Preparation, Mechanical Properties of Waterborne Polyurethane and Crosslinked Polyurethane-Acrylate Composite

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ABSTRACT: The waterborne polyurethane (PU) prepolymer was first prepared based on isophorone diisocyanate, polyether polyol (NJ-210), dimethylol propionic acid (DMPA), and hydroxyethyl methyl acrylate via *in situ* method. The crosslinked waterborne polyurethane-acrylate (PUA) dispersions were prepared with the different functional crosslinkers. The chemical structures, optical transparency, and thermal properties of PU and PUA were confirmed by Fourier transform infrared spectrometry, ultraviolet–visible spectrophotometry, and differential scanning calorimetry. Some physical properties of the aqueous dispersions such as viscosity, particle size, and surface tension were measured. Some mechanical performances and solvent resistance of PUA films were systemically investigated. The experimental results showed that the particle sizes of the crosslinked PUA aqueous dispersions were larger than the PU and increased from 57.3 to 254.4 nm. When the ratios of BA/St, BA/TPGDA, and BA/TMPTA were 70/30, PUA films exhibited excellent comprehensive mechanical properties. The tensile strength and elongation at break of the film were 2.17 MPa and 197.19%. When the ratio of BA/St was 30/70, the film had excellent water resistance and was only 6.47%. The obtained PUA composites have great potential application such as coatings, leather finishing, adhesives, sealants, plastic coatings, and wood finishes. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 958–968, 2012

Key words: polyurethane; polyurethane-acrylate; mechanical property; thermal property

INTRODUCTION

In the last decade, interest in waterborne polyurethane (PU) dispersions has increased because they are environment-friendly materials.[1–5] The unique advantage of PU in relation to surface coatings is their ability to form coherent film and to control the microphase morphology by controlling the relative amounts of soft and hard segments in polymer chain. These features allow PU to be employed in a wide variety of surface coating applications, where mechanical properties are particularly crucial. However, PU suffers from poor water and weather resistance because of the hydrophilic group such as carboxyl group in their molecule chains. Acrylic polymer emulsions (PA) show excellent properties in terms of hardness, weather resistance ability, chemical resistance, and gloss. But, the elasticity and abrasion resistance of acrylic polymer emulsions are inferior to those PU dispersions. In an attempt to overcome these, it is a common practice to combine PU dispersions with PA to be effective to increase the performances of the resulting materials.[6]

Keyvani[7] reported that the waterborne PU modified with acrylic resin had the lowering of cost and the improvements of water resistance, chemical resistance, gloss, hardness, and mechanical properties. So, for the requirements of environmental protection and reducing cost, the polyurethane-acrylate (PUA) hybrid emulsion has been paid more attention as a type of environment-friendly material. It will take the place of the organic solvent-type PU materials in coating, print, ink, and adhesive industries.[8,9] Chai et al.[10] prepared the core-shell composite emulsions with a two component acrylic system of methyl acrylate (MA) and butyl acrylate (BA), and crosslinked PUA with a three component acrylic system of MA, BA, and glycidyl methacrylate using aqueous PU dispersion as seed particles. Lee et al.[11] synthesized a series of latex particles with interpenetrating polymer networks from waterborne PU and polystyrene.

Peruzzo et al.[12] prepared PU/acrylate with different acrylic contents (10, 30, 50, 70, and 90 wt %) by the polymerization of acrylic monomers in the presence of preformed PU chains with polymerizable terminal vinyl groups. Ibarboure et al.[13] reported the preparation and the self-assembly of branch-block PUs with soft poly(n-butyl acrylate) side chains and rigid PCL segments in the main chain. Synthesis and characterization of PU/acrylate hybrid lattices have been discussed in many technical articles.[14–16]

This article reports on the preparation of PU and PUA polymers with BA and different crosslinkers of acrylates. The effects of NCO/OH value and DMPA content on appearances and performance of PU were investigated. The synthesized PU and PUA were characterized using Fourier transform infrared spectrometry (FT-IR), ultraviolet–visible spectrophotometry (UV–vis), and differential scanning calorimetry (DSC) methods. Other properties of PU and PUA films, such as tensile strength, hardness, and water resistance values were also determined.

EXPERIMENTAL

Materials

Polyether polyol (NJ-210, $Mn = 1120$ g/mol) was produced by Ningwu Chemical Co., Jurong, Jiangsu, China; dimethylol propionic acid (DMPA) was produced by PERSTOP Co., Helsingborg, Sweden; isophorone diisocyanate (IPDI) was supplied by Rongrong Chemical Co., Shanghai, China; hydroxyethyl methyl acrylate (HEMA) was provided by Yinlian Chemical Co., Wuxi, Jiangsu, China; styrene (St), BA, triethylamine (TEA), ethylenediamine (EDA), N-methyl-2-pyrrolidone (NMP), acetone, dibutylbis (lauroyloxy) tin (DBLT), and azobisisobutyronitrile (AIBN) were obtained from Sinopharm Chemical Reagent Co., Shanghai, China. Tripropyleneglycol diacrylate (TPGDA) and trimethylolpropane triacrylate (TMPTA) were supplied from Mingda Macromolecule Science and Technology Co., Suzhou, Jiangsu, China.

Preparation of PU dispersion

A certain amount of polyether polyol (NJ-210) and IPDI were added into a four-necked flask equipped with a mechanical stirrer, thermometer, and reflux condenser. Then, DBLT was added as catalyst and the mixture was heated to 60°C, and keeping the temperature for 2 h to prepare the —NCO terminated prepolymer. Next, the above prepolymer was reacted with a certain amount of DMPA dissolved in small amount of NMP at 80–85°C for another 2 h, and the —NCO terminated prepolymer containing carboxyl group was obtained. The obtained —NCO

TABLE I
The Recipe of PU Dispersion

Sample	NCO/OH (R)	DMPA (%)	NJ-210 (g)	IPDI (g)
PU-1	1.4/1	6	22.26	11.10
PU-2	1.6/1	6	19.00	11.10
PU-3	1.8/1	6	16.46	11.10
PU-4	2.0/1	4	13.81	11.10
PU-5	2.0/1	6	14.40	11.10
PU-6	2.0/1	8	24.08	11.10

terminated prepolymer was neutralized by adding TEA at 40°C for about 45 min. Then, a certain amount of the deionized water was poured into the system at the same temperature. Finally, EDA is added as a chain extender into the system. By stirring for 45 min, the waterborne PU dispersion was obtained. The basic recipe is listed in Table I.

Preparation of crosslinked PUA composite dispersion

A certain amount of NJ-210 (10.802 g) and IPDI (8.325 g) were added into a four-necked flask equipped with a mechanical stirrer, thermometer, and reflux condenser. Then, DBLT was added and the mixture was heated to 60°C for 2 h. Next, the above reactants were reacted with a certain amount of DMPA (1.148 g) dissolved in small amount of NMP at 80–85°C for another 2 h. Then, HEMA was added into the system and reacted at 60°C for 5 h. When the temperature was cooled down to 40°C, TEA was added subsequently and reacted for 30 min. After neutralization, a mixture of calculated functional crosslinkers BA and styrene (St), or BA and TPGDA, or BA and TMPTA were added into the prepolymer. The mixture was then dispersed into deionized water under vigorous stirring. AIBN as initiator was added into the dispersion subsequently at 60°C for 4 h. The synthetic route of PUA dispersion is shown in Figure 1. The basic recipes are given in Table II.

Preparation of films

Films were prepared by casting the newly synthesized samples onto a poly(tetrafluoroethylene) at room temperature for 2 days, followed by drying at 80°C for 3 h. This trend of drying is just for slow drying. It is also possible to evaporate the solvent at a fixed temperature, either room or elevated temperature. After demolding, the films were stored in a desiccator at room temperature for further studies.

The solid mass fraction of PU or PUA

PU or PUA dispersion was placed in a 25-mL vessel, keeping in a temperature-controlled oven at 120°C
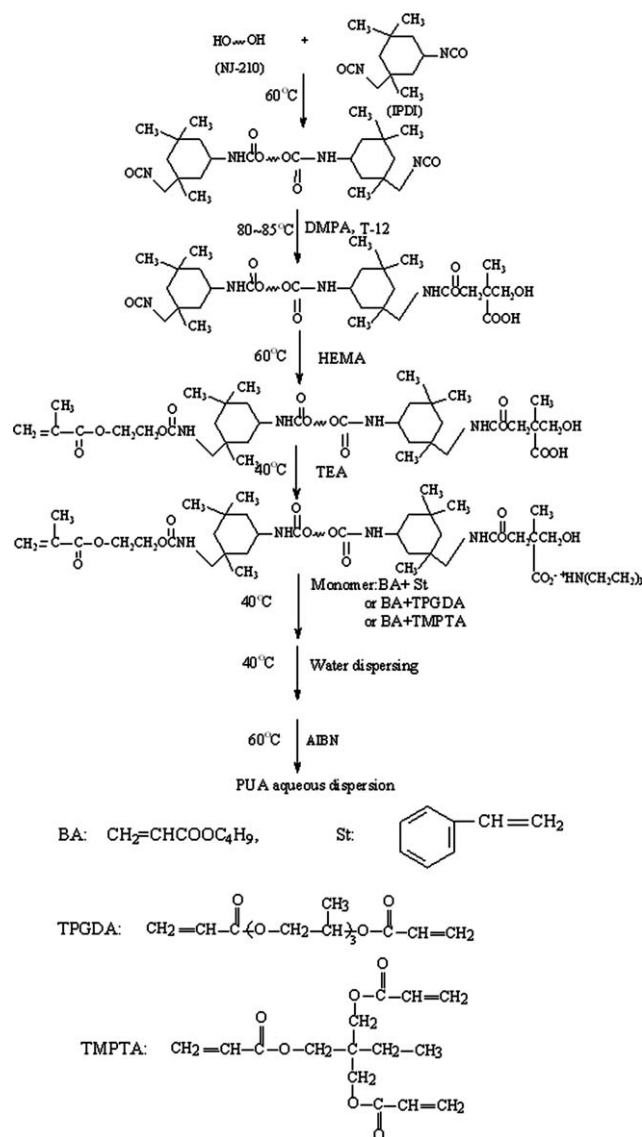
Figure 1 The synthetic route of WPUA dispersion.

after being weighted. Forty-eight hours later, the vessel was taken out, cooled down in desiccators, and then weighed again. When the mass difference

was not above 0.0002 g, the solid mass fraction of PU or PUA dispersion can be calculated by eq. (1):

$$\omega = \frac{W_2}{W_1} \times 100\% \qquad (1)$$

where ω is the solid mass fraction of PU or PUA emulsion, W_1 is the mass of PU or PUA and vessel before being put into the oven, W_2 is the mass of PU or PUA and vessel after being put into the oven.

The apparent viscosity of PU and PUA

The apparent viscosity of PU or PUA aqueous dispersion was measured by a numerical viscometer (NDJ-9S, Shanghai Precision and Scientific Instrument Co., Shanghai, China); when the shear rate was 2000 s^{-1}, the high shear rate warranted highly reliable measurements at a temperature of 25°C.

The particle size and polydispersity of PU and PUA

Particle size is the important parameter in deciding the end use industrial applications of aqueous PU dispersions. PU or PUA samples were added to 100-mL test tubes and diluted with deionized water. The particle diameter and polydispersity were measured by a laser particle size analyzer (BIC-9010, Brookhaven Instrument Co., Holtsville, NY).

The high temperature stability of PU and PUA composite emulsion

PU or PUA composite emulsion was diluted with deionized water until the solid mass fraction was 20%, keeping in a constant temperature oven at 60°C for 24 h. The appearance changes and high temperature stability of the emulsion were observed and recorded.

TABLE II
The Recipes for PUA Series Composite Emulsion

Sample	BA/St	BA(g)	St(g)	BA/TPGDA	TPGDA(g)	BA/TMPTA	TMPTA (g)
PUA-1-1	90/10	11.350	1.261	–	–	–	–
PUA-1-2	70/30	8.828	3.783	–	–	–	–
PUA-1-3	30/70	3.783	8.828	–	–	–	–
PUA-1-4	10/90	1.261	11.350	–	–	–	–
PUA-2-1	–	11.350	–	90/10	1.261	–	–
PUA-2-2	–	8.828	–	70/30	3.783	–	–
PUA-2-3	–	3.783	–	30/70	8.828	–	–
PUA-2-4	–	1.261	–	10/90	11.350	–	–
PUA-3-1	–	11.350	–	–	–	90/10	1.261
PUA-3-2	–	8.828	–	–	–	70/30	3.783
PUA-3-3	–	3.783	–	–	–	30/70	8.828
PUA-3-4	–	1.261	–	–	–	10/90	11.350

The freeze-thaw stability of PU and PUA composite emulsion

For measuring freeze-thaw stability of the aqueous dispersion, PU or PUA aqueous dispersion was cooled to $-20°C$ for 18 h and kept at ambient temperature for 6 h to observe whether the aqueous dispersion deposited or not. The same operation was repeated for five times.

The surface tension of PU and PUA

Surface tension (σ) is a phenomenon caused by the cohesive forces between liquid molecules. It is an effect within the surface film of a liquid that causes the film to behave like an elastic sheet. Commonly, it is measured in mN/m or mJ/m^2. The knowledge of surface tension is useful for many applications and processes as the surface tension governs the chemical and physical behavior of liquids. It can be used to determine the quality of numerous industrial products such as paints, ink jet products, detergents, cosmetics, pharmaceuticals, lubricants, pesticides, and food products. Also, it has profound effect on some steps in industrial processes such as adsorption, distillation, and extraction. Many methods have been established to measure the surface tension of liquids such as the capillary rise method, drop weight method, du Nouy ring method, Wilhelmy plate method, spinning drop method, pendant drop method, and sessile drop method. The choice of the method depends on the nature and stability of the liquid being measured, the measurement conditions, precision, reliability, and the instrumentation cost. Among these methods, drop weight could be considered as one of the oldest and it is still widely used. This method is popular, because it is inexpensive and the set-up is simple. A typical drop weight apparatus consists of a single dripping tip of known diameter, a liquid delivery system, and a weighing balance. In this article, measurement of surface tension was conducted on a single tube manner setup by maximum air bubble method and is shown in Figure 2.

When the liquid end of the capillary was tangent with sample's liquid end, liquid would go up along the capillary. Piston of tap funnel was opened and water could drop slowly, so that the system pressure was reduced. In this way, liquid surface of capillary got a bigger pressure than that of the cuvette and the pressure difference would be formed. When the pressure, which was the result of the pressure difference acting on capillary surface, was a little larger than the surface tension of capillary nozzle liquid, the air bubble would transgress from capillary nozzle. The maximum pressure maximum was obtained from manometer; the value was expressed by eq. (2):
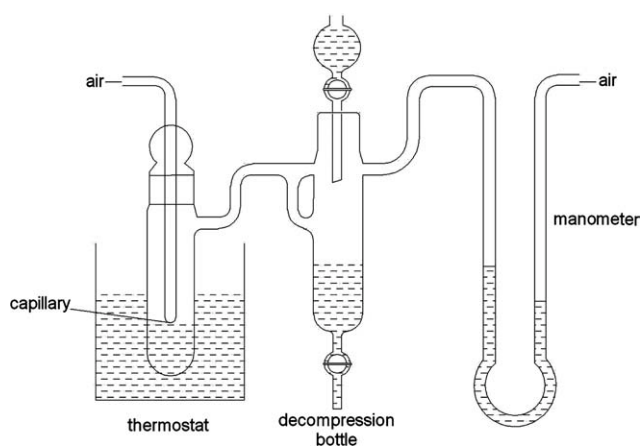

Figure 2 Measurement of surface tension.

$$P_{max} = P_{air} - P_{system} = \Delta P \qquad (2)$$

When the air bubble transgressed from capillary nozzle, all the pressure was $\pi r^2 P_{max}$. The pressure, which was brought by surface tension (σ) of air bubble in capillary, was $2\pi r\sigma_o$. The two pressure values were in equality and described by eq. (3):

$$\pi r^2 P_{max} = \pi r^2 \Delta P = 2\pi r\sigma, \sigma = \frac{r}{2}\Delta P \qquad (3)$$

where r is radius of capillary.

If the same capillary was used, the surface tensions of different liquid were expressed by eq. (4):

$$\frac{\sigma_1}{\sigma_2} = \frac{\Delta P_1}{\Delta P_2} \qquad (4)$$

The surface tension σ of the different liquids could be obtained when the standard substance was measured (e.g., distilled water σ is 72 mN/m).

The tensile strength and elongation at break of PU and PUA composite film

The tensile strength testing and elongation at break testing for all of the specimens were carried out on a tensile tester (KY-8000A, Jiangdu Kaiyuan Test Machine Co., Jiangdu, China) at room temperature, and at a speed of 50 mm/min. All measurements had an average of three runs. The dumbbell-type specimen was 30-mm long at two ends, 0.2-mm thick and 4-mm wide at the neck.

The hardness of PU and PUA composite film

The hardness was measured with a sclerometer (KYLX-A, Jiangdu Kaiyuan Test Machine Co.);

TABLE III
The Effect of R Value on the Properties of PU Samples

Sample	PU-1	PU-2	PU-3	PU-4
R	1.4	1.6	1.8	2.0
Appearance	Semitransparent, slightly yellow	Semitransparent, slightly yellow	Turbid, slightly yellow	Transparent, slightly yellow
Forming film at room temperature	No	No	Yes	Yes

measurements were done three times for each sample, and the average value was calculated.

The water absorption (or swelling degree) of PU and PUA composite film

The water absorption (or swelling degree) values of PU and PUA membranes were obtained as follows. Preweighed dry membranes (30 × 30 mm) were immersed in distilled water and 5% NaOH at 25°C. After 24 h, the membranes were then blotted with filter paper and weighed. The water absorption (or swelling degree) w was calculated as follows:

$$\omega = \frac{m_2 - m_1}{m_1} \times 100\% \qquad (5)$$

where m_1 is the weight of the original dry sample, and m_2 is the weight of the swollen sample.

Structure characterization and optical transparency

FT-IR spectra of PU and PUA samples were obtained between 4000 and 400 cm^{-1} with an FTIR spectrometer (AVATAR 360, Nicolet, Madison, WI). A minimum of 32 scans were signal-averaged with a resolution of 2 cm^{-1} in the 4000–400 cm^{-1} range. UV–vis spectra of PU and PUA samples were recorded with a UV–vis spectrometer (UV2450, Shimadzu, Kyoto, Japan) in the 350- to 800-nm range at 25°C.

Thermal properties

DSC was performed on a Netzsch instrument (204F1, Netzsch, Seligenstadt, Germany). The programmed heating range was from room temperature to 500°C at a heating rate of 10°C/min under a

nitrogen atmosphere. The measurement was taken with 6–10 mg samples. DSC curves were recorded.

RESULTS AND DISCUSSION

The effects of R (NCO/OH) and DMPA on the properties of PU

Fixing the content of DMPA as 6%, a series of PU dispersions and films were prepared by changing the R value. The appearance and film performance are listed in Table III. As shown in Table III, the PU-4 had the best appearance and film-forming ability. In this article, R value was chosen as 2.0.

Fixing the R value as 2.0, a series of PU dispersions and films were prepared by changing the content of DMPA. The appearance and film performance are listed in Table IV. As shown in Table IV, with the increase of DMPA:

1. The particle size of PU dispersion first decreased, and then increased. This was because the content of —COOH in DMPA was increasing, which was hydrophilic and improved the hydrophilicity of PU, so that the particle size of PU will decrease. But, with the content of DMPA increasing, a large chain of hydrophilic PU aggregated and the PU emulsion will become unstable.
2. The PU emulsion viscosity was increasing; this was because the —OH in DMPA was very active and it could accelerate the reaction between the —OH and —NCO.
3. The water absorption of PU film was increasing, which was to say its water resistance was decreasing that was largely affected by the —COOH in DMPA.

TABLE IV
The Effect of DMPA Content on the Properties of Samples

Sample	DMPA (%)	Appearance	Particle size (nm)	Apparent viscosity (Pa s)	Water absorption (%)
PU-4	4	Transparent, slightly yellow	68.2	0.352	36.8
PU-5	6	Transparent, slightly yellow	57.3	0.360	52.6
PU-6	8	Transparent, slightly yellow	79.6	0.375	95.9

TABLE V
The Physical Properties of PU and PUA Dispersions

Sample	PU-5	PUA-1-(1–4)	PUA-2-(1–4)	PUA-3-(1–4)
Solid mass fraction (%)	23.6	20.5	19.5	18.4
		19.8	18.9	21.2
		21.6	20.7	20.3
		18.4	18.2	18.6
Apparent viscosity (Pa s)	0.360	0.184	0.180	0.174
		0.160	0.162	0.163
		0.195	0.182	0.170
		0.176	0.160	0.161
Particle size (nm)	57.3	89.7	254.4	228.8
		94.5	236.3	87.0
		74.8	178.2	133.5
		153.6	107.8	132.3
Polydispersity	0.357	0.220	0.237	0.250
		0.281	0.241	0.239
		0.281	0.315	0.216
		0.244	0.368	0.235
Appearance	#	☆	*	§
		★	□	□
		★	□	§
		*	□	§
Storage stability	▲	▲	▲	▲
		▲	●	▲
		▲	▲	▲
		●	▲	▲
High temperature stability	▲	▲	▲	▲
		▲	▼	▲
		▲	▲	▲
		▼	▼	▲
Freeze–thaw stability	▲	▲	▲	▲
		▲	▼	▲
		▲	▲	▲
		▼	▲	▲
σ (mN/m)	40.09	49.28	45.28	39.02
		65.93	46.88	42.35
		71.12	44.62	38.63
		79.52	47.02	46.75

#, transparent and slightly yellow; ☆, semitransparent and slightly yellow; ★, slightly white, blue, and semitransparent; *, milkiness, blue, and semitransparent; □, slightly white, blue, and semitransparent; §, milkiness and blue; ▲, stable; ▼, precipitate; ●, layering.

According to the above analysis, in this article, the content of DMPA was chosen as 6%.

The physical properties of PU and PUA dispersions

The physical properties of PU and PUA dispersions are listed in Table V.

1. Viscosity is an important feature of dispersions, which affects the processability and properties of coatings. Table V showed the viscosity characteristics of PU and PUA dispersions with the different functional crosslinkers. It could be seen that the apparent viscosities of all PUA dispersions were smaller than that of the pure PU-5 dispersion. Besides, with the increase of average functional groups, their viscosities decrease accordingly. This could be explained by electronic double layer theory and steric hindrance effects. On one hand, PUA samples have the same hard and soft segments but different functional acrylic groups, so they obtained different contents of ionic groups. Since PUA-1(1–4) series were capped with single functional acrylic groups BA and St whereas the double functional acrylic groups of PUA-2(1–4) series were TPGDA, and terminal groups of PUA-3(1–4) series were TMPTA, PUA-1(1–4) series samples possessed relative higher contents of hydrophilic ionic groups. Therefore, the electric stagnant effects were enhanced in PUA-1(1–4) series and their fluid-dynamics volumes were increased, to result in

their increased viscosities. On the other hand, different steric hindrance effects of chains were obtained in PUA samples for their different functional crosslinkers. The samples with higher functional crosslinker will possess less entanglement among polymer chains. This also explains why branched samples have lower viscosity than linear ones even when they have the same content of hydrophilic ionic groups and terminal groups.

2. Obviously, when the amounts of DMPA were the same, the hydrophilic/hydrophobic ratios of the different crosslinked PUA composite emulsions decreased. The numbers of the micelle particles decreased, and the average particle size of PUA composite emulsion increased. With the increase of the particle size, the appearance of emulsion changes from transparence to semi-transparence or slightly transparence.[17] The crosslinked PUA aqueous dispersions had smaller polydispersity than the pure PU.

3. The surface tension (σ) greatly depends on the bulk, amount, and volume of the polar groups on the molecular chains. As shown in Table V, (a) PUA had higher σ than the pure PU. It was mainly because that there were more polar groups in the PA molecular chains than in the PU molecular chains; (b) the σ of PUA dispersions increased with decreasing of the amount of BA. This was because during the particle formation process, the BA had smaller volume and fewer lateral groups; (c) for PUA-1, PUA-2, and PUA-3 series: when the ratios of BA/St, BA/TPGDA, and BA/TMPTA were the same, the surface tension of PUA-1 series was the biggest while PUA-3 was the smallest. This was because TMPTA had the biggest crosslinked degree and formed interpenetrating network structures. When the ratios of BA/TPGDA and BA/TMPTA were 30/70, PUA-2-3 and PUA-3-3 had the biggest σ in their PUA series. The σ of PUA-2 and PUA-3 series was small than those of the author's previous studies.[14,15] With the decrease of σ, the conglutinate property was improved between the glue and fundus material. So, the performance of PUA-3-3 is the best.

The mechanical properties of PU and PUA films

The mechanical properties for PU and different PUA are listed in Table VI. As shown in Table VI:

1. With the increase of St, TPGDA, and TMPTA content, the hardness of PUA films increased obviously in PU matrix. This may be attributed

TABLE VI
Some Mechanical Properties of PU and PUA Films

Sample	PU-5	PUA-1-(1–4)	PUA-2-(1–4)	PUA-3-(1–4)
Hardness (Shore A)	83	89	87	85
		90	89	88
		95	90	91
		97	94	93
Tensile strength (MPa)	0.77	0.68	1.39	1.74
		1.76	1.86	2.17
		1.13	1.63	1.65
		1.37	1.32	1.63
Elongation at break (%)	36.59	39.24	23.03	68.28
		190.02	197.19	76.82
		44.12	76.92	61.07
		82.76	177.63	48.16

to the increase in the interpenetration and entanglement of St (or TPGDA or TMPTA) components into PU matrix, which in turn attributes high degree of compatibility between PU and acrylate phase.[6] The polarity of the hard monomer St (or TPGDA or TMPTA) was familiar with the hard segment of PU. There had been hydrogen bonding and some compatibility between the PU and St (or TPGDA or TMPTA) phases in the systems. With the increase of hard monomer content, the density of the hard segment in the molecular chains increased; the crosslinked degree improved because of the hydrogen bonding formation.[15] At larger hard segment content, the phase of the hard segment exhibited higher impact strength and higher hardness. However, hardness became inferior beyond optimum concentration of acrylate.

2. When the ratios of BA/St, BA/TPGDA, and BA/TMPTA were the same, PUA-1 series had bigger hardness than PUA-1 and PUA-2 series. This was because PUA-1 series were formed with strong strength of rigid aromatic structure. The obtained results showed that PUA films had better hardness than those of the author's previous studies.[14]

3. PUA films had higher tensile strength and elongation at break than pure PU film, which were due to the formation of crosslinked structure between PU and PA and intermolecular hydrogen bonds among PUA molecules. As a result, PUA films exhibited excellent comprehensive mechanical properties. With the increase of crosslinked degree, the density of the crosslinking positions increased, leading to the increase of tensile strength (PUA-1 < PUA-2 < PUA-3). And when the ratios of BA/St and BA/TMPTA were 70/30, the tensile strength and elongation at break of their PUA films achieved the maximum. In PUA-3 series,

TABLE VII
Solvent Resistance of PU and PUA Films

Sample	PU-5	PUA-1-(1–4)	PUA-2-(1–4)	PUA-3-(1–4)
Water absorption (%)	17.42	21.83	16.24	18.05
		14.82	15.35	20.31
		6.47	16.03	13.32
		20.49	17.84	14.55
Swelling degree (5% NaOH) (%)	88.30	126.22	177.43	50.94
		49.95	45.55	43.68
		16.58	148.72	52.85
		39.69	229.50	81.21

elongation at break of PUA changed little with the changing of BA/TMPTA, mainly because the chain of macromolecular acrylic resin had the special flexibility.

The water absorption (or swelling degree) of PU and PUA composite film

As one of the major drawbacks compared with the solvent-based products, the water resistance of WPUA films has attracted extensive attention. Many factors influencing the water resistance of WPUA films, such as hydrophilic groups, polyether or polyester glycols, have been investigated.[4] However, the effects of different functional crosslinkers on the water resistance of PUA have not been reported in the literature. PU and PUA films were put into water and 5% NaOH at 25°C after being weighed. Twenty-four hours later, water absorption or swelling degree of PU and PUA films were measured. The results are shown in Table VII. As shown in Table VII:

1. In PUA-1 series, PUA-1-3 had the lowest water absorption showing that PUA-1-3 had the best

water resistance when the mass ratio of BA/St was 30/70. In PUA-2 series, the water absorption of the PUA changed little with the changing of BA/TPGDA and was close to the pure PU. In PUA-3 series, the water absorption of PUA-3-3 achieved the maximum when the mass ratio of BA/TMPTA was 30/70 and the film had the best water resistance. It was found that the water resistance of three PUA films of 10/90 ratio was in the order of PUA-1-4 > PUA-2-4 > PUA-3-4, in consistency with their functional sequence groups, implying that the functional groups of PUA polymer played an important role in improving the water resistance. Since the functional groups of PUA-3-4 molecule were higher than the functional groups of PUA-1-4 and PUA-2-4, PUA-3-4 could obtain far more contents of unsaturated double bonds and higher crosslinking density than PUA-1-4 and PUA-2-4, and consequently provide more barriers to the migration of water, to result in a much better water resistance. Moreover, the obtained results showed that the PUA films had better water resistance than those of the author's previous studies.[14]
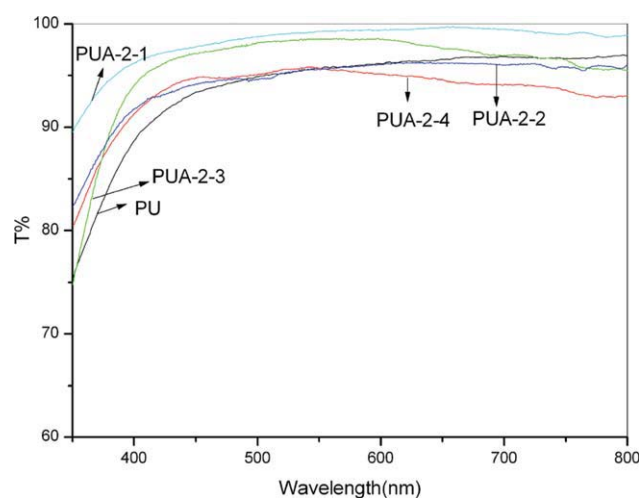

Figure 3 UV–vis spectra of PU and PUA-1 series. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

Figure 4 UV–vis spectra of PU and PUA-2 series. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

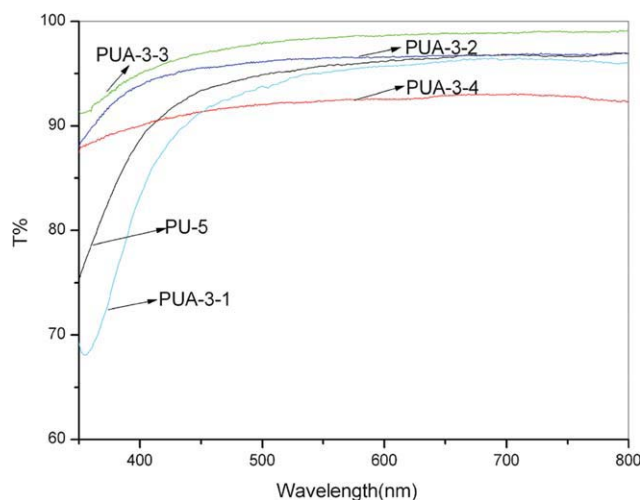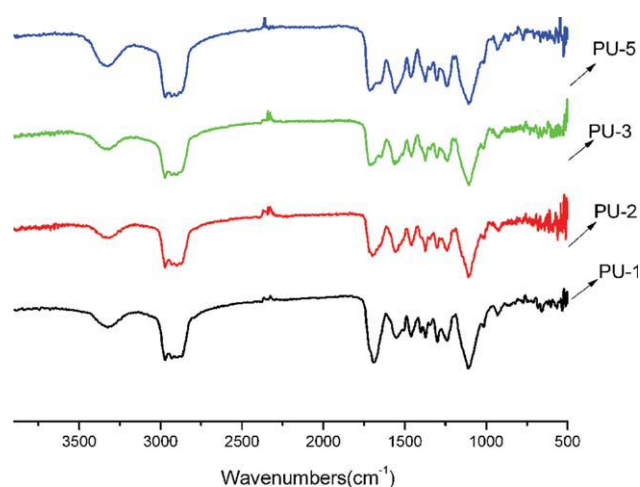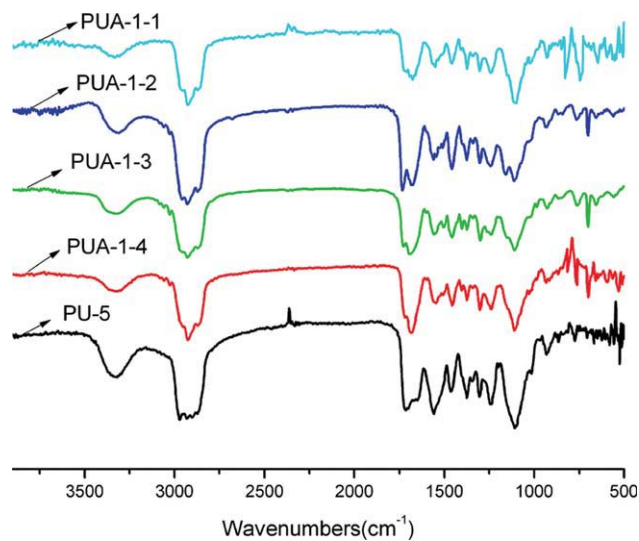**Figure 5** UV–vis spectra of PU and PUA-3 series. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

2. Besides PUA-1-1, PUA-2-1, PUA-2-3, and PUA-2-4, other PUA films had excellent alkalinity resistances compared to pure PU.

Optical transparency and structure characterization

Figures 3–5 showed the UV–vis spectra of PU, PUA-1, PUA-2, and PUA-3 series films, respectively. Based on the UV–vis results, the transmittances of all PUA and PU films were expected to produce more transparent films than 90% at $\lambda \geq 700$ nm wavelength. The UV spectra and the particle size of PUA dispersion were nearly correlative. The result showed that the prepared films had better optical transparency.

Figures 6–9 showed the FT-IR spectra of PU, PUA-1, PUA-2, and PUA-3 series films, respectively.

Figure 6 FT-IR spectra of PU. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

Figure 7 FT-IR spectra of PU and PUA-1 series. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

The spectral analysis was mainly used to check the completion of polymerization reaction, in terms of disappearance of the —NCO peak of all the films at 2270 cm^{-1}, and the appearance of N—H band at 3310–3500 cm^{-1}. The completion of the reaction and the formation of predesigned PUA were confirmed from the following analysis. The spectra of PU and PUA exhibited a strong absorption band at 3383 and 3378 cm^{-1}, respectively, which might be ascribed to the hydrogen bonding between N—H and carbonyl groups. It could be seen that there was a progressive change in the absorption pattern of C=O stretching region, which might be attributed to the presence of acrylate group. The band at about 1735 cm^{-1} was assigned to C=O in the PU and the band at 1741 cm^{-1} to carbonyl C=O stretching vibrations of the
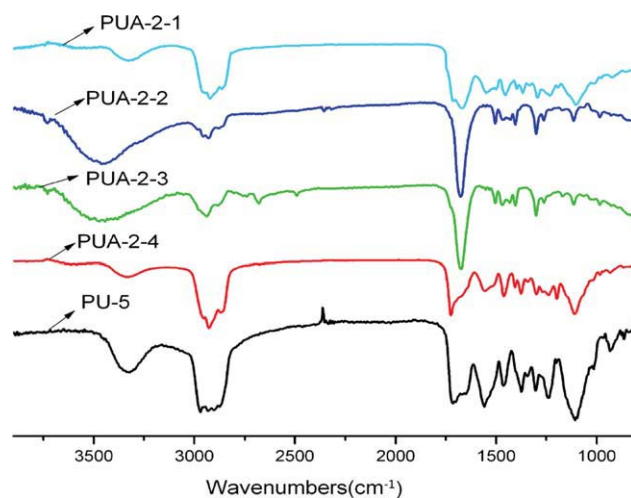

Figure 8 FT-IR spectra of PU and PUA-2 series. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

BA and St (or TPGDA or TMPTA) ester groups. The disappearance of band at 1548–1640 cm^{-1} to —C=C— confirmed the copolymerization between PU and AC components in PUA composite latex.

Thermal properties

The DSC curves of PU and some PUA samples from room temperature to 500°C are shown in Figure 10. As shown in Figure 10:

1. PUA samples had higher glass transition temperature (T_g) of hard segment than PU sample.
2. In the same series, with the increase of the monomer St (or TPGDA or TMPTA) content, the glass transition temperatures of PUA samples increased.
3. From the DSC curve of PUA composite sample, there was only a glass transition temperature in the temperature range of 50 to 55°, between the glass temperature of acrylate copolymer and the glass temperature of hard segment of seed probably arise from the micro-Brownian motion of polyacrylate copolymer and the micro-Brownian motion of the hard segment of the seed PU. This shows that hard domains of seed PU contain polyacrylate molecules. Furthermore, the glass transition temperature of hard segments in crosslinked PUA-1 series connect together and form a big step, showing that the phase separation of crosslinked PUA is not very obvious. This is probably due to the fact that the hard domains of the seed PU have carried out the crosslinking reaction with the polyacrylate copolymer, leading to the increase of the degree of phase uniformity of the crosslinked PUA. The result indicated that crosslinked structure and intermolecular hydrogen
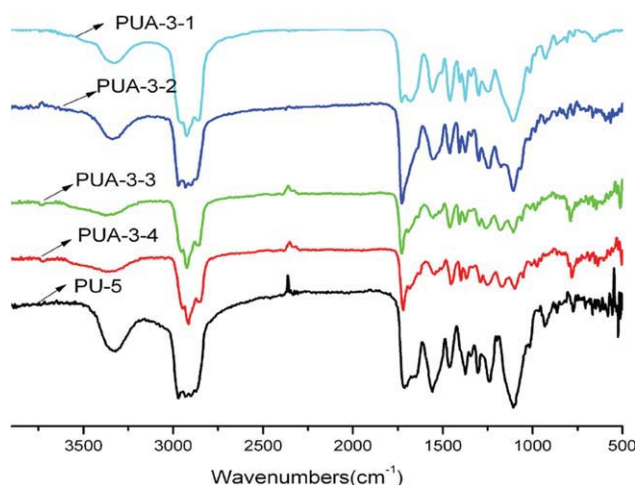
Figure 9 FT-IR spectra of PU and PUA-3 series. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]
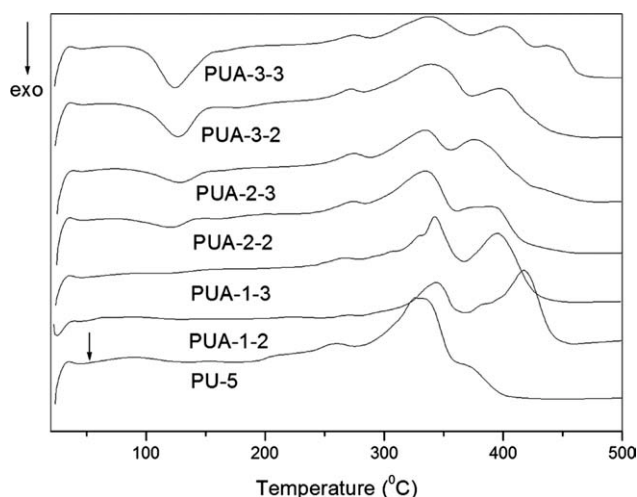
Figure 10 The DSC curves of PU and some PUA.

bonds among PUA molecules enhanced miscibility.

4. All PUA materials had higher decomposition temperatures (T_d) than PU sample, resulting in the formation of crosslinked PUA structure in the composite PUA system.
5. The decomposition temperature of PUA sample decreased with the increase of soft monomer BA content in the same PUA series.

CONCLUSION

The waterborne PU dispersion was prepared and had excellent performance when R value was 2.0 and the content of DMPA was 6%. The waterborne crosslinked PUA composite was prepared with different functional crosslinkers. The experimental results indicate that the crosslinked PUA aqueous dispersion has larger particle-size, smaller polydispersity, bigger hardness, and tensile strength than the pure PU. With the increase of crosslinked degree, the tensile strength increases (PUA-1 < PUA-2 < PUA-3). When the ratios of the BA/St and BA/TMPTA were 70/30, the mechanical properties of PUA films were the best. When the ratios of the BA/St and BA/TMPTA were 30/70, PUA films have excellent water resistance. UV–vis spectra show that the prepared films have better optical transparency. The PUA samples have higher glass transition temperature (T_g) of hard segment and good thermal property than PU sample. The obtained PUA have great potential application such as coatings, leather finishing, adhesives, and wood finishes.

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