

Dual-Curing of Anionic Aqueous-Based Polyurethanes at Ambient Temperature

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ABSTRACT: Polyurethane (PU) prepolymers are prepared by a polyaddition of isophorone diisocyanate, polypropylene glycol-1000, and 2,2-dimethylolpropanic acid. The anionic aqueous-based PU dispersions are derived from a water dispersion process of these NCO-terminated PU prepolymers together with a neutralization and a chain extension. They have both terminal amino and pendent carboxylic groups which are potentially reactive sites toward a di-functional epoxy and a tri- or di-aziridinyl compound of a dual-curing PU system, respectively. The stabilities of the resulting PU dispersions on zeta potential and particle size distributions are investigated. The improvements on mechanical, physical, and thermal properties of these dual-cured PU systems are also evaluated. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 1661–1671, 1998

Key words: aqueous-based PU; epoxy; aziridinyl latent curing; dual-curing

INTRODUCTION

Polyurethanes (PUs) have been widely accepted for various applications due to their versatile properties which can be tailor-made. PUs have been modified for wide ranging applications during the past 60 years, such as textile treatments, synthetic leathers, coatings, adhesives, foams, membranes, elastomers, and so on.¹

The solvent-based PUs will be restricted in their traditional applications sooner or later because of the demands of economics, safety, and environmental regulations.^{2–6} Aqueous-based PUs could replace them and play an important role in their applications in the near future. However, concerns of shelf-life and batch variation of the current aqueous-based PUs have to be overcome; furthermore, their mechanical and other performance properties are lower than the conventional solvent-based PUs,

caused by their low molecular weight with thermoplastic characters. However, PU prepolymers with a higher molecular weight or a partial crosslinking will have a viscosity too high to be dispersed homogeneously by water. Even further, it creates instability factors, such as coarse particle sizes of the resulted PU dispersions. An introduction of a post-curing system could be one of the practicable solutions to compensate for the deficiencies of these prepared anionic aqueous PU dispersions.^{2–6}

An anionic aqueous-based PU system used in this article was prepared by a two-stage PU prepolymer process. It is from a polyaddition of isophorone diisocyanate, polypropylene glycol-1000, and 2,2-dimethylol propanic acid, then followed by a neutralization with triethylamine and a chain extension with ethylenediamine during a water dispersion process (see Scheme 1). The resulting anionic aqueous-based PU is a solvent-free and self-emulsified dispersion system. There are terminal amino and pendent carboxylic reactive groups which coexist in these aqueous PU dispersions. A di-functional epoxy and a tri- or di-aziridinyl compound is chosen for a selective

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Table I Mechanical and Physical Properties of PU with Various Dosages of Di-functional Epoxy Compounds

Properties	PU with Epoxy Resin Curing Agents												Original PU
	3.3 phr			8.3 phr			16.7 phr			25.0 phr			
	-901	-902	-903	-901	-902	-903	-901	-902	-903	-901	-902	-903	
	Tensile Strength (kg/cm ²)												
Elongation (%)													
100	5.3	4.8	4.1	6.2	7.4	4.9	7.5	8.8	4.2	7.6/45	8.0/94	4.6	4.7
200	8.0	7.3	6.2	9.5	12.1	7.5	—	—	—	—	—	7.0	6.9
300	10.7	10.2	8.4	13.1	—	10.2	—	—	—	—	—	—	8.0
400	14.0	13.7	11.1	—	—	—	—	—	—	—	—	—	10.4
500	18.0	17.4	14.5	—	—	—	—	—	—	—	—	—	13.4
600	—	—	—	—	—	—	—	—	—	—	—	—	17.0
Contact Angle (°)	74.6	79.2	75.4	79.6	80.6	76.2	82.2	82.2	81.2	85.8	85.4	79.4	76.0
Water uptake (<i>w_a</i> %)	9.7	10.5	10.0	7.1	7.5	6.9	6.9	7.2	5.8	7.0	7.0	5.7	19.0
Polym. Wt. Loss (<i>w_x</i> %)	0.5	0.1	0.5	0.2	0.1	0.6	0.4	0.1	0.3	0.1	0.1	0.6	0.7
Gel Content (%)	88.6	89.6	85.4	92.4	93.7	89.8	93.6	93.6	84.1	93.7	94.2	81.9	85.4
Hardness (Shore A)	15.2	15.2	16.0	16.0	16.5	16.2	15.8	16.2	16.8	17.5	17.8	17.8	14.6

Di-functional epoxy compounds NPES-901, -902, and -903 were used; their "epoxy equivalent weights" (ew) were 458, 613, and 738, respectively.

curing reaction toward each individual PU reactive site, as a part of dual-curing PU system.

An addition reaction of an amino group of PU with a hydrophobic difunctional epoxy compound takes place in the PU particle core at ambient temperature. However, a tri- or di-aziridinyl compound is soluble in an aqueous phase and serves as a latent curing agent for the aqueous PU system. The carboxylic groups of the polymer will react with an aziridinyl compound only under an acidic environment or on the air drying stage.²⁻⁶ These two types of curing agents have different chemical characters and the curing reactions occurred in their own conditions as a single-curing or a dual-curing system. Both epoxy and aziridinyl compounds play important roles in a dual-curing system.

The PU dispersion properties after the treatment either with a single-curing or dual-curing system were monitored by a particle sizer and zeta potential meter. The cured PU films were evaluated by the measurements of tensile strength, contact angle, water uptake, gel content, dynamic mechanical, and thermogravimetric analyses.

EXPERIMENTAL

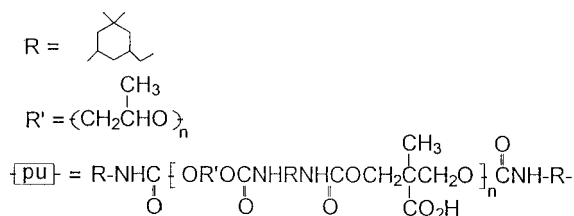
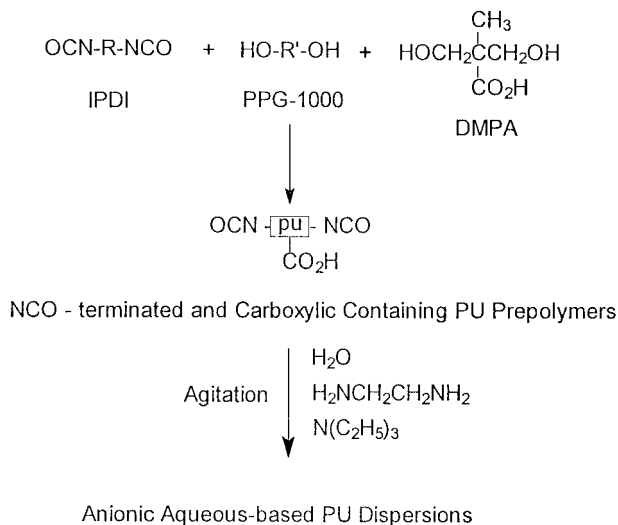
Instruments

Dynamic mechanical behaviors of PU films were performed by dynamic mechanical thermal ana-

lyzer (DMTA) (Polymer Laboratories, MK-II). Thermogravimetric data were obtained from a Perkin-Elmer 7 thermal analysis system. Stress-strain curves of PU films were measured by a Shimadzu Autograph S-100-C. Particle size and zeta potential distributions of PU dispersions were taken by Zetamaster and Zeta Sizer ZEM 5002 (Malvern Instruments Limited). Contact angles of pure water droplets on a dried PU film were measured by FACE contact angle meter, model CA-A (Kyowa Kaimenkagaku Co., Ltd.).

Materials

Triethylamine (TEA) and ethylenediamine (EDA) were supplied by Junsei Chemical Co.; 2,2-dimethylpropanoic acid (DMPA) was supplied by Aldrich Chemical Co.; these were distilled or recrystallized before use. Isophorone diisocyanate (IPDI) was supplied by Olin Chemical Co.; polypropylene glycol-1000 (PPG-1000) was supplied by Arco Chemical Co.; Difunctional epoxy compounds, NPES-901, -902, -903, and NPEW-254 were from Nan-Ya Plastics Industrial Co.; Tri- and di-aziridinyl compounds, TMPTA-AZ-0 and HDDA-AZ-0, were prepared by Gelie Co., all these were used as received without further purification.



Scheme 1 Preparations of aqueous-based PU ionomers.

Preparations of Anionic Aqueous-Based PU Dispersion⁷

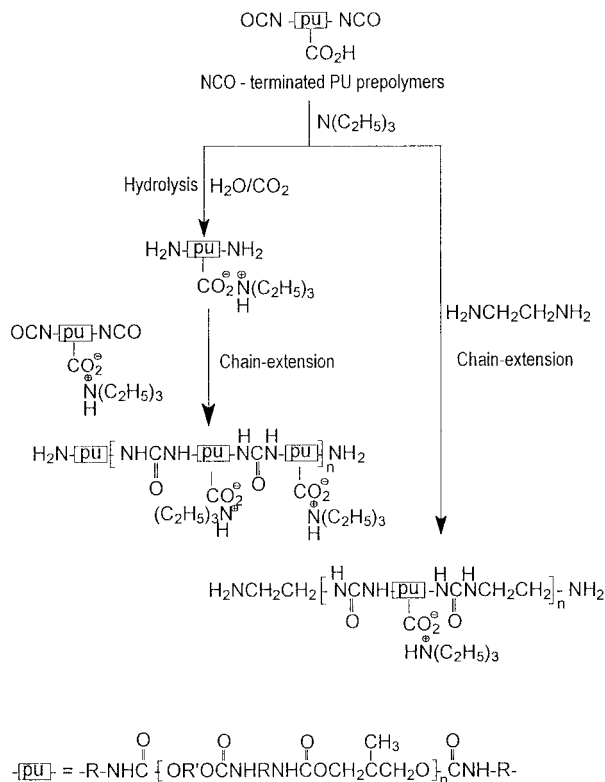
PPG-1000 (0.1 mol) and DMPA (0.1 mol) were dried at 110°C overnight before they were mixed with IPDI (0.3 mol) in a 500-mL 4-necked resin flask. The resin flask was equipped with a mechanical stirrer, thermometer, nitrogen inlet, and condenser with a CaCl₂ drying tube. The reaction was carried out and kept at 90°C for ~ 4 h, or until NCO% dropped below 3.0 (according to ASTM D1638 NCO determination method), which took another half hour. Then freshly dried acetone (230 mL) was added in the reaction flask in order to adjust the viscosity of PU prepolymers. The PU dispersions resulted from a high shear rate mixing of these PU prepolymers with a 450-mL aqueous solution of EDA (0.08 mol) and TEA (0.1 mol). The final amino-terminated PU dispersions (see Schemes 1 and 2) had 30% solid contents and the pH 8.0 to 9.0 after acetone was removed under vacuum.

Curings of Aqueous PU with a Difunctional Epoxy Compound

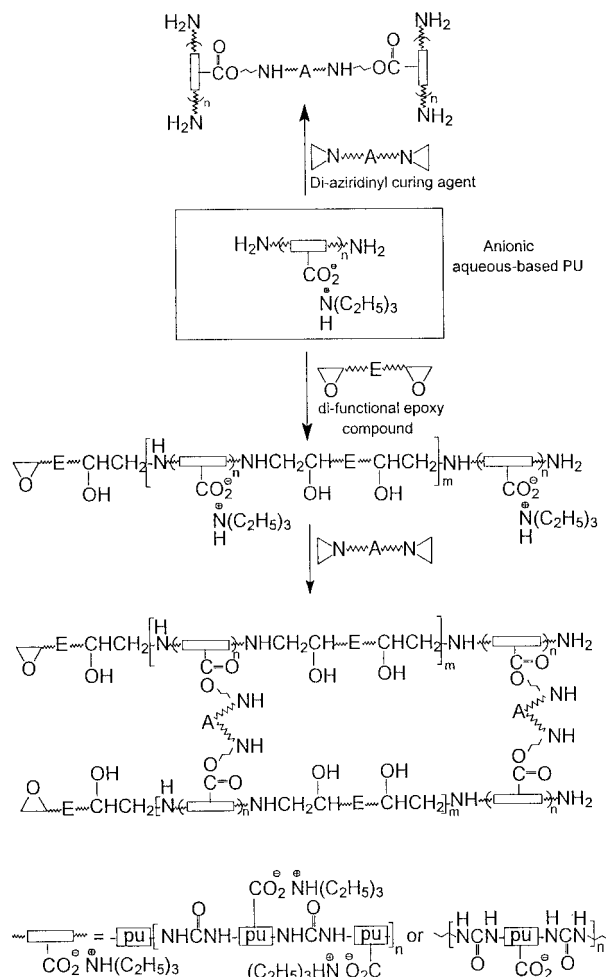
The prepared aqueous-based PU dispersion was treated with a di-functional epoxy compound (NPEW-254, NPES-901, -902, or -903) (see Scheme 4) in various dosages (3.3, 8.3, 16.7, and 25.0 phr). Their epoxy equivalent weight (ee) was determined according to the published method.¹¹ Each difunctional epoxy compound was diluted with a 20-fold amount of acetone before its addition. The addition mixture was kept stirring for additional 2 h and then acetone was removed from the dispersions under low pressure. The resulted PU dispersions were sampled for film casting and other testings.

Self-Curable PU System with a Multi-Aziridinyl Compound

The prepared aqueous-based PU dispersion was treated with a tri- or di-aziridinyl compound, TMPTA-AZ-0 (3.3 phr) or HDDA-AZ-0 (8.3 phr) (see Scheme 5) as a latent curing agent. The aziridinyl compound was diluted with a 10-fold amount of deionized water before its addition



Scheme 2 PU chain-extension reactions on water dispersion process.



Scheme 3 Dual-curing of anionic aqueous-based PU system.

into PU dispersion. The addition mixture was kept at constant agitation under a nitrogen blanket for one hour. It is necessary to maintain a pH value of PU dispersions at 8.0 or above. The resulting PU dispersion becomes a single-pack self-curable aqueous-based PU system and it is stored in a tightly closed container for film casting and other tests.

Dual-Curing System of Aqueous-Based PU Dispersions

The prepared aqueous-based PU dispersion was treated with a di-functional epoxy compound, NPEW-254 or NPES-901, as the first PU curing agent. This resulted dispersion was treated further with TMPTA-AZ-0 or HDDA-AZ-0 as a latent curing agent in various dosages (3.3, 5.0, 6.7, and 8.3 phr). This final addition mixture became an

one-component dual-curing aqueous-based PU system. The proceeding addition procedure for each curing agent was followed for this dual-curing PU system.

Physical Properties of PU Dispersions

Anionic aqueous-based PU dispersion was treated with either a single-curing or the dual-curing agent at ambient temperature. The particle size and zeta potential distributions of each resulting aqueous-based PU dispersion were monitored by a particle sizer and zeta potential meter. Each test specimen was prepared from a PU dispersion sample with a 200-fold dilution of de-ionized water. All the measurements were carried out at 25°C.

Particle Size Measurements

The measurements of an average particle size and particle size distributions of PU dispersions were performed by a dynamic light scattering method. A diode laser with the power of 4 mW on a 670 nm light beam was used.

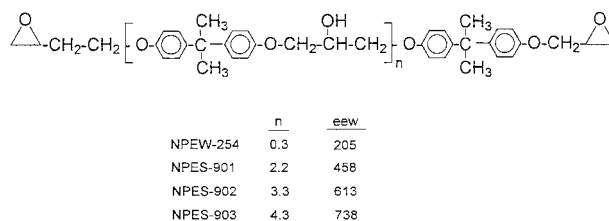
Zeta Potential of PU Dispersions

A particle electrophoresis analyzer with a 5-mW He-Ne laser on a 633-nm light beam was used for the zeta potential measurement of each PU sample.

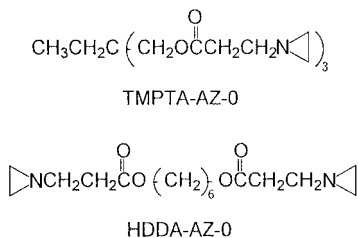
Mechanical and Physical Properties of PU Films

Tensile Strength and Elongation

PU films were cast and air dried from these prepared PU dispersions at ambient temperature and then dried at 50°C for 24 h. These PU films were conditioned in a 75% relative humidity chamber at 25°C for 72 h before the measurement. Each test specimen in a dumbbell shape with 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. Six tests of each PU sample



Scheme 4 Di-functional epoxy compounds.



Scheme 5 Aziridinyl compounds.

were taken and the three measurements which showed the high tensile strength for calculating the mean value were selected.

Gel Content

A known weight of dried PU film was extracted for 24 h in a Soxhlet extractor with tetrahydrofuran. PU gel remained after extraction was dried and calculated. Gel content of PU films are shown in Table I.

Contact Angle

PU film was cast on a glass plate from PU dispersions and dried at ambient temperature. Sets of distilled water droplets on the film surface were used for the contact angle measurements at 25°C. The dimensions of the water droplets were measured ~ 10 s after placing the water droplet. Five measurements of each sample were performed and the three closest results were chosen and averaged for a mean value. The contact angle was calculated by the following equation:

$$\text{Contact angle } (^\circ) = 2 \tan^{-1} (h/r)$$

Where h is a height of the spherical segment of water droplet and r is a radius of the spherical segment.

Water Uptake of PU Film

A known weight (W_0) dried PU film with a dimension of $60 \times 60 \times 1$ mm was immersed in distilled water bath for 8 days. The towel-wiped dry sample weight (W_1) and oven-dried PU film weight (W_2) were obtained. Water uptake ($W_a\%$) and the weight loss ($W_x\%$) of PU film in water were calculated according to the following equations.

$$W_a\% = \frac{W_1 - W_2}{W_2} \times 100\%$$

where W_a is the amount of water uptake by PU film.

$$W_x\% = \frac{W_0 - W_2}{W_0} \times 100\%$$

where W_x is the amount of PU dissolved in water.

Thermal Behaviors

Dynamic Mechanical Analysis

The PU films were dried at 50°C for 24 h and conditioned in a 75% relative humidity at 25°C for 72 h before testing. DMTA measurement in bending mode was used for PU film with a heating rate at 3°C/min from -80 to 150°C on 1.0 Hz frequency.

Thermogravimetric Analysis

Each dried PU sample (~ 10 mg) was taken and measured by a thermogravimetric analyzer with a heating rate of 20°C/min from ambient temperature to 600°C under nitrogen or normal atmosphere.

RESULTS AND DISCUSSION

These self-emulsified and solvent-free anionic aqueous-based PU dispersions were prepared by

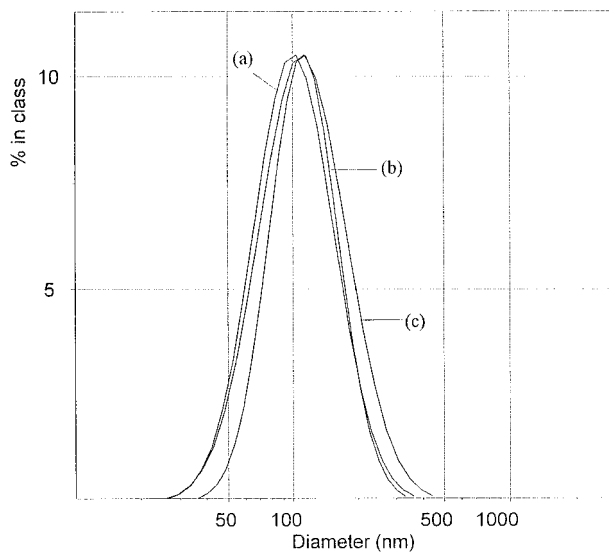


Figure 1 Particle size distributions of PU dispersions. Curves: (a) original PU; (b) with 8.3 phr NPEW-254; (c) with 8.3 phr NPEW-254 and with 8.3 phr HDDA-AZ-0.

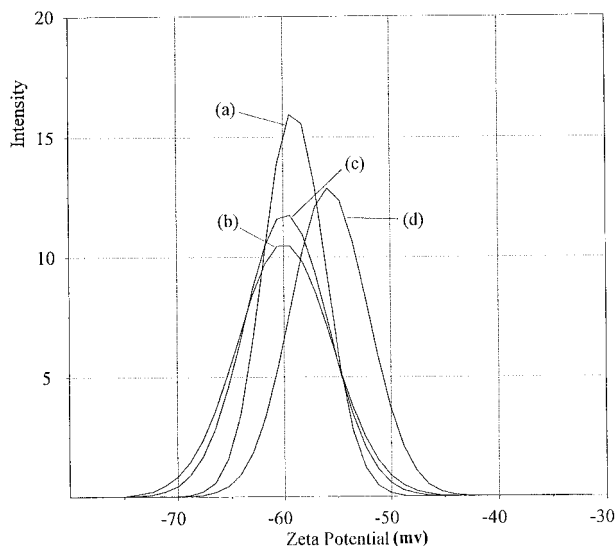


Figure 2 Zeta potential distributions of PU dispersions. Curves: (a) original PU; (b) with 8.3 phr NPEW-254; (c) with 8.3 phr HDDA-AZ-0; (d) with a dual-curing system (8.3 phr HDDA-AZ-0 and 8.3 phr NPEW-254).

a PU prepolymer process followed by a neutralization with triethylamine and a chain extension with ethylenediamine during a water dispersion process (Scheme 1). These PU dispersions had 30% solids. PU films derived from these PU dispersions had 85.4% gel content and 14.6 Shore A hardness; it had 19.0% water uptake and 0.7% polymer loss in water after 8 days' water immersion. There are two potentially reactive sites, primary amino and pendent carboxylic groups coexisted in these prepared aqueous PU dispersions.

Terminal amino groups, the reactive site of the aqueous PU dispersions, were from a hydrolysis and a partial chain extension of ethylenediamine with NCO-terminated PU prepolymers during the water dispersion process (Scheme 2). Both of these amino-terminated polymers existed in the PU dispersions. These terminal amino groups were entangled with the polymer chain and trapped inside the hydrophobic PU particle core in the aqueous PU dispersions. The amino group content is 3.8×10^{-3} equivalents per 100 grams of PU dispersions, which was estimated by a styrene oxide titration method.⁸ The evidence of its fluorescence spectrum indicated that a hydrophobic epoxy curing agent diffused into PU particle of the dispersions.¹⁰ In the mean time, reaction takes place between the epoxy compound and the primary amino groups inside PU particles.¹² Each PU particle of the dispersions serves as a microre-

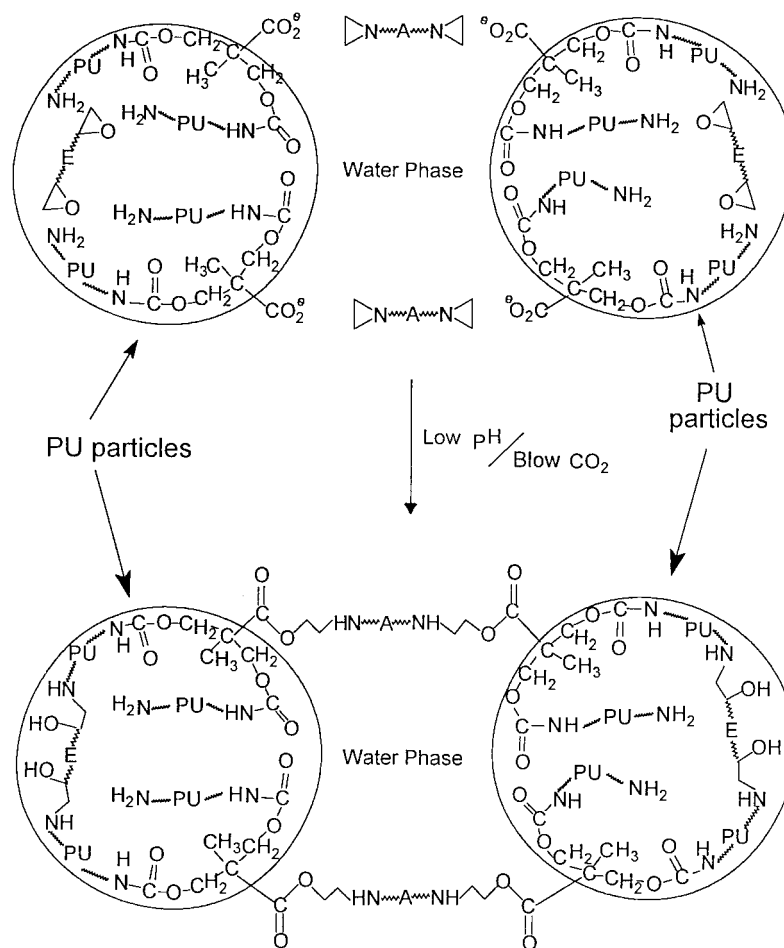
actor for an "amine/epoxy" ring-opening curing reaction (Scheme 3).

Carboxylic pendant, reactive sites of the PU dispersions come from one of the PU ingredients, 2,2-dimethylolpropanoic acid. The hydrophilic carboxylic ions on the PU particle surface extended toward the water phase of aqueous-based dispersion system.¹³ The concentration of that carboxylic ion is 1.5×10^{-2} equivalents per 100 grams of PU dispersions. These ionic groups provide the electronegative charges for a repulsive force among PU particles, which stabilized the final PU dispersions. However, the incorporation of these hydrophilic groups in polymers also brought about the deficiencies on PU water resistance and other application properties. A reaction took place between a carboxylic acid of polymer and a multi-aziridinyl compound which demonstrated an effective way to improve these PU properties^{7-9,14} (Scheme 3). A hydrophilic tri- or di-aziridinyl compound, TMPTA-AZ-0 or HDDA-AZ-0, was selected and added to these PU dispersions as a latent curing agent. It remained stable in the water phase at pH 8.0 or above.⁷

Both reactive sites, carboxylic and amino groups in the aqueous PU system, have curing reaction patterns which are different from each other. PU terminal amino groups react with a hydrophobic di-functional epoxy compound inside the PU particle after they contact each other. The curing reaction takes place between carboxylic groups of polymer and aziridinyl latent curing agent during the drying stage. Their curing behavior on a single-curing and a dual-curing PU system are discussed in this article.

Properties of Aqueous-Based PU Dispersions

The average particle size of the prepared PU dispersion is 110.6 nm in diameter. It changes to 119.8 nm after the treatment with 8.3 phr of NPEW-254 (Scheme 4). This hydrophobic epoxy compound diffused into PU particles in an aqueous dispersion as the first curing agent for the PU system and its average particle size had increased by 9.2 nm. Then a hydrophilic diaziridinyl compound, HDDA-AZ-0 (Scheme 5), is chosen to serve as a latent curing agent for this epoxy-cured PU dispersion. Its size changed to 123.3 nm after the addition of 8.3 phr HDDA-AZ-0, it had an increase of 3.5 nm only. The hydrophilic HDDA-AZ-0 is non-electrolyte and water-soluble. It stayed in the aqueous phase after its addition as a part of this dual-curing PU system. The average particle



Scheme 6 Scheme illustration of dual-curing anionic aqueous-based PU.

size distributions of these resulted PU dispersions were illustrated in Figure 1.

These PU dispersions are self-emulsified with the internal hydrophilic carboxylic groups. Their mean zeta potentials remained at 59 ± 4 mV after the treatment with either a single-curing agent, NPEW-254 or HDDA-AZ-0, or a dual-curing system with NPEW-254 and then HDDA-AZ-0, respectively. The zeta potential distributions of the PU dispersions are shown in Figure 2. Its value remained constant for more than a week if it was kept in a closed container. It is suggested these two different curing agents work independently in a dual-curing system for the aqueous-based PU dispersions. The stability of the resulting PU dispersions are not affected by the addition of this type dual-curing agent.

Mechanical and Physical Properties of PU Films

A series of difunctional epoxy compounds used for PU curings are NPES-901, -902, and -903, their

epoxy equivalent weights (eew) are 458, 613, and 738, respectively (Scheme 4). Each of them owns difunctional epoxy endgroups which are reactive toward the terminal amino groups of PU molecules. A hydrophobic epoxy compound reacts with the amino-terminated polymer after they come into contact with each other inside the PU particles of the aqueous dispersions (Scheme 6).

The original PU had an ultimate tensile strength of 17.0 kg/cm^2 and 600% elongation. The epoxy-cured PU films exhibited some improvements on their stress/strain curves (Fig. 3). For instance, when 8.3 phr of epoxy curing agent, NPES-901 (eew 458) was applied, the resulting PU had 6.2 kg/cm^2 modulus at 100% elongation and 92.4% gel contents. When its epoxy dosage increased to 16.7 phr, its tensile strength (100% elongation) increased to 7.5 kg/cm^2 , and its gel content reached 93.6% (Table I). For other higher eew epoxy curing agents, their mechanical and physical properties of PU films are improved only

at a lower dosage. The higher eew results in a phase separation from the PU system when a higher epoxy dosage is used. It is possibly due to a high eew epoxy compound has a poor acetone (or other hydrophilic solvents) solubility and solidified after its addition into the aqueous PU dispersions.

The most epoxy-cured PU films had the higher contact angle, especially, with a high dosage (e.g., 25.0 phr NPES-902) epoxy compound, as it had a higher contact angle than the original PU film (Table I). These epoxy-cured PU films also had less water uptake and also less polymer loss in water than the original PU. Most of them had <10% of water uptake. This indicated the curing reaction by one of these di-functional epoxy compounds which caused an increase in PU molecular weight and also a decrease on the hydrophilicity of the epoxy-cured PU.

A tri-aziridinyl compound, TMPTA-AZ-0 (Scheme 5), was used as a latent curing agent for the aqueous-based PU system. It reacted with carboxylic pendants of PU on the drying process. The tensile strength of 3.3 phr TMPTA-AZ-0 cured PU film was 5.5 kg/cm² (100% elongation), it had 90.5% gel contents, 77.4° contact angle, and 10.4% water uptake.

TMPTA-AZ-0 was used as one of the parts of a dual-curing PU system. PU was cured with 3.3 phr of NPES-901 and then with 3.3 phr of TMPTA-AZ-0. The final dual-cured PU film had a modulus at 5.4 kg/cm² (with 100% elongation) (Fig. 4); its contact angle increased to 80.4° and the gel contents reached 96.0% (Table II). The

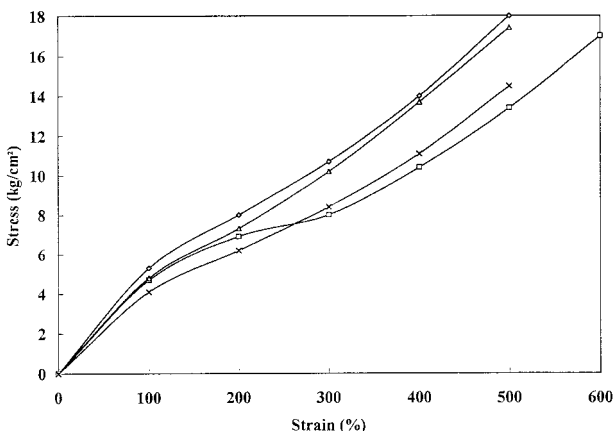


Figure 3 Stress-strain curves of PU treated with 3.3 phr various di-functional epoxy compounds. (a) Original PU (□); (b) with NPES-901 (◇); (c) with NPES-902 (△); (d) with NPES-903 (×).

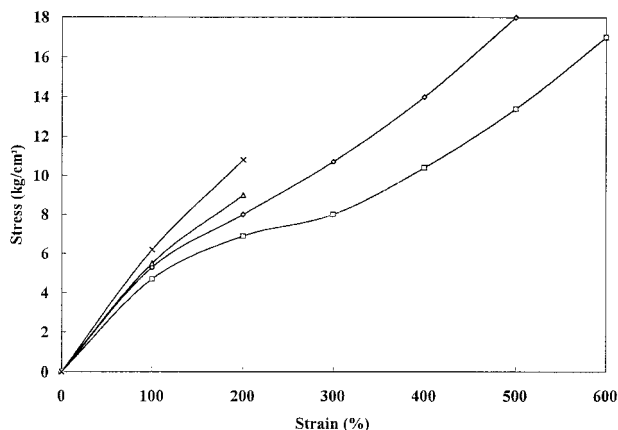


Figure 4 Stress-strain curves of single- and dual-cured PU films. (a) Original PU (□); (b) treated with 3.3 phr NPES-901 (◇); (c) treated with 3.3 phr TMPTA-AZ-0 (△); (d) with dual-curing system (3.3 phr NPES-901 and 3.3 phr TMPTA-AZ-0) (×).

contact angle of the dual-cured PU increased to 83.6° with 5.0 phr of TMPTA-AZ-0, but it decreased to 76.0° with 8.3 phr of TMPTA-AZ-0. This maybe due to a partial homopolymer formation from an excess amount of TMPTA-AZ-0. Its homopolymer had good hydrophilicity⁷⁻⁹ which provides a lower contact angle and higher water uptake for the resulting PU film. However, the gel contents and polymer loss in water had only a slight change with an increase of TMPTA-AZ-0 dosage because of the partial homopolymers formation from TMPTA-AZ-0 as parts of PU structural networks.

Thermal Behavior

The dynamic mechanical data indicated that a higher epoxy dosage of PU system had a higher storage modulus. However, when the dosage of NPES-902 (eew 613) was increased to 25.0 phr, a phase separation from the PU system occurred on its storage modulus curve (Figs. 5 + 6), due to an excess amount of the unreacted epoxy compound¹⁵ present in the PU system.

The DMTA curves of the original PU film had a low temperature damping peak at -38.7°C that is the glass transition temperature (T_g) of PU soft segments. It also had a broad hump around 42.0°C that might be due to the hydrogen-bond relaxation on PU main chain. Its low temperature damping peak intensity decreased with as the epoxy dosage increased. This indicated the curing

Table II PU Properties with a Single- or Dual-Curing System

Properties	PU with Single- or Dual-Curing Agent						Original PU
	PU-E ^a	PU-A ^b	PU-EA ^c				
			3.3 phr	5.0 phr	6.7 phr	8.3 phr	
Tensile Strength (kg/cm ²)							
Elongation (%)							
100	5.3	5.5	5.4	6.2	6.2	5.3	4.7
200	8.0	9.0	—	10.8	—	—	6.9
300	10.7	—	—	—	—	—	8.0
400	14.0	—	—	—	—	—	10.4
500	18.0	—	—	—	—	—	13.4
600	—	—	—	—	—	—	17.0
Contact Angle (°)	74.6	77.4	80.4	83.6	80.6	76.0	76.0
Water uptake (<i>w_a</i> %)	7.1	10.4	8.9	8.7	8.6	10.7	19.0
Polym. Wt. Loss (<i>w_x</i> %)	0.5	0.3	0.4	0.3	0.6	0.4	0.7
Gel Content (%)	88.6	90.5	96.0	95.5	96.8	96.5	85.4
Hardness (Shore A)	15.2	15.5	16.0	16.5	16.8	17.2	14.6

^a PU-E, PU with 3.3 phr di-functional epoxy compound NPES-901.

^b PU-A, PU with 3.3 phr tri-aziridinyl compound, TMPTA-AZ-0.

^c PU-AE, Dual-curing of PU with 3.3 phr NPES-901 and TMPTA-AZ-0 in various dosages.

reaction between epoxy-curing agent and amino groups of the PU main chain; moreover, its free volume decreased as the degree of crosslinking increased. For instance, when NPES-903 is added, the intensity of its damping peak at -38.7°C decreased with the increase in epoxy dosage. When its dosage increased to 25.0 phr, a new

broad peak appeared and centered at 100.9°C on the DMTA curve of PU. That is due to a microgel formation of an unreacted epoxy-curing agent and resulted in a phase separation occurring from its cured PU film (Fig. 6).

The PU films are also cured with 16.7 phr of NPES-901, -902, and -903, respectively. Each epoxy-cured PU also showed a new broad damping

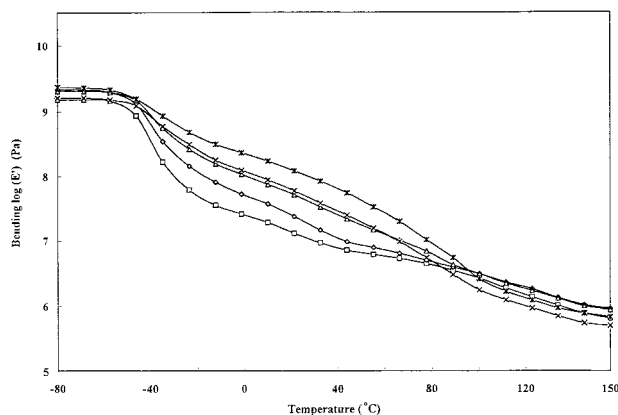


Figure 5 Storage moduli of PU treated with various dosages of NPES-902. (a) Original PU (□); (b) with 3.3 phr NPES-902 (◇); (c) with 8.3 phr NPES-902 (Δ); (d) with 16.7 phr NPES-902 (×); (e) with 25.0 phr NPES-902 (*).

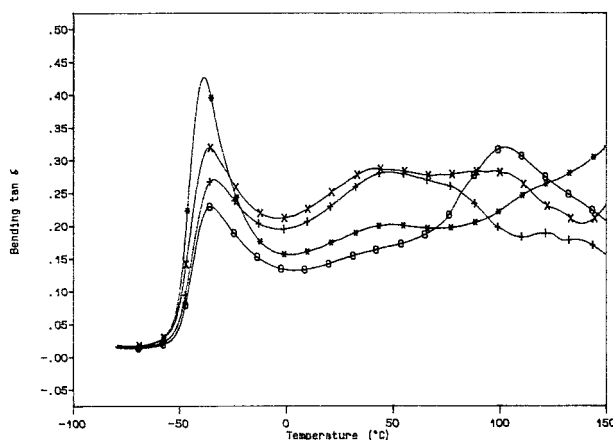


Figure 6 Damping curves of PU treated with various dosages of NPES-903. (a) Original PU (*); (b) 3.3 phr (×); (c) 8.3 phr (+); (d) 25.0 phr (○).

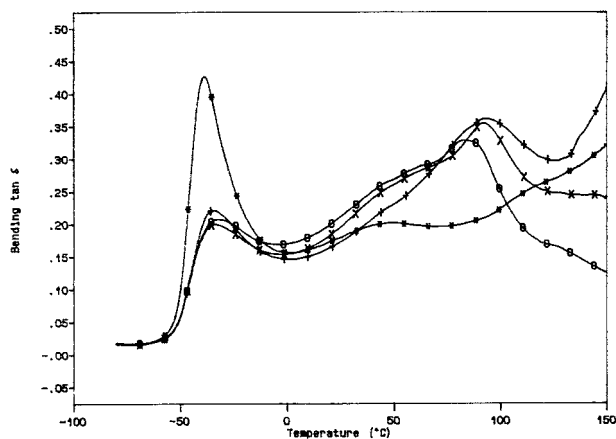


Figure 7 Damping curves of PU treated with 16.7 phr of various di-functional epoxy compounds. (a) Original PU (*); (b) with NPES-901 (+); (c) with NPES-902 (×); (d) with NPES-903 (○).

peak in the 80–100°C range (Fig. 7). That peak was derived from the partial-cured and unreacted epoxy compound in each individual epoxy-curing PU system.

For epoxy-cured PU with 25.0 phr of NPES-902, low-temperature T_g shifted to -34.9°C and the peak intensity decreased on its DMTA curve. Furthermore, a new additional damping peak on 96.3°C and a peak shoulder on 67.6°C (Fig. 7) appeared on the curve. The peak on 96.3°C could be from the unreacted epoxy curing agent, and the peak shoulder could be a partially reacted epoxy compound. Its damping peak broadened and cen-

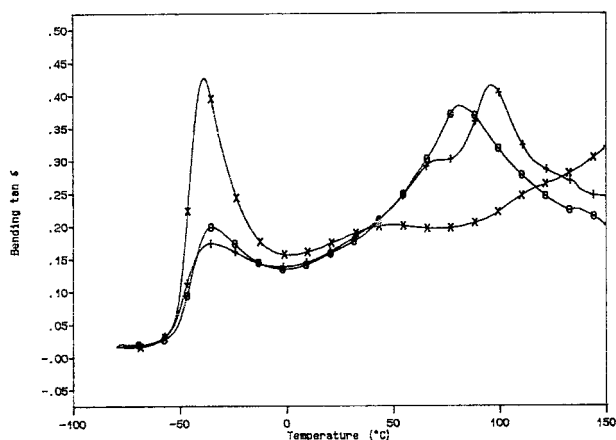


Figure 8 Damping curves of PU treated with NPES-902 and a heat treatment. Curves: (a) original PU (×); (b) with 25.0 phr NPES-902 (+); (c) heat treatment of (b) at 140°C for 20 min (○).

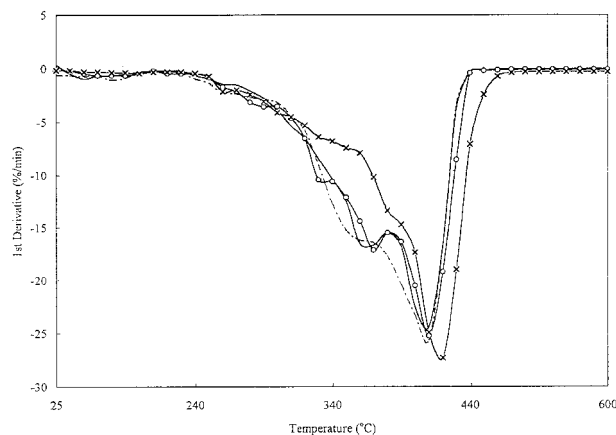


Figure 9 Differential thermogravimetric analysis curves of PU films under N_2 . (a) Original PU (—); (b) with 3.3 phr NPES-901 (— · —); (c) with 3.3 phr TMPTA-AZ-0 (○); (d) with a dual-curing system (3.3 phr NPES-901 and 3.3 phr TMPTA-AZ-0) (×).

tered at 81.2°C after the sample was heated at 140°C for 20 min (Fig. 8). That post-heating drives the curing reaction further for this epoxy-cured PU film.

The DMTA curve of a dual-cured PU film with a low curing dosage (for example, 3.3 phr), has a lower damping peak intensity than a single-cured or the original PU. In a similar phenomenon, the differential thermogravimetric analysis data indicated the thermal stability of the dual-cured PU film is better than the single-cured or the original PU film (Fig. 9). That is also the evidence that the dual-cured PU film had a better polymeric network build-up than the single-cured or the original PU film.

CONCLUSIONS

The aqueous PU dispersions consist of terminal amino and pendent carboxylic groups, they are reactive toward a difunctional epoxy and a triaziridinyl curing agents, respectively.

The curing reaction of difunctional epoxy curing agent with the terminal amino groups of PU main chain takes place within the hydrophobic PU particles of the aqueous dispersions at ambient temperature, whereas TMPTA-AZ-0, a hydrophilic triaziridinyl curing agent, is added as a latent curing agent. It is stable in the aqueous phase and the curing reaction with carboxylic group of PU occurred only under an acidic environment or

on the air-drying stage at ambient temperature. The stabilities of these single- and dual-curing PU systems are proved by their zeta potential and particle size distributions of the resulted PU dispersions.

The final dual-cured PU film has exhibited improvements both in its mechanical and physical properties as well as thermal behavior because of the polymeric networks' formation from this effective "epoxy/aziridinyll dual-curing system" for these anionic aqueous-based PU dispersions. The improvements in the properties of the dual-cured PU systems depend not only on the availability of the reactive sites in the polymer, but also on the nature and functionality of the curing agent.

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