Hybridization of Aqueous PU/Epoxy Resin via a Dual Self-Curing Process

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ABSTRACT: Amino-terminated and carboxyl-containing polyurethane (PU) is prepared by an isocyanate-terminated PU prepolymer process. Carboxyl-containing epoxy resin is obtained from a half-esterification of epoxy resin with maleic anhydride. These two aqueous resins are obtained after neutralization with triethylamine and dispersion into water phase, respectively. A latent curing agent (TMPTA-AZ) is prepared by a Michael addition of aziridine with trimethylolpropane triacrylate (TMPTA). A self-curing system of PU/epoxy hybrid is obtained from a blending of these two aqueous resins with latent curing agent. PU/epoxy hybrid is derived from two self-curing reactions on drying. The first curing for hybridization between PU amino groups with oxirane groups of epoxy resin is via a ring-opening reaction and the secondary curing takes place on carboxyl groups of PU/epoxy hybrid with aziridine of TMPTA-AZ. The final properties of these dual self-cured PU/epoxy hybrids are reported. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 147–155, 2008

Key words: aziridine; dual-curing; PU; epoxy resin; hybrid

INTRODUCTION

Although the application technology of conventional solvent-based PU is well established, it has been phasing out and replaced by an environmental friendly aqueous-based PU resin, because of the requirements of environment, economics, and safety, However, aqueous-based PU resin has low average molecular weight, poor organic solvent resistance, and inferior mechanical properties, etc., comparing with the solvent-based PU. Posttreatments of aqueous-based PU have been proven to be effective methods to improve PU properties; a postcuring reaction with multiaziridine curing agent is one such example.[1–3] Polymer hybridization is another method to enhance PU performance properties. A polymer hybridization process[4–10] of aqueous-based PU with a self-emulsified polymer dispersion in aqueous phase and a self-curing reaction take place on drying. A most popular self-emulsified aqueous PU dispersion containing carboxyl group is obtained from a water dispersion process of NCO-terminated PU prepolymer (NCO-PU) with ethylenediamine (EDA), a chain-extender. NCO-PU is prepared by a polyaddition reaction of isophorone diisocyanate (IPDI) with poly(propylene glycol)-2000 (PPG-2000) in the presence of 2,2'-dimethylolpropanoic acid (DMPA). Isocyanate terminal groups of NCO-PU are chain-extended or hydrolyzed, becoming amino groups during water dispersion process (Scheme 1). Because of the ionic character of carboxyl group, this PU becomes self-emulsified or water-reducible in the water phase. Furthermore, most of aqueous-based PU dispersions are linear thermoplastic polymers and bear lower average molecular weight, and these characters induce their poor solvent resistance, low mechanical properties, etc.[11] The property improvements of aqueous-based PU are normally carried out by postcuring reaction[1–5,12–17] or polymer hybridization process[6–10,18–25] to enhance its crosslinking density, molecular weight, and performance properties.

EXPERIMENTAL

Materials

Isophorone diisocyanate (IPDI) was supplied by Hul Chemical Co., Germany. Epoxy resin-128 (equivalent epoxy weight, EEW = 188) was obtained from Formosa Plastic Co. 2,2'-Dimethylolpropanoic acid (DMPA), triethylamine (TEA), maleic anhydride acetone, tetrahydrofuran (THF), and methyl isobutyl ketone (MIBK) were purchased from Aldrich Chemical Co., USA. Polypropylene glycol-2000 (PPG-2000) is obtained from Arco Chemical Co., Taiwan. Latent curing agent TMPTA-AZ was prepared according to the method stated in our published work[20]. All solvents

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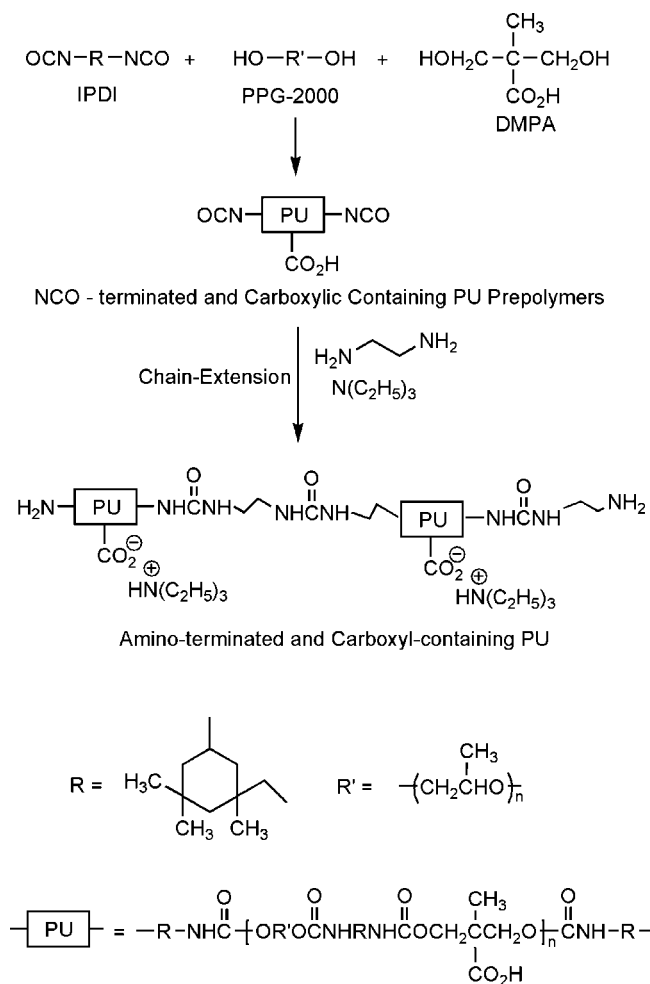
Scheme 1 Preparation of amino-terminated and carboxyl-containing PU resin.

were purified before use according to the published method.

Instruments

Dynamic mechanical analysis (DMA) data are obtained from TA-Q800, USA. Thermogravimetric data are obtained from Hi-Resolution TGA 2950 TG-DTA Thermogravimetric Analyzer, USA. Infrared spectra of cast dry PU and epoxy resins on KBr disc were measured, respectively, by a Biorad FTIR spectrophotomer FTS-40, USA. ^{1}H- and ^{13}C NMR spectra were recorded by Bruker AC-300 spectrometer, Germany. Chemical shifts are reported in parts per million (ppm) relative to residual CHCl$_3$ (δ = 7.26, for ^{1}H; δ = 77.0, for ^{13}C). Stress and strain curves of PU and its hybrids were taken with Shimadzu Autograph S-100-C, Japan.

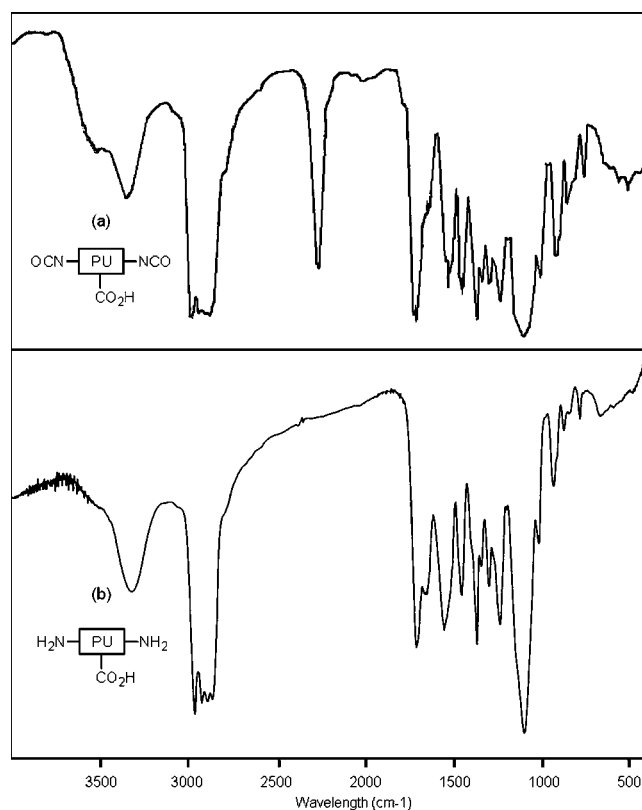## Preparation of amino-terminated and carboxyl-containing PU

A mixture of PPG-2000 (0.1 mol) and DMPA (0.1 mol) were dried at 110°C overnight before being mixed

with IPDI (0.3 mol) in a 500-mL 4-necked resin flask. The resin flask was equipped with a mechanical stirrer, a thermometer, a nitrogen inlet, and a condenser with a CaCl$_2$ drying tube. The reaction mixture was heated slowly, raised to 90°C, and kept at that temperature for about 4 h, until NCO% dropped below 3.0 (ASTM D 1638) and remained constant for another half hour. Then, freshly dried acetone was added into the reaction flask (after it was cooled below 50°C) for adjusting PU prepolymer (NCO-PU) viscosity to 2000 cps (solid content = 50%). Triethylamine (0.05 mol) and ethylenediamine (EDA, 0.07 mol) were added into acetone solution of PU-NCO (100 g) at room temperature and the reaction was kept at that temperature until NCO% dropped to zero [the absorption peak of NCO group at 2267 cm^{-1} disappeared, Fig. 1(a), Scheme 1].

Preparation of carboxyl-containing epoxy resin

A methyl isobutyl ketone (MIBK) solution of epoxy resin-128 (0.80 mol) and maleic anhydride (0.24 mol) was put into a 500-mL three-necked round bottom flask that equipped with a mechanical agitator, a thermometer, and a condenser. The reaction was kept at 120°C for 20 h. The crude materials obtained were washed with deionized water several times to remove the residual melaic acid and the solvent was removed

Figure 1 FTIR spectra of (a) PU prepolymer and (b) amino-terminated PU.
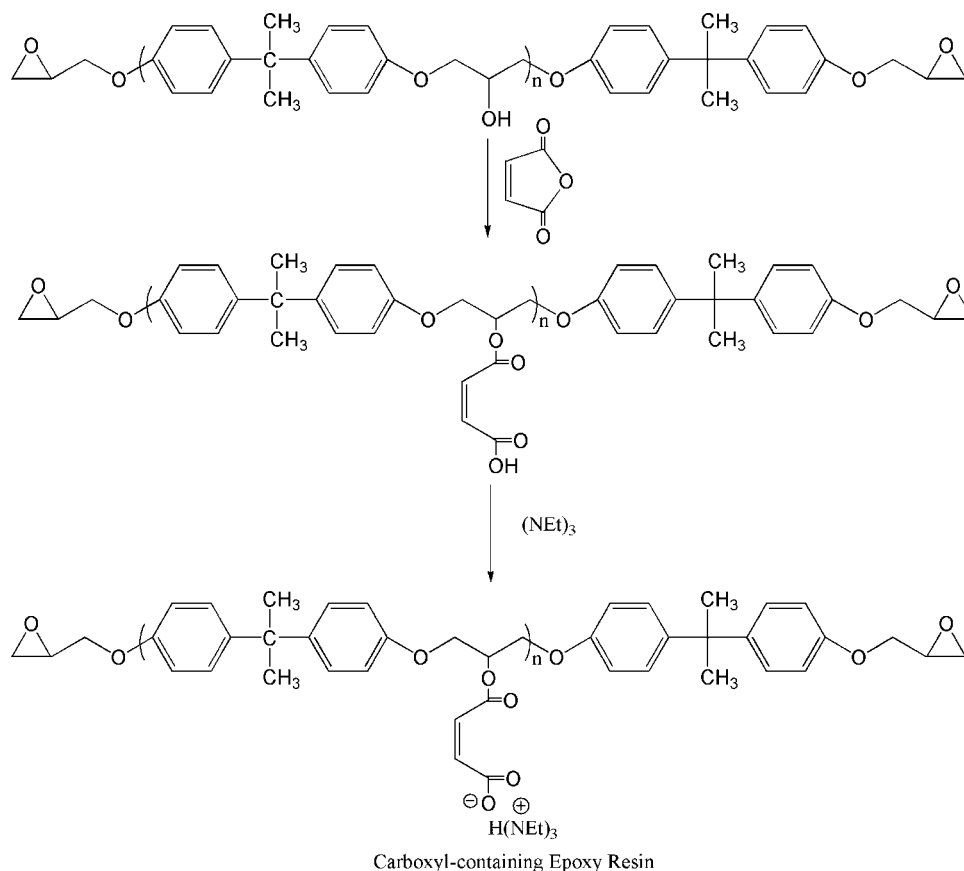
Scheme 2 Preparation of carboxyl-containing epoxy resin.

by reduced pressure. TEA (0.2 mol) was added into reaction system to neutralize the pendent carboxylic acid groups of epoxy resin and dried acetone was added to adjust the viscosity. Finally, the carboxyl-containing epoxy was obtained, which had a solid content at 40% (Scheme 2).

Preparation of self dual-curing PU/epoxy hybrid dispersion

The mixtures of PU/epoxy (amino/oxirane equivalent ratio = 1.5/1.0, 1.0/1.0, 1.0/1.5) were treated with various dosages (0–5 phr) of a latent curing agent TMPTA-AZ and dispersed into deionized water with mechanical agitation. The resulting self dual-curing PU/epoxy hybrid dispersion had 20% solid content after acetone removal under reduced pressure. This aqueous-based PU/epoxy hybrid dispersion remains stable when its pH value is maintained at 8.0 or above. And its PU/epoxy hybrid film was obtained from casting of PU/epoxy hybrid dispersion into glass plate and dried at ambient temperature. The PU/epoxy hybrid film was dried further in a 50°C vacuum oven for 24 h and then was conditioned in a 75% relative humidity environment for 1 day before testing.

Performance properties

Gel content

A known weight of oven-dried film (W_1) was put into a Soxhlet extractor for continuous extraction with THF for 24 h. The polymer gel that 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 $60 \times 60 \times 1$ mm^3 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, and

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

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

Ethanol swelling

A known weight (W_0) of dried PU film sample with a dimension of $60 \times 60 \times 1$ mm^3 was immersed in a 95% ethanol bath for 24 h. The towel-down dry sample weight (W_1) and the oven-dried sample weight (W_2) were obtained. Ethanol-swollen (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 and

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

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

Tensile strength and elongation

Each PU film was cast and dried from these prepared self-curable PU dispersions at room temperature. The PU films were then kept in an oven at 25°C for 24 h and conditioned at a 75% relative humidity environment for 1 day before testing. Dumbbell-shaped specimens of 1.0 mm thickness were 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 measurement, and the mean results were calculated.

Dynamic mechanical analysis

Air-dried PU films were dried further at 50°C in an oven for 24 h before testing. DMA was carried out in film tension mode at a heating rate of 3°C/min from −70 to 100°C at 1.0 Hz frequency for each testing sample.

Thermogravimetric analysis

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

RESULTS AND DISCUSSION

An aqueous-based amino-terminated and carboxyl containing PU dispersion was obtained from a water dispersion process of NCO-terminated PU prepolymer (NCO-PU) with EDA as a chain extender (Scheme 1). The average molecular weight of NCO-terminated PU prepolymer is about 30,000 before chain-extension with EDA, which is determined by an end-group analysis method.

A water-reducible epoxy resin was prepared by a half-esterification of maleic anhydride with hydroxyl group of epoxy resin. The carboxyl group was neutralized with TEA and then dispersed into water phase, becoming a water-reducible epoxy resin and the epoxy (oxirane) terminal groups remained intact (Scheme 2).

Both aqueous-based PU dispersion and water-reducible epoxy resin are miscible in aqueous phase. A single component self-curable aqueous PU/epoxy hybrid dispersion was obtained from a blending of these two aqueous-based polymer dispersions with a latent curing agent (a polyaziridine compound). The latent curing agent TMPTA-AZ was prepared by a Michael addition of aziridine with trimethylolpropane triacrylate (Scheme 3).[1–5,12–17] PU/epoxy hybrid is derived from two self-curing reactions on drying (Scheme 4). First curing for hybridization between PU amino groups with oxirane groups of epoxy resin was via a ring-opening reaction and the second curing takes place on carboxyl groups of PU/epoxy hybrid with aziridine of TMPTA-AZ. The performance properties of PU/epoxy hybrids via the dual-curing process are evaluated in this report.

Self-emulsified aqueous-based PU dispersion

A self-emulsified PU dispersion was obtained from a conventional PU prepolymer process (Scheme 1).[1–5,12–17] Its NCO absorption peak of PU prepolymer appears at 2267 cm^{-1} on FTIR [Fig. 1(a)]. An aqueous solution of TEA and ethylene diamine is added for neutralization and chain extension reaction, respectively, during water dispersion. And it results in a formation of amino-terminated and carboxyl group containing aqueous-based PU dispersion [Fig. 1(b)].

Water-reducible epoxy resin[7–10]

A half-esterification reaction of epoxy resin with maleic anhydride and then neutralized with TEA and it becomes water-reducible epoxy resin (Scheme 2).[7–10] The oxirane absorption of epoxy resin remains at 915 cm^{-1} and a new absorption of carboxyl peak appears at 1740 cm^{-1} on FTIR spectra [Fig. 2(a,b)].
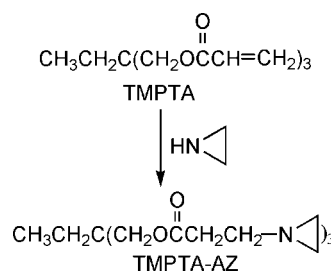

Scheme 3 Preparation of TMPTA-AZ.
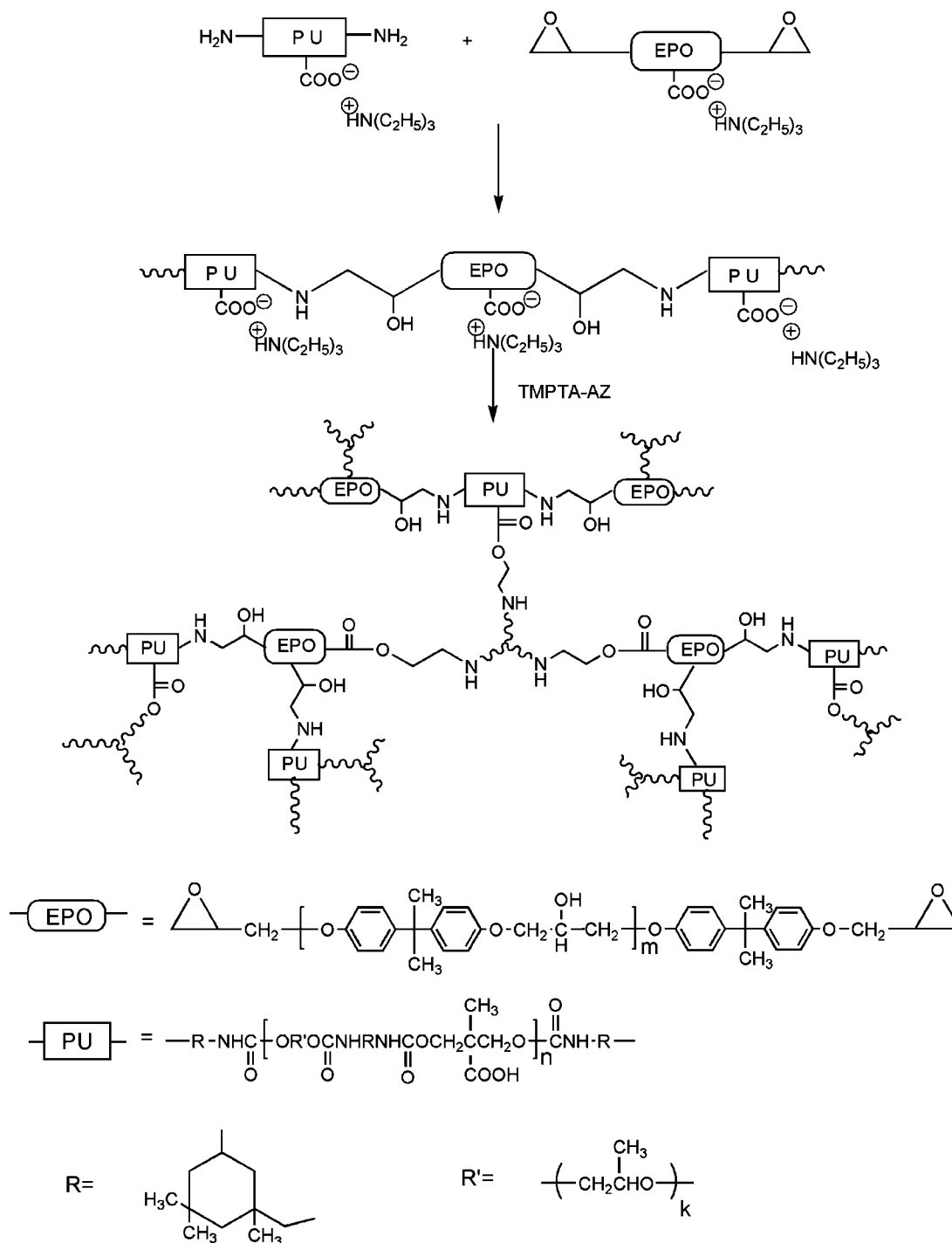
Scheme 4 Dual curing reaction of PU/epoxy hybridization.

Physical properties of PU/epoxy hybrids

Either original aqueous-based PU or water-reducible epoxy resin without curing or hybridization is dissolved in THF and ethanol. That indicates a linear structure of both of these two polymers with low average molecular weight and lack of organic solvent resistance.

For PU/epoxy hydrid with amino/oxirane equivalent ratio 1.0/1.0 without curing agent, the gel content is 66.3% and the ethanol swollen is 472%; its gel content decreases to 15.7% and ethanol swollen increases to 1582% with an amino/oxirane equivalent ratio at 3/2. These results demonstrate that a chain extension reaction of epoxy resin with PU takes place between
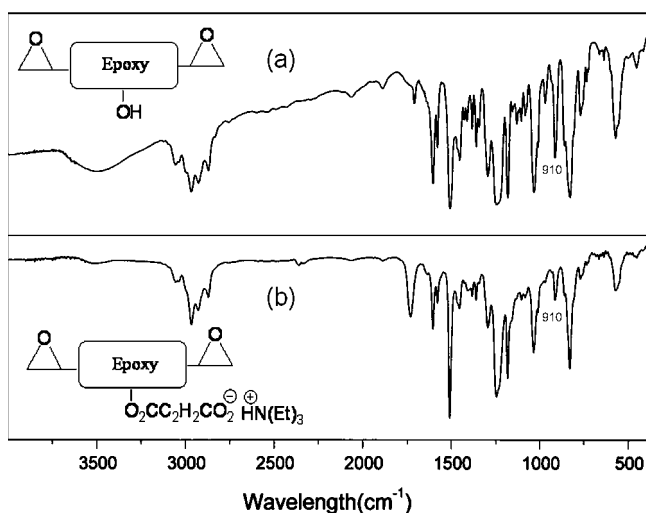
Figure 2 FTIR spectra of (a) epoxy resin and (b) carboxyl-containing epoxy resin.

the amino terminal groups of PU and the oxirane of epoxy resin via a ring-opening reaction (Scheme 4), and its gel content and ethanol swollen depend on epoxy resin dosage. However, its ratio is 2/3 and its gel content increases to 68.4% and ethanol swollen decreases to 288% (Table I); The primary amino group of PU reacts with oxirane group of epoxy resin, resulting in a ring-opening reaction and formation of a secondary amino group, which also reacts further toward the excess oxirane group of epoxy resin (PU/epoxy hybrid in amino/oxirane = 2/3).

The gel content of PU/epoxy hybrid cured by TMPTA-AZ increases. For example, in PU/epoxy hybrids (amino/oxirane ratio = 1.0/1.0) with curing dosage of 1.0 and 5.0 phr TMPTA-AZ, respectively, the gel content increases from 75.1 to 85.5%. This is because the multiaziridine ring of TMPTA-AZ reacts with carboxyl groups of both PU/epoxy hybrid, resulting in the networked structure formation between polymers. The ethanol swollen also decreases

with increasing TMPTA-AZ dosage. For example, the ethanol swollen is 379% for the same PU/epoxy hybrid with 1.0 phr of TMPTA-AZ, and when the TMPTA-AZ dosage is increased to 5.0 phr, its ethanol swollen decreases to 153%.

Mechanical properties of PU/epoxy hybrid

Original PU has a tensile stress of 30.3 kgf/cm^2 at 100% elongation (Table II). Both its tensile stress and tensile strength increase with increasing dosages of epoxy resin or/and curing agent, TMPTA-AZ (Table 2).

For example, the tensile stress increases to 45.6 kgf/cm^2 at 100% elongation and its tensile strength is 65.2 kgf/cm^2 at 287% elongation of PU/epoxy hybrid (in amino/oxirane = 3/2) without curing agent. Its tensile stress increment is due to the polymer chain-extension from hybridization of amino-termninated PU with oxirane terminal group of epoxy resin on drying. Furthermore, its tensile stress increases to 80.2 kgf/cm^2 and tensile strength is 122.4 kgf/cm^2 at 140% elongation of same PU/epoxy hybrid with 5.0 phr curing agent; that is because of the contribution of curing agent TMPTA-AZ, which reacts with carboxylic acid of PU/epoxy hybrid for a postcuring treatment.

PU/epoxy hybrid with a higher epoxy ratio (in amino/oxirane = 2/3) without curing agent has a tensile stress of 80.5 kgf/cm^2 at 100% elongation and its tensile strength is 120.9 kgf/cm^2 at 196% elongation. PU/epoxy hybrid with 5.0 phr curing agent, TMPTA-AZ, has a tensile stress of 134.2 kgf/cm^2 at 100% elongation and its tensile strength is 147.5 kgf/cm^2 at 114% elongation.

The improvement of mechanical properties of PU/epoxy hybrid are limited by the ratio of amino and oxirane groups of PU and epoxy resin, respectively. And further improvements are caused by the postcuring reaction of TMPTA-AZ with carboxylic acid, the curing sites of PU/epoxy hybrid.

TABLE I
Physical Properties of PU/Epoxy Hybrid with Various Dosages of TMPTA-AZ

| | | [Amino]/[oxirane] equivalent ratio of PU/epoxy hybrids | | | | | | | | | | | |
| | | 3/2 | | | | 1/1 | | | | 2/3 | | | |
	WPU	0.0^a	1.0	3.0	5.0	0.0	1.0	3.0	5.0	0.0	1.0	3.0	5.0
Gel content (%)	0.0^b	15.7	70.7	77.1	78.0	66.3	75.1	84.5	85.5	68.4	78.6	87.2	87.6
W_w (%)	31.4	24.1	19.4	18.3	17.8	23.8	14.2	12.5	10.9	22.8	15.0	13.7	10.4
W_x (%)	3.6	2.1	1.8	1.5	1.5	1.6	1.1	0.8	0.8	1.5	0.8	0.7	0.6
W_e (%)	–^{c}	1582	934	893	360	472	379	285	153	288	215	201	158
W_y (%)	100.0	55.7	29.2	25.2	20.8	18.5	11.4	11.2	10.4	18.2	10.8	8.4	8.1

WPU, original aqueous-based PU (without curing or hybridization).
^{a} Values in this row are the amount of latent curing agent TMPTA-AZ (phr).
^{b} Polymer 100% dissolved in THF.
^{c} Polymer 100% dissolved in ethanol.

TABLE II
Mechanical Properties [Stress (kgf/cm²)] of PU/Epoxy Hybrid with Various Dosages of TMPTA-AZ

Elongation (%)	WPU	[Amino]/[oxirane] equivalent ratio of PU/epoxy hybrids											
		3/2				1/1				2/3			
		0.0ᵃ	1.0	3.0	5.0	0.0	1.0	3.0	5.0	0.0	1.0	3.0	5.0
100	30.3	45.6	55.8	70.1	80.2	60.0	62.4	81.4	120.1	80.5	121.6	131.2	134.2
200	33.4	57.9	70.2	–	–	79.0	–	–	–	–	–	–	–
300	34.2	–	–	–	–	–	–	–	–	–	–	–	–
400	36.2	–	–	–	–	–	–	–	–	–	–	–	–
500	38.8	–	–	–	–	–	–	–	–	–	–	–	–
Tensile strength at break (kgf/cm²)/% elongation	39.6/690	65.2/287	76.5/214	100.2/192	122.4/140	81.4/286	83.1/178	113.5/132	142.1/104	120.9/196	133.5/143	141.0/125	147.5/114

WPU, original aqueous-based PU (without curing or hybridization).
ᵃ Values in this row are the amount of latent curing agent TMPTA-AZ (phr).
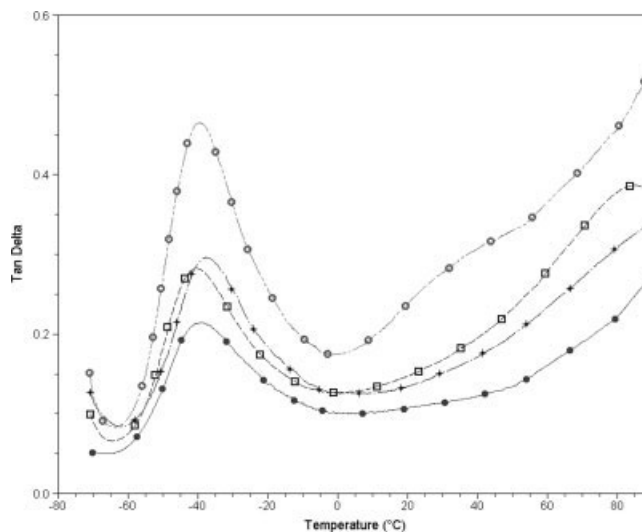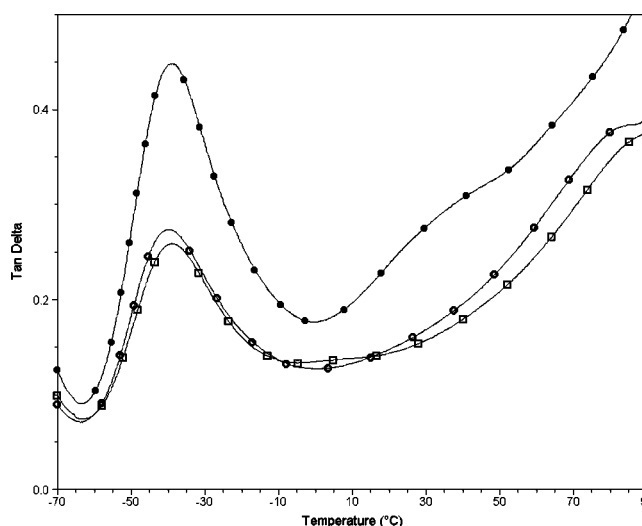

Figure 3 DMA curve of PU and PU/epoxy hybrids without TMPTA-AZ. (○), PU; (+), PU/epoxy = 3/2; (□), PU/epoxy = 1/1; (●), PU/epoxy = 2/3.

Dynamic mechanical analysis

Original PU has a damping peak at −40.3°C and the peak intensity decreases in PU/epoxy hybrid, which demonstrates that a decreasing molecular mobility due to chain extension reaction took place between PU amino groups with oxirane groups of epoxy resin. PU/epoxy hybrid with a higher epoxy resin dosage and a lower damping peak intensity is obtained. For example, a damping peak intensity of PU/epoxy hybrid with amino/oxirane = 3/2 is lower than that of PU/epoxy hybrid with amino/oxirane = 2/3 (Fig. 3).

The curing agent TMPTA-AZ provides a curing reaction between aziridine rings of TMPTA-AZ with

Figure 4 DMA curve of PU, PU/epoxy hybrid, and PU/epoxy hybrid with TMPTA-AZ. (●), PU; (○), PU/epoxy hybrid; (□), PU/epoxy hybrid with TMPTA-AZ.

carboxyl groups of PU/epoxy hybrids on drying. This curing reaction caused the damping peak intensity to decrease further, compared with that of PU/epoxy hybrid without TMPTA-AZ (Fig. 4). These phenomena are the emphatic verification proving the curing reaction has taken place between PU/epoxy hybrid and TMPTA-AZ.

Thermogravimetric analysis

The initial 20% thermal degradation temperature ($T_{d20\%}$) was 314°C and the maximum decomposition temperature (T_{dmax}) was 397°C for original aqueous PU resin, and those for water-reducible epoxy resin were 273 and 310°C respectively. The thermal stability of PU/epoxy hybrid (without TMPTA-AZ) is improved because of the hybridization with epoxy resin, and its $T_{d20\%}$ increases to 324 and 330°C, respectively, with various epoxy resin dosages (amino/oxirane = 3/2 and 2/3) (Table III and Fig. 5). However, its T_{dmax} remains at 400°C of this PU/Epoxy hybrid. An excess amount of epoxy resin serves further curing reaction with the secondary amino group that is derived from the chain extension of PU terminal amino groups with oxirane of epoxy resin at its first ring opening reaction.

The thermal stability of PU/epoxy hybrid is improved slightly with various TMPTA-AZ dosages. $T_{d20\%}$ and T_{dmax} of PU/epoxy hybrid are increased to 341 and 402°C, respectively, with 7.0 phr TMPTA-AZ (Table III).

According to the thermogravimetric analysis, the thermal stability of aqueous-based PU was improved via polymer hybridization with water-reducible epoxy resin and further cured by TMPTA-AZ.

CONCLUSIONS

Water-reducible epoxy resin is obtained from a half-esterification reaction of epoxy resin with maleic anhydride. Amino-terminated and carboxyl containing aqueous-based PU dispersion is blended with this water-reducible epoxy resin in aqueous phase and

Figure 5 TGA thermograms of PU, PU/epoxy hybrid, and PU/epoxy hybrid with TMPTA-AZ. (●), PU; (○), PU/epoxy hybrid; (□), PU/epoxy hybrid with TMPTA-AZ.

treated with a latent curing agent, TMPTA-AZ. It results in the formation of a single component self-curable PU/epoxy hybridization system. The first curing for hybridization between PU amino groups with oxirane groups of epoxy resin was via a ring-opening reaction and the secondary curing takes place on carboxyl groups of PU/epoxy hybrid with aziridine of TMPTA-AZ. These dual self-curing reactions result in the formation of high crosslinking density polymer network of hybrids. Final dual-cured PU/epoxy hybrids show improvements in their physical and mechanical properties as well as their thermal stability. This hybridization process offers an alternative for improving aqueous-based PU resin.

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TABLE III
Thermal Stability of PU/Epoxy Hybrid with Various Dosages of TMPTA-AZ

	PU[a]	Epoxy resin[b]	PU/epoxy hybrids[c]		
			3/2	1/1	2/3
$T_{d20\%}$	314	273	324	324	330
T_{dmax}	397	310	400	400	401

Thermal stability of polymer is measured under N_2 atmosphere.
[a] Carboxyl-containing PU.
[b] Carboxyl-containing epoxy resin (EP-128).
[c] PU/epoxy hybrids without curing agent TMPTA-AZ.

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