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Xia Kong<sup>a</sup>; Shaomao Li<sup>a</sup>; Jinqing Qu<sup>a</sup>; Huanqin Chen<sup>a</sup>

<sup>a</sup> School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, China

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# Self-emulsifying Hydroxy Acrylic Polymer Dispersions for Two Component Waterborne Polyurethane Coatings

XIA KONG, SHAOMAO LI, JINQING QU\* and HUANQIN CHEN

School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China

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Novel self-emulsifying acrylic polymer aqueous dispersions (NPAD) for two component waterborne polyurethane coatings (2K-WPU) were prepared by the emulsification of self-emulsifying polymer blends in water, which the polymer blends typically consist of two acrylic polymers, one is a salt group containing polymer (P1), the other is a polymer without salt groups (P2). The dynamic light scattering (DLS) analysis showed that the NPAD have a bimodal particle size distribution and the particle diameters can be controlled by the amount of salt group containing polymer and the concentration of salt groups in this polymer. Transmission electron microscopy (TEM) images also testified that the NPADs possess small particles consisted of P1 and core-shell structure large particles which are composed of the P1 in the shell parts and the P2 in the core parts. The property comparisons of the NPAD, conventional polyacrylic dispersion (CPAD) and polyacrylic emulsion (PAE) for 2K-WPU disclosed that the NPADs possess higher solid contents up to 45 wt% and much lower carboxy salt contents than those of the CPAD, and the NPAD-based 2K-WPU films display much better performance including 90% of the gloss, 0.81 of the pendulum hardness, much better solvent- and water-resistance than those of the CPAD and PAE. The TGA curves indicated the NPAD-based 2K-WPU films display good thermal stability.

**Keywords:** Aqueous acrylic polymer dispersions, two component waterborne polyurethane, core-shell particles, waterborne coatings

## 1 Introduction

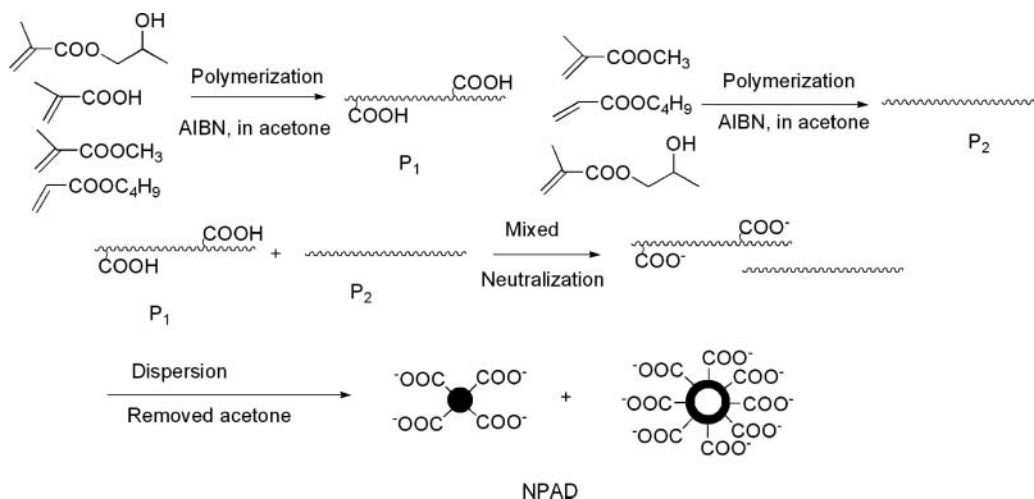
Polyurethane (PU) coatings possess excellent properties and have established an important place in the coatings industry due to their micro-phase separated domains from immiscibility of soft and hard blocks, hydrogen bonding, and chemically induced separation of urethane-rich and urea-rich domains (1–3). Among them, the two component solvent-borne PU coatings display a maximum performance and appearance which satisfied the main market requirements. Due to increasingly stringent legal requirements, two component waterborne polyurethane coatings (2K-WPU) have become increasingly popular over the last several years, driven by market demands for higher-performance, formaldehyde free, thermosetting water-based coatings (4).

The basic components of 2K-WPU systems are a hydroxy-functional waterborne polymer (polyol), an oligomeric polyisocyanate crosslinker derived from hexamethylene diisocyanate (HDI) or isophorone diisocyanate (IPDI) which may or may not be hydrophilically-modified, optional co-solvent(s), and water (5). Various

types of hydroxy-functional waterborne polymers including polyester, polyacrylate, polyurethane, and their hybrids can be used in 2K-WPU systems (6). Among them, waterborne acrylic polymers get more attentions because of their excellent resistance to hydrolysis and low cost (7). These are two kinds of hydroxy-functional waterborne acrylic polymers differ in preparation methods (8), namely, acrylic polymer emulsions (PAE) and acrylic polymer dispersions (PAD) (9). The PAE possess high molecular weight and glass transition temperature give PAE-based 2K-WPU film rapid physical drying properties at room temperature before the onset of chemical crosslinking. However, it is difficult to achieve an acceptable film appearance and fulfill most of customer needs due to some remaining surfactants and protective colloids in the drying films which come from the PAE (10). Thus, PADs are free of any surfactants and protective colloids, the high concentration of hydrophilic acid groups in PADs often lead to a decrease in water-/ethanol-resistance properties of the film (11). much research had focused on overcoming the disadvantages including carboxyl groups in the acrylic polymers could be crosslinked by aziridine, polycarbodiimides and their derivatives (12, 13). On the other hand, the decreasing of the hydrophilic salt group contents in the polymers also lead to hydrophobic films, this would be a good method.

In the present paper, we describe a new preparation process of hydroxy functional acrylic polymer dispersions

\*Address Correspondence to: Jinqing Qu, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China. E-mail: cejqqu@scut.edu.cn



Sch. 1. The synthetic routes of NPAD.

(NPAD), namely, the preparation of self-emulsifying polymer blends, which consist of two polymers which differed in their salt group contents, and only one of the polymers contains the salt groups, which are required for the stabilization of the dispersions. The synthetic process was listed in Scheme 1. The properties of the NPAD, conventional acrylic polymer dispersion (CPAD) and PAE for 2K-WPU coatings were also compared.

## 2 Experimental

### 2.1 Material

Methacrylic acid (MAA), methyl methacrylate (MMA), butyl acrylate (BA), styrene (St), and hydroxypropyl methacrylate (HPMA) are all commercial products purchased from Mitsui Co. (Japan). Dodecyl mercaptan, 2, 2-azobisisobutyronitrile (AIBN), dimethylethanolamine (DMEA), and acetone are provided by Guangdong Carpoly Chemical CO., Ltd. (Jiangmen, China). Hydrophilic modified polyisocyanurate based on HDI trimers (Bayhydur XP2655) was purchased from Bayer CO. (German). All the materials were used without further purification.

### 2.2 Measurements

#### 2.2.1. Particle sizes and distributions

Particle sizes and distributions were measured using a dynamic light scattering (DLS) technique (Malvern Laser Particle Sizer). Samples were diluted with water into an appropriate concentration as indicated by the instrument. Test specification: 0.6–6000 nm; temperature: 25°C.

Transmission electron microscopy (TEM) was used to determine the particle morphologies. TEM were acquired on a Zeiss EM 109T microscope using an accelerating voltage of 80 kV. Samples of colloidal dispersion used for TEM

analysis were prepared by making a 1:10 000 dilution in deionized water followed by casting onto Formvar-coated copper grids (Ted Pella, Inc.).

#### 2.2.2. Film property measurements

Dry times were determined using an automatic drying time recorder on the glass panel according to GB/T 1728–1989; gloss was read directly at 60° on the glass panel using a glossmeter (GB/T 9754–1988); the hardness was tested with a pencil (provided by Zhonghua Pencil Factory in Shanghai, China) having a different hardness on a glass panel (GB/T 1730–93); the adhesion was determined using the cross-hatch method at a distance of 1 mm on tinplate (GB/T 9286–1998); the flexibility was tested with a T-bend tester (GB/T 9755–2001); and the impact resistance was measured with an impact tester on a tinplate; refer to the GB/T 4893.9–1992.

#### 2.2.3. Water/ethanol Uptake

A known weight ( $W_1$ ) of a dried polymer film (60 mm × 60 mm × 1 mm) was immersed in a distilled water bath for 8 days for water uptake, or immersed in an ethanol (95%) bath for 48 h for ethanol absorption, followed by wiping off the surface water or ethanol with a piece of filter paper to determine the weight  $W_2$ , three measurements were averaged for each sample. The percentage of the water and the ethanol uptake were calculated according to the following equations:

$$W_{A/E}\% = \frac{W_2 - W_1}{W_1} \times 100\% \quad (1)$$

where  $W_A$  and  $W_E$  are the water and ethanol absorption, respectively.

#### 2.2.4. Gel contents of the film

The crosslinking degree of 2K-WPU films was determined with gel contents and evaluated on the basis of swelling

experiments using 2K-WPU films, which were dried at 25°C for 3 days, followed by annealing latex films at 50°C for 4 h. 2K-WPU films (0.1–0.2 g,  $W_3$ ) were immersed in acetone for 48 h at room temperature. Samples were reweighed after drying at 50°C for 24 h ( $W_4$ ), and the gel content ( $\alpha$ ) was determined using the following equation:

$$\alpha = \frac{W_4}{W_3} \times 100\% \quad (2)$$

### 2.2.5. IR analysis

The infrared (IR) spectra were recorded with a Spectrum 2000 FTIR instrument in the 400–4000  $\text{cm}^{-1}$  region. A NPAD and a mixed 2K-WPU paint were coated directly on to the surface of a KBr crystal, respectively, and measured after film forming and drying (a simple IR measurement method for liquid sample).

### 2.2.6. TGA analysis

Thermal stability of dried films were determined by the Thermo gravimetric analyzer (TG/DSC, STA449C, NET-ZSCH Co. Germany) by heating the sample (2–4 mg) under a flow of air (40 mL/min) and protective nitrogen (30 mL/min) at 15°C/min from 40 to 650°C. The TGA samples were prepared by the method described in the film preparation.

## 2.3 Synthesis of the NPAD

Acrylic copolymers with varying monomer contents were synthesized by well-known solution copolymerization technique in acetone using AIBN as an initiator (14). The comonomer contents were adjusted by calculating the  $T_g$  of the copolymers from the Fox equation. Polymerizations were carried out in a four-necked flask equipped with a reflux condenser, stirrer and thermometer at 65°C in an inert atmosphere of nitrogen. 50 g of acetone as a solvent was taken in the reactor. AIBN as an initiator (1.0 g) was dissolved in 75 g of the monomers and the mixture was added dropwise to the reactor for an initial 3 h followed by a further 2 h reaction with a continuous stirring condition. The reaction was stopped at 98% monomer to polymer conversion. Table 1 reports the composition of the copolymers synthesized for this study in detail.

NPAD was prepared as follow: P1 and P2 were mixed with the mass ratio in the range of 0.3:0.7–1:0 and then neutralized with dimethylethanolamine, the polymer solutions

**Table 1.** The compositions of P1-P3

Copolymers	MMA, wt%	BA, wt%	ST, wt%	MAA, wt%	HPMA, wt%
P1	21.5	30.0	12.0	3.5	33.0
P2	37.0	30.0	0.0	0.0	33.0
P3	20.0	30.0	12.0	5.0	33.0

were dispersed in water, and then the acetone was distilled by a vacuum evaporator, and dimethylethanolamine was added to control the pH of NPAD to 7–9.

The CPAD and PAE were synthesized according to reference (15), and their formula were the same as that of P1.

## 2.4 Preparation of 2K-WPU Coatings

The defoamer and leveling agent were first added to the NPAD (0.02 wt% based on the NPAD), then the XP2655 was added into the NPAD according to 1.5:1 of the molar ratio of NCO and OH groups, and stirred for another 10 min before the films were made, water was added to control the application viscosities. Although in an idea system, an equal stoichiometry of polyisocyanate and polyol is desired, in reality, 2k-WPU systems are usually mixed with a large molar excess of polyisocyanate to competing reactions of isocyanate with water according to references (8–10). The preparation of CPAD and PAE based 2K-WPU were same as those of the NPAD-based 2K-WPU coatings.

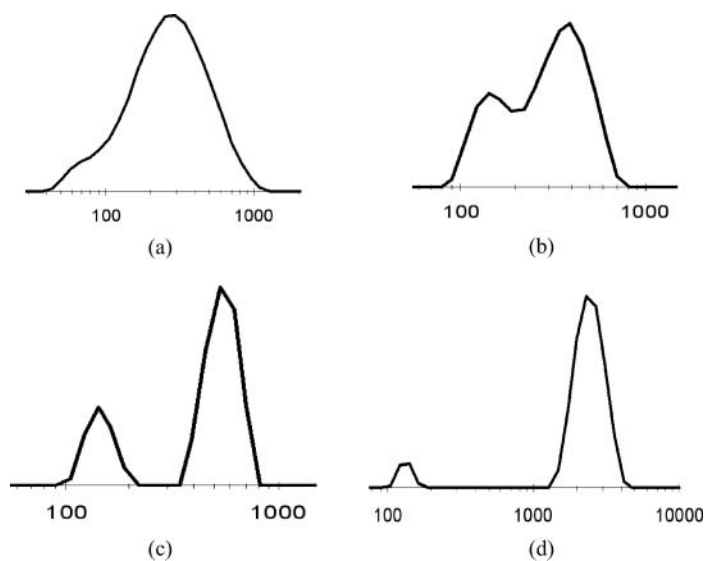
## 2.5 Preparation of 2K-WPU Films

The coatings were brushed onto clean glass panels and sand-treated thin tinplate panels kept the thickness of the dry film at  $20 \mu\text{m} \pm 3 \mu\text{m}$ , and then dried at room temperature. The gloss, adhesion, flexibility, and impact resistance of films were measured after the panel was dried for 48 h, and the pencil hardness was measured after 48 h and 7 days, respectively. The water and chemical resistance were determined after 7 days.

# 3 Results and Discussion

## 3.1 Preparation and Particle Size Distribution of NPAD

Scheme 1 illustrated the synthetic routes of NPAD. The acrylic copolymers P1, P2 and P3 were synthesized independently by free radical solution copolymerization using the AIBN as an initiator in the acetone, which the –COOH groups are concentrated only on the P1 and P3. Mixed P1 and P2 were placed in a separate reaction vessel and then neutralized with a DMEA with the aid of a stirrer, emulsified it with water and the acetone was removed to afford NPAD systems with 40–45% solid contents. Obviously, the ratios of MMA to BA have a drastic impact on the physical mechanical properties of acrylic copolymers and 2K-WPU. The incorporation of the hard monomer (MMA) results in the rigidity and good adhesion of the acrylic copolymers and 2K-WPU. However, the flexibility of the acrylic copolymers and 2K-WPU is improved while the strength decreased with the incorporation of the soft monomer (BA). We also found that the ratios of MMA to



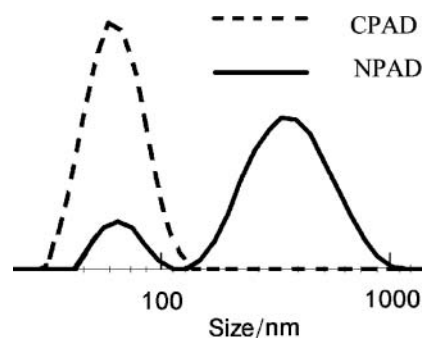
**Fig. 1.** The particles size distributions of NPAD with vary mass ratios of P1 and P2. [(a) P1/P2 = 7:3,  $d_p = 224$  nm,  $\alpha = 91\%$ ; (b) P1/P2 = 6:4;  $d_{p1} = 147$  nm,  $d_{p2} = 367$  nm,  $\alpha = 93\%$ ; (c) P1/P2 = 4:6,  $d_{p1} = 146$  nm,  $d_{p2} = 552$  nm,  $\alpha = 86\%$  (d) P1/P2 = 3:7,  $d_{p1} = 134$  nm,  $d_{p2} = 2000$  nm,  $\alpha = 82\%$ ].

BA slightly affect particle sizes and distributions of NPAD and CPAD.

Since NPADs were prepared by the combination of different amounts of a salt group contain in P1 and without salt groups P2, the particle sizes and distributions of NPAD can be controlled by both the amount of the P1 and the concentration of salt groups in the P1. Figure 1 illustrates the particle sizes and distributions changed with the mass ratios of P1 and P2 in the range of 30–70% along with gel contents of NPAD-based 2K-WPU.

Figure 1 clearly demonstrates that all NPAD have a bimodal particle distribution. The small particle average diameters were similar in the range of 130–150 nm, while the larger particle average diameters were changed with the content of P1 ranging from 224 nm to 2000 nm. The gel contents of NPAD-based 2K-WPU were in the range of 82–93% which are listed in Figure 2. The NPAD become unstable with the content of P1 below 30 wt%, it is attributed to the fact that the hydrophilicity of NPAD increased along with the particle sizes which decreased with an increasing amount of P1, and increasing the stability of NPAD. The mass ratio between P1 and P2 has a great influence on both particle populations. With an increasing amount of P1, the larger particles get smaller. The small particle fraction slightly changes its diameter, but the number of small particles is growing. Shear energy has no influence on the particle size distribution of the dispersions. This means that these dispersions are thermodynamically stable systems.

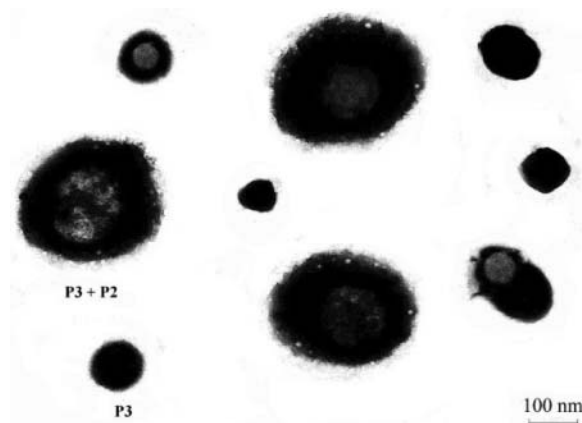
We also synthesized the P3 with 5.0 wt% MAA content and the other monomers composition are the same as P2, and then we prepared P3 dispersion (CPAD) and NPAD



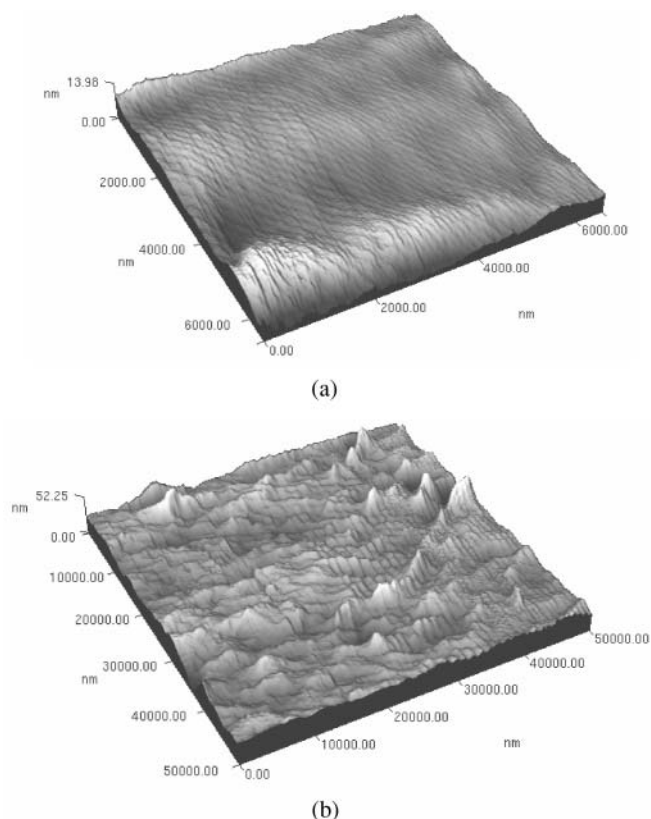
**Fig. 2.** The particle sizes and distributions of CPAD and NPAD synthesized with 5.0 wt% MAA. [CPAD (P3/P2 = 1:0,  $d_p = 56$  nm); NPAD (P3/P2 = 1:1,  $d_{p1} = 60$  nm;  $d_{p2} = 300$  nm)].

with 50 wt% of the P3 and 50 wt% of the P2. Figure 2 shows the particle sizes and distributions of CPAD and NPAD. The NPAD exhibits larger particle sizes ( $d_p = 160$  nm) and a continued bimodal particle size distributions in contrast to CPAD ( $d_p = 56$  nm). However, the smaller particle average diameter of NPAD is similar to that of the CPAD. It could be concluded that the larger particles ( $d_p = 300$  nm) formed core-shell structures, and the hydrophilic P3 forms the shell, and the P2 forms the core during emulsifying process. It was proven by the TEM picture of NPAD (P3 and P2) in Figure 3. The TEM image shows that NPAD contains the small particles and the larger particles, and the small particles are stable and stained, which consisted only of hydrophilic P3 (containing St). While the larger particles have a clear core-shell structure, which is formed by the P3 (stained domains) and P2 (unstained domains).

In most 2K-WPU systems, the polyols and polyisocyanates are not distributed homogeneously in the film, and the 2K-WPU film appearances are not as good, which was testified by atomic force microscopy (AFM). The condition can be improved to by using NPAD with good self-emulsified ability. Thus, the special morphology of the NPAD, the NPAD possess a much better emulsifying



**Fig. 3.** TEM picture of the NPAD (P3/P2 = 1:1).

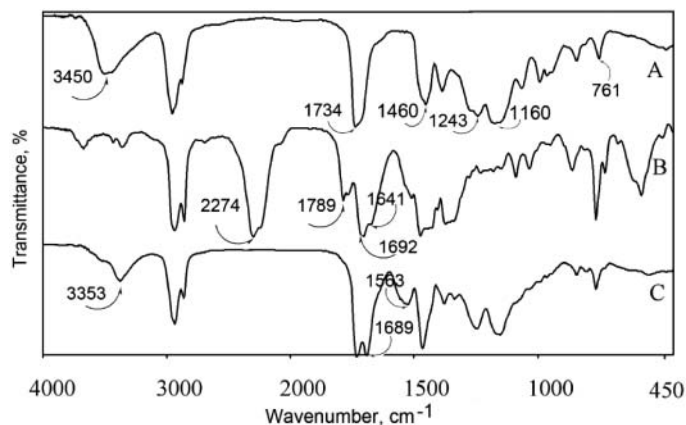


**Fig. 4.** The three-dimensional AFM images of 2K-WPU film (a) NPAD-based (P3/P2 = 1:1); and (b) PAE-based (P3/P2 = 0:1).

ability to the polyisocyanate crosslinker than that of the PAE, probably due to the presence of a large number of small hydrophilic particles. The AFM topographic images of NPAD- and PAE-based 2K-WPU film are shown in Figure 4. Figure 4 demonstrated that the average roughness ( $R_a$ ) and root mean square roughness ( $R_q$ ) in the NPAD-based 2K-WPU film were 1.61 and 2.15 nm, respectively, while the responding value of the PAE-based film was 3.62 and 4.25 nm, respectively in Figure 4(b). It was found that the NPAD-based 2K-WPU film was uniform, and the boundaries between the polyols and polyisocyanates were ambiguous.

### 3.2 IR Analysis

Figure 5 depicts the FTIR spectra of NPAD (A), XP2655 (B) and cured NPAD-based 2K-WPU (C). Trace A shows that the band at  $3450\text{ cm}^{-1}$  attributes to the OH group stretching vibration; the band  $1734\text{ cm}^{-1}$  due to C=O stretching mode, and the bands at  $1243\text{ cm}^{-1}$  and  $1166\text{ cm}^{-1}$  are attributed to the C–O stretching vibrations of acrylic ester groups; and the  $-\text{CH}_2-$  bending deformation mode is detected at  $1460\text{ cm}^{-1}$ . Trace B indicated the band  $2274\text{ cm}^{-1}$  responsible for NCO group. The bands at  $1789\text{ cm}^{-1}$ ,  $1692\text{ cm}^{-1}$  and  $1641\text{ cm}^{-1}$  represent asymmetric and symmetric C=O stretching modes of the HDI trimer, re-



**Fig. 5.** FTIR spectra of NPAD (P3/P2 = 1:1) (A), XP2655(B) and cured 2K-WPU(C).

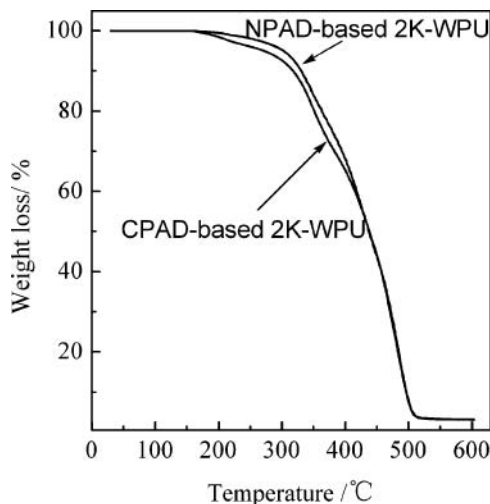
spectively (16). In the trace C, the wide and strong  $-\text{OH}$  absorptions between  $3444\text{ cm}^{-1}$  and  $3533\text{ cm}^{-1}$  disappeared and a new sharp peak appeared at  $3353\text{ cm}^{-1}$ , which was attributed to N–H absorption. The NCO absorption peak at  $2273\text{ cm}^{-1}$  disappeared, indicating that the  $-\text{NCO}$  group reacted completely. A new stronger peak at  $1689\text{ cm}^{-1}$  was attributed to C=O stretch vibration, which meant that a reaction between water and  $-\text{NCO}$  took place. The absorption peak at  $1563\text{ cm}^{-1}$  was attributed to N–H bond vibration and C–N symmetry stretch vibration, and the sharp and strong peak at  $761\text{ cm}^{-1}$  was absorption due to C–N bond vibration. These indicated the presence of urethane bond and urea bond formation. A new peak appeared at  $1168\text{ cm}^{-1}$  that was attributed to the C–N–C stretch vibration in the isocyanurate ring in the hydrophilic-modified curing agent.

### 3.3 TGA Analysis

Figure 6 illustrates the TGA curves of the NPAD- and CPAD-based cured 2K-WPU films which formulated with an  $-\text{NCO}/\text{OH}$  molar ratio of 1.5:1. It shows that the initial decomposition temperature of NPAD-based 2K-WPU was about  $225^\circ\text{C}$ , slightly higher than that of CPAD-based ( $220^\circ\text{C}$ ), indicating that the NPAD-based 2K-WPU film possesses good thermal stability.

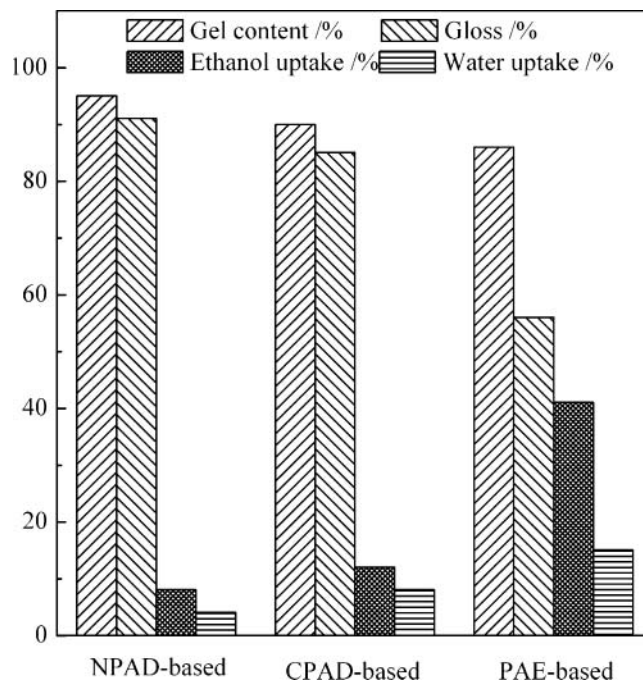
### 3.4 The Film Properties of 2K-WPU

NPAD- (P3 and P2), CPAD-(P3), and PAE-based (P1) 2K-WPU were prepared with 1.5:1 of the molar ratio of NCO and OH groups, and the film properties including the gross, water- and ethanol-absorption, and gel content were illustrated in Figure 7. It was clearly demonstrated that NPAD-based 2K-WPU films displayed the higher gloss and gel contents, the lower water- and ethanol-uptake than those of CPAD- and PAE-based. It was probably attributable to the NPAD with a bimodal particle size



**Fig. 6.** TGA curves of 2K-WPU films (NPAD: P3/P2 = 1:1; CPAD: P3/P2 = 1:0).

distribution which possesses a favorable emulsifying ability and complete miscibility to the crosslinker, which leads to minimizing the side reaction between NCO groups and water and increase the crosslinking degree of film. In addition, the gel content of NPAD based 2k-WPU film was high, about 95%, it also provided evidence that HPMA units dispersed uniformly in the polymer chains and all hydroxy groups in polymer chains could crosslink with isocyanate groups. PAE-based 2K-WPU exhibits rapid physical drying properties at room temperature due to the high molecular weight of PAE, but PAE-based 2K-WPU film possesses poor appearance and water-/ethanol-resistance due to the presence of surfactants remaining in the drying film. The appearance of the CPAD-based 2K-WPU film was similar to that of NPAD, while the water-/ethanol resistance of CPAD-based 2K-WPU film was inferior to those NPAD-based due to higher carboxy group contents in the CPAD. Table 2 also demonstrated that the NPAD-based 2K-WPU film displays good appearance, high hardness, and excellent water-/ethanol-resistance properties.



**Fig. 7.** The properties of NPAD- (P3/P2 = 1:1), CPAD- (P3/P2 = 1:0) and PAE (P1/P2 = 1:0)-based 2K-WPU films.

#### 4 Conclusions

Novel self-emulsifying aqueous acrylic polymer dispersions for two component waterborn polyurethane coatings were prepared by the emulsification of self-emulsifying polymer blends in water. The blends typically consist of two polymers, one is a salt group containing P1, and the other P2 is free of salt groups. The DLS analysis data disclosed that the NPAD have a bimodal particle size distribution, which can be controlled by the amount of salt group containing polymer and the concentration of salt groups in this polymer. TEM images showed that the NPAD contains small particles from P1 and a core-shell structure larger particle. AMF pictures showed the films of NPAD-based 2K-WPU display excellent appearance. The NPAD-based

**Table 2.** The properties of NPAD-, CPAD- and PAE-based 2K-WPU films

Item	CPAD <sup>a</sup>	PAE <sup>b</sup>	NPAD <sup>c</sup>
Dispersion appearance	Transparent	Milky	Translucent
Dispersion solid content/%	33	45	45
Touch drying time/min	60	20	30
Hard drying time/d	3	7	3
Films appearance	Translucent no crack	Translucent slight crack	Brilliant, no crack
Damping hardness	0.75	0.72	0.81
Water-resistance (100°C)	No change	Some bubbles	No change
Ethanol-resistance	No change	Become crisp	No change

<sup>a</sup>CPAD: conventional acrylic polymer dispersion, P3/P2=1:0;

<sup>b</sup>PAE: acrylic polymer emulsion, P1/P2 =1:0;

<sup>c</sup>NPAD: Novel acrylic polymer dispersion P3/P2 = 1:1.

2K-WPU possessed high performance films including 90% of the gloss, 0.81 of the pendulum hardness, 4.2 wt% of the water uptake, and 8.5 wt% of the ethanol absorption. TGA curves showed that NPAD-based 2K-WPU film display good thermal stability up to 225°C.

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### References

1. Qu, J. and Chen, H. (2002) *J. Chem. Eng. Chin. Univ.*, 16, 570–574. (in Chinese).
2. Chattopadhyay, K. and Raju, K.V.S.N. (2007) *Prog. Polym. Sci.*, 32, 352–418.
3. Nanda, A. K. and Wicks, D.A. (2006) *Polymer*, 47, 1805–1811.
4. Charles, R.H., Andrew, G.G. and Robert, J.H. (1996). *J. Coatings Tech.*, 68, 51–61.
5. Michael, J.D. (1997) *J. Coatings Tech.* 69, 47–52.
6. Feng, S.X., Dvorchak, M. and Hudson K.E. (1999) *J. Coatings Tech.*, 71, 51–57.
7. Martin, M., Michael, S., Claus, K. and Eberhard, J. (2000) *Prog. Org. Coat.*, 40, 99–109.
8. David, A.L., Richard, J. Q. and Denise, E.F. (1999) *Prog. Org. Coat.*, 35, 109–116.
9. Nabuurs, T., Pears, D. and Overbeek, A. (1999). *Prog. Org. Coat.*, 35, 129–140.
10. Melchioris, M., Sonntag, M. and Kobusch, C. (2000) *Prog. Org. Coat.*, 40, 99–109.
11. Zeno, W., Wicks, J. and Douglas, A. (2002) *Prog. Org. Coat.*, 44, 161–183.
12. Brinkman, E. and VandeVoord, P. (1998) *Prog. Org. Coat.*, 34, 21–25.
13. Wang, S.C., Chen, P.C., Yeh, J.T. and Chen, K.N. (2007) *Reactive & Functional Polymers*, 67, 299–311.
14. Patel, S., Bandyopadhyay, A., Vijayabaskar, V. and Bhowmick A.K. (2005) *Polymer*, 46, 8079–8090.
15. Zhang, F.A., Wang, Y.P. and Yuan, L. (2004). *Journal Macromolecular Science, Part A: Pure and Applied Chemistry*, 41, 15–27.
16. Zhao, Y. and Sun, X. Spectrum identification of organic molecular structure. Beijing: Science Press, (2003) 15–65.