively high cost of fluorinated monomers (FAs), which are not stable in systems and also lead to long curing time. Therefore, the content of FAs should be

minimized while maintaining famous surface tension (water/oil).

Compared with the traditional waterborne emulsions, the technology of one component crosslinking waterborne emulsions based on the ambient temperature has many characteristics, such as energy conservation, environmental protection, and low price. Various crosslinking systems and mechanisms including crosslinking of acetyl acetoxy group/polyamine, *N*-methylol acrylamide and its derivatives, and epoxy groups, siloxanes,¹⁴ hydrazine or ketone groups, and auto-oxidation of unsaturated fatty acids. It is known that ketone or hydrazine groups are stable in aqueous phase and easy to control because it is affected by pH at ambient temperature.¹⁵ In this study, crosslinking can provide materials with fast curing time and ensure that fluorinated polymer can work better in only low content of FA.

In our research, a series of crosslinking (based on ketone or hydrazine groups) waterborne fluorinated polyurethane-acrylate (WFPUA) emulsions were prepared via soapless emulsion polymerization without the necessity of a heat treatment. Meanwhile, the performances of the films with and without the FA were compared with each other.

EXPERIMENTAL

Materials and Reagents

Isophorone isocyanate (IPDI) and polyester polyol (PCL1000) were purchased from Shengfang Chemical Reagent (Guangdong, China); dibutyltin dilaurate (DBTDL) was from Tianjin damao Chemical Reagent Factory (Tianjin, China); butanediol and 2,2-dimethylol propionic acid (DMPA) was from Kelong Chemical Reagent (Sichuan, China); 1H,1H,2H,2H-perfluorooctyl acrylate (FA) was purchased from Harbin Xeogia Group (Harbin, China); butyl acrylate and methyl methacrylate were from Tianjin Chemical Reagent (Tianjin, China); trimethylolpropane and 2-hydroxyethyl acrylate (HEA) were from Beijing Chemical Reagent (Beijing, China); triethylamine (TEA) and potassium persulfate (KPS) was purchased from Tianjin Hongyan Chemical Reagent (Tianjin, China); diacetone acrylamide (DAAM) and adipic dihydrazide (ADH) were from Jinan Taihua Chemical Reagent (Shangdong, China). All chemicals were from analytical pure and used as received without further purification except PCL1000. It was dried at 120°C under vacuum for 4 h until no bubbling was observed. Deionized water was used for whole experiments.

Preparation of Crosslinking WPUA and its Films

Preparation of Crosslinking WPUA. A series of crosslinking WPUA emulsion were synthesized using a solvent-free method.

A mixture of core monomers solution consisting of IPDI, PCL1000, DMPA, and chain extender (butanediol) in the vinyl monomer system was placed in a four-neck, round-bottom flask (500 mL) fitted with a thermometer, a mechanical stirrer (150 rpm), a reflux condenser, and nitrogen gas inlet. After adding the catalyst (DBTDL, 0.03 wt % based on the total reaction mass), and the content was stirred for 1.5 h at 80°C. A certain amount of the branching unit (trimethylolpropane) was added to the prepolymer at 80°C for another 1 h, so that the NCO-terminated polyurethane (NCO-PU) prepolymer including network structure was obtained. Then, grafting of HEA to the NCO-PU, and the reaction mixture was allowed to react at 80°C for 1 h. In this procedure, 1,4-benzoquinone (500 ppm based on the mass of total monomers) was added as a inhibitor to stop the vinyl monomers from polymerizing by high temperature in the system. Then, the HEA-terminated polyurethane (HEA-PU) was obtained and cooled to 40°C with the moderating stirring. TEA, as a neutralization agent, was then dropped slowly into the flask to neutralize the carboxyl group while maintain the aforementioned temperature. After 30 min neutralization, deionized water was used to emulsify the reaction mixture with vigorous stirring (3000 rpm). The crosslinker of DAAM was added to the dispersion and a water/radical initiator (KPS, 2.5 wt % based on the acrylate-content) was added to the emulsion subsequently. The radical polymerization of acrylate groups (vinyl group) was performed by heating the mixture to 80°C and maintaining the temperature 4 h. The resulting products were stable dispersion with a solid content 30%. The whole synthetic route was depicted in Figure 1. The proportion of FA monomer was range from 0.0% to 9.2%.

Preparation of Crosslinking WPUA and WPUA Films.

WPUA and WPUA films were prepared by pouring the newly emulsions into clean poly(tetrafluoroethylene) molds at room

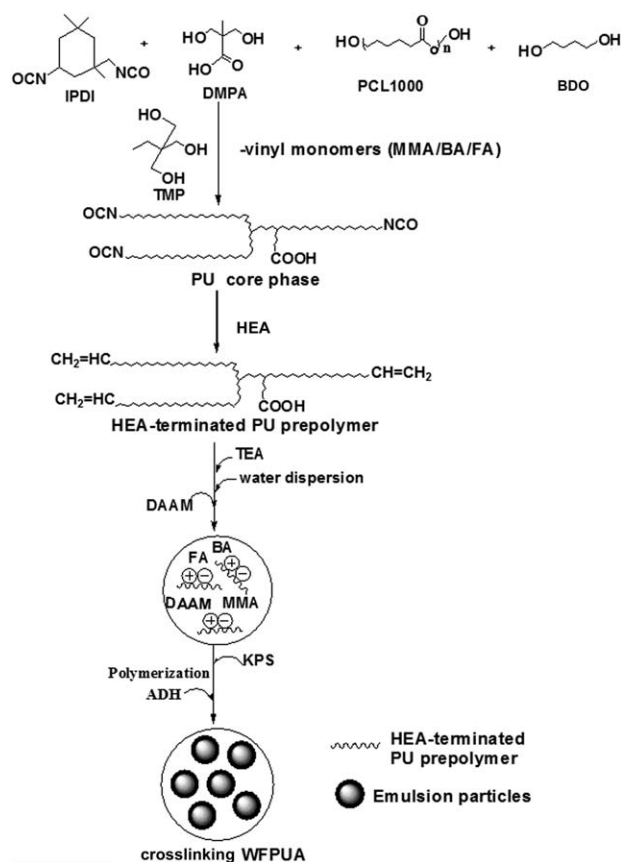


Figure 1. Synthesis process of crosslinking WPUA hybrid emulsion.

temperature for 3 days. The films were then vacuum dried by gradient heating process (increment rate of temperature was 10°C per 2 h) and were finally kept in an oven at 70°C for 5 h. Then, the films were stored in a desiccator under ambient conditions. The thickness of the film was about 0.4 mm.

Characterization

Measurements of Crosslinking WPUA or WPUA Physics Structure. The average particle size was measured using Nano-ZS particle sizer (Malvern Instruments Company, United Kingdom) at 25°C after the samples were diluted with deionized water.

The viscosity of the crosslinking WPUA and WPUA copolymer emulsions was recorded by DV-3+pro digital viscometer (Shanghai Nirun Scientific Company, China). The measurements were obtained at 25°C and under 100 rpm.

Transmission electron microscopy (TEM) micrographs of the WPUA particles were observed through H-600 TEM (Hitachi Company, Japan) with an acceleration voltage of 200 kV.

Measurements of Crosslinking WPUA or WPUA Chemical Structure. The chemical components of the crosslinking WPUA and WPUA latex films were confirmed by VETOR-2 Fourier transform infrared spectrometer (Bruker company, Germany) in the range from 4000 cm^{-1} to 600 cm^{-1} using attenuated total reflectance (ATR) (ZnSe crystal) apparatus.

Surface analysis was examined by X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). XPS survey

Table I. Sample, Composition, Viscosity, Particle Size, and Stability of Crosslinking WPUA and WFPUA

Sample	IPDI/PCL1000/DMPA/ BDO/TMP (Molar ratio)	w (FA) (wt %)	DAAM : ADH	Viscosity (cP/25°C)	Inherent viscosity (dL/g)	Average particle size (nm)	Stability
WPUA-1	1.1/0.3/0.4/0.2/0.06	0.0	1 : 1	33.4	0.98	36.3	Stable
WFPUA-2	1.1/0.3/0.4/0.2/0.06	1.8	1 : 1	32.7	0.98	50.5	Stable
WFPUA-3	1.1/0.3/0.4/0.2/0.06	4.6	1 : 1	29.1	0.97	74.2	Stable
WFPUA-4	1.1/0.3/0.4/0.2/0.06	7.4	1 : 1	28.7	0.97	95.6	Stable
WFPUA-5	1.1/0.3/0.4/0.2/0.06	9.2	1 : 1	23.1	0.97	102.8	Stable
WFPUA-6	1.1/0.3/0.4/0.2/0.06	12.0	1 : 1	-	-	-	Unstable

spectra were confirmed by AXIS ULTRA X-ray photoelectron spectrometer (Kratos Analytical, United Kingdom) using a ALKa achromatic X-ray source and a spot size $100 \times 100 \mu\text{m}^2$. The compositions of film-air surface were measured. AFM was determined by a SPA-400 AFM (Seiko Instruments, Japan). Images were acquired under room temperature.

Measurements of Crosslinking WPUA or WFPUA Properties.

The contact angles of water and methylene iodide were measured using a JJC-I contact angle goniometer (Changchun Optical Instrument Company, China) at 25°C and the reported were the mean of three replicates. The contact angle which can be used to calculate the surface free energy of the solid film through the following equation¹⁶:

$$\gamma = \gamma_d + \gamma_p \quad (1)$$

$$(1 + \cos\theta_{\text{liquid}})\gamma_{\text{liquid}} = 2(\gamma_{\text{liquid}}^d \gamma^d)^{1/2} + 2(\gamma_{\text{liquid}}^p \gamma^p)^{1/2} \quad (2)$$

where $\gamma_{\text{liquid}} = \gamma_{\text{liquid}}^d + \gamma_{\text{liquid}}^p$, γ was surface energy of solid film, γ_d was the emulsion component, and γ_{liquid}^p was the polarity component, θ_{liquid} was contact angle of the latex film with water or methylene iodide and $\gamma_{\text{H}_2\text{O}}^d = 22.1 \text{ mJ/m}^2$, $\gamma_{\text{H}_2\text{O}}^p = 50.7 \text{ mJ/m}^2$, $\gamma_{\text{CH}_2\text{I}_2}^d = 44.3 \text{ mJ/m}^2$, $\gamma_{\text{CH}_2\text{I}_2}^p = 6.50 \text{ mJ/m}^2$.

The water absorption (W_a) was expressed as the weight percentage of water in the swollen film samples. The latex films were cut into $20 \times 20 \text{ mm}^2$ and immersed in deionized water for 24 h under ambient condition. The formula of W_a as follows:

$$W_a(\%) = (M_1 - M_0) / M_0 \times 100 \quad (3)$$

where M_0 was the weight of film sample and M_1 was the swollen film sample in water.

Thermogravimetry analysis (TGA) of the crosslinking WPUA or WFPUA was performed on a Q500 thermogravimeter (TA Instruments Company). The heating range from 25°C to 600°C at a heating rate of 10°C/min under the nitrogen atmosphere.

The tensile properties were recorded under ambient temperature using a tensile tester (KY-8000A, Jiangdu Kaiyuan Test Machine) at a speed of 50 mm/min to determine the final tensile strength as well as the elongation at break. The quoted measurements had an average of three runs.

The hardness was recorded using a SDI-TH200 shore A type durometer. The quoted values were the average of three measurements.

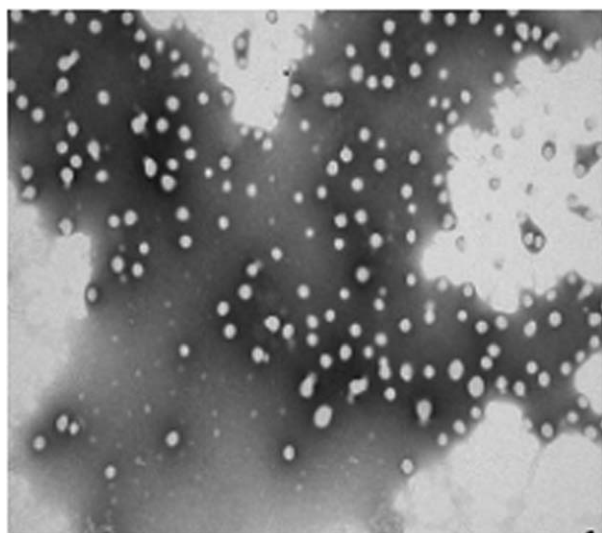
RESULTS AND DISCUSSION

Average Particle Size, Viscosity, and Morphology of the WPUA/WFPUA Hybrid Emulsions

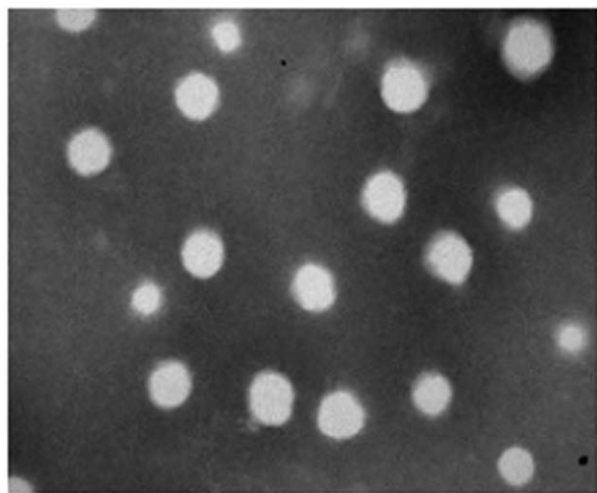
The physical properties of hybrid emulsions, including the average particle size, stability, and viscosity were listed in Table I. With the increase of the FA, the average particle size of the dispersions increased, such as the average particle size are increased from 36.3 nm to 102.8 nm with the increase of FA content in the range of 0%–9.2%. The result may be ascribed to the improvement of the hydrophobic FA monomer, which will increase the length of the polymer and lead to the relatively higher hydrophobic units in the hybrid emulsion. Besides, with FA content increased to 12% in the hybrid emulsion was beyond the self-emulsifying ability at the hydrophilic monomer (DMPA) content (5 wt %) in the crosslinking WFPUA prepared in the study. These reasons will cause the bigger average particle sizes and the unstable existence as a result of the increase of FA monomer.

The viscosity of crosslinking WFPUA is decreased with the increasing content of FA.¹⁷ Generally, the bigger the particle sizes, the less stretched the molecular chains, the less the surface areas, and the less the charges. At this time, the hydration shell on the surface areas becomes thinner, and the continuous phase in the middle of particles is increased, thus the work of latex particles is decreased along with motion of the latex particles in the hybrid emulsion. On the contrary, the smaller particle sizes, the more work among them in the system. Therefore, the lower viscosity of the hybrid emulsion was recorded along with the higher particle size. The inherent viscosities of WFPUA in this study were in the range of 0.98–0.97 dL/g. These values were used for indicating the information of polymers with relatively high molecular weight.

The morphology of crosslinking WFPUA containing 9.2 wt % of FA hybrid sample synthesized in this study was observed by TEM in Figure 2(a) (magnification: 50,000) and Figure 2(b) (magnification: 200,000). The magnification of Figure 2(a) shows the relatively good dispersing and regularity of the particle sizes. Besides, from the magnification of Figure 2(b) was observed obviously core-shell structure of the latex particles because of the difference of electron transmission to the core phase and shell phase.¹⁸ Therefore, the crosslinking core-shell WFPUA was successfully synthesized.



(a)



(b)

Figure 2. TEM photograph of crosslinking WFPUA-5 latexes (a) magnification: 30,000 and (b) magnification: 200,000.

FT-IR Spectra of WPUA and WFPUA Films

Figure 3 displayed Fourier transform infrared spectroscopy (FT-IR) spectra of (a) WPUA film, (b) WFPUA film, (c) DAAM contained WFPUA film, and (d) crosslinking WFPUA film. All FT-IR spectra exhibit the characteristic stretching peaks of N—H ($\nu_{\text{N-H}}$) at 3200–3400 cm^{-1} , stretching peaks of C—H (CH_2) at 2860–2950 cm^{-1} , stretching vibration of C=O (amide I, $\nu_{\text{C=O}}$) at 1724 cm^{-1} , the bands of (amide II, δ N—H and $\nu_{\text{C-H}}$) at 1535 cm^{-1} which confirmed the carbonyl group of urethane.¹⁹ Moreover, in these four spectra the characteristic absorption band of isocyanate group disappeared at 2270 cm^{-1} indicated that the —NCO groups had reacted completely.

Compared with the Figure 3(a), the characteristic absorption band in Figure 3(b) changed. The stretching vibration of CF_2 group and CF_3 group were overlapped the ester carbonyl (O—C—O) at 1150 cm^{-1} but the rocking and wagging vibrations of the CF_3 group at 660 and 702 cm^{-1} in the fingerprint

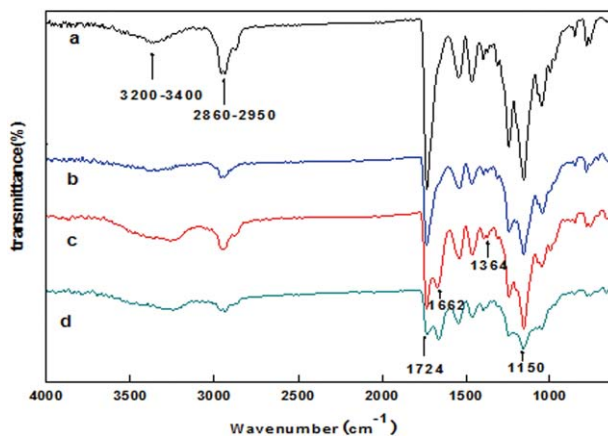


Figure 3. FT-IR spectrum of (a) WPUA film, (b) WFPUA film, (c) DAAM contained WFPUA film, and (d) crosslinking WFPUA film. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

region can indicate the fluorinated groups were be reacted in the system. In comparison with the FT-IR spectrum of (b), the appearance of the stretching vibrations of C—N groups at 1362 cm^{-1} and keto group (—C=O) at 1710 cm^{-1} in FT-IR spectrum of (c) which can manifest DAAM maybe polymerized in hybrid film. Compared with Figure 3(c), the disappearance of 1710 cm^{-1} (—C=O), 3314 cm^{-1} (N—H) and the enhancement of 1662 cm^{-1} (C—N) confirmed the crosslinking reaction between DAAM and ADH in the Figure 3(d).²⁰

Surface Analysis of the Crosslinking WPUA and WFPUA Hybrid Films

The XPS and AFM survey spectra of the WPUA and WFPUA hybrid films are used to indicate the film-air interface chemical composition and morphologies. As shown in Table II and Figure 4, the change of the molar ratio of FA will surely influence the distribution of elements in hybrid films. Along with the increase of the ratio, the peak intensity of F1s in samples will be increased from 1.98% to 26.17%. Besides, the element F1s content of hybrid films on the air-film interface were eight times than the theoretical content in the average hybrid films. When the FA monomer was increased to 9.2%, the increasing times can reach to 22 times. The results demonstrate that the fluorine content presented obviously aggregation of fluorine element on the film-air interface, and with the improvement of FA content, the increasing times of the F1s element on the air-film interface will be bigger.^{17,19}

Table II. Element Content of the Crosslinking WPUA and WFPUA Hybrid Films on the Air-Film Surface

Element (%)	Sample designation		
	WPUA-2	WFPUA-3	WFPUA-5
F1s	1.98	4.67	26.17
C1s	92.90	86.71	56.77
O1s	4.68	2.99	12.91
N1s	0.44	5.63	4.15

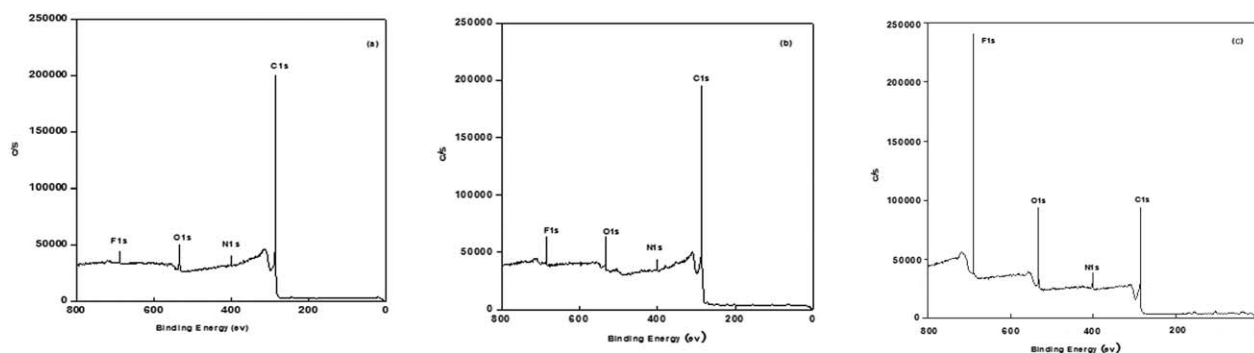


Figure 4. XPS spectra of (a) surface of crosslinking WPUA-2, (b) surface of WPUA-3, and (c) surface of WPUA-5.

The surface morphologies of the WPUA and WPUA hybrid films are showed in Figure 5. The two-dimensional images (2D) were on the left and the three images (3D) were on the right. Some important parameters such as roughness average (R_a), root-mean-square, maximum peak height (R_p), roughness factor ($R = 1 + Sdr$), and 10 point height (R_z) were recorded from AFM software analysis in Table III.

The roughness is influenced greatly by the amount of FA. With the increase of the FA content, the roughness was also increased obviously (Figure 3). It was clearly shown in Table III that almost parameters potential highly was augmented from WPUA-1 to WPUA-5. For example, roughness averages (R_a) are increased from 2.98 to 9.32 nm with an increase in FA content in the range of 0–9.2%. The surface morphologies of the hybrid films were varied from smooth states to roughness ones. The reason maybe that the fluorinated group presented obvious enrichment on the air-film surface with the increasing of the FA content.²¹ The result of the AFM is in accordance with the analysis of the XPS.

DSC and TG Analysis

The thermal properties of fluorinated copolymer materials are the important factor to measure the application. Thus, thermal properties of the sample films with different content of FA were measured by differential scanning calorimetry (DSC) and TGA. Figure 6 shows the DSC scan curves of crosslinking WPUA and WPUA. Figure 6 shows that the sample films had two glass transition temperatures T_g (soft segments T_{gs} and hard segments T_{gh}). Generally, the T_{gs} and T_{gh} were influenced by chemical composition, phase mixing/separation and the molecular weight of PU and PA. Moreover, with increasing FA content, the T_{gs} was enhanced from 29.50°C to 34.97°C, the T_{gh} shifted from 96.21°C to 94.58°C. These results suggested that the interaction between FA monomers and the soft segments are elevated due to hydrogen bonding effect, so the T_{gs} was raised with the augment of FA monomers. However, the introduction of FA monomers had almost no effect on the hard segment, which lead to the little change of T_{gh} .

The thermogravimetric curves of crosslinking WPUA and WPUA sample films were displayed in Figure 7. The TGA results showed that the thermal stability of the hybrid films were gradually elevated with the fluorinated content of the sam-

ple films increased, but the increase was not obvious at the beginning of the decomposition of the hybrid films. At the same time, as the decomposition was processed, the thermal stability of the hybrid films was more and more apparent. It can be explained that the early stage decomposition occurred mainly in the hard segments where FA had little effect, and then the degradation occurred in the soft segments where the $-\text{CF}_2$ and $-\text{CF}_3$ with high bond energy of the FA monomers can restrain the hybrid films decomposition, and therefore enhance thermal stability of the hybrid films.^{22,23}

Water Repellent/Antifouling Property of Crosslinking WPUA and WPUA

The high contact angles/low surface free energy as important criteria were used to measure water repellent/antifouling in this study. The water/methylene iodide contact angles, surface free energies, and water absorption of the crosslinking WPUA and WPUA hybrid films was displayed in Figure 8 and Table IV, respectively. The water/methylene iodide contact angles were increased to some extent as the FA content was raised in the crosslinking WPUA hybrid films. For example, the water contact angle and methylene iodide contact angle have been raised to 18.7° and 17.9°, respectively, when the FA content increased from 1.8% to 9.2%. Meanwhile, the surface free energies are decreased from 31.76 to 21.89 mJ/m² and the water absorption also reduced from 16.2% to 7.4%, when the FA content increased from 0% to 9.2%. The results demonstrate that there will include more hydrophilic units on the film surface as the FA content increased in the hybrid films. The reasons of the changes should be attributed to the enrichment of fluorinated groups on the hybrid films as well as the increase of FA content.²⁴

Mechanical Properties of the Crosslinking WPUA and WPUA Films

The tensile strength, the elongation at break, and shore hardness of the hybrid films are listed in Table IV. Figure 9 shows the tensile stress-strain curves of the crosslinking WPUA and WPUA. The tensile strength and shore hardness of the hybrid film was decreased with the increasing FA content but the elongation at break of the hybrid film was raised. The phenomena of the decrease in tensile strength but the higher elongation at break might be due to the higher softness and the lower hardness in the hybrid films. It is well known that the PU is made

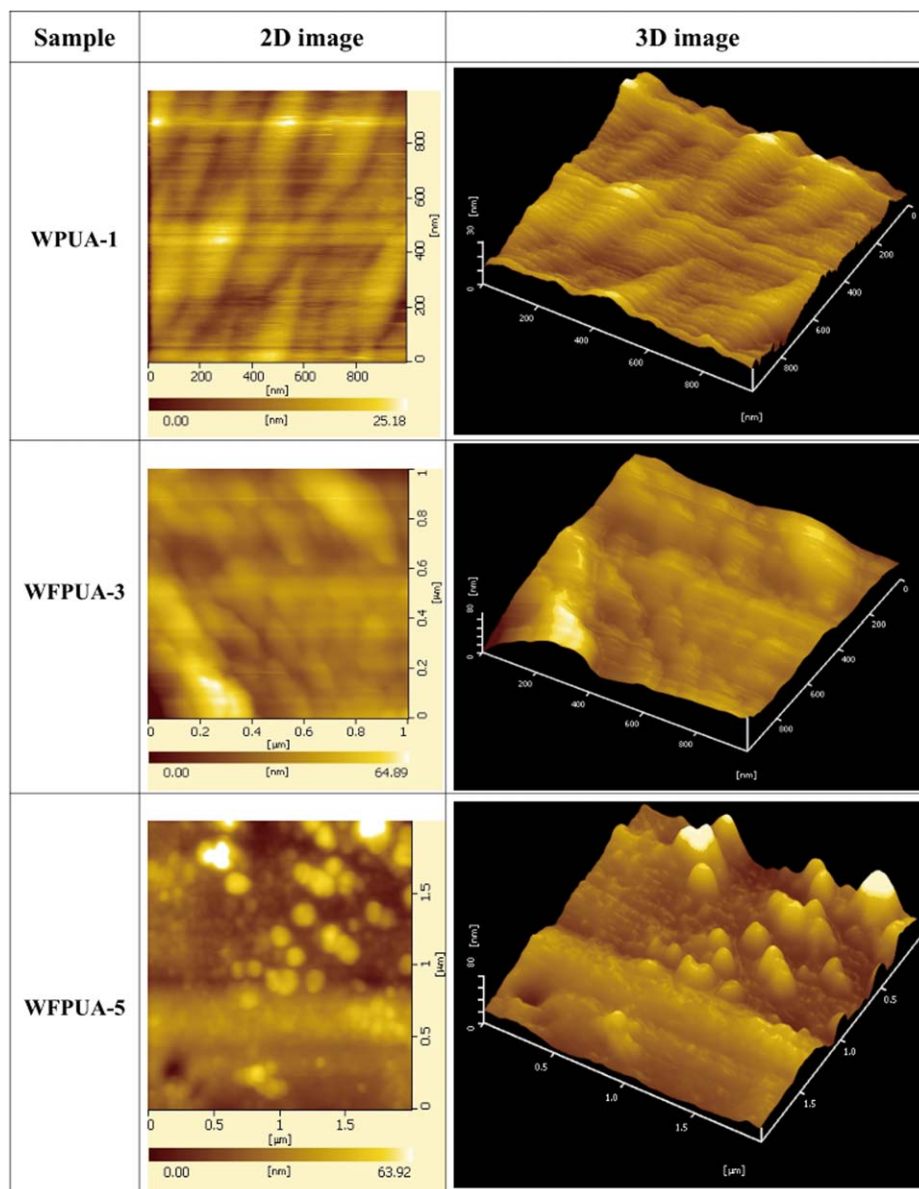


Figure 5. AFM images of polymer films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

up of hard segment and soft segments, and the hard segments mainly influences the strength and the soft segments mainly affects the flexibility of the hybrid films. The raising of FA content leads to the increase of soft segments, so that the tensile strength was decreased and the elongation at break was increased. Meanwhile, as to the no evident changes of hardness,

Table III. The Various Roughness Parameters for Crosslinking WPUA and WFPUA Films of Figure 5

Factors	Ra (nm)	RMS (nm)	Rz (nm)	Rp (nm)	R
WPUA-1	2.98	9.45	39.73	30.68	1.02
WFPUA-3	7.21	9.77	40.28	66.36	1.03
WFPUA-5	9.32	11.86	56.93	80.5	1.05

the shore hardness of the decrease of hybrid films are also unapparent.²⁵ The changes of the hybrid films were coincident with the results of DSC.

CONCLUSIONS

A series of crosslinking WFPUA dispersions were synthesized using a solvent-free method and the properties were confirmed by all characterization methods. The physical properties of hybrid emulsions which indicated that with the raising of FA content, the particle and viscosity also increased but the emulsion became unstable. Then, the core-shell of crosslinking WFPUA emulsion synthesized in this study was observed. FT-IR, AFM, and XPS indicated that FA had been polymerized into the crosslinking WPUA polymer and the fluorinated groups have evident enrichment on the film-air surface with the

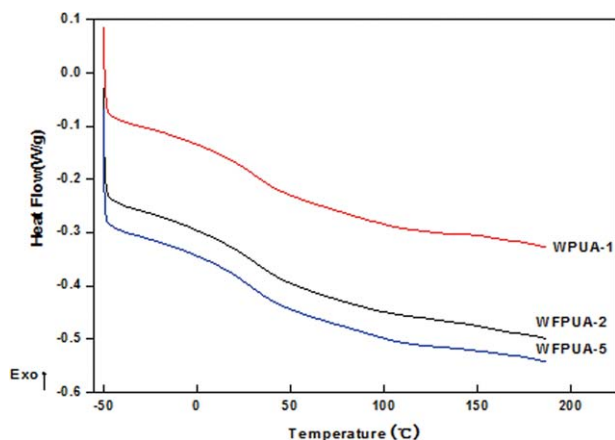


Figure 6. DSC curves of crosslinking WPUA and WPUA films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

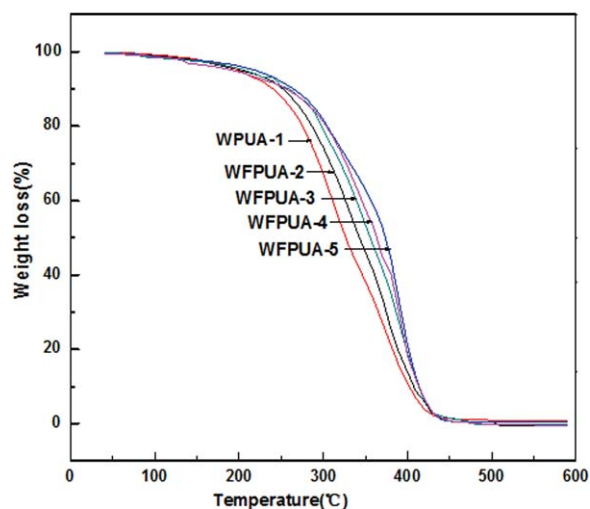


Figure 7. TGA curves of crosslinking WPUA and WPUA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

increase of FA content. When the content of the FA in the crosslinking WPUA is increased from 0% to 9.2%, the water contact angle and methylene iodide contact angle have been

Table IV. Mechanical Properties and Shore Hardness of Crosslinking WPUA and WPUA Hybrid Films

Sample	Mechanical properties			Shore hardness
	Tensile stress (MPa)	Elongation at break (%)	Water absorption (%)	
WPUA-1	27.49	270.9	16.2	93
WFPUA-2	26.51	330.3	12.1	91
WFPUA-3	23.31	364.9	9.6	88
WFPUA-4	14.64	395.0	8.5	86
WFPUA-5	10.49	410.5	7.4	85

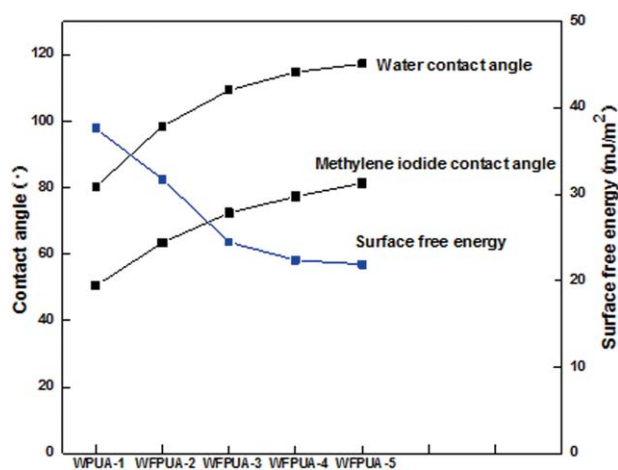


Figure 8. Water/methylene iodide contact angles and surface free energies of crosslinking WPUA and WPUA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

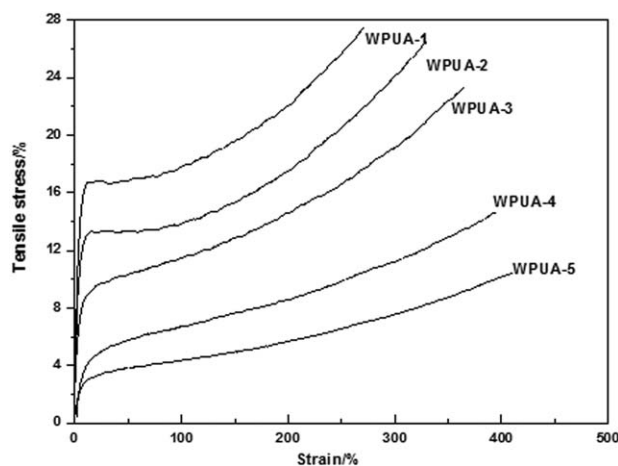


Figure 9. Strain-stress curves of crosslinking WPUA and WPUA hybrid films.

raised to 36.8° and 30.9°, respectively. Meanwhile, the surface free energies are decreased from 37.61 to 21.89 mJ/m² and the water absorption also is reduced from 16.2% to 7.4%. At the same time, the thermal properties and the elongation are raised but tensile stress and shore hardness are decreased with the increase of FA content. Moreover, the glass transition temperature of the T_{gs} and T_{gh} of the hybrid films is increased and slightly reduced, respectively. In summary, the results indicated as the FA content was 9.2%, the film exhibited the best mechanical properties, thermal properties, and water repellent/antifouling properties.

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