

A New Tri-functional Azetidine Compound for Self-Curing Aqueous-Based PU System

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ABSTRACT: A mono-azetidine compound had been demonstrating a ring opening reaction with carboxylic acid (e.g., trimethylacetic acid, TMAA) and that resulted in an amino ester bond formation at ambient temperature. A triazetidine compound (trimethylolpropane tris(1-azetidynyl)propionate, TMPTA-AZT) was obtained via Michael addition of azetidine (AZT) to trimethylolpropane triacrylate (TMPTA). The carboxylic groups of anionic aqueous-based polyurethanes (PU) served as internal emulsifier, which stabilized PU dispersion and also served as PU curing sites. The triazetidine compound (TMPTA-AZT) was introduced into anionic

aqueous-based PU dispersion as a new latent curing agent and that mixture became a single-component self-curable aqueous PU system. A crosslinked PU film was obtained from this PU system on drying at ambient temperature. The final polymer performance properties demonstrated the crosslinking behaviors of this new curing agent, TMPTA-AZT, with carboxylic ion-containing aqueous-based PU resins. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 175–181, 2012

Key words: self-curing; azetidine; ring-opening; aqueous-based PU; Michael addition

INTRODUCTION

Traditional solvent-based polyurethanes (PUs) have been widely accepted by the market for more than decades. Because of their flexible properties, they can be tailor-made from various available raw materials.¹ Due to the concerns of safety, economic, and environmental impact, the solvent-based PUs have been being gradually phased out and replaced by aqueous-based PU system.

A most popular self-emulsified carboxyl groups containing aqueous-based PU dispersion is obtained from the water dispersion process of isocyanate (NCO)-terminated PU prepolymer (NCO-PU). NCO-PU is prepared by a conventional process of polyaddition reaction of isophorone diisocyanate (IPDI) with poly(propylene glycol)-2000 (PPG-2000) in the presence of 2,2'-dimethylolpropanoic acid (DMPA). NCO terminal groups of NCO-PU are hydrolyzed and become amino groups during water dispersion process. Then part of these amino groups react

further with the remaining NCO groups for a self-chain extension to form urea bonding.

The pendent carboxylic ions stabilized aqueous PU dispersion provide the surface charges of PU micelles (particles) that cause the repulsion among PU particles and stabilizes PU dispersion in the water phase. Furthermore, because of the ionic character of carboxylic groups, this PU becomes self-emulsified or water-reducible. Such aqueous-based PU resin has a common disadvantage similar to that of a polymeric surfactant in that, after drying to result in a film, such film still exhibits the high hydrophilic properties due to the presence of hydrophilic carboxylic groups in PU molecules. Furthermore, most of aqueous-based PUs are linear thermoplastic with a lower average molecular weight, and these characters induce the poor water or solvent resistance and low mechanical properties which are not compatible with the solvent-based PU.²

There are several chemical modifications to solve these deficiencies of aqueous-based PU, including a postcuring reaction^{3–12} and polymer hybridization^{13–16} that have been proven to be effective methods for enhancing its crosslinking density, average molecular weight, and further for the performance properties. Therefore, a curing agent is a key compound for improving performance properties of aqueous-based PU resin.

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$$\text{Gel content \%} = (W_2/W_1) \times 100\%$$

Water-uptake

A known weight (W_0) of dried PU film sample with a dimension of 60 mm × 60 mm × 1 mm was immersed in de-ionized water bath for 7 days. The towel-dried sample weight (W_1) and the oven-dried sample weight (W_2) were obtained. Water-uptake ($W_w\%$) and weight loss ($W_x\%$) of the PU film in water were calculated according to the following equation.

$$W_w\% = [(W_1 - W_2)/W_2] \times 100\%$$

W_w : amount of water-uptake by PU film

$$W_x\% = [(W_0 - W_2)/W_0] \times 100\%$$

W_x : amount of PU film dissolved into the water.

Ethanol swollen

A known weight (W_0) of dried PU film sample with a dimension of 60 mm × 60 mm × 1 mm was immersed in a 95% ethanol bath for 24 h. The towel-dried sample weight (W_1) and the oven-dried sample weight (W_2) were obtained. Ethanol-absorption ($W_e\%$) and the weight loss ($W_y\%$) of PU film in ethanol were calculated according to the following equation.

$$W_e\% = [(W_1 - W_2)/W_2] \times 100\%$$

W_e : amount of ethanol absorption by PU film

$$W_y\% = [(W_0 - W_2)/W_0] \times 100\%$$

W_y : amount of PU film dissolved into the ethanol solution.

Thermogravimetric analysis

The thermal stability of each PU sample (about 10 mg) was measured by a TA thermogravimetric analyzer with a heating rate of 10 °C/min from room temperature to 600°C under nitrogen atmosphere with flow rate at 1 mL/s.

RESULTS AND DISCUSSION

The ambient temperature curing reaction of aqueous-based PU has proven to be an effective method to enhance the PU properties, such as postcuring²⁻¹⁰ and polymer hybridization¹³⁻¹⁶ are the alternative efficient and convenient process for improving PU

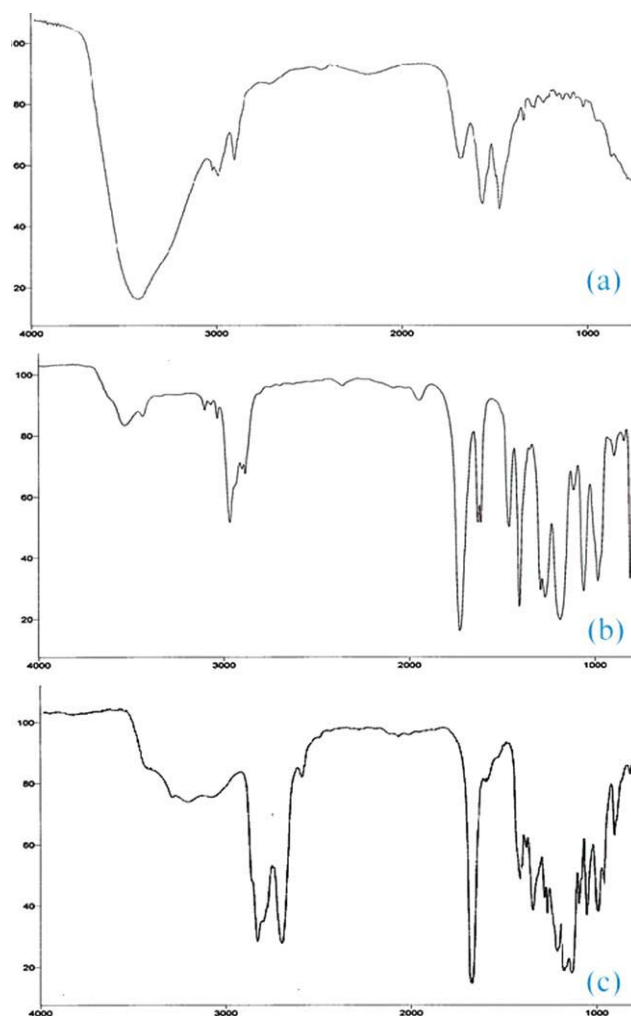


Figure 1 FTIR spectra of (a) AZT, (b) TMPTA, and (c) TMPTA-AZT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

properties. AZT-containing compounds also have been used as a latent curing agent for improving polymer properties in our previous publications.^{17,18}

A new triazetidine compound, TMPTA-AZT, has been synthesized via Michael addition reaction of AZT to TMPTA (Scheme 2). TMPTA-AZT is compatible and stable in anionic aqueous-based PU dispersion system (its pH value ~ 8.0). A different dosage of TMPTA-AZT is added into aqueous-based PU dispersion and forming a self-curable aqueous-based PU system, respectively. The self-curing behaviors of aqueous-based PU system with TMPTA-AZT are investigated.

Characterizations of TMPTA-AZT

Original TMPTA had characteristic absorption peaks of acrylic C=C bond absorption peak at 1631 cm⁻¹ and carbonyl absorption peak at 1736 cm⁻¹ on FTIR spectrum (Fig. 1). AZT was prepared by a modified

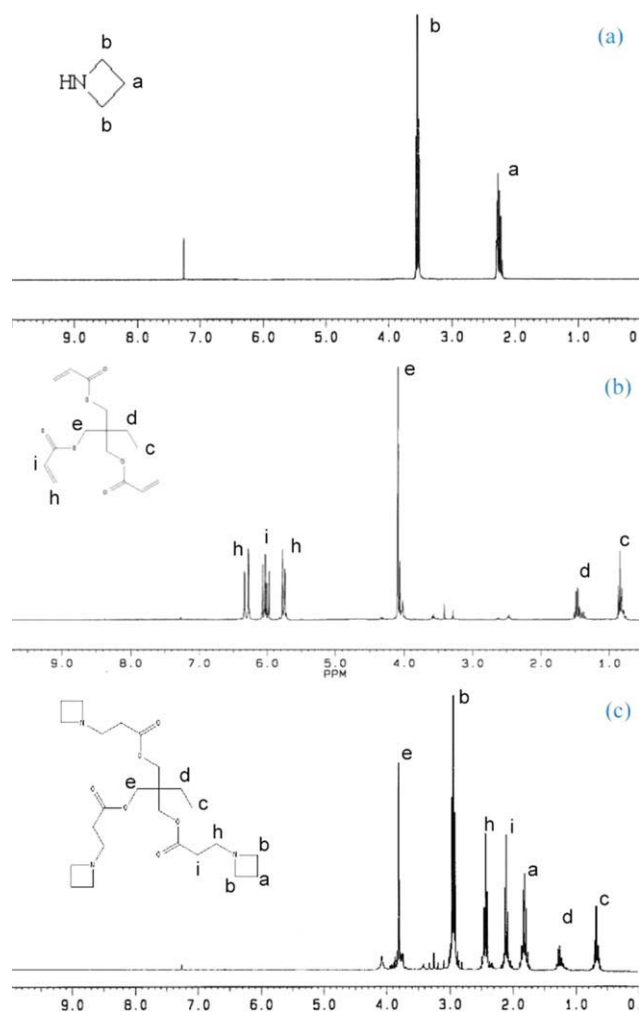


Figure 2 ¹H-NMR spectra of (a) AZT, (b) TMPTA, (c) TMPTA-AZT. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](#).]

process of the published method.^{19,21} The TMPTA-AZT was obtained from Michael addition reaction of AZT to TMPTA (Scheme 2) and its absorption peak

TABLE I
Physical Properties of PU Resins with TMPTA-AZT

| | WPU ^a | WPU with TMPTA-AZT (phr) ^b | | | | |
|-----------------|------------------|---------------------------------------|------|------|------|------|
| | | 1.0 | 2.0 | 3.0 | 4.0 | 5.0 |
| Gel content (%) | 0 | 43.4 | 57.2 | 66.1 | 70.4 | 77.5 |
| W_e (%) | — ^c | 1404 | 720 | 512 | 415 | 380 |
| W_y (%) | 100 | 54.4 | 36.4 | 25.1 | 23.6 | 22.7 |
| W_w (%) | 23.9 | 16.1 | 9.3 | 8.2 | 7.1 | 6.2 |
| W_x (%) | 2.1 | 1.7 | 1.4 | 0.9 | 0.7 | 0.6 |

W_e : ethanol absorption by PU resin; W_y : PU resin dissolved in ethanol; W_w : water-uptake by PU resin; W_x : PU resin dissolved in water.

^a WPU was the original PU without curing agent, TMPTA-AZT.

^b Curing dosages (phr) based on grams per 100 g PU resin.

^c PU resin dissolved in ethanol completely.

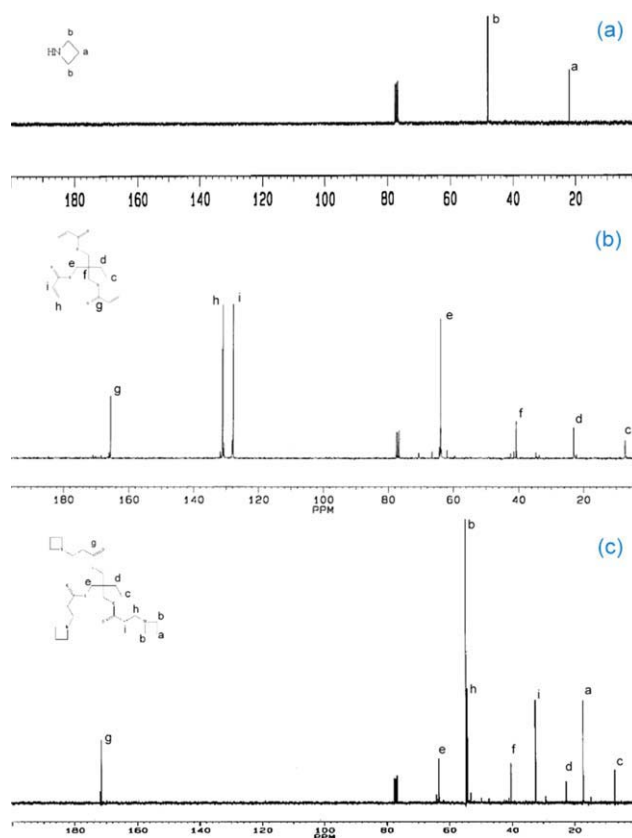


Figure 3 ¹³C-NMR spectra of (a) AZT, (b) TMPTA, (c) TMPTA-AZT. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](#).]

at 1631 cm^{-1} disappeared and a carbonyl absorption peak remained at 1736 cm^{-1} of TMPTA-AZT (Fig. 1). Due to Michael's addition of amino group of AZT to acrylic C=C bond, its absorption peak vanished from FTIR spectrum after the addition reaction is completed.

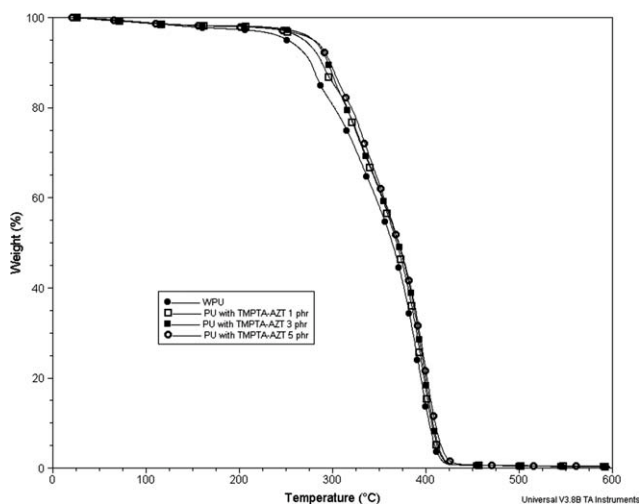


Figure 4 TGA of PU resins with TMPTA-AZT under nitrogen Original PU (●); with 1.0 phr (□); with 3.0 phr (■); with 5.0 phr (○) TMPTA-AZT.

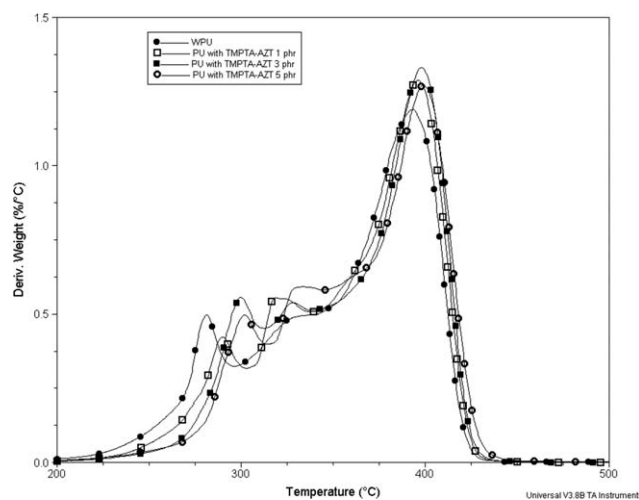


Figure 5 DTA of PU resins with TMPTA-AZT under nitrogen. Original PU (●); with 1.0 phr (□); with 3.0 phr (■); with 5.0 phr (○) TMPTA-AZT.

The chemical shifts (ppm) at 1.77 (m) and 2.98 (m) indicated the protons on AZT ring of TMPTA-AZT on $^1\text{H-NMR}$ spectra [Fig. 2(c)], which are slightly different from the original AZT ring [2.23 and 3.54 ppm, Fig. 2(a)]. The chemical shifts of protons on $\text{C}=\text{C}$ bond (between 5.5 and 6.5 ppm) of TMPTA disappeared and resulted in new chemical shifts at 2.12 (m) and 2.41 (m). These were methylene protons next to the carbonyl group and AZT of TMPTA-AZT, respectively.

The chemical shifts at 17.8 and 55.1 ppm of $^{13}\text{C-NMR}$ spectra [Fig. 3(c)] belonged to AZT of two different carbons of TMPTA-AZT, which are slightly different from original AZT [24.0 and 47.2 ppm, Fig. 3(a)]. There were two new chemical shifts at 33.0 and 55.0 ppm, which were the carbons adjacent to carbonyl group and AZT of TMPTA-AZT, respectively.

Physical properties

Gel content and ethanol swollen of PU resin indicated a relative degree of crosslinking density of polymer. Gel content of this self-cured PU resin increased with increasing the dosage of curing agent, TMPTA-AZT (Table I). Original PU resin (WPU) was soluble in THF completely, however, its gel content increased to 43.4 and 77.5% which cured with 1.0 and 5.0 phr of TMPTA-AZT, respectively.

WPU was completely dissolved in ethanol and it demonstrated that PU is linear and low molecular weight. The ethanol-swollen of self-cured PU by 1.0 and 5.0 phr of TMPTA-AZT, were 1404 and 380%, and their weight-loss in ethanol were 54.4 and 22.7%, respectively, (Table I).

The water-uptake of WPU was 23.9%. Its value decreased to 16.1 and 6.2% with increasing the dosages of TMPTA-AZT (1.0 and 5.0 phr, respectively).

The weight-loss in water of WPU was 2.1% and decreased to 1.7 and 0.6% with the corresponding dosage of TMPTA-AZT (Table I).

The increasing gel content, the decreasing ethanol-swollen, and water-uptake of self-cured PU resin were the evidence of the self-curing reaction occurred within the aqueous-based PU system with TMPTA-AZT.

Thermal properties

Thermal stabilities of original aqueous-based PU before and after cured with TMPTA-AZT have only slight differences, which are not easy to differentiate from each other on thermogravimetric analysis (TGA) thermograms (Fig. 4); however, it is quite obvious on DTA thermograms (Fig. 5). Thermal stability of original aqueous PU (WPU) had two major decomposition temperatures at 281.1 and 392.5°C on TGA thermogram (Table II, Fig. 5). These were ascribed to the different thermal degradations of urethane and polyether chemical bonds of WPU, respectively. As the increasing TMPTA-AZT dosages, their thermal degradation temperature, $T_{d10\%}$, $T_{d1stmax}$ and $T_{d2ndmax}$ were all slightly shifted to a higher temperature, these three peaks belong to urethane, urea, and ethers linkages of self-cured PU (Fig. 5). For example, $T_{d10\%}$ was 276.3°C for WPU, it increased to 297.2°C of WPU with TMPTA-AZT (5.0 phr) and its $T_{d1stmax}$ and $T_{d2ndmax}$ reached to 302.0 and 400.5°C, which compared to 281.1 and 392.5°C of WPU (Table II). These thermal degradation temperature changes due to the chemical bond (amino ester bond) formation among PU containing carboxyl pendent groups after curing with TMPTA-AZT enhance the thermal stability.

CONCLUSIONS

A model reaction of mono-AZT containing compound, MA-AZT, with trimethyl acetic acid (TMAA) demonstrates a ring-opening product, which was

TABLE II
Thermal Degradation Temperatures of PU Resins with TMPTA-AZT

| | WPU ^a | WPU with TMPTA-AZT (phr) ^b | | | | |
|--------------------|------------------|---------------------------------------|-------|-------|-------|-------|
| | | 1.0 | 2.0 | 3.0 | 4.0 | 5.0 |
| T_{donset} (°C) | 252.2 | 268.3 | 274.2 | 278.3 | 278.8 | 279.1 |
| $T_{d10\%}$ (°C) | 276.3 | 288.1 | 290.3 | 294.8 | 296.8 | 297.2 |
| $T_{d1stmax}$ (°C) | 281.1 | 290.4 | 295.3 | 299.7 | 301.3 | 302.0 |
| $T_{d2stmax}$ (°C) | 392.5 | 396.3 | 397.2 | 398.0 | 398.2 | 400.5 |

^a WPU was the original PU without curing agent, TMPTA-AZT.

^b Curing dosages (phr) based on grams per 100 g PU resin.

characterized as an amino ester bond formation.¹⁸ A trifunctional AZT compound, TMPTA-AZT, was synthesized and served as a latent curing agent for carboxyl group containing aqueous-based PU dispersion. It resulted in a convenient single-component self-curing aqueous-based PU system. A self-cured PU resin was obtained from drying of this aqueous PU dispersion at ambient temperature. Physical properties of self-cured PU resin were improved depending on the TMPTA-AZT curing dosages. For example, the gel content increases from 0% of WPU resin to 77.5% of self-cured PU resin with 5.0 phr TMPTA-AZT. Thermal stabilities of self-cured PU resins were slightly better than WPU, such as the maximum decomposition temperatures ($T_{d1stmax}$ and $T_{d2ndmax}$) reached to 302.0 and 400.5°C, respectively, compared to that of (281.1 and 392.5°C) of WPU. These PU properties improve due to the positive contribution of new trifunctional AZT compound, TMPTA-AZT, as the latent curing agent.

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