Self-Curable System of an Aqueous-Based Polyurethane Dispersion via a Ring-Opening Reaction of Azetidine End Groups

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ABSTRACT: An azetidine (AZT) containing compound, 3-azetidinyl propanol was synthesized from methyl acrylate with 3-amino-1-propanol in a four-step reaction. It was introduced into an isocyanate-terminated carboxylic acid containing polyurethane (PU) prepolymer as the end group. A single-component, AZT-terminated self-curable aqueous-based PU dispersion was obtained from the water dispersion process after it was neutralized with triethylamine. Its carboxylic groups served not only as the internal emulsifier stabilizing the aqueous PU dispersion but also as PU self-curing sites toward its AZT end groups via a ring-opening reaction. The curing reaction took place on drying and resulted in polymeric network structure formation among the polymers. The performance properties of this self-cured PU were evaluated in this study. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 4383–4393, 2006

Key words: crosslinking; dispersions; functionalization of polymers; polyurethanes

INTRODUCTION

Traditional solvent-based polyurethane (PU) has been widely accepted by the market for more than half a century. Because of its flexible properties, it can be tailor-made from available raw materials.[1] PU has been used extensively for various applications, such as coatings, adhesives, foams, textiles, and membranes. Because of the environmental impact and health and safety concerns, solvent-based PU has been being gradually phased out from the market and replaced by aqueous-based PU. The most popular aqueous-based PU dispersion is a self-emulsified and organic solvent-free system.

An anionic self-emulsified PU dispersion containing carboxyl groups was prepared from an isocyanate-terminated carboxylic acid containing polyurethane prepolymer (NCO-PU), which was prepared by a polyaddition reaction of isophorone diisocyanate (IPDI) with poly(propylene glycol) (PPG-2000) and dimethylolpropanic acid (DMPA). Some isocyanate (NCO) terminal groups were hydrolyzed to amino groups when they were dispersed into the water phase after being neutralized with triethylamine (TEA). These amino groups may have reacted further with the remaining NCO groups for self-chain extension to form urea bonding. The pendent carboxyl groups of aqueous PU provided the particle surface charges, thereby causing repulsion between PU particles and stabilizing PU dispersions in the water phase. Because of the ionic character of the carboxyl group, this PU became self-emulsified in the water phase. However, because of its hydrophilic character with lower average molecular weight characteristics, the physical and mechanical properties of aqueous-based PU were still not compatible with the solvent-based PU resin.

There are several different chemical modifications, including a postcuring reaction[2–11] and polymer hybridization,[12–16] that have been proven to be effective methods for enhancing the crosslinking density and performance properties of aqueous-based PU. The convenient postcuring reaction of an anionic aqueous-based PU dispersion is mainly based on its pendent carboxyl groups reacting with a multiaziridine latent curing agent in various dosage on drying,[2–6] and the resulting aqueous-based PU has its properties modified accordingly.

Azetidine (AZT), also called trimethyleneimine, was first prepared by Gabriel and Weiner in 1888.[17] AZT and its derivatives are stable in alkaline systems and undergo ring opening by nucleophilic addition at the C_2 position of the AZT ring for ring-opening reactions at pH values below 6.0. Few studies have reported the formation of polypropyleneimine[18] and betaine.[19,20]

The AZT moiety is one ideal reactive group toward carboxyl groups at a low-pH (e.g., 6.0) conditions at ambient temperature. Because of its ring-opening reac-

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tion with carboxylic acid and the formation of amino ester bonding, this is similar to the azirdine moiety. Therefore, AZT was introduced to NCO-PU to form an azetidine-terminated self-curable anionic polyurethane dispersion (AZT-PU), which was stable at pH values below 6.0. This AZT-PU was self-cured via an AZT ring opening by the carboxylic acid of the PU pendent on drying. The performance properties, including as gel content, water uptake (W_w), ethanol swelling, tensile strength, and thermal behaviors, of this self-cured PU were evaluated in this study.

EXPERIMENTAL

Materials

IPDI was supplied by Hul Chemical Co. (Germany). DMPA, TEA, 3-amino-1-propanol, methyl acrylate (MA), thionyl chloride, lithium aluminum hydride (LAH), sodium hydrogen carbonate, anhydrous sodium carbonate, dichloromethane, methanol, tetrahydrofuran (THF), pentaerythritol, anhydrous sodium sulfate, sodium sulfate decahydrate, and ethanol were supplied by Aldrich Chemical Co. PPG-2000 was supplied by Arco Chemical Co. (Taiwan). All solvents were purified before use.

Instruments

Thermogravimetric data were measured with a Hi-Resolution TGA 2950 TG-DTA thermogravimetric analyzer. IR spectra were recorded by a Bio-Rad Fourier transform infrared (FTIR) FTS-40 spectrometer. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker AC-300 spectrometer (Germany). Chemical shifts are reported in parts per million relative to residual $CHCl_3$ ($\delta = 7.26$ for ^{1}H; $\delta = 77.0$ for ^{13}C). Multiplicities are shown as singlets (s), doublets (d), triplet (t), quartet (q), and multiple splits (m). Stress and strain curves of the PU films were taken with a Shimadzu Autograph S-100-C (Japan).

Preparation of 3-azetidinyl propanol (AZT-OH; Scheme 1)

Step 1: Dimethyl 3-*N*-(3-hydroxypropyl) iminodipropinate

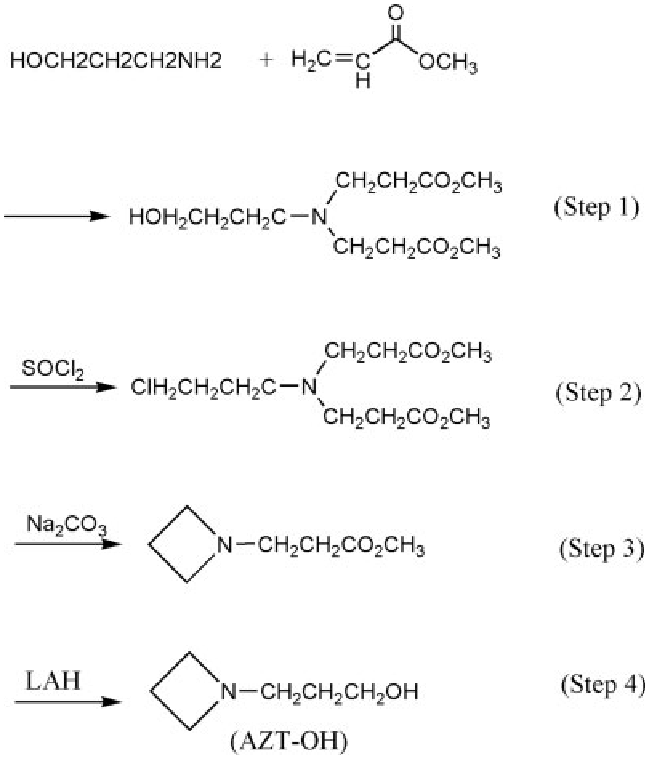
3-Amino-1-propanol (150 g, 2.00 mol) was added dropwise to 430 g of MA and refluxed 12 h in a 1-L round-bottom flask. Excess MA was removed under reduced pressure, and 478 g of dimethyl 3-*N*-(3-hydroxypropyl) iminodipropinate was obtained.

Yield = 96.8%. ^{1}H-NMR ($CDCl_3$, 300 MHz, δ): 1.54 (m, 2H), 2.35 (t, J = 7.0 Hz, 4H), 2.47 (t, J = 6.1 Hz, 2H), 2.64 (t, J = 7.1 Hz, 4H), 3.54 (s, 6H), 3.55 (t, J = 5.6 Hz, 2H). ^{13}C-NMR ($CDCl_3$, 75 MHz, δ): 28.4, 31.8, 49.0, 51,3, 52.2, 62.0, 172.5. IR (KBr, cm^{-1}): 3420, 1953, 2843, 1735, 1438, 1200, 1175, 1049, 843.

Step 2: Dimethyl 3-*N*-(3-chloropropyl) iminodipropinate

A solution of 478 g (1.94 mol) of dimethyl 3-*N*-(3-hydroxypropyl) iminodipropinate in 800 mL of CH_2Cl_2 was added dropwise to a CH_2Cl_2 solution of 262 g (2.2 mol) of thionyl chloride in an ice bath; the reaction mixture was kept below 25°C. The reaction mixture was stirred for another 6 h at room temperature after the addition. Then, it was neutralized with an aqueous solution 400 g of $NaHCO_3$. The organic layer was separated and washed with deionized water and then dried with Na_2SO_4. The residue was obtained after the solvent was removed. The reaction product, dimethyl 3-*N*-(3-chloropropyl) iminodipropinate (473 g), was obtained.

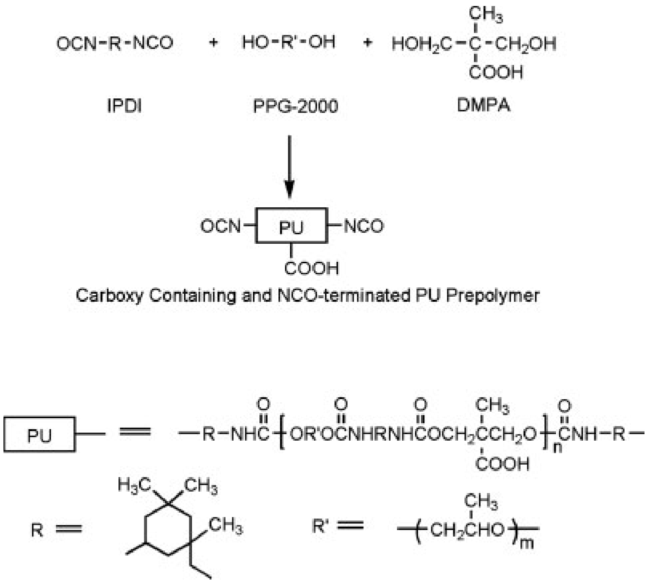
Yield = 92.05%. ^{1}H-NMR ($CDCl_3$, 300 MHz, δ): 1.80 (m, 2H), 2.37 (t, J = 6.9 Hz, 4H), 2.48 (t, J = 6.4 Hz, 2H), 2.67 (t, J = 7.0 Hz, 4H), 3.49 (t, J = 6.3 Hz, 2H), 3.61 (s, 6H). ^{13}C-NMR ($CDCl_3$, 75 MHz, δ): 30.2, 32.4, 42.7, 49.2, 50.3, 51.4, 172.7. IR (KBr, cm^{-1}): 2953, 2828, 1738, 1437, 1253, 1199, 1174, 1043,842, 718, 648.



Scheme 1 Preparation of AZT-OH.

Step 3: Methyl 3-(1-azetidinyl) propionate (MA-AZT)

Dimethyl 3-*N*-(3-chloropropyl) iminodipropinate (473 g, 1.78 mol) obtained from step 2, Na_2CO_3 (286 g), and



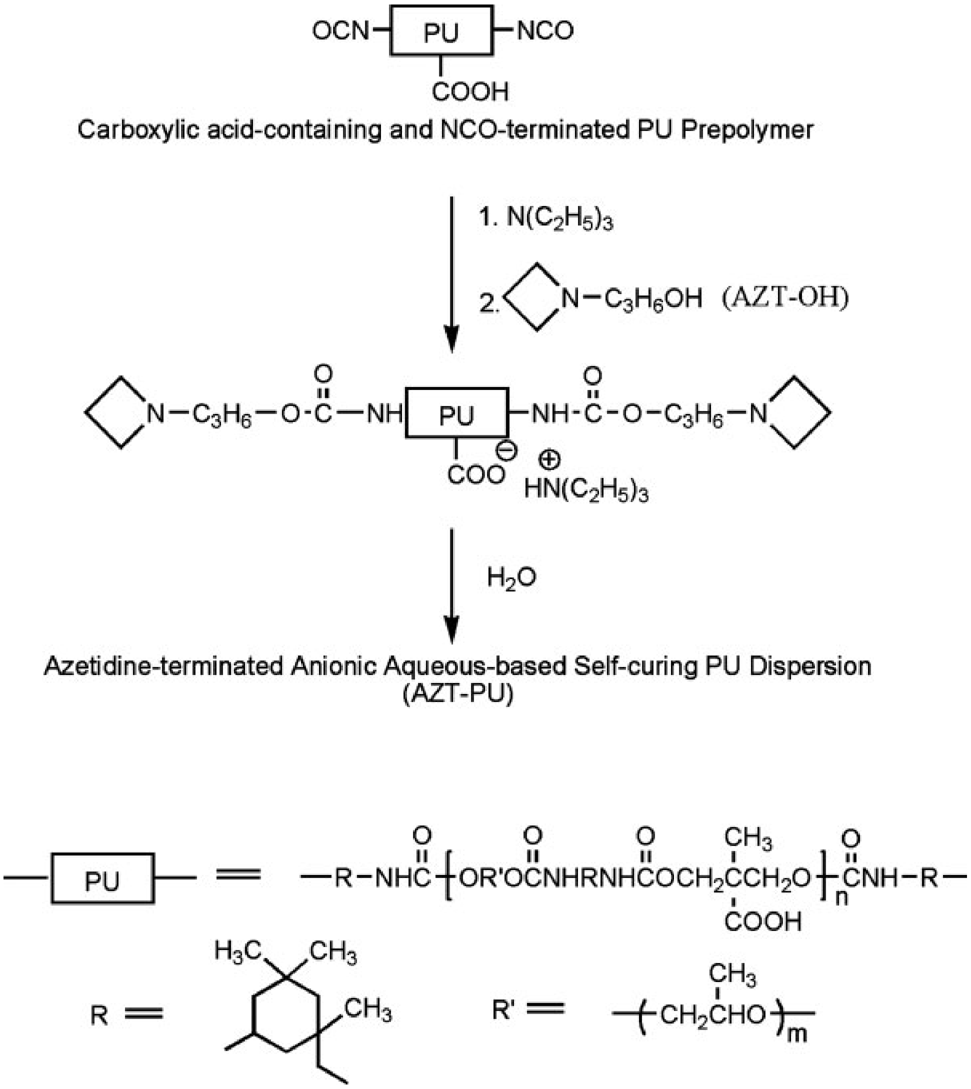
Scheme 2 Preparation of NCO-PU.

pentaerythritol (10 g) were placed in a 1-L, three-necked, round-bottom flask fixed with a mechanical stirrer, a thermometer, and a vacuum-distillation head. The crude product was distilled at 150°C/15 mmHg. The crude distillation product was purified by fractional distillation, and we collected 118 g of MA-AZT.

Yield = 45.45%. ^{1}H-NMR ($CDCl_3$, 300 MHz, δ): 1.92 (m, 2H), 2.20 (t, J = 7.3 Hz, 2H), 2.55 (t, J = 7.2 Hz, 2H), 3.05 (t, J = 7.1 Hz, 4H), 3.54 (s, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz, δ): 17.3, 32.6, 51.3, 54.7, 54.9, 172.5. IR (KBr, cm^{-1}): 2998, 2957, 2827, 1739, 1438, 1325, 1307, 1258, 1209, 1167, 1122, 1082, 1020, 986, 648.

Step 4: AZT-OH

A THF solution (200 mL) of MA-AZT (14.3 g, 0.10 mol) was added dropwise to a THF (100 mL) solution of 4.56 g of LAH in a 500-mL, three-necked, round-bottom flask. The reaction was kept in an ice



Scheme 3 Preparation of AZT-PU dispersion.

bath during the addition, and it was stirred for an additional 1 h after the addition was complete. An aqueous suspension of Na_2SO_4 was added slowly to the reaction mixture to quench excess LAH and filtered. The organic solution was separated and dried with Na_2SO_4. The residue, AZT-OH (9.2 g), was obtained after the solvent was removed (Scheme 1):

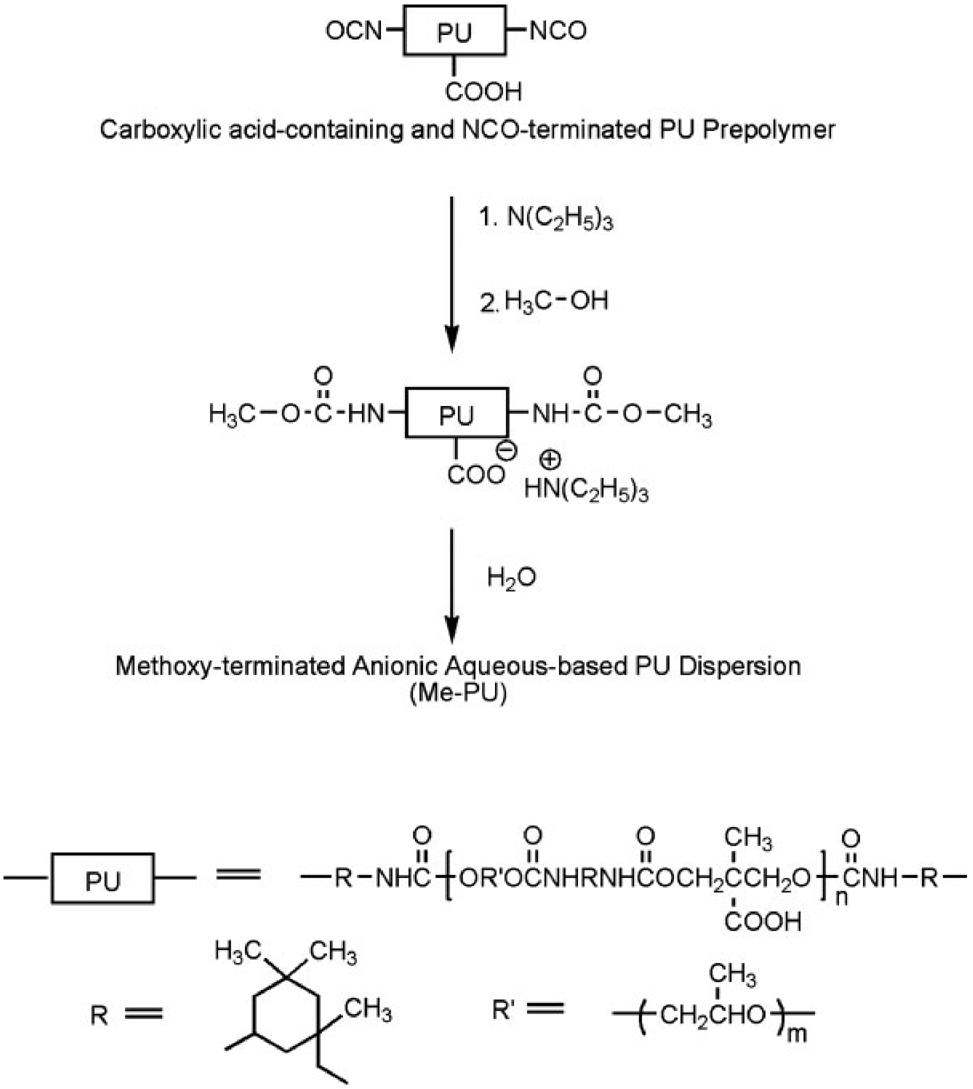
Yield = 79.50%. ^{1}H-NMR ($CDCl_3$, 300 MHz, δ): 1.50 (m, 2H), 2.01 (m, 2H), 2.59 (t, J = 7.2 Hz, 2H), 3.13 (t, J = 7.1 Hz, 4H), 3.68 (t, J = 5.5 Hz, 2H). ^{13}C-NMR ($CDCl_3$, 75 MHz, δ): 17.3, 28.3, 55.1, 59.6, 64.0. IR (KBr, cm^{-1}): 3369, 2997, 2956, 2840, 1656, 1449, 1381, 1126, 1066, 1018, 981, 770.

Preparation of NCO-PU (Scheme 2)

PPG-2000 (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, four-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 kept at 90°C for about 4 h, until the NCO percentage dropped below 3.0% (ASTM D 1638 NCO determination method) and remained constant for another half hour. Then, freshly dried acetone was added to the reaction flask (when it was cooled below 50°C) to adjust the viscosity of NCO-PU.

Preparation of AZT-PU (Scheme 3)

An excess amount of TEA was added to the acetone solution (130 g) of PU-NCO (65 g, prepared previously) to neutralize the pendent carboxylic acid, and then, an acetone solution of AZT-OH (5.35 g) was added dropwise through an addition funnel. The reaction mixture was kept at an acetone refluxing temperature for 2.5 h. The reaction was completed when its NCO number dropped to zero (the NCO absorption peak at 2260 cm^{-1} disappeared in FTIR). The



Scheme 4 Preparation of Me-PU dispersion.

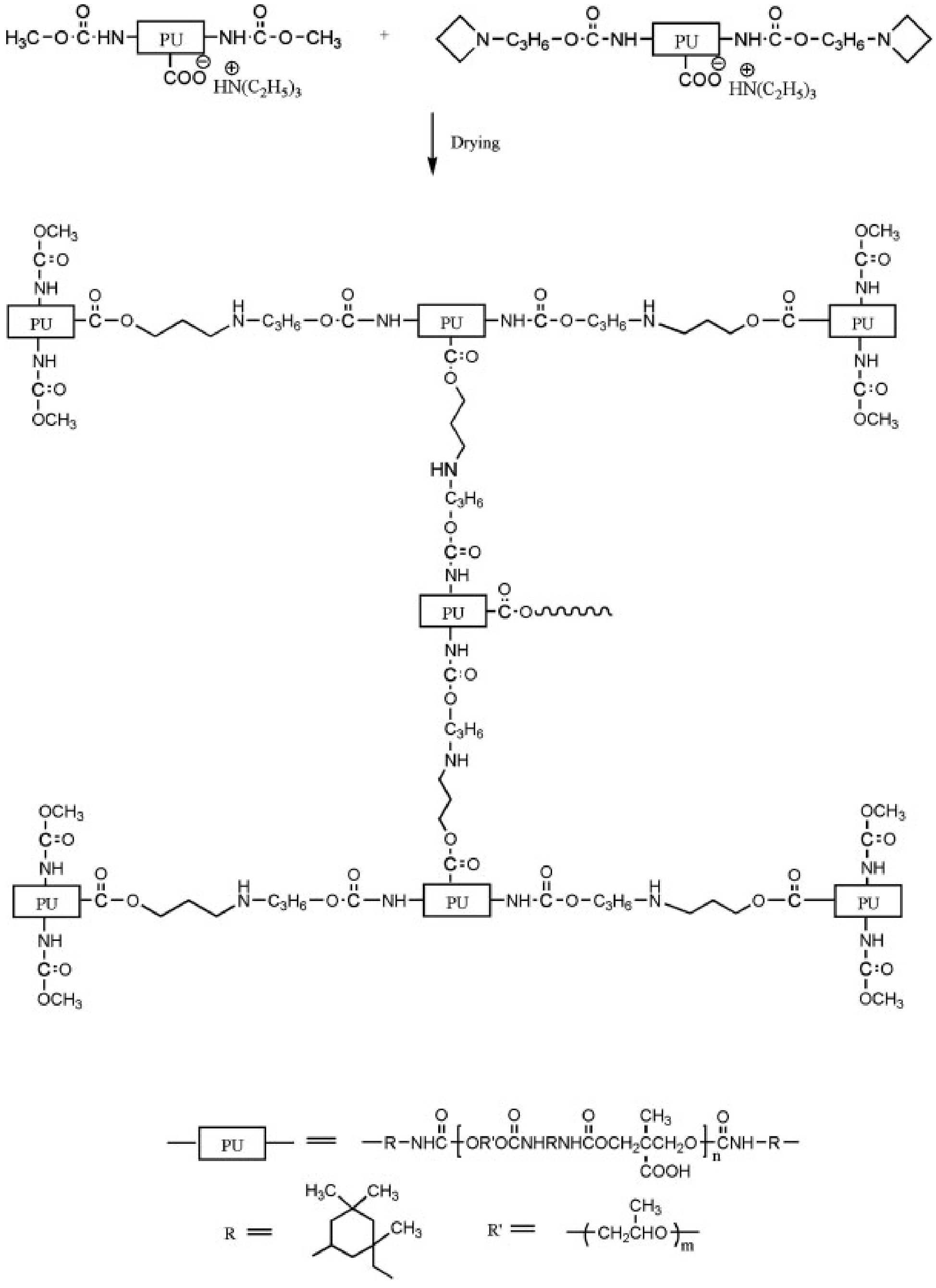
reaction mixture was added to deionized water with agitation. This resulted in the formation of AZT-PU with 30% solid content after acetone was removed.

Preparation of the methoxy-terminated aqueous-based polyurethane dispersion (Me-PU; Scheme 4)

An excess amount of TEA was added to a PU-NCO (65 g) acetone solution to neutralize the pendent carboxylic acid, and then, excess methanol (10 g) was added dropwise through an addition funnel. The reaction mixture was kept at an acetone refluxing temperature for 2.5 h. The reaction was completed when its NCO number dropped to zero. The reaction mixture was added to deionized water, similar to the preparation of AZT-PU. This resulted in the formation of Me-PU with 30% solid content after acetone was removed.

Hybridization of AZT-PU with Me-PU (Scheme 5)

AZT-PU and Me-PU were mixed in various ratios with stirring, and the resulting homogeneous aqueous PU dispersion was cast and dried at ambient



Scheme 5 Cross-self-curing of AZT-PU/Me-PU hybrids.

temperature. This resulted in a hybridized and crosslinked PU resin. It was heated in a 50°C oven for 24 h and conditioned in a 75% relative humidity chamber at ambient temperature for 24 h before testing.

Properties of the PU resin

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 remaining after extraction was dried and calculated according to the test result. Three tests were carried out and averaged for each PU sample:

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

where W_2 is the oven-dried sample weight.

W_w

A known weight of dried PU film sample with dimensions of 60 × 60 × 1 mm (W_0) was immersed in a deionized water bath for 7 days. W_1 and W_2 were obtained. W_w (%) and the weight loss of the PU film in water could be calculated according to the following equation:

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

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

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

Ethanol swelling

W_0 of the dried PU film sample with dimensions of 60 × 60 × 1 mm was immersed in a 95% ethanol bath for 24 h. W_1 and W_2 were obtained. Ethanol absorption by the PU film (W_e) and the weight loss

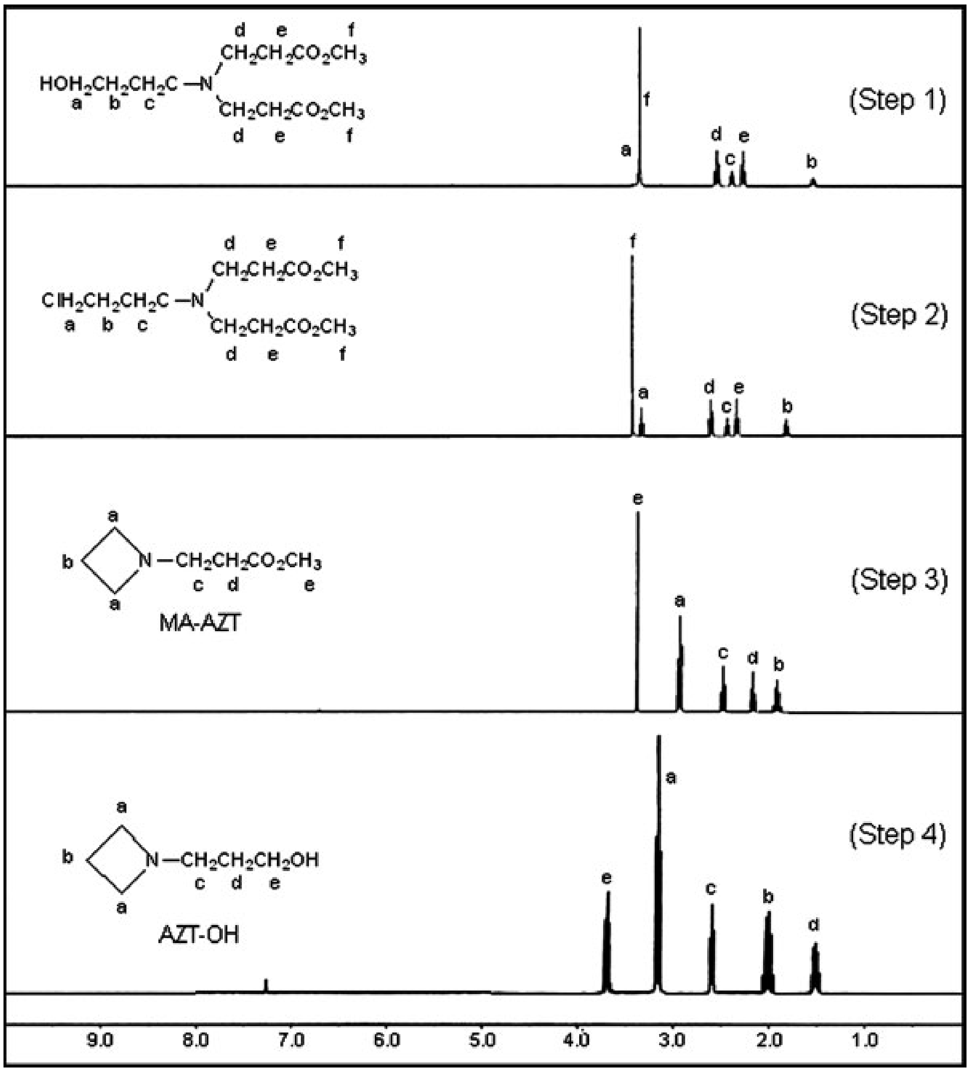


Figure 1 ^{1}H-NMR spectra of each step product toward AZT-OH.

of the PU film in ethanol could be calculated according to the following equations:

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

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

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

Tensile strength and elongation

Each PU film was cast and dried from these prepared self-curable PU dispersions at room temperature and were then kept in an oven at 25°C for a week before the tests. 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 the measurement, and we calculated the mean results.

Thermogravimetric analyses

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

RESULTS AND DISCUSSION

Because of the environmental impact and health and safety concerns of traditional solvent-based PU, it has been replaced by environmentally friendly aqueous-based PU dispersions. However, aqueous-based PUs are hydrophilic with lower molecular weights, which cause some insufficient properties compared to traditional solvent-based PUs. Postcuring reactions of aqueous-based PUs have been proven to be an effective method for improving PU properties, for example, a curing reaction with a multiaziridine curing agent.[2–11] Furthermore, polymer hybridization is another effective process for improving the PU properties.[12–16]

A model reaction product of a monoazetidine compound, MA-AZT, with trimethylacetic acid demonstrated the AZT ring opening by carboxylic acid of trimethylacetic acid.[21] A diazetidine containing curing agent was applied for aqueous PU dispersion as a latent curing agent.[21]

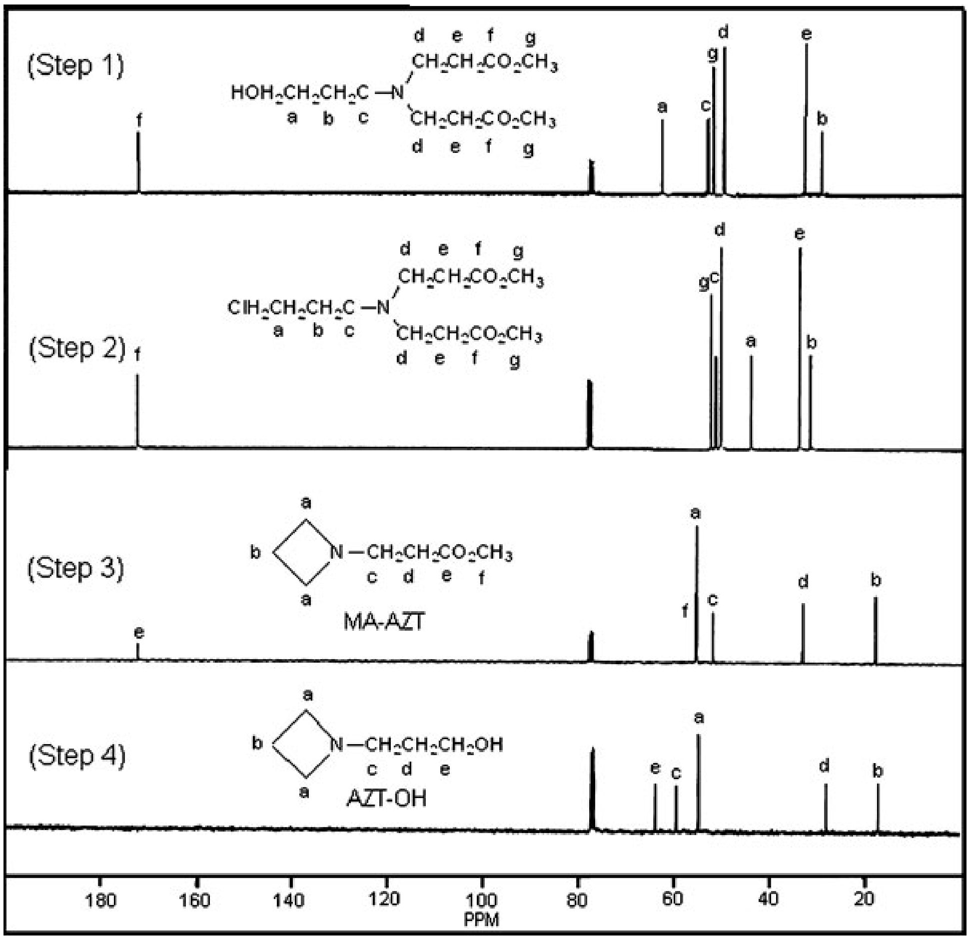


Figure 2 ^{13}C-NMR spectra of each step product toward AZT-OH.

A new AZT-containing compound, AZT-OH, was synthesized and introduced to NCO-PU; this resulted in an AZT-PU that was self-curable due to the presence of AZT and carboxylic acid. The self-curing reaction of AZT-PU took place on drying. The curing behaviors of the self-cured PU were evaluated in this study.

Characterization of AZT-OH

MA-AZT was prepared by a modified process of published methods[21–23] (step 3, Scheme 1). AZT-OH was obtained from a reduction reaction of MA-AZT in the presence of LAH (step 5, Scheme 1). The chemical shift at 3.54 ppm (s) of ^{1}H-NMR spectra indicated three protons on the methyl ester of MA-AZT, and the chemical shifts at 1.92 and 3.05 ppm indicated two and four protons on AZT of MA-AZT (Scheme 1 and Fig. 1). The chemical shift (3.54 ppm) of the methyl group disappeared after LAH reduction, and a new chemical shift appeared at 3.68 ppm (t); this indicated the two protons on the carbon atom next to the hydroxyl group. The chemical shifts of the AZT ring were slightly downfield shifted to 2.01 and 3.13 ppm.

The chemical shifts at 17.3 and 54.9 ppm indicated two different AZT carbons of MA-AZT on the ^{13}C-NMR spectra (Fig. 2). The chemical shifts at 54.7 and 172.5 ppm indicated carbons on the methyl ester and the carbonyl group of MA-AZT, respectively. The chemical shifts of the methyl ester (54.7 ppm) and carbonyl group (172.5 ppm) disappeared, and a new chemical shift at 64.0 ppm appeared after MA-AZT was reduced. Both the ^{1}H-NMR and ^{13}C-NMR spec-

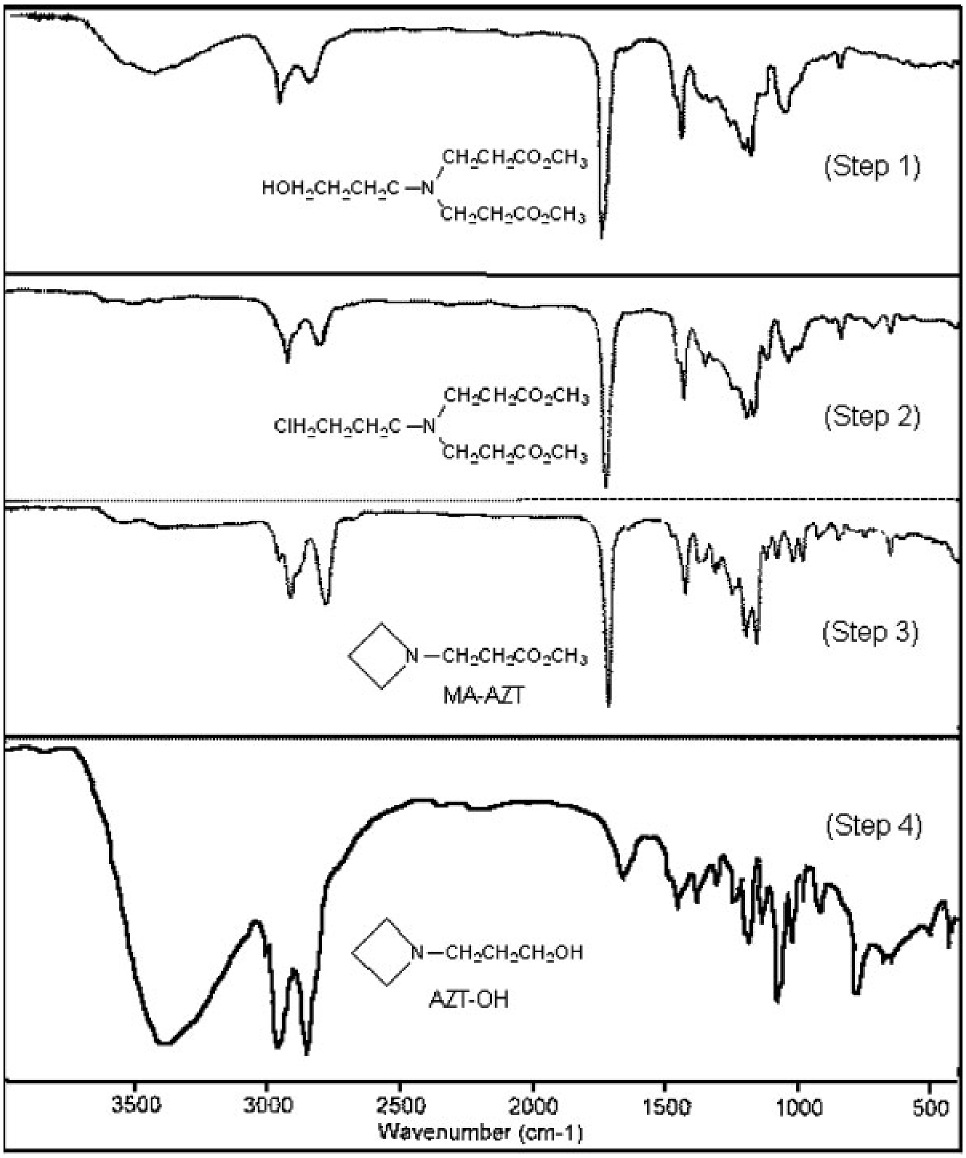


Figure 3 FTIR spectra of each step product toward AZT-OH.

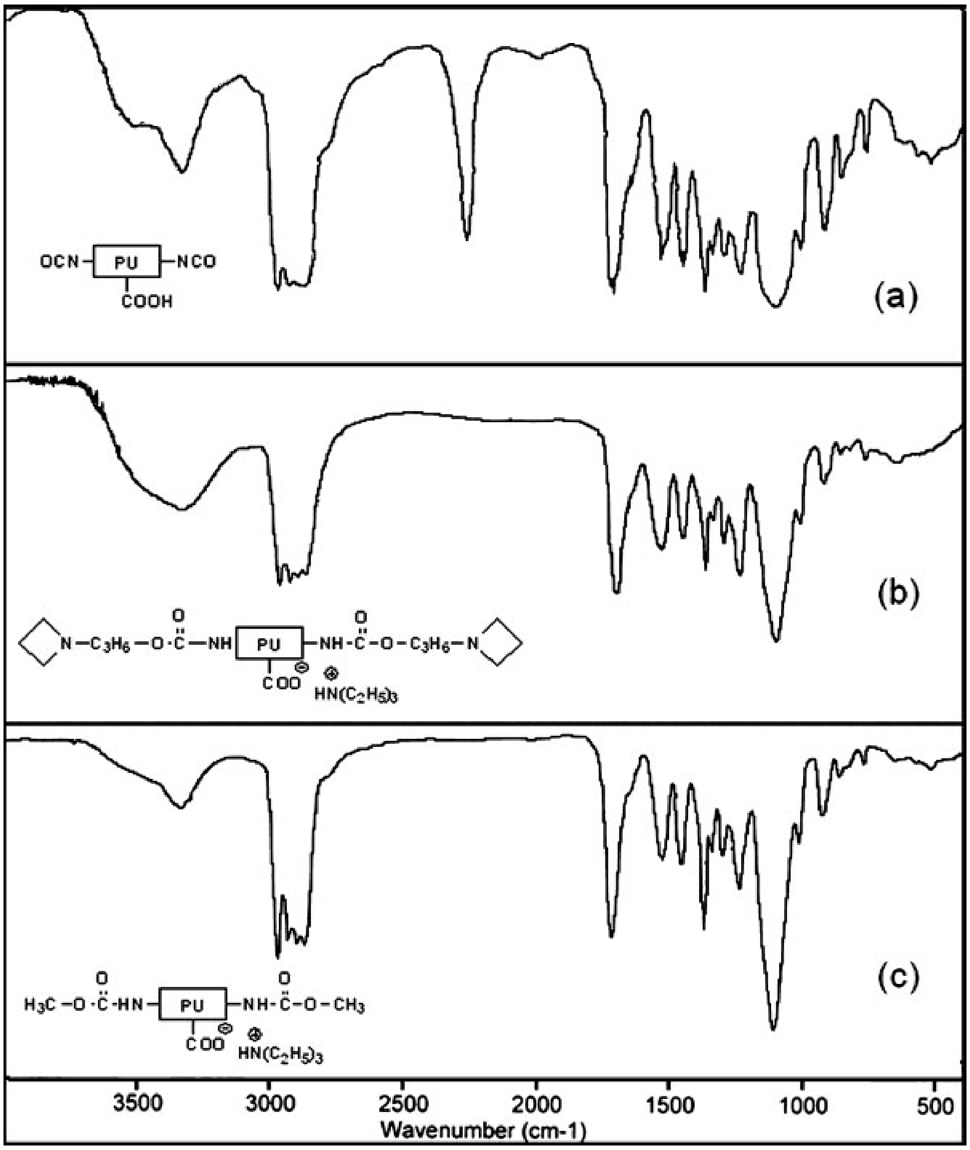


Figure 4 FTIR spectra of (a) NCO-PU, (b) AZT-PU, and (c) Me-PU.

tra demonstrated that AZT-OH was obtained by LAH reduction.

The carbonyl absorption peak of MA-AZT at 1739 cm^{-1} disappeared and was replaced by a new absorption peak of a hydroxyl group at 3369 cm^{-1} on the FTIR spectra (Figs. 3,4) when MA-AZT was reduced to AZT-OH.

Physical properties

The gel content and ethanol swelling of AZT-PU resin were 82.7 and 258.2%, respectively, when we compared Me-PU resin that dissolved completely in THF and ethanol (Table I). These indicate that the Me-PU resin was poor in solvent resistance due to

TABLE I
Physical Properties of Me-PU/AZT-PU Hybrids

		Me-PU/AZT-PU[a]			
Property	Me-PU	5 : 1	3 : 1	1 : 1	AZT-PU
COO^-/AZ[d]	0	1.8	1.2	0.6	0.3
Gel content (%)	0	57.1	64.0	74.9	82.7
W_w (%)	24.1	19.9	18.4	17.1	15.3
W_x (%)	2.6	2.2	2.0	1.7	1.0
W_e (%)	—[b]	868.5	422.6	368.6	258.2
W_y (%)	100	34.3	22.3	16.4	6.7
Hardness[c]	24	28	38	48	54

[a] Weight ratio of Me-PU/AZT-PU.
[b] One hundred percent of PU film dissolved into ethanol.
[c] Hardness of the polymer was measured with a Shore A durameter.
[d] Molar ratio of carboxyl/azetidine.

its low molecular weight without crosslinking. AZT-PU was obtained from a self-curing reaction between PU AZT terminal groups with its own carboxylic acid intermolecularly and intramolecularly on drying. The AZT-PU demonstrated a higher crosslinking density. The mixing of these two (Me-PU and AZT-PU) PU dispersions at 5 : 1, 3 : 1, and 1 : 1 ratios resulted in various extents of cross self-cured PU hybrid formations with 57.1, 64.0, and 74.9% gel contents, respectively. The increasing gel content of the hybridized PU resin depended on the amount of AZT-PU.

W_w values of Me-PU and AZT-PU were 24.1 and 15.3%, respectively. The value decreased with increasing AZT-PU dosage for the Me-PU/AZT-PU hybrids. There were also slight improvements in W_x of the Me-PU/AZT-PU hybrids compared to that of Me-PU. These were due to the different crosslinking densities of the PU hybrids from the contribution of AZT-PU.

Because of the AZT moiety, the AZT-PU served as a self-curing agent. Ethanol swelling of the hybridized PU also decreased from 868.5 to 368.6% with increasing AZT-PU ratio from 5 : 1 to 1 : 1.

The hardness of the AZT-PU resin was 54, and the hardness of the Me-PU resin was 24. The hardnesses of hybridized PU resins were 28, 38, and 48, and their ratios were 5 : 1, 3 : 1, and 1 : 1, respectively. The hybridized PU resin with a greater AZT-PU dosage exhibited a higher hardness due to the highly extent network structure formation.

These physical phenomena represent the evidence of the curing reaction of PU-terminal AZT with its carboxylic acid intermolecularly and intramolecularly for the AZT-PU and Me-PU/AZT-PU hybrids.

Mechanical properties

The tensile strength at break of AZT-PU resin was 34.3 kgf/cm^2 at 208% elongation, and the Me-PU resin was unbreakable at greater than 1300% elongation. The tensile strength at break changed to 33.0 kgf/cm^2 at 588%, 41.0 kgf/cm^2 at 498%, and 55.4 kgf/cm^2 at 398%, respectively, for PU hybrids with Me-PU/AZT-PU ratios of 5 : 1, 3 : 1, and 1 : 1 (Fig. 5). The tensile stress was 0.4 kgf/cm^2 at 100% elongation of Me-PU resin, and that of AZT-PU increased to 17.2 kgf/cm^2 (Table II). These data demonstrate the higher tensile strength of AZT-PU and Me-PU/AZT-PU hybrids compared to that of the Me-PU resin. This was due to the curing reaction of PU-terminal AZT with its carboxylic acid of AZT-PU and Me-PU/AZT-PU hybrids.

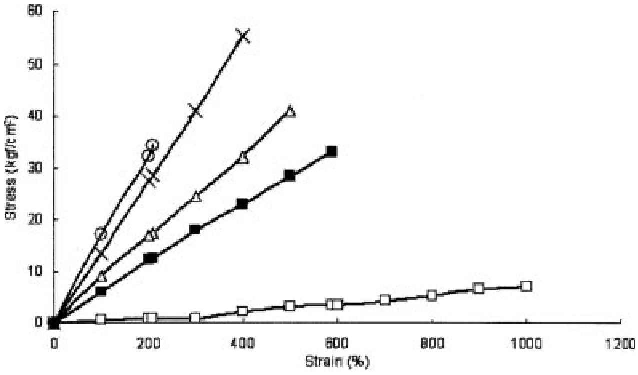


Figure 5 Stress–strain curves of (○) AZT-PU, (□) Me-PU, and Me-PU/AZT-PU hybrids in various ratios: (■) 5 : 1, (△) 3 : 1, and (×) 1 : 1.

Thermal properties

The thermal degradation temperatures at an initiator weight loss of 5% of Me-PU and AZT-PU were 246 and 265°C, respectively. The major decomposition temperatures of Me-PU and AZT-PU were both at 367°C. TGA thermograms indicated that the AZT-PU and Me-PU/AZT-PU hybrids had better thermal sta-

TABLE II
Mechanical Properties of Me-PU/AZT-PU Hybrids

		Me-PU/AZT-PU[a]			
Properties	Me-PU	5 : 1	3 : 1	1 : 1	AZT-PU
Tensile stress (kgf/cm^2)					
100% elongation	0.4	6.1	9.0	13.5	17.2
200% elongation	0.8	12.1	16.8	27.5	32.2
300% elongation	0.9	17.9	24.3	41.1	—
400% elongation	2.2	22.9	32.2	—	—
500% elongation	3.1	28.3	—	—	—
600% elongation	3.4	—	—	—	—
700% elongation	4.2	—	—	—	—
800% elongation	5.1	—	—	—	—
900% elongation	6.4	—	—	—	—
1000% elongation	7.1	—	—	—	—
Tensile strength at break (kgfcm^{-2}/%)	—[a]	33.0/588	41.0/498	55.4/398	34.3/208

[a] Elongation greater than 1300% without break.

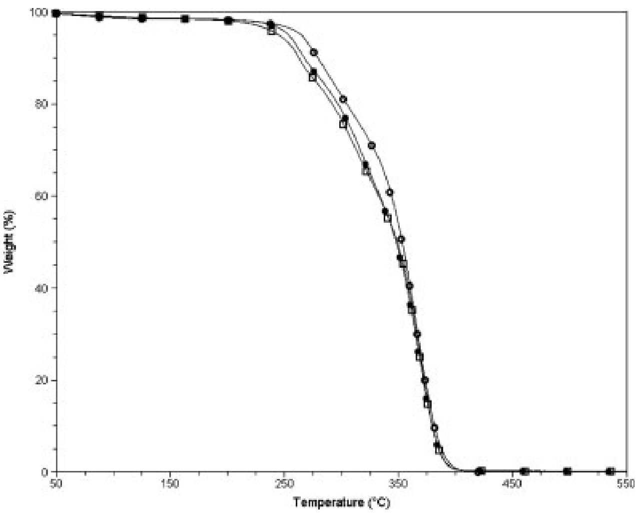


Figure 6 Thermogravimetric analysis of (□) Me-PU, (○) AZT-PU, and (●) 1 : 1 Me-PU/AZT-PU hybrid under nitrogen.

bility than noncrosslinked Me-PU resin, and thermal stability increased with increasing AZT-PU dosage (Fig. 6). These improved thermal properties were caused by the interpenetrating polymer network formation of Me-PU/AZT-PU hybrids via a self-curing reaction.

CONCLUSIONS

AZT-PU served as an internal polymeric self-curing agent, and its self-curing reaction took place with AZT and carboxylic acid within polymers intermolecularly and intramolecularly. Both aqueous-based self-curable AZT-PU and Me-PU were self-emulsified and compatible with each other in any ratios. The self-curable AZT-PU served as a polymeric curing agent and formed a cross-self-curable PU system with Me-PU. The curing reaction took place intermolecularly and intramolecularly and resulted in the formation of the cross-self-cured PU hybrid of Me-PU and AZT-PU on drying. The physical, mechanical, and thermal properties of AZT-PU and cross-self-cured Me-PU/AZT-PU hybrids were improved compared to the original uncured Me-PU resin. The AZT terminal group of the polymer offered an alternative self-curing system for carboxylic acid containing aqueous-based polymers.

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