

A Cross Self-Curing System for an Aqueous-based PU Hybrid

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ABSTRACT: Isocyanate (NCO)-terminated polyurethane (PU) prepolymer comprises carboxylic acid, which is obtained from a conventional PU preparation procedure. Aziridine-terminated PU oligomer is prepared by an addition reaction of aziridine to NCO-terminated PU prepolymer after it is neutralized with triethylamine. This PU oligomer is then dispersed with water and becomes a single-component self-curable aqueous-based PU dispersion (PU-AZ). PU carboxyl groups are not only the ionic centers stabilizing the aqueous polymer dispersion, but also serve as PU curing sites toward the curing reaction with its aziridine terminal

groups on drying. This self-curable PU-AZ dispersion is miscible and compatible with other carboxyl groups containing aqueous-based PU dispersion in any ratio, which results in a cross self-cured PU hybrid formation on drying. This cross self-cured PU hybridization process allows property modification and the curing of PU simultaneously without the addition of any external curing agent. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 550–558, 2005

Key words: self-curing; PU hybrid; aziridine

INTRODUCTION

Applications and production processes of solvent-based polyurethane (PU) have been well developed for the last several decades. However, due to environment and safety regulations, as well as health considerations, the applications of aqueous-based PU are gradually becoming the world market trend.¹

This trend has put a great demand on the environmentally friendly aqueous-based PU resins. However, their physical and mechanical properties are still insufficient in comparison with those of the solvent-based PU. Furthermore, difficulties also have been encountered in producing a reliable aqueous-based PU in enhancing the molecular weight and crosslinking density.

A conventional self-emulsified PU dispersion containing carboxylic acid is prepared from an isocyanate (NCO)-terminated PU prepolymer, which is an addition reaction adduct of isophorone diisocyanate (IPDI) with polypropylene glycol-2000 (PPG-2000) and 2,2-dimethylolpropanoic acid (DMPA). Some of its NCO terminal groups are hydrolyzed to amino groups when it is dispersed into water after neutralization with triethylamine. A fraction of these amino groups may react further with the remaining NCO terminal groups for PU chain extension.^{2,3} The carboxylic ions of aqueous-based

PU provide surface charges of PU micelles (particles), thereby causing repulsion between PU particles and stabilizing PU dispersion in the water phase. Because of the ionic character of the carboxyl group, this PU becomes self-emulsified or water-reducible in the water phase. Such aqueous-based PU has a common disadvantage similar to that of a polymeric surfactant in that, after drying into a film, such film still exhibits the high hydrophilic properties due to the presence of carboxyl groups in the PU molecule.

The processes of postcuring reaction^{2–9} or polymer hybridization^{10–14} are proven to be effective methods to improve molecular weight, crosslinking density, and subsequent performance properties of aqueous-based PU so as to broaden the polymer applications.

A convenient postcuring reaction of aqueous-based PU is mainly based on its carboxyl group reacting with a multifunctional aziridinyl latent curing agent on air drying,^{2–5} while aqueous-based PU terminal amino groups react with the epoxide groups containing polymers. These PU dual-curing reactions result in PU hybrid formation of PU/epoxy resin⁴ or PU/glycidyl methacrylate (GMA) copolymer.^{11,12} The property improvement of these dual-cured PU hybrids depends on the dosages of aziridinyl curing agent and epoxide-containing polymer.

There is an alternative of PU hybrid formation: introducing an aziridine-terminated PU oligomer serves as a polymeric curing agent and becomes a different self-curable aqueous-based PU system. This self-cured PU resin results from a curing reaction taking place between

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the PU terminal aziridine and pendent carboxyl groups without the addition of any external curing agent. This self-curable aqueous-based PU system is compatible with other conventional aqueous-based PU comprising carboxyl groups and forms a cross self-cured PU hybrid on drying. The results of this unique cross self-curing PU hybrid system will be discussed in this article.

EXPERIMENTAL

Materials

Triethylamine (TEA), ethylenediamine (EDA), and 2,2-dimethylolpropanoic acid (DMPA) are supplied by the Aldrich Chemical Co. Inc. Isophorone diisocyanate (IPDI) is supplied by Dow Chemical Co. Polypropylene glycol-2000 (PPG-2000) is supplied by Arco Chemical Co. All of the materials are used as received without further purification. Acetone, methanol, and other solvents are dried and distilled over anhydrous calcium chloride before use.

Instruments

Dynamic mechanical thermal behavior of the polymer films was performed with a Dynamic Mechanical Thermal Analyzer, MK-II, Polymer Laboratories. Thermogravimetric data were measured by a Hi-Resolution TGA 2950 Thermogravimetric Analyzer (TA). Stress and strain curves of PU films were taken with a Shimadzu Autograph S-100-C. NMR spectra were measured by a Bruker 300 MHz.

Preparation of NCO-terminated PU prepolymer² (PU-NCO)

PPG-2000 (0.2 mol.) and DMPA (0.1 mol.) were dried at 110°C overnight before being mixed with IPDI (0.4 mol) in a 1-L four-necked resin flask. The resin flask is equipped with a mechanical stirrer, a thermometer, a nitrogen inlet, and a condenser with a CaCl₂ drying tube. The reaction mixture was kept at 110°C for about 4 h under nitrogen, until NCO% dropped below 3.5 (ASTM D 1638 NCO determination method) and remained constant for another 30 min and then was cooled down at ambient temperature for the next process (Scheme I and Figure 1).

Preparation of self-cured aqueous-based PU (PU-AZ) resin

Ethyleneimine (aziridine) was prepared from ethanolamine according to the published method.¹⁵ The acetone solution (200 mL) of PU-NCO (100 g, prepared above) was neutralized with triethylamine and then aziridine (4 g) acetone solution was added through an addition funnel. The reaction mixture was kept at 50°C under nitrogen for an additional 1 h after the

addition was completed. The reaction was completed when the NCO number of the reaction mixture dropped to zero (which is the absorption peak of the NCO group and was not observed at 2265 cm⁻¹ in FT-IR spectrum; Figure 2). The reaction mixture was added to 250 mL deionized water with agitation. The resulting self-curing PU dispersion had 30% solids after acetone was removed and its pH value was maintained at 8.0 or above (Scheme I). The self-cured PU film was obtained from the cast of this self-curing PU dispersion on drying at ambient temperature.

Preparation of conventional aqueous-based PU (PU²) resin

Acetone solution of PU-NCO (100 g, prepared above) was dispersed into 250 mL aqueous amines solution, which consisted of 0.04 mol of ethylenediamine and 0.05 mol of triethylamine. The water dispersion process was carried out with a 1,000 rpm agitation. The final aqueous-based PU dispersion had 30% solids after acetone was removed and its pH value was maintained at 8.0 or above (Scheme II). The conventional aqueous-based PU resin was cast dry from this PU dispersion at ambient temperature.

Cross self-cured PU hybrids (PU-AZ/PU)

Self-curing and conventional aqueous-based PU dispersions were mixed in various ratios with gentle agitation. The resulting homogeneous PU dispersion was cast and dried at ambient temperature. The resulting cross self-cured PU hybrid (PU-AZ/PU) films (Scheme III) were then heated at 50°C for 24 h. These PU hybrid films were ready for testing after conditioning in a 75% relative humidity chamber at 25°C for 72 h.

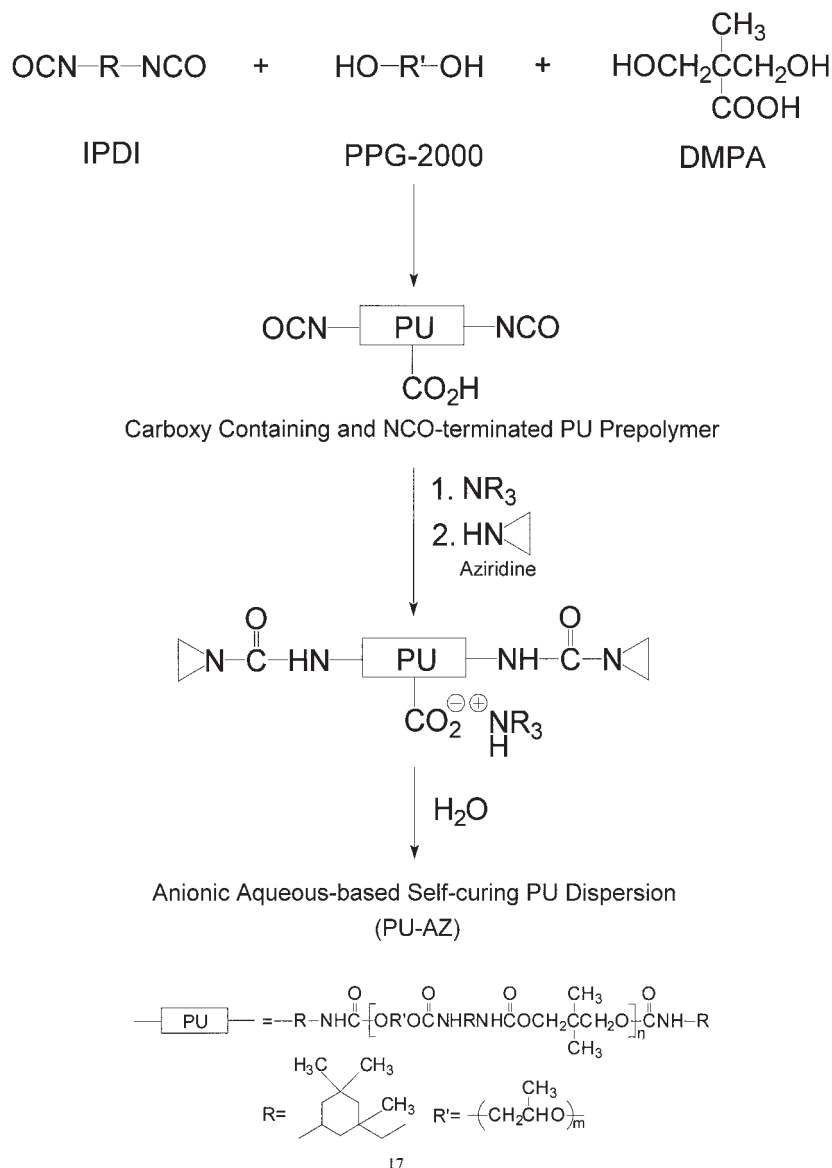
Properties of PU-AZ/PU hybrids

Tensile strength and elongation

Each specimen was cut in a dumbbell shape at 1.2 ± 0.1 mm thickness. The gauge length was 40 mm and the measurement was performed at a cross-head speed of 40 mm/min. Six specimens for each sample were taken, and the three measurements that showed the medium value of tensile strength were selected for calculating the mean value according to the method of ASDM D 412-92.

Gel content

A known weight of oven-dried film was put into a Soxhlet extractor for a continuous extraction with THF for 24 h. Polymer gel remaining after extraction was dried and calculated according to the test results. Three tests were carried out and averaged for each sample.



Scheme 1 Preparation of aqueous-based self-curing PU-AZ dispersion.

Ethanol uptake

A known weight (W_0) of $60 \times 60 \times 1$ mm dried polymer film was immersed in a distilled water bath for 8 days for water uptake. It was also immersed in an ethanol (95%) bath for 48 h for ethanol absorption. The towel-dried sample weight (W_1) and the oven-dried film weight (W_2) were obtained. Three measurements were averaged for each sample. The percentage of water uptake (W_A), ethanol absorption (W_E), and weight losses (W_x , W_y) of the polymer films in water and in ethanol were calculated according to the following equations, respectively:

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

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

where W_A and W_x are the amount of water uptake by the polymer film and the amount of polymer dissolved into water, respectively; and

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

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

where W_E and W_y are the amount of ethanol absorption by the polymer film and the amount of polymer dissolved into ethanol, respectively.

Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis measurements were carried out in bending mode with a heating rate of

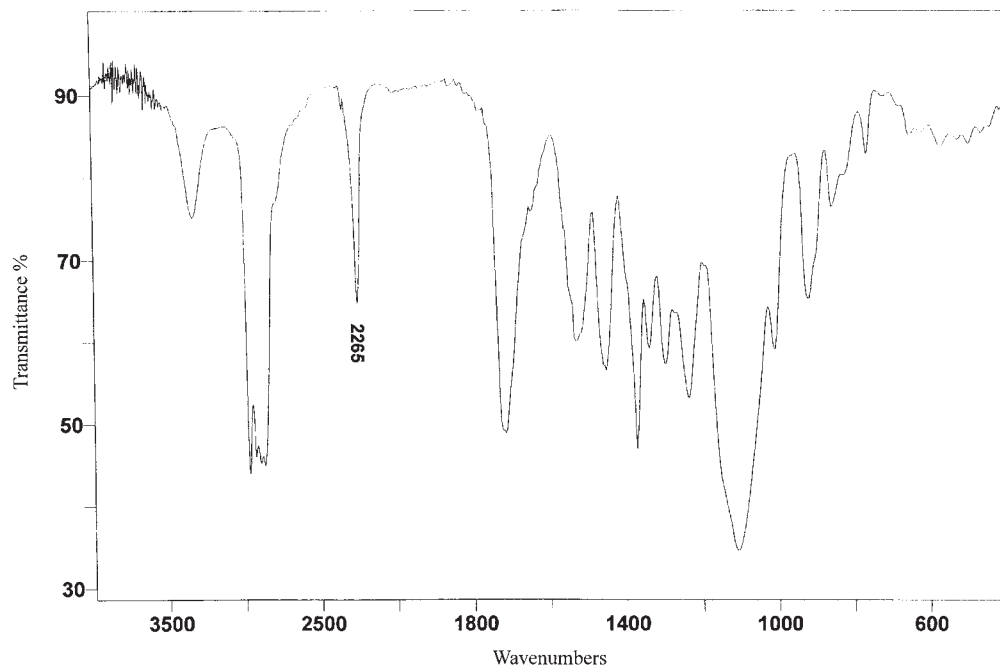


Figure 1 FT-IR spectrum of NCO-terminated PU prepolymer.

3°C/min from -80 to 150°C at a 1.0-Hz frequency for each sample.

Thermogravimetric analysis (TGA)

PU samples were measured by a thermogravimetric analyzer with a heating rate of 20°C/min from ambient temperature to 500°C. These were carried out un-

der a nitrogen atmosphere for the measurement of polymer thermal stabilities.

RESULTS AND DISCUSSION

The postcuring reactions of aqueous-based PU have been proven to be an effective chemical process for improving PU properties, as are curing reactions with

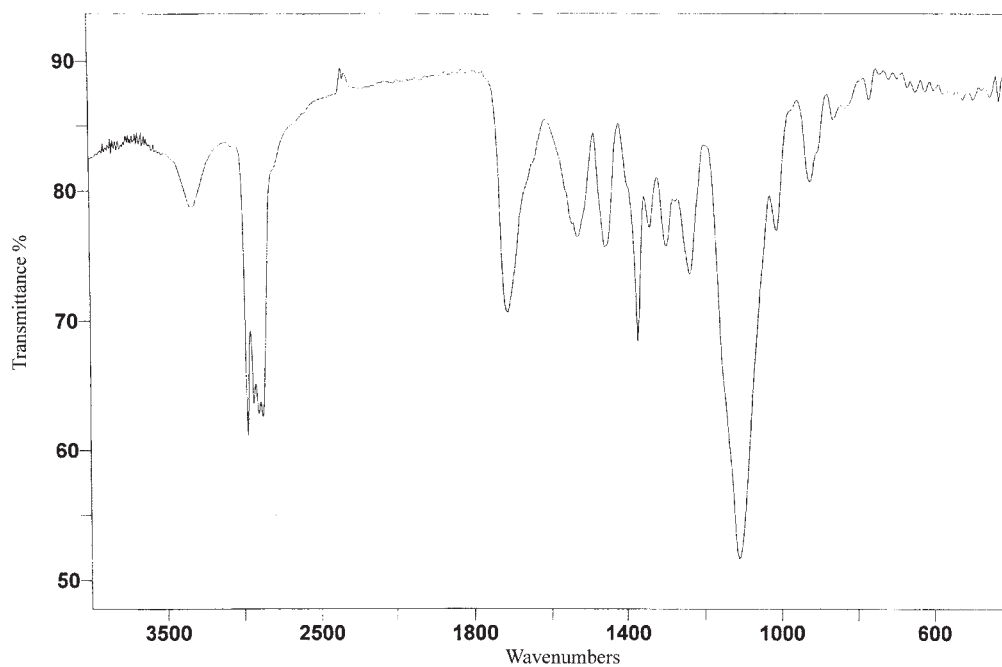
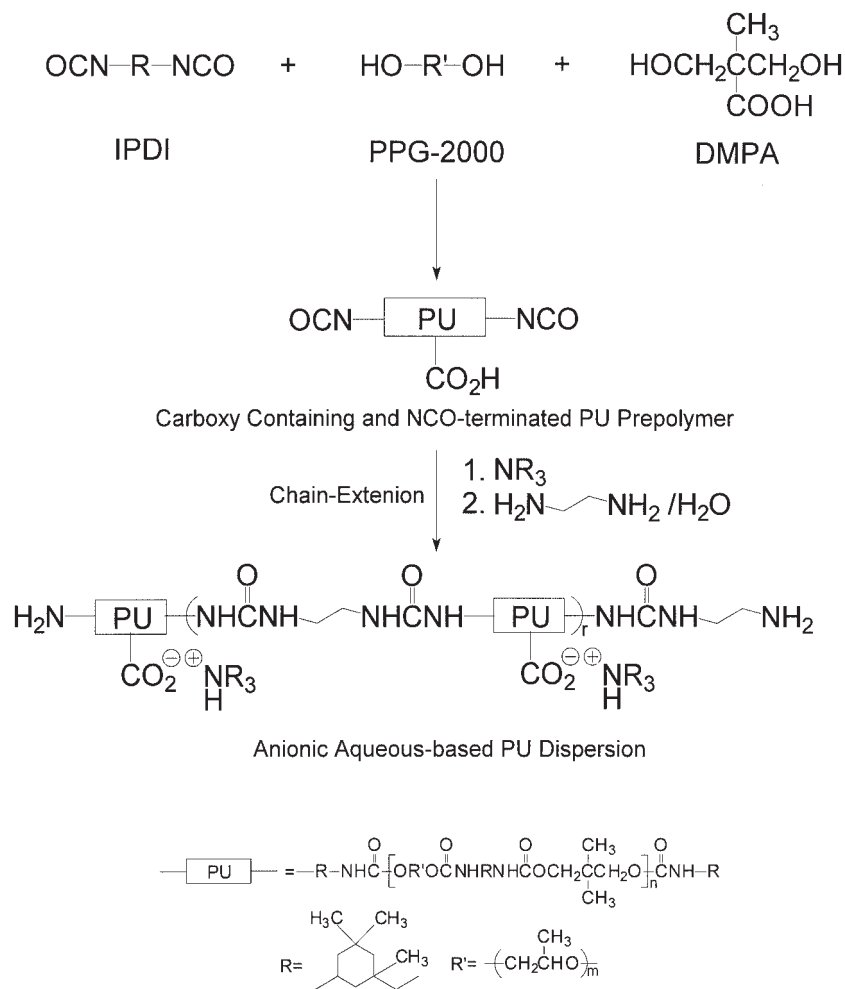


Figure 2 FT-IR spectrum of aziridine-terminated PU oligomer.



Scheme 2 Preparation of anionic aqueous-based PU dispersion.

a multifunctional aziridine curing agent²⁻⁵ or a phosphorus containing aziridine curing agent, which also serves as a reactive flame retardant.⁸⁻¹⁰ Furthermore, PU properties have been improved from a polymer hybridization process simply by mixing an aqueous-based PU dispersion with epoxy resins,⁴ glycidyl methacrylate (GMA)-copolymer emulsion,^{11,12} and water-reducible epoxy dispersion,¹³ respectively, in the aqueous phase and drying at ambient temperature. These are energy-saving polymer hybridization processes and provide alternatives for modifying aqueous-based PU resin.

Conventional aqueous-based PU dispersions were prepared from a PU prepolymer process.³ The PU carboxyl group served as an ionic center and a curing site that is derived from one of PU ingredients: 2,2-dimethylolpropanic acid (DMPA) (Schemes I and II). It results in the formation of a self-emulsified aqueous-based PU dispersion. This PU dispersion consists of 30% solids and 3.5×10^{-2} equivalents of carboxyl group per 100 g of solid PU resin.

A self-curing aqueous-based PU dispersion was obtained from a subsequent reaction of NCO-terminated

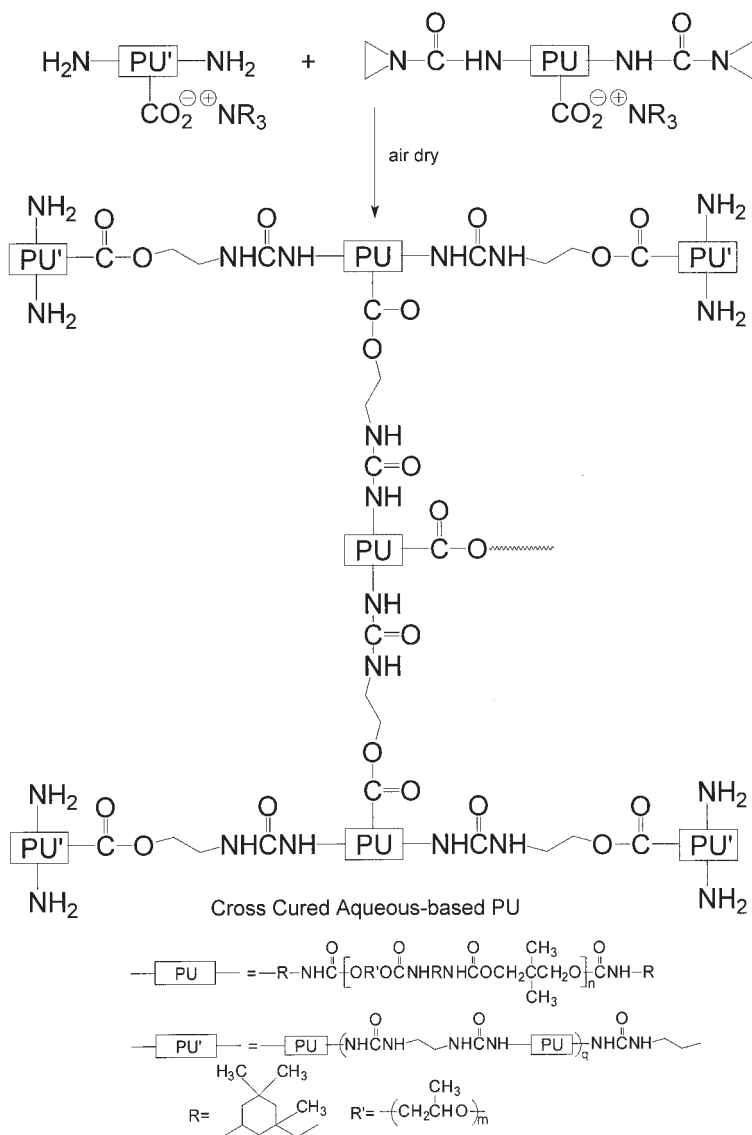
PU prepolymer to an aziridine-terminated PU oligomer by an addition reaction of aziridine and then by the water dispersion (Scheme I). This self-cured PU (PU-AZ) resin was prepared directly from this aqueous-based aziridine-terminated PU dispersion on drying.

Both self-curing PU-AZ (Scheme I) and conventional aqueous-based PU (Scheme II) dispersions are self-emulsified aqueous dispersions, which are compatible with each other. The self-curing process of PU-AZ was derived from a reaction intra- or intermolecularly between the PU terminal aziridine and its pendent carboxyl group and served as a polymeric curing agent. Various cross self-cured PU hybrids (PU-AZ/PU, Scheme III, Table I) can be obtained from the polymer hybridization process of this self-curing PU dispersion (PU-AZ, Scheme I) with a conventional aqueous-based PU dispersion (PU, Scheme II) in various ratios.

Characterizations of the self-curing PU system

Monitoring self-curing PU (PU-AZ) system by FT-IR

The NCO absorption peak (at 2265 cm^{-1}) of PU-NCO (Figure 1) disappeared after aziridine addition and



Scheme 3 Cross self-curing between carboxyl group containing aziridine-terminated and conventional aqueous-based PU.

resulted in an aziridine-terminated PU oligomer formation (Scheme I and Figure 2). The amide N-H stretching frequency appeared at 3332 cm^{-1} , after aziridine addition to NCO (Figure 3), replacing the terminal amine (at 3352 cm^{-1}) of the conventional aqueous-based PU (Figure 4).

Physical properties

The gel content and ethanol uptake of PU-AZ resin were 94.9 and 224.5%, respectively, compared to those of the uncured conventional aqueous-based PU resin, which dissolves completely in THF or ethanol (Table I). This demonstrates the relative degree of crosslinking density of PU-AZ by the curing reaction of PU aziridine groups. These two PU dispersions (PU-AZ/PU) were mixed in 1 : 2 and 2 : 1 ratios and resulted in the cross self-cured PU hybrid formation with 80.3 and 89.9% gel contents, respectively (Table I). The

increasing gel content of the PU hybrid depends on the dosage of PU-AZ. The amount of ethanol uptake also decreased from 1000.5 to 373.6% with increasing the PU-AZ/PU ratio from 1 : 4 to 2 : 1. The hardness of PU-AZ was 72 compared to 61 of the original PU and those of 64, 67, 67, and 70 of cross self-cured PU hybrid with PU-AZ/PU hybridization ratios of 1 : 4, 1 : 2, 1 : 1, and 2 : 1, respectively. The higher PU-AZ dosage created a higher hardness due to a greater polymeric network formation. This represents the evidence of the intermolecular crosslinking reaction taking place between PU-AZ and PU within this cross self-curing PU system.

Mechanical properties

The tensile strength at break of conventional PU resin was 4.4 kg/cm^2 at 1530% elongation and its value of PU-AZ was 2.0 kg/cm^2 at 135% elongation. Its value

TABLE I
Properties of PU-AZ/PU Hybrids

Properties	Original PU ^a	PU-AZ ^b	PU-AZ/PU ^c , tensile stress (kg/cm ²)			
			1 : 4	1 : 2	1 : 1	2 : 1
Elongation (%)						
100	0.6	1.5	1.3	1.5	1.8	1.9
200	1.1	—	2.4	2.6	3.1	3.4
300	1.4	—	3.1	3.5	4.3	4.6
400	1.8	—	3.8	4.3	5.5	—
500	2.0	—	4.5	5.2	—	—
600	2.3	—	5.2	6.2	—	—
700	2.5	—	6.0	7.6	—	—
800	2.7	—	6.5	—	—	—
900	2.9	—	—	—	—	—
1000	3.1	—	—	—	—	—
Tensile strength at break (kg cm ⁻² /%)	4.4/1530.0	2.03/135.0	7.5/876.7	8.0/753.0	6.8/480.0	5.4/375.0
Gel content (%)	0	94.9	73.1	80.3	85.7	89.9
Ethanol uptake (%)	— ^d	224.5	1005.5	568.2	472.9	373.6
Polymer wt. dissolved in ethanol (%)	100	4.7	20.6	15.3	9.8	7.7
Hardness ^e	61	72	64	67	67	70

^a PU, conventional aqueous-based PU.

^b PU-AZ, self-cured aqueous-based PU.

^c Weight ratio of PU-AZ/PU.

^d Original aqueous-based PU dissolves in ethanol (95% w/w).

^e Hardness of polymer is measured by Shore A Durometer.

changed to 8.0 kg/cm² at 753% and 5.4 kg/cm² at 375% elongation, respective to the PU-AZ/PU ratios of 1 : 2 and 2 : 1. The tensile stress at 0.6 kg/cm² with 100% elongation of original PU and its value of PU-AZ/PU (2 : 1) hybrid increased to 1.9 kg/cm² (Table I). These data

demonstrate the better mechanical properties of PU-AZ and PU-AZ/PU hybrids compared to the original aqueous-based PU resin. These are due to the cross self-curing reaction taking place between PU-AZ and PU within these self-curing polymer systems.

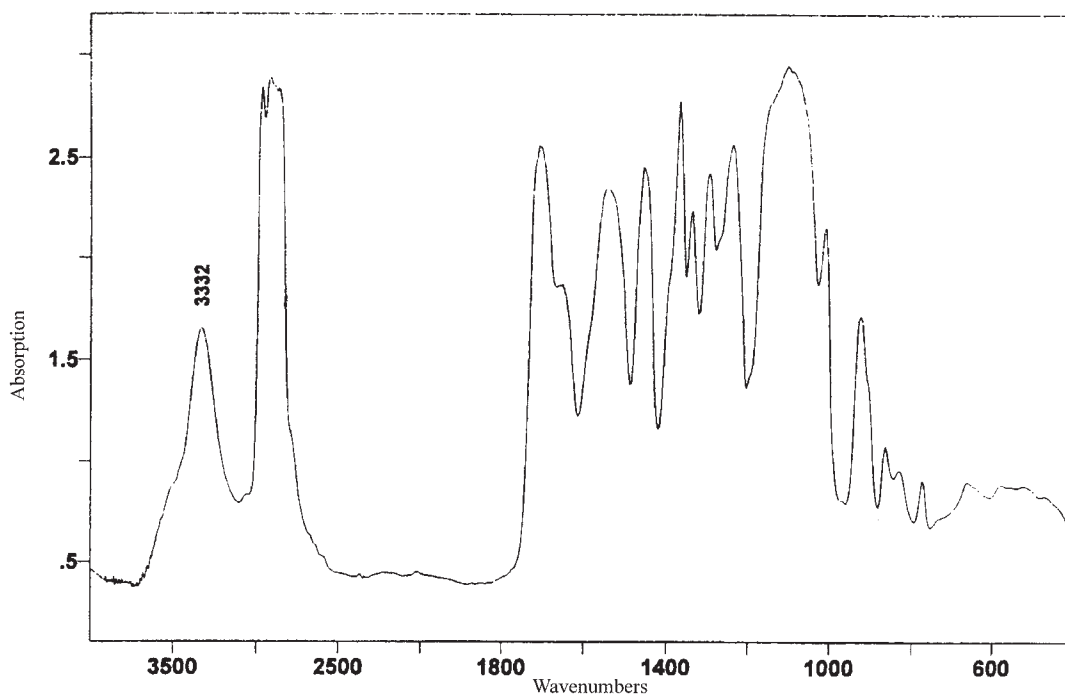


Figure 3 FT-IR spectrum of self-cured PU resin.

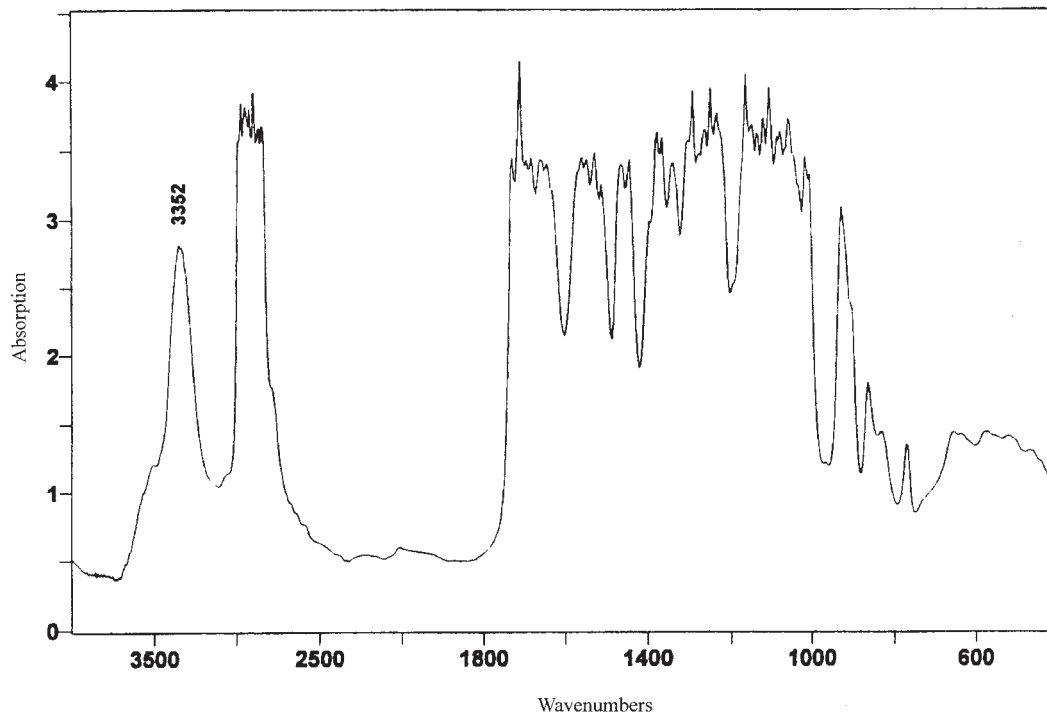


Figure 4 FT-IR spectrum of aqueous-based PU resin.

Thermal behavior

The major decomposition temperatures of PU and PU-AZ are 357 and 385°C, respectively. Its TGA thermogram indicates the PU-AZ/PU hybrid has a better ther-

mal stability than the original PU, and its thermal stability increases with increasing PU-AZ dosage (Figure 5). These improved properties are caused by the self-curing reaction, which helps the interpenetrating polymeric network formation within these PU-AZ/PU hybrids.

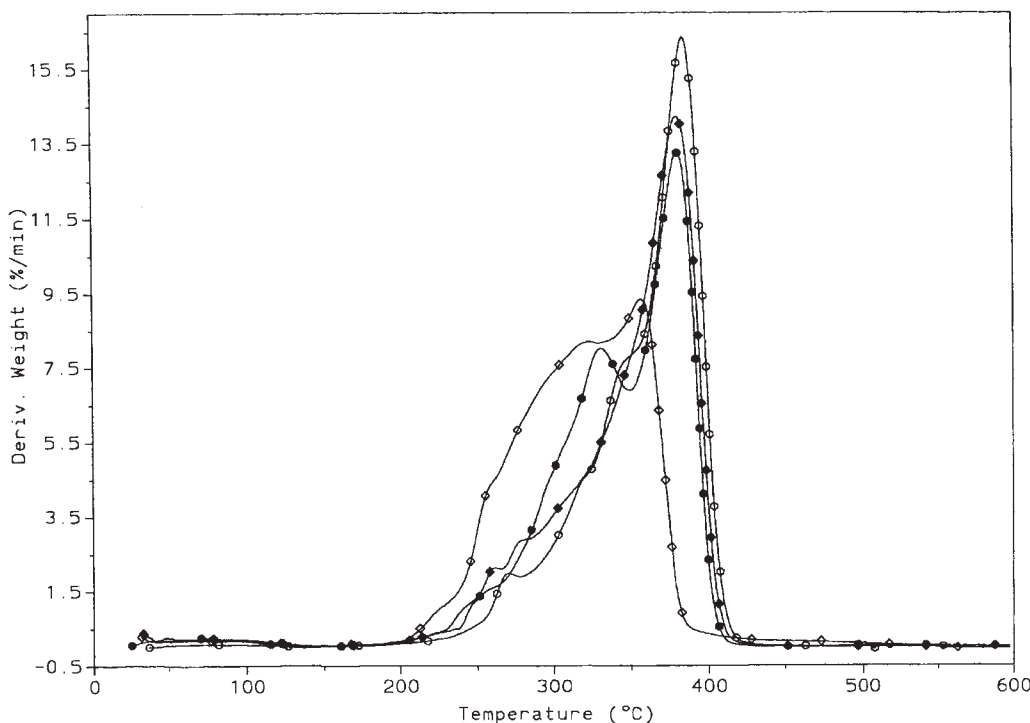


Figure 5 Differential thermogravimetric analyses of PU-AZ/PU hybrids.

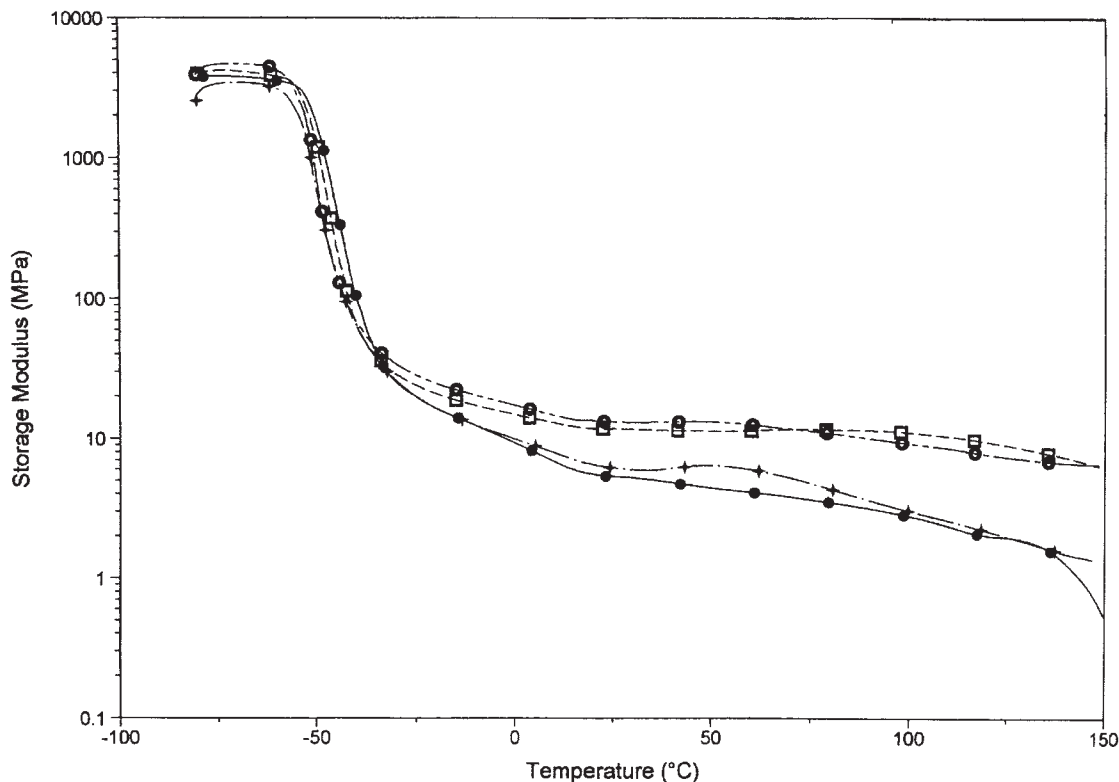


Figure 6 DMA storage moduli of PU-AZ/PU hybrids.

Dynamic mechanical analysis indicated a self-curing PU system having a higher storage modulus of PU-AZ than that of original PU (Figure 6). The self-cured PU-AZ was found to be much stiffer than original PU, due to the restricted polymer mobility with less free volume of PU-AZ having a higher crosslinking density. Higher storage modulus was also obtained from a higher ratio of PU-AZ/PU hybrid, for example, the PU-AZ/PU (2 : 1) hybrid was closer to that of PU-AZ. This thermal behavior was also coincident with PU mechanical and physical properties, such as tensile strength, hardness, gel content, and ethanol uptake (Table I).

CONCLUSIONS

The aziridine-terminated PU oligomer (PU-AZ) serves as an internal polymeric curing agent and the self-curing reaction takes place within its polymer. Both aqueous-based PU-AZ and PU dispersions are self-emulsified and compatible with each other in any ratios. PU-AZ serves as a polymeric curing agent and forms a cross self-curing PU system. The curing reaction takes place intra- and intermolecularly, which results in the formation of the cross self-cured PU hybrid (PU-AZ/PU) on drying. The thermal behavior, physical, and mechanical properties of PU-AZ resin or PU-AZ/PU hybrids are improved compared to those of conventional aqueous-based PU resin. This PU-AZ/PU hybridization process

has been shown to be one of options for improving the conventional aqueous-based PU resin.

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