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-azetidinyl)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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Azetidine (AZT)[17,18] reacts with carboxylic acid containing compound and it also undergoes self-polymerization at a pH value lower than 7.0; it is similar to a rapid polymerization of triaziridine compound with acrylic acid.[17,19] However, either AZT or aziridine moiety containing compound is stable in an alkaline system. Now, a triazetidine containing compound (e.g., TMPTA-AZT) has been synthesized and introduced into the aqueous-based PU dispersion as a latent curing agent and that results in a single component self-curable aqueous-based PU system. This self-curing aqueous-based PU system remains stable while keeping its pH value around 8.0 at ambient temperature. A self-curing reaction will take place on drying or lowering its pH value lower than 7.0. The crosslinking reaction mechanism was proposed according to a designed model reaction of methyl 3-azetidinyl propionate (MA-AZT) and trimethylacetic acid (TMAA) that has been published.[18] A triazetidine containing compound (TMPTA-AZT) has been prepared and it serves as a new latent curing agent for aqueous-based PU dispersion. The properties of the resulting single component self-curing aqueous-based PU system are evaluated in this report.

EXPERIMENTAL

Materials

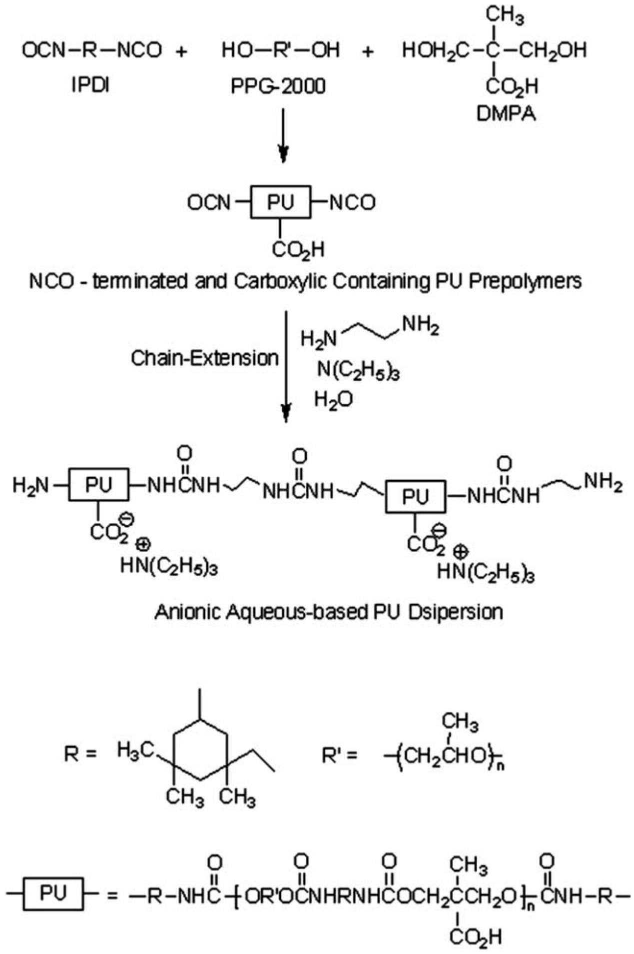
IPDI was supplied by Hul Chemical, Germany. DMPA, ethylenediamine (EDA), triethylamine (TEA), 3-amino-1-propanol, methyl acrylate, thionyl chloride, and trimethylol propane triacrylate (TMPTA) were supplied by Aldrich Chemical, Co., (St. Louis, Misouri). Polypropylene glycol-2000 (PPG-2000) was obtained from Arcos Chemical Co., Taiwan. All solvents were purified before use, which were purified according to the standard method.

Instruments

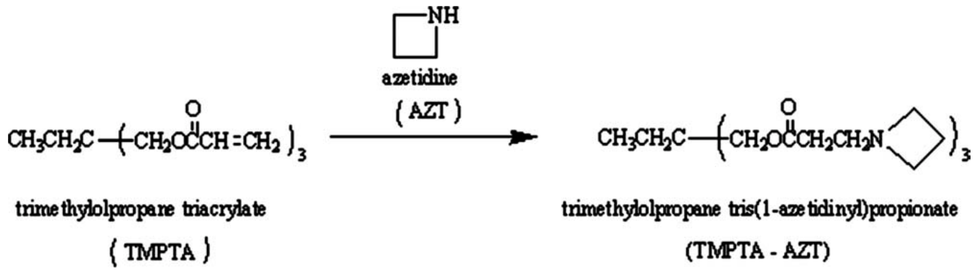
Thermogravimetric data were obtained from Hi-Resolution TGA 2950 TG-DTA Thermogravimetric Analyzer (TA Instrument Co., New Castle, Delaware). Each sample was carried out at a heating rate 10 °C/min under nitrogen atmosphere. Infrared spectra were measured by a HORIBA FTIR FT-720, Japan. Each IR spectrum was measured with a resolution of 4 cm^{-1}. FT-NMR spectra were recorded by Brucker AC-300 spectrometer, Germany. Chemical shifts were reported in ppm relative to residual $CHCl_3$ ($\delta = 77.0$, for ^{13}C).

Preparation of anionic aqueous-based PU dispersions

PPG-2000 (0.1 mol) and DMPA (0.1 mol) were dried at 110°C overnight before mixed with IPDI (0.3 mol) in a 500 mL four-necked reaction flask. The reaction flask was equipped with a mechanical stirrer, a thermometer, a nitrogen inlet, and a condenser with $CaCl_2$ drying tube. The reaction mixture was kept at 110°C and stirred at 300 rpm under nitrogen for about 4 h, until NCO% drops to 3.0 (ASTM D1638 NCO determination method) and remained constant for another half-hour. Following, the freshly dried acetone (230 mL) was added into the reaction flask (when the system cooled down below 50°C) to adjust the viscosity of PU prepolymer. Furthermore, TEA (0.11 mol) and EDA (0.2 mol) were introduced into PU-prepolymer to neutralize the carboxylic acid and chain-extension process. The reaction was kept at room temperature until the NCO value dropped to zero (the NCO absorption peak at 2267 cm^{-1} disappeared in FTIR spectrum). An aqueous-based PU dispersion was obtained from a high shear rate (about 3000 rpm) mixing of PU with 900 mL de-ionized water. The anionic PU dispersion was obtained after acetone was removed and it contained 25% solid contents with a pH value at 8.5 (Scheme 1).



Scheme 1 Preparation of anionic aqueous-based PU dispersion.



Scheme 2 Preparation of TMPTA-AZT curing agent.

Preparation of tri-functional azetidine compound, TMPTA-AZT

AZT was synthesized by a modified process,[18,20,21] which had four reaction steps. The detail synthesis conditions were also published in our previous work.[18] A new triazetidine containing compound, TMPTA-AZT, was prepared via the Michael addition reaction of AZT with trimethylolpropane triacrylate (TMPTA) (Scheme 2).

A CH_2Cl_2 solution (20 mL) of AZT (0.066 mol) was added drop-wise into a CH_2Cl_2 solution (30 mL) of TMPTA (0.02 mol). When the addition completed, the reaction mixture was kept at room temperature for another 12 h. The solvent (CH_2Cl_2) and un-reacted AZT were removed under reduced pressure and the final product, TMPTA-AZT (its ^{1}H-NMR and ^{13}C-NMR spectra on Figures 2(c) and 3(c), respectively) was obtained in 97% yield.

^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): 0.65 (t, 3H), 1.26 (m, 2H), 1.77 (m, 6H), 2.12 (m, 6H), 2.41 (m, 6H), 2.98 (m, 12H), 3.79 (s, 6H).

^{13}C-NMR ($CDCl_3$, 60 MHz, ppm): 7.2, 17.8, 23.0, 33.0, 40.0, 55.0, 55.1, 63.5, 171.5.

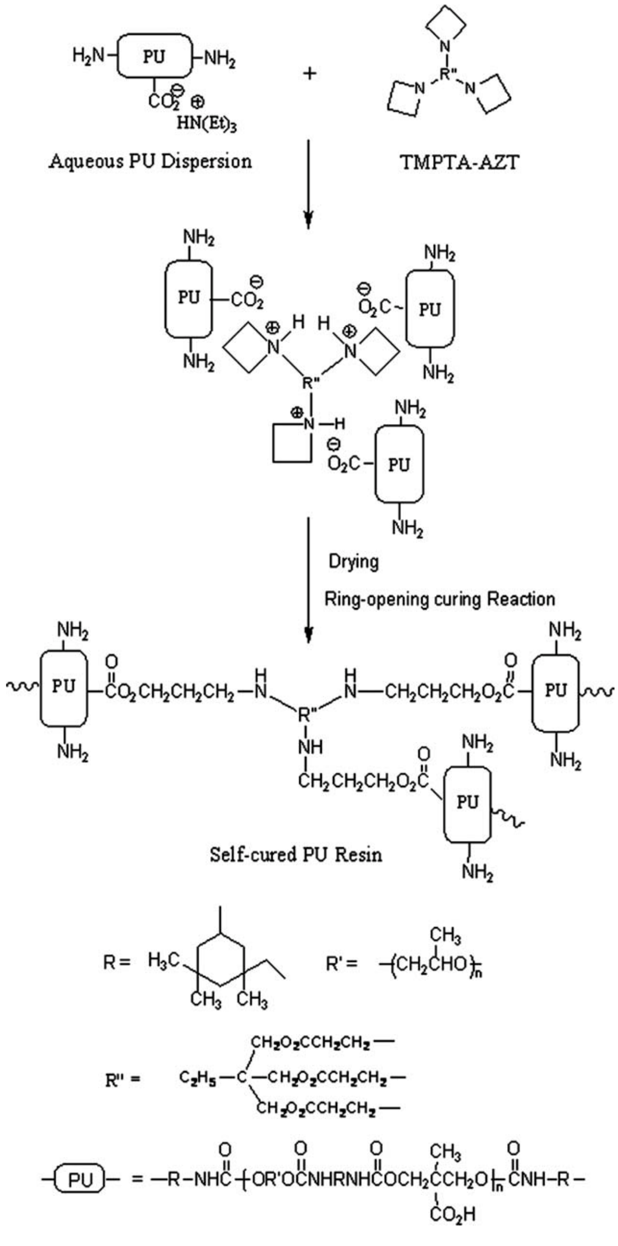
Self-curing aqueous-based PU system with TMPTA-AZT

Various dosages of TMPTA-AZT (1.0–5.0 phr) were diluted with a 10-fold acetone and added into aqueous PU dispersion with stirring. The mixtures were kept stirring under nitrogen for additional 30 min. It became a single-component self-curable aqueous-based PU system after acetone was removed. The self-cured PU resins were obtained from this aqueous PU system on drying at ambient temperature. These cured PU resins were placed in a vacuum oven at 50°C for 24 h and conditioned in a 75% relative humidity chamber for one day before testing. Its self-curing reaction with TMPTA-AZT is shown in Scheme 3.

Physical properties

Gel content

A known weight of oven-dried film (W_1) was put into a Soxhlet extractor for continuous extraction with tetrahydrofuran (THF) for 24 h. The polymer gel remained after extraction was dried (W_2) and calculated according to the test result. Three tests were carried out and averaged for each PU sample.



Scheme 3 Self-curing aqueous-based PU system with TMPTA-AZT.

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

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 postcuring[2–10] and polymer hybridization[13–16] are the alternative efficient and convenient process for improving PU properties. AZT-containing compounds also have been used as a latent curing agent for improving polymer properties in our previous publications.[17,18]

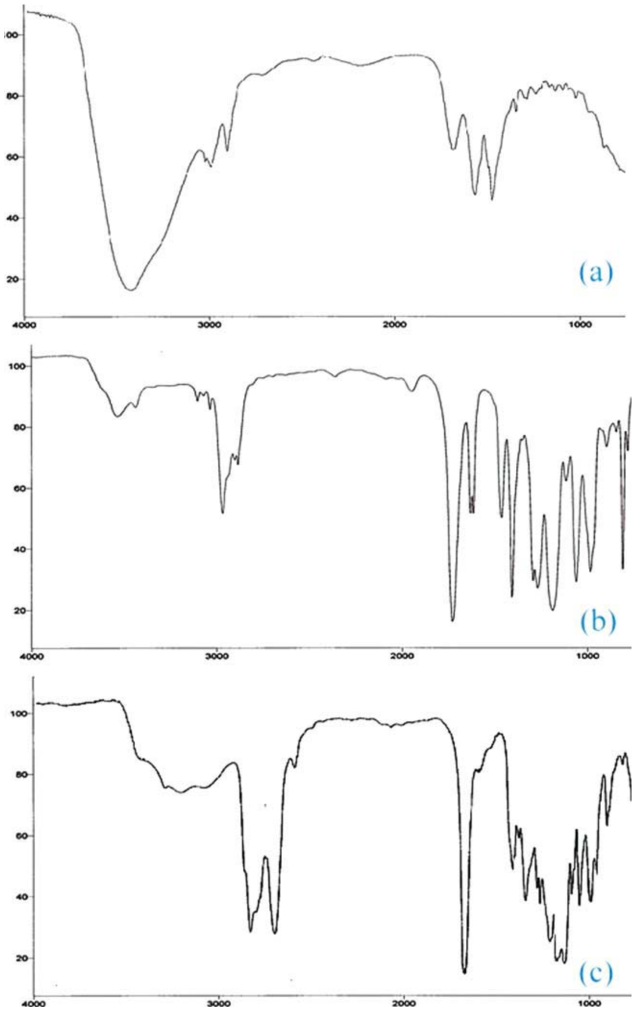


Figure 1 FTIR spectra of (a) AZT, (b) TMPTA, and (c) TMPTA-AZT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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

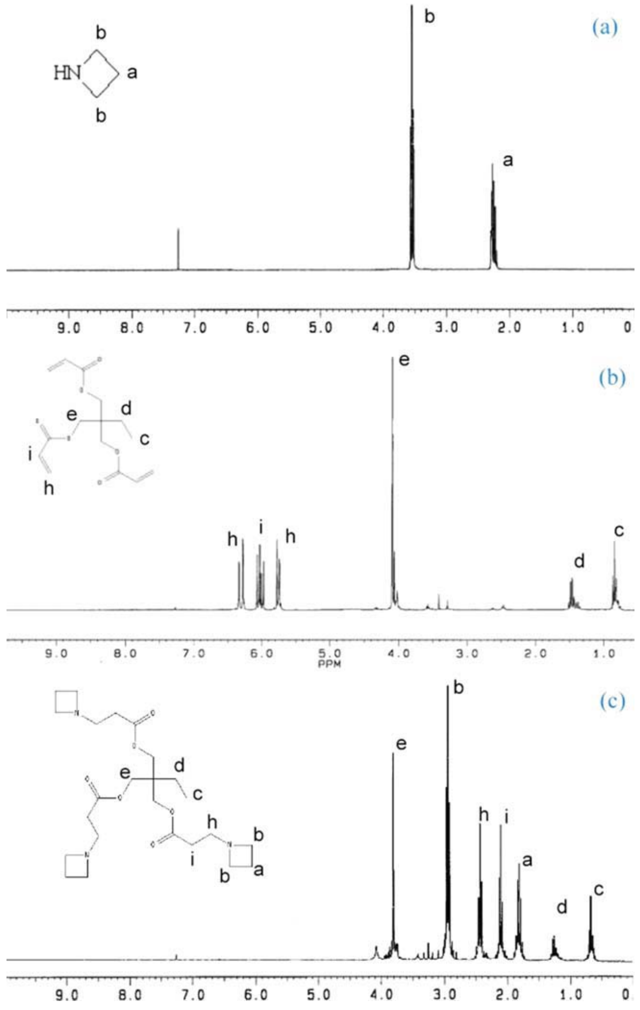


Figure 2 ^{1}H-NMR spectra of (a) AZT, (b) TMPTA, (c) TMPTA-AZT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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 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.

TABLE I
Physical Properties of PU Resins with TMPTA-AZT

		WPU with TMPTA-AZT (phr)[b]				
	WPU[a]	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.

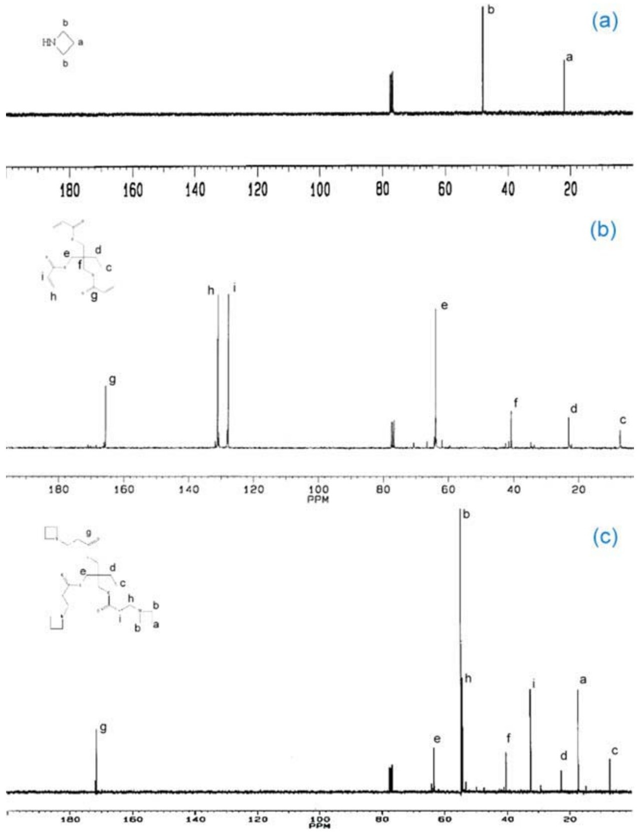


Figure 3 ^{13}C-NMR spectra of (a) AZT, (b) TMPTA, (c) TMPTA-AZT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

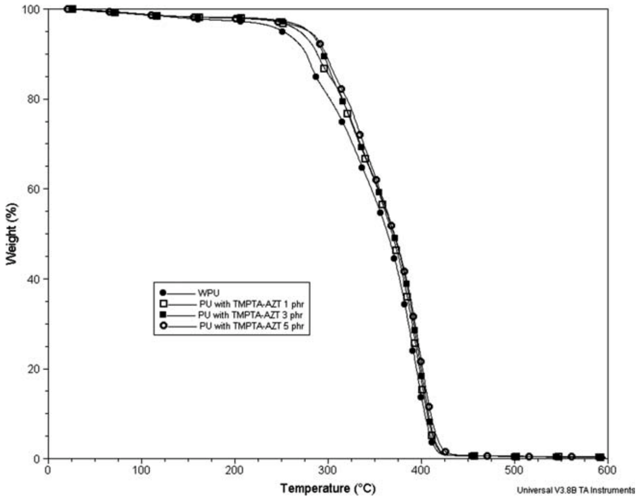


Figure 4 TGA of PU resins with TMPTA-AZT under nitrogen Original PU (●); with 1.0 phr (□); with 3.0 phr (■); with 5.0 phr (○) TMPTA-AZT.

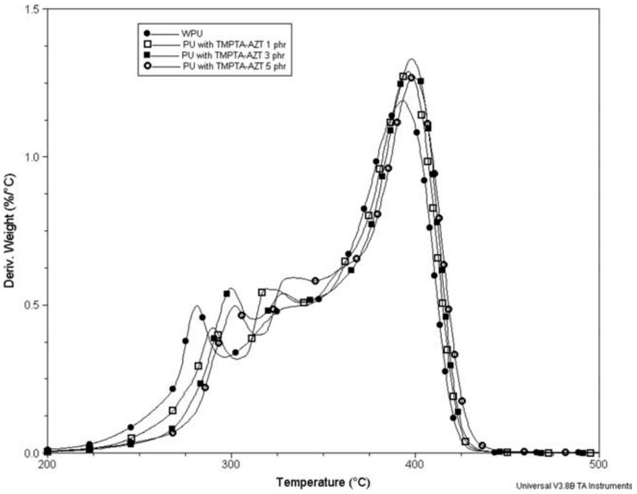


Figure 5 DTA of PU resins with TMPTA-AZT under nitrogen. Original PU (●); with 1.0 phr (□); with 3.0 phr (■); with 5.0 phr (○) TMPTA-AZT.

The chemical shifts (ppm) at 1.77 (m) and 2.98 (m) indicated the protons on AZT ring of TMPTA-AZT on ^{1}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 C═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}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, $T_{d10\%}$, $T_{d1\mathrm{stmax}}$ and $T_{d2\mathrm{ndmax}}$ 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 $T_{d1\mathrm{stmax}}$ and $T_{d2\mathrm{ndmax}}$ 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 with TMPTA-AZT (phr)[b]				
	WPU[a]	1.0	2.0	3.0	4.0	5.0
$T_{d\mathrm{onset}}$ (°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
$T_{d1\mathrm{stmax}}$ (°C)	281.1	290.4	295.3	299.7	301.3	302.0
$T_{d2\mathrm{stmax}}$ (°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 ($T_{d1\mathrm{stmax}}$ and $T_{d2\mathrm{ndmax}}$) 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.

References

1. Dieterich, D. In Polyurethane Handbook; Oertel, G., Ed.; Hanser: New York 1985, Chapter 2.
2. Coogan, R. G. Prog Org Coat 1997, 32, 51.
3. Lai, J. Z.; Chen, P. J.; Yeh, J. T.; Chen, K. N. J Appl Polym Sci 2005, 97, 550.
4. Lai, J. Z.; Ling, H. J.; Yeh, J. T.; Chen, K. N. J Appl Polym Sci 2004, 94, 845.
5. Lai, J. Z.; Ling, H. J.; Yeh, J. T.; Chen, K. N. J Appl Polym Sci 2004, 1997, 91.
6. Chen, G. N.; Chen, K. N. J Appl Polym Sci 1997, 63, 1609.
7. Chen, K. N.; Liu, P. H.; Chen, M. S.; Chen, K.-N. J Polym Res 1997, 4, 165.
8. Chen, G. N.; Chen, K. N. J Appl Polym Sci 1998, 67, 1661.
9. Huang, C. T.; Chen, K. N. J Appl Polym Sci 2006, 100, 3741.
10. Wang, S. C.; Chen, P. C.; Yeh, J. T.; Chen, K. N. J Appl Polym Sci 2006, 102, 4383.
11. Wang, T. Z.; Chen, K. N. J Appl Polym Sci 1999, 74, 2499.
12. Shao, C. H.; Wang, T. Z.; Chen, G. N.; Chen, K. J.; Yeh, J. T.; Chen K. N. J Polym Res 2000, 7, 41.
13. Huang, W. K.; Yeh, J. T.; Chen, K. J.; Chen, K. N. J Appl Polym Sci 2001, 79, 662.
14. Chen, G. N.; Chen, K. N. J Appl Polym Sci 1999, 71, 903.
15. Ling, H. J.; Chen, G. N.; Chen, K. N. Adv Eng Mater 1999, 1, 114.
16. Chen, T. W.; Yeh, J. T.; Chen, K. N.; Lin, Y. S. U.S. Pat. 6,291,554 (1976).
17. Chen, P. C.; Wang, S. C.; Yeh, J. T.; Chen, K. N. J Appl Polym Sci 2007, 104, 809.
18. Wang, S. C.; Chen, P. C.; Yeh, J. T.; Chen, K. N. React Funct Polym 2007, 67, 299.
20. Wadsworth, D. H. J Org Chem 1967, 32, 1184.
19. Chen, P. C.; Wang, S. C.; Hwang, J. Z.; Yeh, J. T.; Huang, C. Y.; Chen, K. N. J Chin Chem Soc 2011, 57, 901.
21. Wadsworth, D. H. Org Synth 1973, 53, 13.