

Curing Reaction of Amino-Terminated Aqueous-Based Polyurethane Dispersions with Triglycidyl-Containing Compound

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ABSTRACT: Amino-terminated anionic aqueous-based polyurethane (PU) dispersion was obtained from NCO-terminated PU prepolymer, which was neutralized with an excess triethylamine (TEA) and chain extended by ethylenediamine (EDA) during water dispersion process. That PU prepolymer was obtained from a polyaddition reaction of isophorone diisocyanate (IPDI), polypropylene glycol-2000 (PPG-2000), and 2,2'-dimethylol propanoic acid (DMPA). This aqueous-based PU dispersion was treated with trimethylolpropane triglycidyl ether (TMPTGE) as a latent curing

agent and resulted in a self-cured PU resin on drying. A model ring-opening curing reaction between oxirane group of TMPTGE with terminal amino group of PU was demonstrated by glycidol with *n*-butyl amine. The physical and mechanical properties as well as thermogravimetric analyses of these self-cured PU resins were evaluated in this article. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 725–731, 2008

Key words: curing of polymers; dispersions; polyurethanes; mechanical properties; oxirane

INTRODUCTION

Polyurethane (PU) is widely accepted because of their versatile properties and can be tailor-made. PU has been modified for wide applications, such as textile treatments, coating, adhesives, elastomer, membranes, foam, and so on.¹ Because of the demands of safety, economic, and environmental protection, traditional solvent-based PU has been restricted since last decade and been gradually replaced by aqueous-based PU. Aqueous-based PU becomes the world market popularly because it is a kind of ecofriendly product.

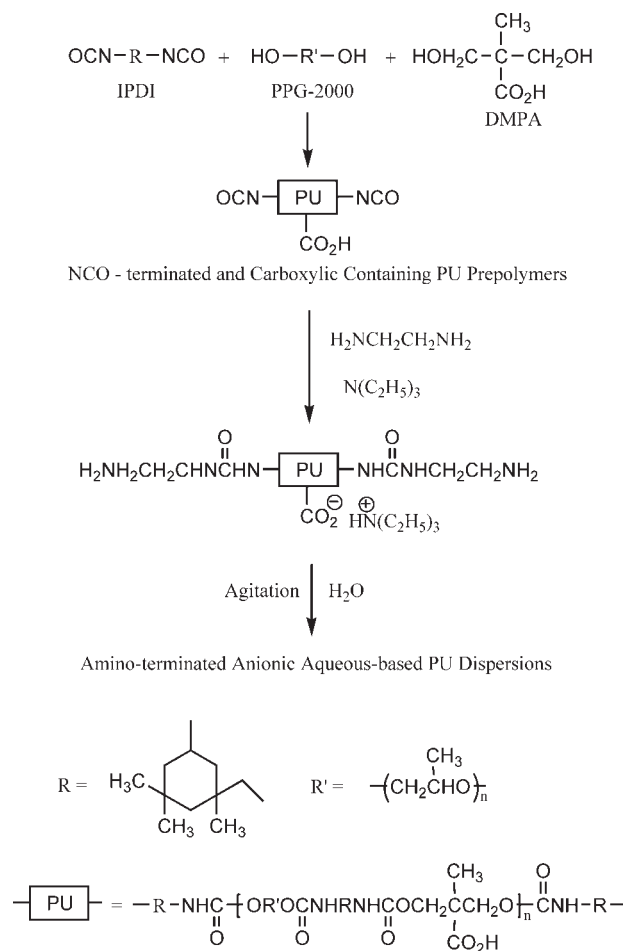
Although aqueous-based PU plays important role in many applications, however, its chemical resistance, physical, and mechanical properties are still insufficient comparing to solvent-based PU. This is because of its linear thermoplastic polymer with lower average molecular weight of aqueous-based PU. To overcome the problems, the improvements of aqueous-based PU are carried out by the postcuring

reaction^{2–6} or polymer hybridization^{7–11} to increase polymer crosslinking density and enhance the performance properties.

Several postcuring treatments were designed and proved that improved the performance of aqueous-based PU, such as aziridine-, azetidino- or oxirane-containing curing agent. The carboxylic acid of PU reacted with aziridine or azetidino curing agent.^{12,13} The amino group reacted with oxirane group containing compound.^{7–11,14} We found amino-terminated aqueous-based PU resin was modified by oxirane-terminated epoxy resin and the curing reaction took place within PU particles of aqueous PU dispersion at ambient temperature that was monitored by fluorescence spectra.^{3,4} A triglycidyl-containing compound, trimethylolpropane triglycidyl ether (TMPTGE) was introduced into amino-terminated aqueous-based PU dispersion and results in a single component self-curing PU system. The self-curing reaction took place between oxirane groups of TMPTGE and amino groups of PU within PU particles on drying. A model curing reaction was demonstrated by glycidol with *n*-butyl amine, which was identified by FT-NMR. The self-cured PU films were evaluated by the measurements of gel content, water-uptake, alcohol-swollen, tensile strength, dynamic mechanical analysis, and thermogravimetric analysis.

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Scheme 1 Preparation of amino-terminated anionic aqueous-based PU dispersions.

EXPERIMENTAL

Materials

Isophorone diisocyanate (IPDI) was obtained from Dow Chemical Co., USA. 2,2'-dimethylol propanoic acid (DMPA), triethylamine (TEA), ethylenediamine, *n*-butyl amine, and trimethylolpropane triglycidyl ether (TMPTGE) were supplied by Aldrich Chemical Co., USA. Glycidol, polypropylene glycol-2000 (PPG-2000) were supplied by Arcos Chemical Co., Taiwan. Acetone and other solvents were dried and distilled over calcium chloride before used. Glycidol was purified by vacuum distillation.

Instruments

Thermogravimetric data were obtained from Hi-Resolution TGA 2950 TG-DTA, TA, USA. Infrared spectra were measured by a Biorad FTIR FTS-40, USA. ^{13}C -NMR spectra were recorded by Bruker AC-300 spectrometer, Germany. Chemical shifts were reported in ppm relative to residual CHCl_3 (δ

= 77.0, for ^{13}C). Stress and strain curves of PU films were taken with Shimadzu Autograph S-100-C, Japan. Dynamic mechanical analysis data are obtained from Dynamic Mechanical Analyzer, TA-Q800, USA.

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 under nitrogen for about 4 h, until NCO% drops to 3.0 (ASTM D1638 NCO determination method) and remained constant for another half an 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. Then, water solution of TEA (0.11 mol) and EDA (0.2 mol) were introduced into PU prepolymer for neutralization and chain-extension during water dispersion process with a high shear rate mixing. The anionic PU dispersion was obtained after acetone was removed and it contained 25% solid content with a pH value at 8.5 (Scheme 1) (Fig. 1).

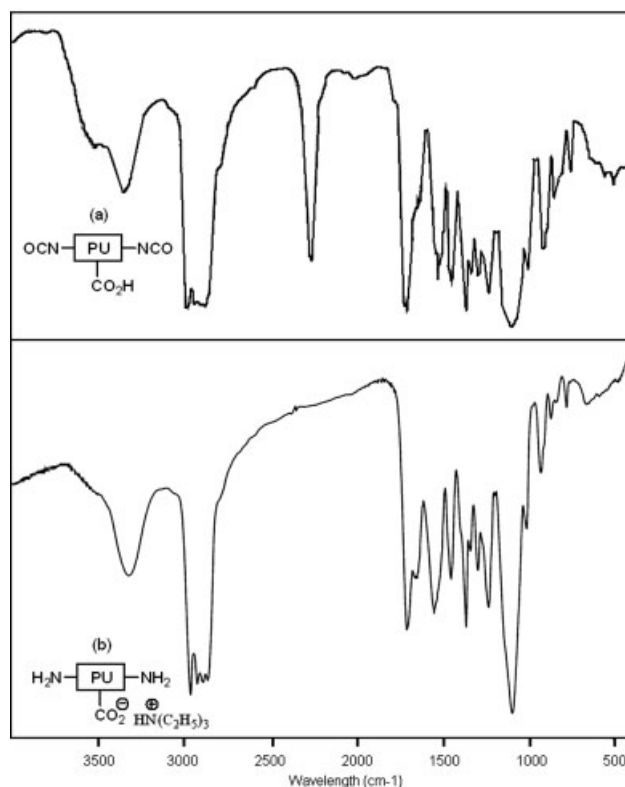


Figure 1 FTIR of (a) PU NCO terminated prepolymer; (b) Amino-terminated PU.

Treatment of aqueous-based PU dispersion with TMPTGE

A various dosages (1, 2, 3, 4, and 5 phr) of TMPTGE were diluted with acetone and added drop-wise into aqueous-based PU dispersion, respectively. After the addition, acetone was removed in a rotary evaporator. The final PU dispersion were cast on the glass plate and dried at ambient temperature. The final PU films were further dried in a 50°C vacuum oven for 24 h and conditioned at a 75% relative humidity environment for 1 day before testing.

Model reaction of glycidol with *n*-butyl amine

n-Butyl amine (0.25 mol) was placed into a 50-mL three-necked round-bottom flask and equipped with a condenser, an addition funnel, and a magnetic stirrer bar in an ice bath. Glycidol (0.05 mol) was added drop-wise into the reaction system via an addition funnel. After the addition, the reaction mixture was kept at 50°C for 6 h and then cooled down to room temperature, the excess *n*-butyl amine was removed by reduced pressure. The ring-opening product was isolated and identified by FT-NMR.

Physical and mechanical 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.

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

Water-uptake

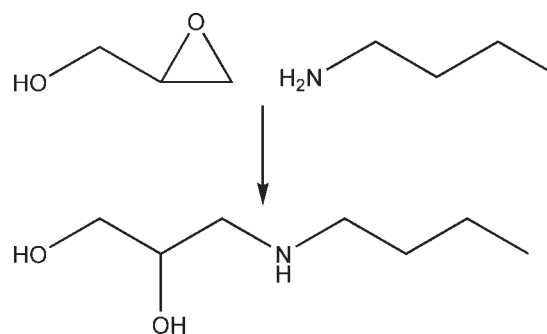
A known weight (W_0) of dried PU film sample with a dimension of 60 mm × 60 mm × 1 mm was immersed in deionized water bath for 7 days. The towel-dried sample weight (W_1) and the oven-dried sample weight (W_2) were obtained. Water-uptake (W_w %) and weight loss (W_x %) of the PU film in water were calculated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

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

where W_w is the amount of water-uptake by PU film.

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

where W_x is the amount of PU film dissolved into the water.



Scheme 2 Model reaction of glycidol with *n*-butyl amine.

Ethanol swelling

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 wiped 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 equations.

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

where W_e is the amount of ethanol absorption by PU film.

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

where W_y is the amount of PU film dissolved into the ethanol solution.

Tensile strength and elongation

Each PU film was cast from this prepared self-curable PU dispersion and dried at room temperature then was kept in an oven at 50°C for 24 h and conditioned at a 75% relative humidity environment at 25°C for 1 day before testing. Dumbbell-shaped specimen of 1.0-mm thickness was used. The gauge length was 40 mm, and the test was performed at a crosshead speed of 40 mm/min. Three test specimens of each sample were taken for the measurement, and calculated the mean results.

Thermogravimetric analysis (TGA)

Each PU sample (about 10 mg) was measured by a thermogravimetric analyzer with a heating rate of 10°C/min from room temperature to 600°C under nitrogen.

Dynamic mechanical analysis (DMA)

Air-dried PU films were dried further in 50°C oven for 24 h before testing. Dynamic mechanical analysis

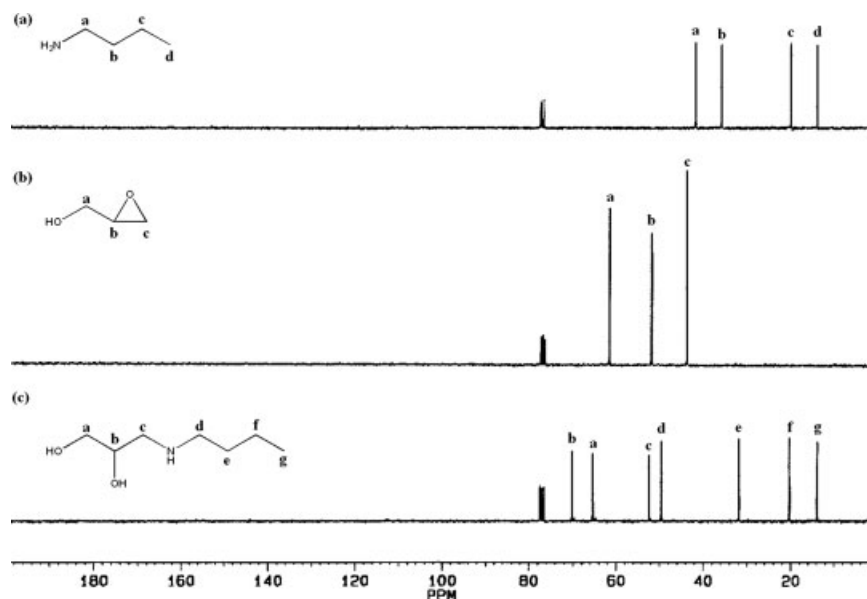


Figure 2 ^{13}C -NMR of (a) butyl amine; (b) glycidol; (c) 3-(butylamino)-propane-1,2-diol.

(DMA) was carried out in film tension mode with a heating rate of $3^\circ\text{C}/\text{min}$ from -70 to 100°C at 1.0 Hz frequency for each testing sample.

RESULTS AND DISCUSSION

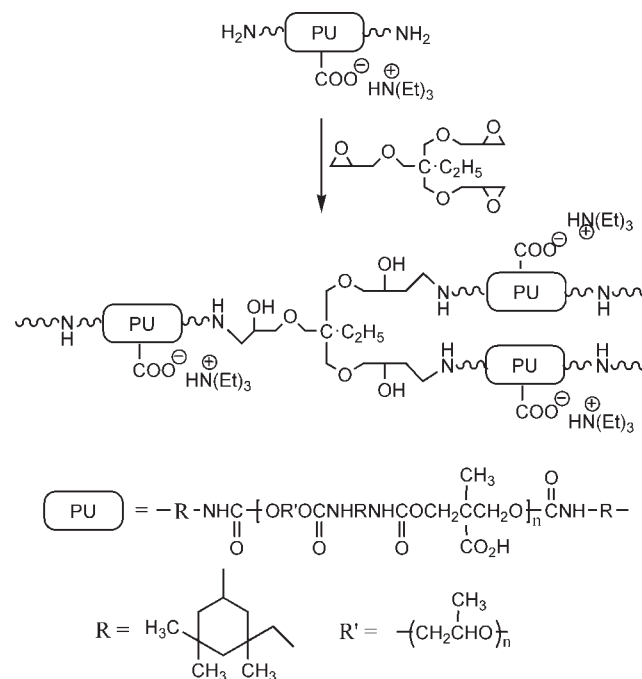
Amino-terminated anionic aqueous-based PU dispersion was obtained from a conventional PU prepolymer process and followed by neutralization with TEA and chain-extension with EDA during the water dispersion process (Scheme 1). This aqueous-based PU dispersion consisted of about 1.06% of terminal amino groups.

Model reaction of glycidol with *n*-butyl amine

A model reaction (Scheme 2) of glycidol with *n*-butyl amine was monitored by ^{13}C -NMR (Fig. 2). The chemical shift of carbon atom next to amino group of *n*-butyl amine was 41.6 ppm while the two carbon atoms on the oxirane ring and carbon atom next to hydroxyl group of glycidol were at 44.0, 52.2, and 61.9 ppm on ^{13}C -NMR spectrum, respectively. After ring-opening reaction the chemical shift of carbon atom next to amino group of *n*-butyl amine was shifted downfield to 49.5 ppm. At this meantime, original chemical shifts at 44.0 and 52.2 ppm of oxiranyl ring were disappeared and two new chemical shifts appeared at 52.3 and 70.1 ppm. The chemical shift of carbon atom next to primary hydroxyl group was shifted from 61.9 to 65.3 ppm. The ^{13}C -NMR spectra confirmed the formation of ring-opening product, 3-(butylamino)-propane-1,2-diol (Scheme 2).

Posttreatment of aqueous PU dispersion with TMPTGE

The treatment of trimethylolpropane triglycidyl ether (TMPTGE) with amino-terminated aqueous-based PU dispersion at ambient temperature that resulted in a formation of postcured PU resin on drying. The curing reaction between the oxirane ring of TMPTGE and amino terminated PU (Scheme 3) is similar to the model reaction of glycidol with *n*-butyl amine (Scheme 2).



Scheme 3 Postcuring of amino-terminated aqueous-based PU with TMPTGE.

TABLE I
Physical Properties of PU with TMPTGE Curing Agent

| | Original PU | PU with TMPTGE (phr) ^a | | | | |
|-------------------------------|----------------|-----------------------------------|------|------|------|------|
| | | 1.0 | 2.0 | 3.0 | 4.0 | 5.0 |
| Gel contents ^b (%) | 0.0 | 66.2 | 84.9 | 87.7 | 90.8 | 92.1 |
| W_w (%) | 23.9 | 14.2 | 10.9 | 9.6 | 9.1 | 8.0 |
| W_x (%) | 2.1 | 1.7 | 1.1 | 1.0 | 1.0 | 0.7 |
| W_z (%) | – ^c | 1204 | 586 | 431 | 359 | 323 |
| W_y (%) | 100.0 | 25.7 | 14.9 | 10.9 | 8.2 | 7.2 |

^a Curing dosage based on one hundred solid of aqueous-based resins.

^b Soxhlet extraction with THF.

^c PU Films 100% dissolved in ethanol.

Physical properties of postcured PU film with TMPTGE

Gel content

Gel content of dried PU film from original aqueous-based PU is zero (soluble in tetrahydrofuran, THF completely), which indicated original PU was a linear thermoplastic resin with low molecular weight. Each postcured PU films had greater gel content than the original PU. For example, the treatments with 3 and 5 phr of TMPTGE, the resulted PU films had 87.7% and 92.1% gel content, respectively. These were contributions from the curing reaction between oxirane groups of TMPTGE with amino-terminated groups of PU and resulting in the formation of polymeric networked PU resin (Table I).

Ethanol swollen

Original PU film dissolved in ethanol completely. However, after the treatments with various dosages of TMPTGE, the amount of ethanol absorption was

reduced with increasing TMPTGE dosage (Table I). Ethanol absorption of PU film with 1.0 phr TMPTGE was 1204% and the value decreased to 323% with 5.0 phr TMPTGE. The results of PU film dissolved into ethanol (W_y %) has a similar pattern of ethanol swollen with different TMPTGE dosages.

Water-uptake

The water-uptake of original PU film was 23.9% and it decreased with increasing TMPTGE dosages (Table I). Water-uptake of postcured PU film was 14.2% with 1.0 phr of TMPTGE and decreased further to 8.0% with 5.0 phr TMPTGE. The treatment of TMPTGE also demonstrated the postcuring reaction and forming polymeric network structure of final PU resin.

Mechanical properties of TMPTGE cured PU film

Tensile stress at 400% elongation was 27.0 kgf/cm² of original PU resin and it increased with increasing

TABLE II
Mechanical Strength of PU with Curing Agent TMPTGE Series

| | Original PU | PU with TMPTGE (phr) ^a | | | | |
|---|---|-----------------------------------|---------------|---------------|---------------|---------------|
| | | 1.0 | 2.0 | 3.0 | 4.0 | 5.0 |
| Elongation (%) | Tensile Strength (kgf/cm ²) | | | | | |
| 100 | 10.7 | 21.5 | 24.1 | 26.1 | 26.7 | 32.5 |
| 200 | 18.0 | 38.8 | 44.5 | 48.2 | 51.6 | 58.9 |
| 300 | 23.1 | 51.3 | 61.7 | 67.9 | 78.3 | 84.6 |
| 400 | 27.0 | 61.4 | 77.3 | 89.3 | 108.1 | 116.7 |
| 500 | 30.4 | 72.9 | 96.2 | 117.9 | – | – |
| 600 | 33.2 | 83.2 | 116.6 | – | – | – |
| 700 | 36.3 | 95.7 | 141.4 | – | – | – |
| 800 | 39.4 | 109.6 | 171.7 | – | – | – |
| 900 | 42.2 | 126.2 | – | – | – | – |
| 1000 | 45.0 | 144.9 | – | – | – | – |
| 1100 | 47.8 | – | – | – | – | – |
| 1200 | 50.6 | – | – | – | – | – |
| Tensile strength ^b (kgf/cm ² /%) | 50.8/ 1206 | 148.4/ 1026 | 178.6/ 823 | 120.8/ 509 | 114.5/ 420 | 116.7/ 400 |

^a Curing dosage based on one hundred solid of aqueous-based resins.

^b Tensile strength at breaking.

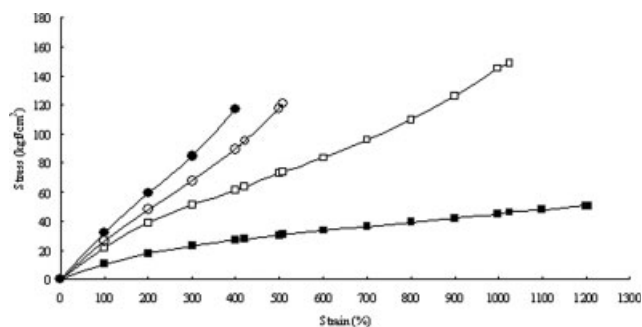


Figure 3 Stress–strain curves of PU with various dosages of TMPTGE PU (■); with 1.0 phr (□); 3.0 phr (○); 5.0 phr (●) phr TMPTGE.

the dosages of TMPTGE. For example, the tensile stress at 400% elongation increased to 89.3 and 116.7 kgf/cm² when PU treated with 3.0 and 5.0 phr of TMPTGE, respectively (Table II and Fig. 3). These mechanical properties improvement also due the evidence of polymeric network structure formation when aqueous-based PU cured by TMPTGE.

Thermal behaviors

Dynamic mechanical analysis (DMA) curves of original PU had a higher damping peak at 46.5°C that belonged to T_g of PU resin. The peak intensity decreased with increasing the dosages of TMPTGE (Fig. 4). Its lower damping intensity is due to PU crosslinking density increased with increasing TMPTGE curing dosage.

Thermal stability of PU film was investigated by the thermogravimetric analysis (TGA) under nitrogen atmosphere. The initial decomposition temperature (T_{onset}) of PU film was increased with

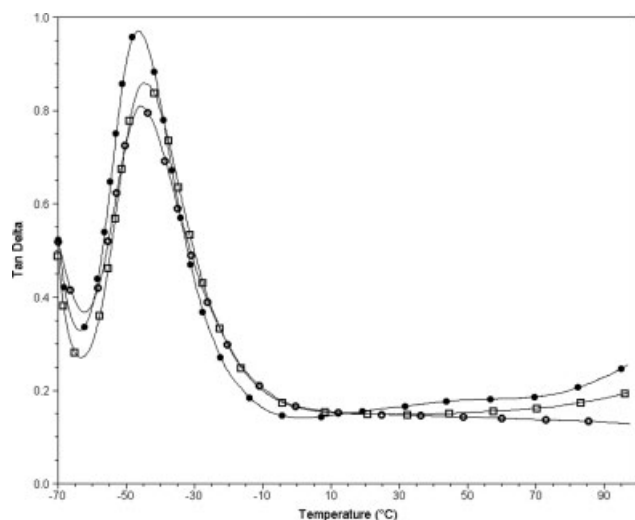


Figure 4 Dynamic mechanical analysis of PU with various dosages of TMPTGE. PU (●); with 1.0 phr (□); with 5.0 phr (○) TMPTGE.

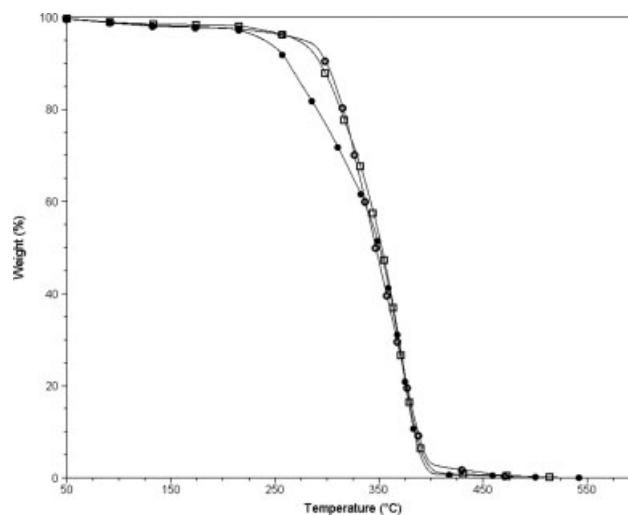


Figure 5 Thermogravimetric analysis of PU with various dosages of TMPTGE under nitrogen. PU (●); with 3.0 phr (□); with 5.0 phr (○) TMPTGE.

increasing the dosages of TMPTGE (Fig. 5). For example, T_{onset} of original PU was at 247.8°C and that of cured PU increased to 274.2 and 307.7°C with 3.0 and 5.0 phr of TMPTGE curing dosages, respectively (Table III). These phenomena also proved the curing between PU and TMPTGE.

CONCLUSIONS

A triglycidyl-containing compound, TMPTGE served as a convenient postcuring agent for amino-terminated anionic aqueous-based PU dispersion. Its postcuring reaction had been taking place between oxirane of TMPTGE and amino groups of aqueous-based PU on drying. The crosslinking density of this self-cured PU film depended on the amount of TMPTGE dosages. The physical and mechanical properties as well as thermal behaviors were directly related to the crosslinking density of resulted PU resin. TMPTGE functioned as an alternative convenient postcuring agent for aqueous-based PU dispersion.

TABLE III
Thermal Properties of PU with Various Dosage of TMPTGE

| | PU with TMPTGE (phr) ^a | | | | | |
|--------------------------|-----------------------------------|-------|-------|-------|-------|-------|
| | Original PU | 1.0 | 2.0 | 3.0 | 4.0 | 5.0 |
| T_{onset} ^b | 247.8 | 264.4 | 266.6 | 274.2 | 306.7 | 307.7 |
| T_{dmax} ^c | 372.1 | 371.3 | 374.3 | 370.7 | 370.1 | 372.4 |

^a Curing dosage based on one hundred solid of aqueous-based resins.

^b The initial decomposition temperature.

^c The temperature of the maximum decomposition rate.

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