

Single Component Self-Curable Aqueous-based PU System with New Aziridinyl Curing Agent

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ABSTRACT: The self-emulsified aqueous-based polyurethane (PU) consists of carboxyl group, which is an ionic center not only stabilizing the aqueous polymer dispersion but also serving as the curing site toward aziridinyl curing agent. Two new aziridinyl curing agents, HDI-AZ and ADA-AZ, are prepared from an addition reaction of aziridine to hexamethylene diisocyanate (HDI) and adipic acyl chloride (ADA), respectively. These curing agents are added separately into NCO-terminated PU prepolymer before or after the water dispersion process. The resulting PU disper-

sion becomes a single component self-curable aqueous-based PU system. The cured PU is obtained from this single component PU dispersion on drying at ambient temperature. The improved PU properties demonstrate the feasibility of this convenient single component self-curable aqueous-based PU system. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 1997–2007, 2004

Key words: self-curing, aqueous-based PU, aziridinyl curing agent

INTRODUCTION

Applications and production process of solvent-based polyurethane (PU) are well developed. However, due to the concerns of environment, economy, and safety, the solvent-based PU tends to be gradually replaced by aqueous-based PU. The applications of aqueous-based PU are becoming the world market trend, which is an environmental friendly product that eliminates the use of organic solvent.

There has been a great demand for aqueous-based PU, however, its physical and mechanical properties are still insufficient in comparison with those of the solvent-based PU. Difficulties have been encountered for current technologies for producing aqueous-based PU in enhancing the molecular weight and crosslinking density of PU.

A conventional self-emulsified PU dispersion containing carboxyl group is obtained from a PU prepolymer process by reacting isophorone diisocyanate (IPDI) with polypropylene glycol (PPG-2000) in the presence of 2,2-dimethylolpropanic acid (DMPA). The isocyanate terminal groups of PU prepolymer are hydrolyzed to amino groups by water addition.^{1,2} These amino groups may react further with the remaining NCO groups for self-chain extension to form urea

bonding or may be present in the water phase without further reaction.

The carboxyl groups containing aqueous-based PU provide surface charges to the surrounding PU micelles (particles), thereby causing repulsion between PU particles and resulting uniform distribution of PU particles in water phase. Because of the hydrophilic properties of the carboxyl group, this PU becomes self-emulsified or water-reducible in water phase. Such aqueous-based PU has a common disadvantage similar to that of a polymer surfactant in that, after drying into a film, such film exhibits a high hydrophilicity.

The improvements on aqueous-based PU^{1,2} are normally performed by postcuring reaction^{3–9} or polymer hybridization^{10–14} to enhance the molecular weight and the crosslinking density of polymer.

A convenient postcuring reaction of aqueous-based PU is mainly based on its carboxyl group reacting with an aziridinyl curing agent when its pH value drops below 6.0 or on air drying.^{2,3} The resulting aqueous-based PU has the properties modified accordingly to its curing dosage.

Two new curing agents are prepared from an addition of aziridine respective to hexamethylene diisocyanate (HDI) and adipic acyl chloride (ADA) to form aziridinyl moiety containing compounds, respectively. Various amount of aziridinyl compounds are added separately into aqueous-based PU as an latent self-curing agent. The resulting PU dispersion be-

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comes a single component self-curable PU system. The detailed investigation will be evaluated in this report.

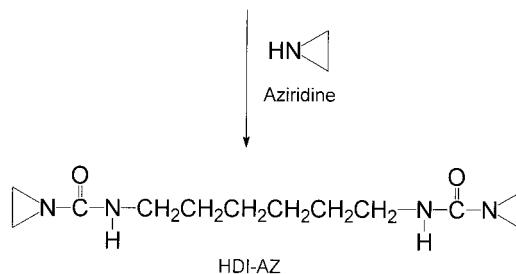
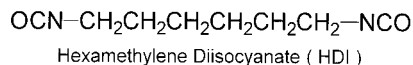
EXPERIMENTAL

Materials

Triethylamine (TEA), ethylenediamine (EDA), adipic acid, thionyl chloride, and 2,2-dimethylolpropanoic acid (DMPA) are supplied by the Aldrich Chemical Co. Inc. Isophorone diisocyanate (IPDI) and hexamethylene diisocyanate (HDI) are supplied by Hul Chemical Co. Polypropylene glycol-2000 (PPG-2000) is supplied by Arco Chemical Co. These 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 polymer film is performed with Dynamic Mechanical Thermal Analyzer, MK-II, Polymer Laboratories. Thermogravimetric data are measured by Hi-Resolution TGA 2950 Thermogravimetric Analyzer, TA. Stress and strain



Scheme 1 Preparation of HDI-AZ Curing Agent.

curves of PU films are taken with Shimadzu Auto-graph S-100-C. NMR spectra are measured by Bruker 300 MHz.

Preparation of HDI-AZ curing agent

Ethyleneimine (aziridine) is prepared from ethanolamine according to the published method.¹⁵ Toluene solution (20 mL) of aziridine (0.2 mol) is added into

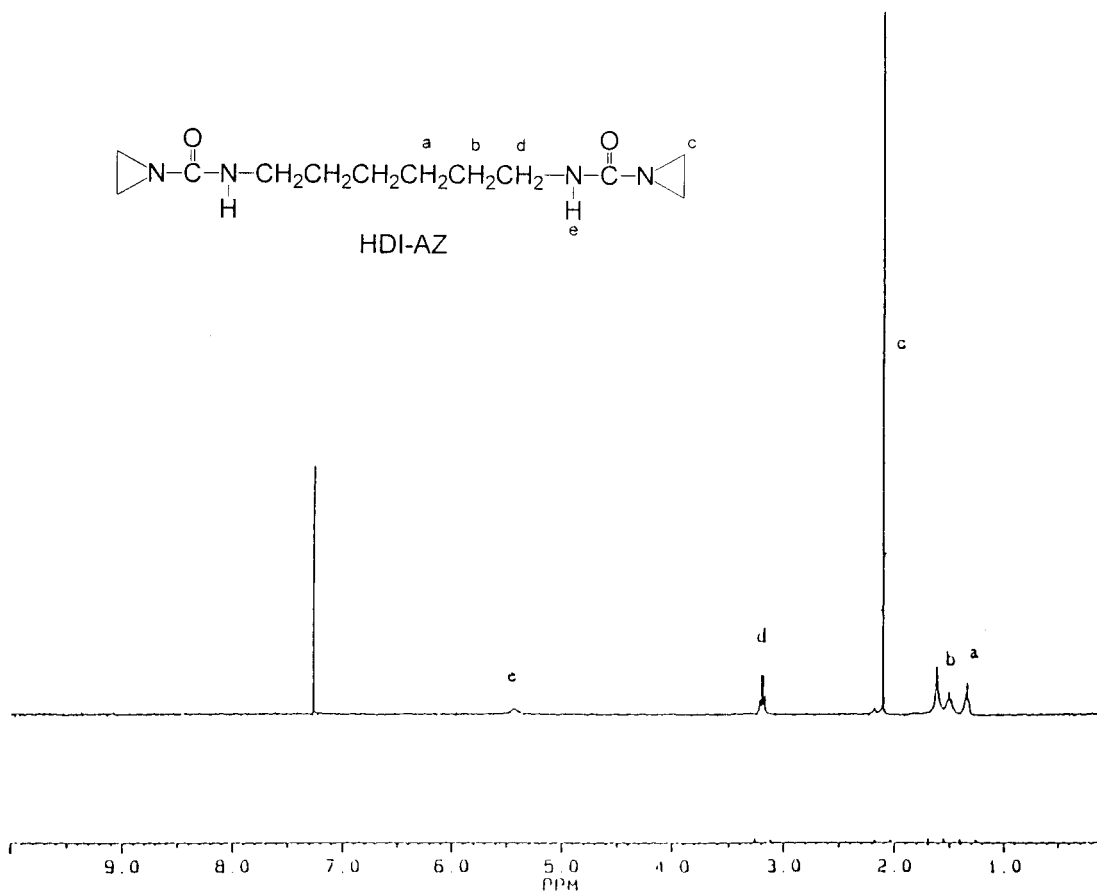


Figure 1 Proton NMR spectrum of HDI-AZ

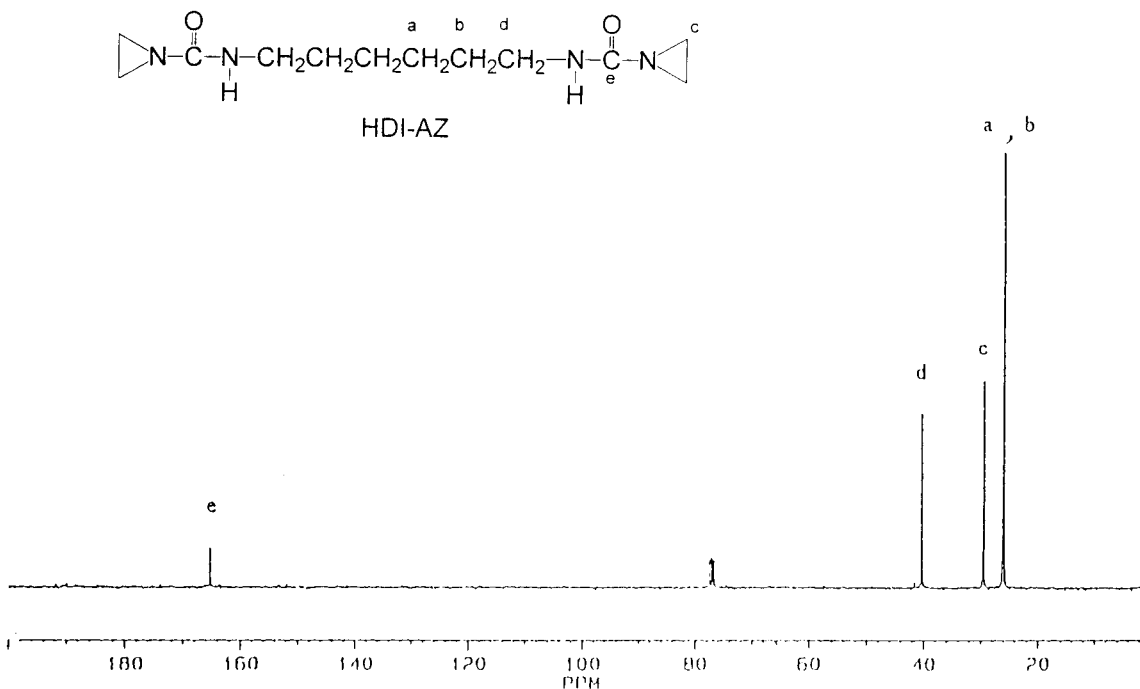


Figure 2 ^{13}C NMR spectrum of HDI-AZ

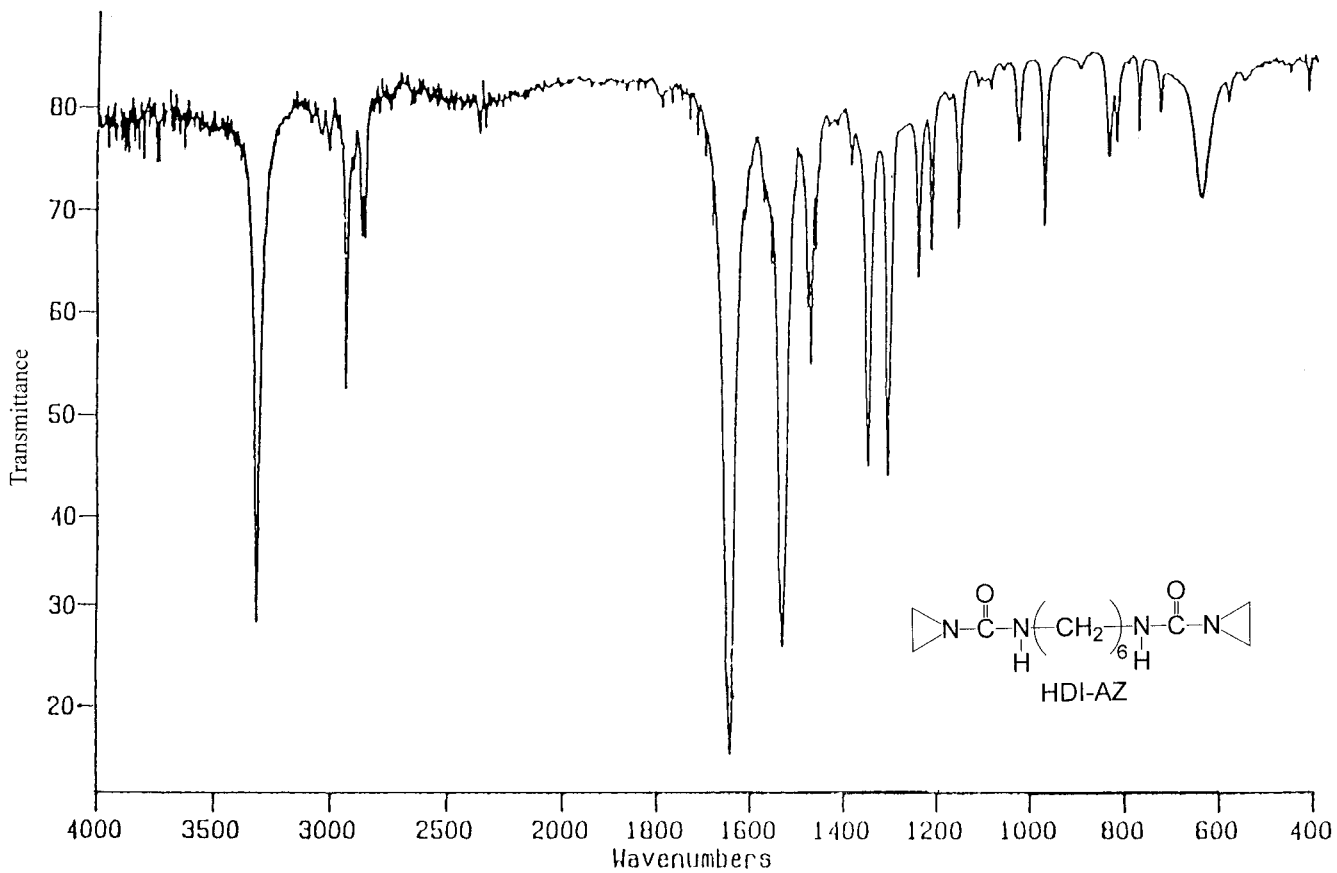
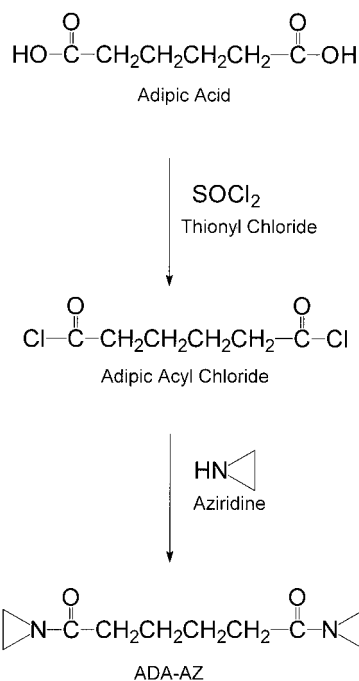


Figure 3 FT-IR spectrum of HDI-AZ



Scheme 2 Preparation of ADA-AZ Curing Agent.

toluene solution (100 mL) of hexamethylene diisocyanate (HDI, 0.1 mol) through an addition funnel. The reaction mixture is kept at 50 °C for an additional 4 h after the addition is completed. The reaction is com-

pleted when the NCO number of the reaction mixture dropped to about zero (when the absorption peak of NCO group is not observed at 2261 cm^{-1} in FTIR spectrum measurement). A white solid product (HDI-AZ) is obtained from filtration with 98% yield after drying under vacuum. A white crystalline product is obtained by recrystallization from cyclohexane and it melts at around 105–106 °C.¹⁶

Preparation of ADA-AZ curing agent

A mixture of adipic acid (0.1 mol) and thionyl chloride (SOCl_2 , 0.25 mol) is kept at 50–60 °C for 5 h. The evolving gases (SO_2 and HCl) are trapped with NaOH solution. Adipic acid is converted slowly and becomes liquid adipoyl chloride (ADA) after the reaction is completed. The excess amount of thionyl chloride is removed by vacuum stripping. An ethereal solution of aziridine (AZ, 0.2 mol) and TEA (0.25 mol) then is added into the liquid ADA, which was prepared previously in an ice bath for 2 h. After the reaction is completed, TEA/ HCl salt is removed by filtration. The filtrate is concentrated by vacuum and the ADA-AZ white solid is obtained with 95% yield. A white crystalline product is obtained by recrystallization from cyclohexane and it melts at around 40–41 °C.¹⁷

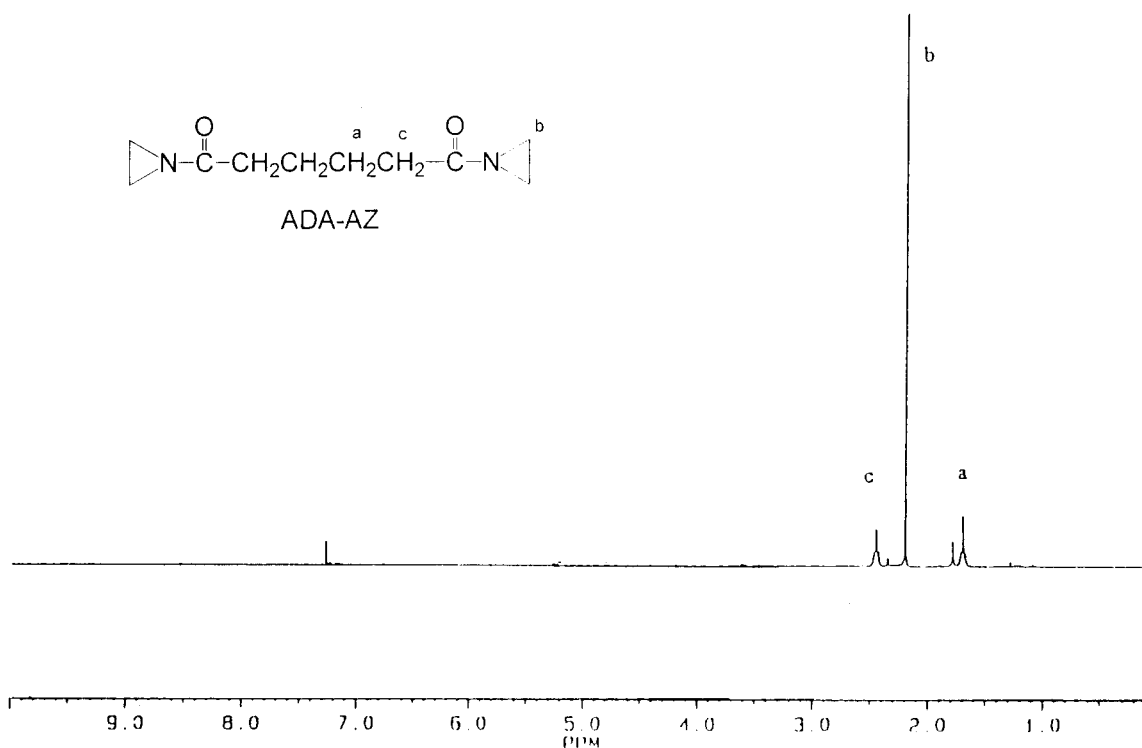


Figure 4 Proton NMR spectrum of ADA-AZ

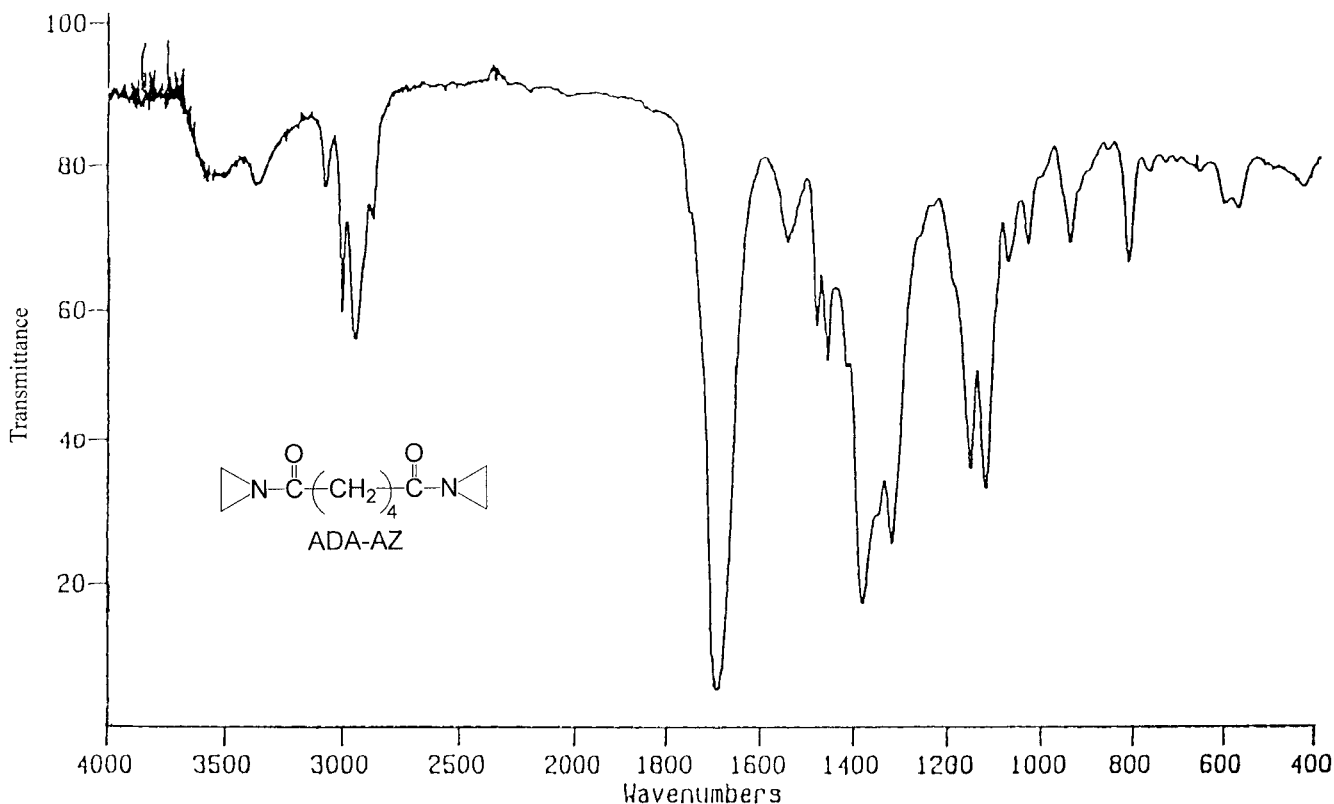


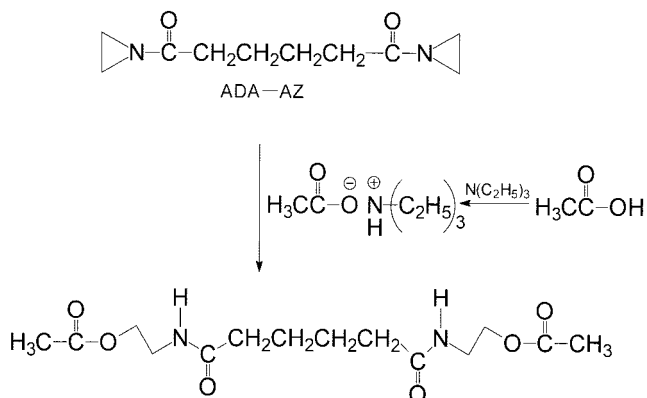
Figure 5 FT-IR spectrum of ADA-AZ

Preparation of single-component self-curable aqueous-based PU dispersion

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 500-mL four-necked resin flask. The resin flask is equipped with a mechanical stirrer, a thermometer, a nitrogen inlet, and a condenser with CaCl₂ drying tube. The reaction mixture is kept at 110°C for about 4 h under nitrogen, until NCO % drops below 3.5 (ASTM D1638 NCO determination method) and remains constant for

another 0.5 h. The thus formed NCO-terminated PU prepolymer is cooled to room temperature and then diluted with dry acetone to obtain a workable viscosity (e.g., 1000 cps) PU solution.

The diluted mixture is neutralized with TEA, and then various dosages of HDI-AZ and ADA-AZ are added, respectively. The final self-curable aqueous-based PU dispersion is obtained from a high shear rate mixing with deionized water (Scheme IV). The aqueous-based PU dispersion is obtained after acetone is distilled off under vacuum and trapped with liquid nitrogen. The pH value of this self-curable aqueous-based PU dispersion is kept higher than 8.0 for storage.

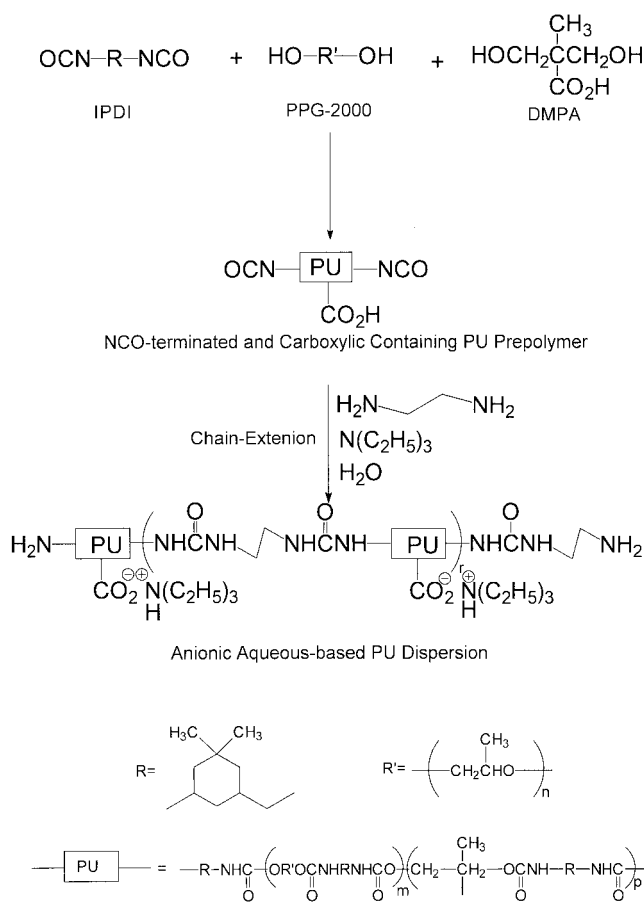


Scheme 3 Model Reaction of ADA-AZ with Acetic Acid.

Properties of the self-cured aqueous-based PU

Tensile strength and elongation

The cast films are air dried at room temperature and then at 50°C for 24 h. They are conditioned in a 75% relative humidity chamber at 25°C for 72 h before the measurements. Each specimen is cut into a dumbbell shape of 1.2 ± 0.1 mm thickness. The gauge length is 40 mm and the measurement is performed at a cross-head speed of 40 mm/min. Six specimens for each



Scheme 4 Preparation of Aqueous-based PU Dispersion.

sample are taken, and the three measurements that showed the highest tensile strength are selected for calculating the mean value.

Gel content

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

Ethanol uptake

A known weight (W_0) of $60 \times 60 \times 1$ mm dried polymer film is immersed in a distilled water bath for 8 days for water uptake. It is 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) are obtained. Three measurements are 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 are 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 thermal analysis (DMTA)

Air-dried PU films are dried further at 50°C oven for 24 h and then conditioned in a 75% relative humidity chamber at 25°C for 72 h before testing. Dynamic mechanical thermal analysis measurements are carried out in bending mode with a heating rate of $3^\circ\text{C}/\text{min}$ from -80 to 150°C at a 1.0 Hz frequency for each sample.

Thermogravimetric analysis (TGA)

The conditioned samples are measured by a thermogravimetric analyzer with a heating rate at $20^\circ\text{C}/\text{min}$ from ambient temperature to 500°C . These are carried under a nitrogen or air atmosphere for the measurements of polymer thermal stabilities, respectively.

RESULTS AND DISCUSSION

The posttreatments of aqueous-based PU proved to be the effective method for improving PU properties. Such as an aziridinyl compound serves as the postcuring agent for the carboxyl group containing aqueous-based PU.¹⁻⁵ Phosphorus-containing aziridinyl curing agents also serve as a reactive flame retardant.^{8,9} PU properties are modified further by the polymer hybridization of glycidyl methacrylate-copolymer emulsion,^{10,11} aqueous-based epoxy resins,¹² and acrylic copolymers,¹³ respectively. This polymer hybridization process provides an alternative for modifying aqueous-based PU properties.

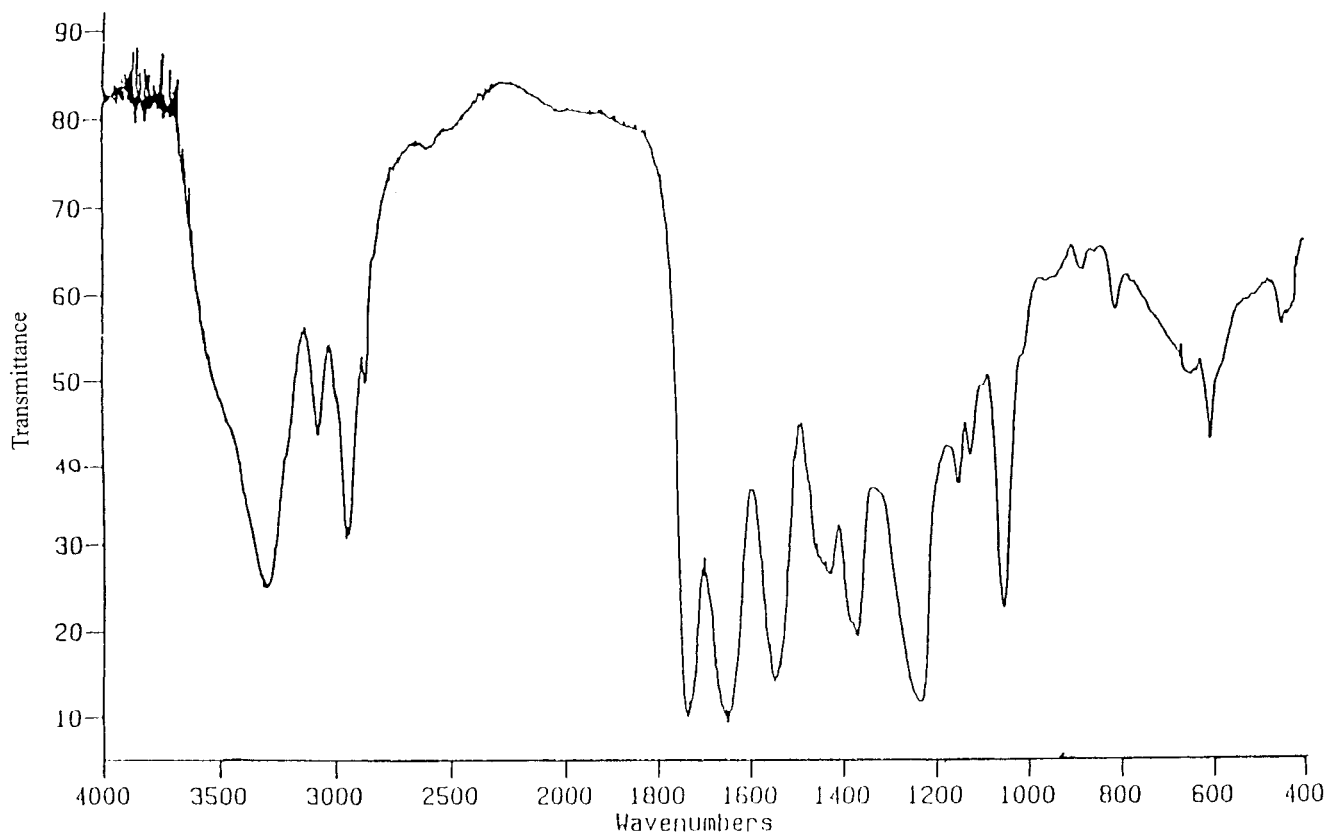


Figure 6 FT-IR spectrum of the reaction Adduct of ADA-AZ and Acetic Acid

The aqueous-based PU dispersion is prepared from a conventional PU prepolymer process.^{1,2} PU carboxyl group is the ionic center and the curing site that comes from one of PU ingredients, DMPA.

Two new curing agents, HDI-AZ and ADA-AZ, are synthesized and are compatible with aqueous-based PU dispersion, respectively. This curing agent comprises the aziridinyl functional group, which is reactive toward the carboxyl group of aqueous-based PU on air drying and becomes a latent curing agent for this single component self-curable PU system.

Characterization of the aziridinyl curing agents

HDI-AZ curing agent

HDI-AZ is obtained from an addition reaction of aziridine to HDI (Scheme I). The chemical shifts on ¹H-NMR of HDI-AZ at 1.42, 1.62, and 3.20 ppm indicates six protons on the hexamethylene chain, and on 2.09 ppm is four methylene protons on the aziridinyl group (Figure 1). On ¹³C-NMR chemical shifts at 25.99 ppm for hexamethylene four carbons and at 40.25 ppm for two carbons adjacent to ureas' nitrogen. The chemical shift of aziridinyl carbons at 29.38 ppm and ureas' carbonyl carbon at 165.24 ppm (Fig. 2).

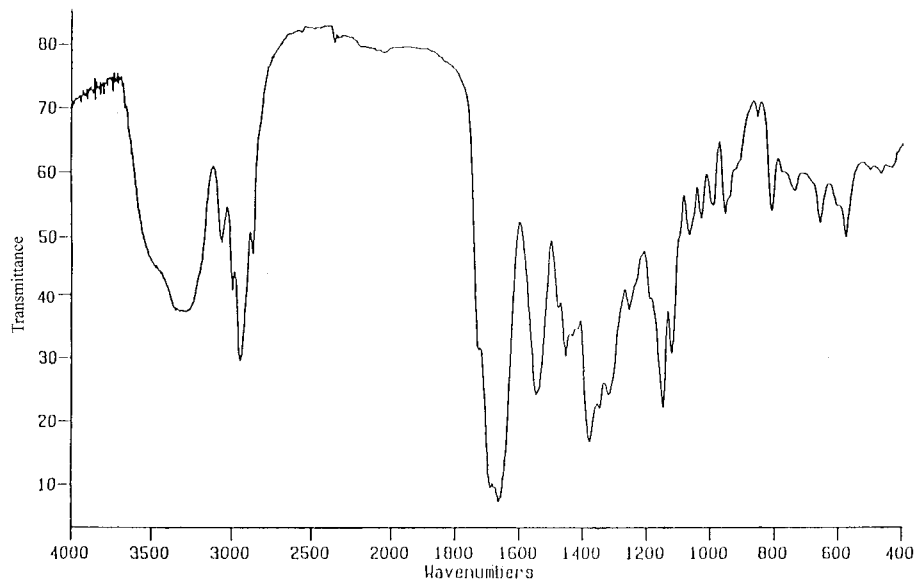
HDI-AZ has no NCO absorption peak at 2280 cm⁻¹ exists but has new amide I and II bands at 1648 and 1536 cm⁻¹, respectively, on FT-IR spectrum (Fig. 3). These indicate the urea formation from the addition reaction of aziridine toward HDI isocyanate group and no trace of original HDI left. Aziridinyl group of the compound shows the characteristic absorption peaks at 981 and 1310 cm⁻¹.

ADA-AZ curing agent

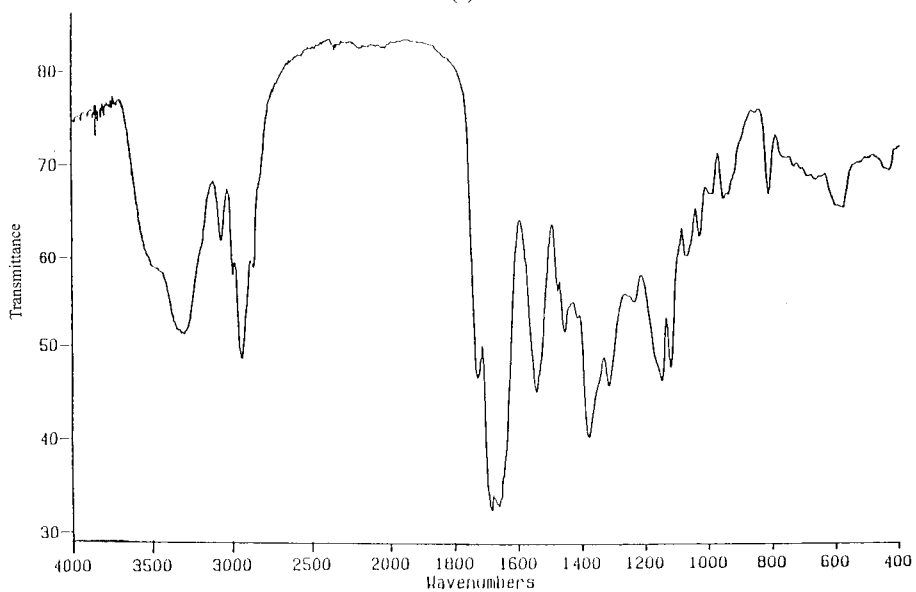
ADA-AZ is prepared from a consequent reaction of adipic acid and thionyl chloride and then a substitution of adipic acyl chloride by aziridine (Scheme 2). The chemical shifts on ¹H-NMR of ADA-AZ at 2.21 and 2.43 ppm which indicates four methylene protons on aziridinyl group of ADA-AZ curing agent (Fig. 4).

ADA-AZ has the absorption peak at 1689 cm⁻¹ for amide I band and free of O-H (for carboxylic acid) stretching band between the ranges of 2500–3300 cm⁻¹ on FT-IR (Fig. 5).

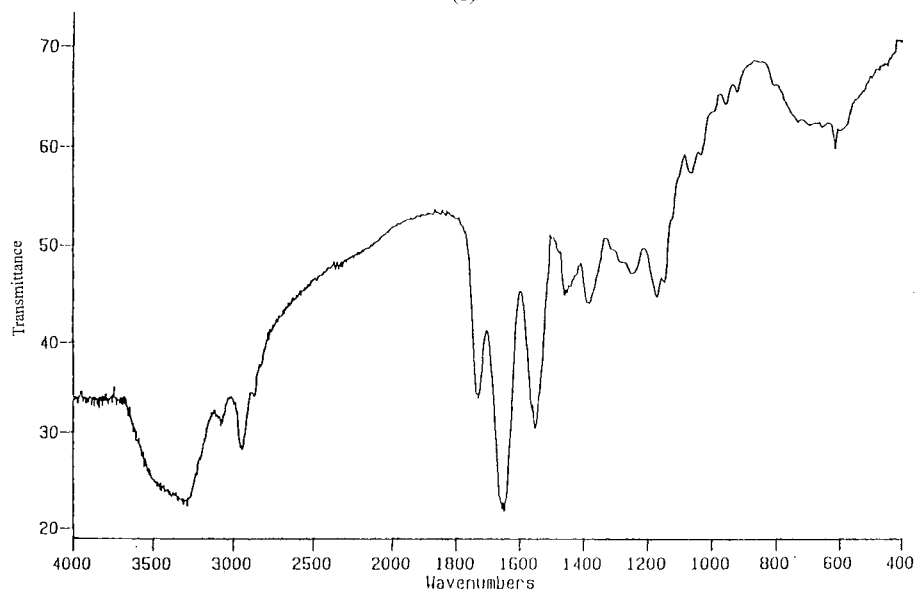
A model reaction adduct of ADA-AZ with acetic acid (Scheme III) which indicates the formation of a new ester carbonyl stretching at 1740 cm⁻¹, a new amide II band and N-H stretching at 1550 and 3306 cm⁻¹, respectively. And the original amide I band shifts from 1689 to 1640



(a)



(b)



(c)

Figure 7 FT-IR spectra of the adduct of ADA-AZ and acetic acid (a) after 1 day, (b) after 4 days, (c) after 7 days air exposure.

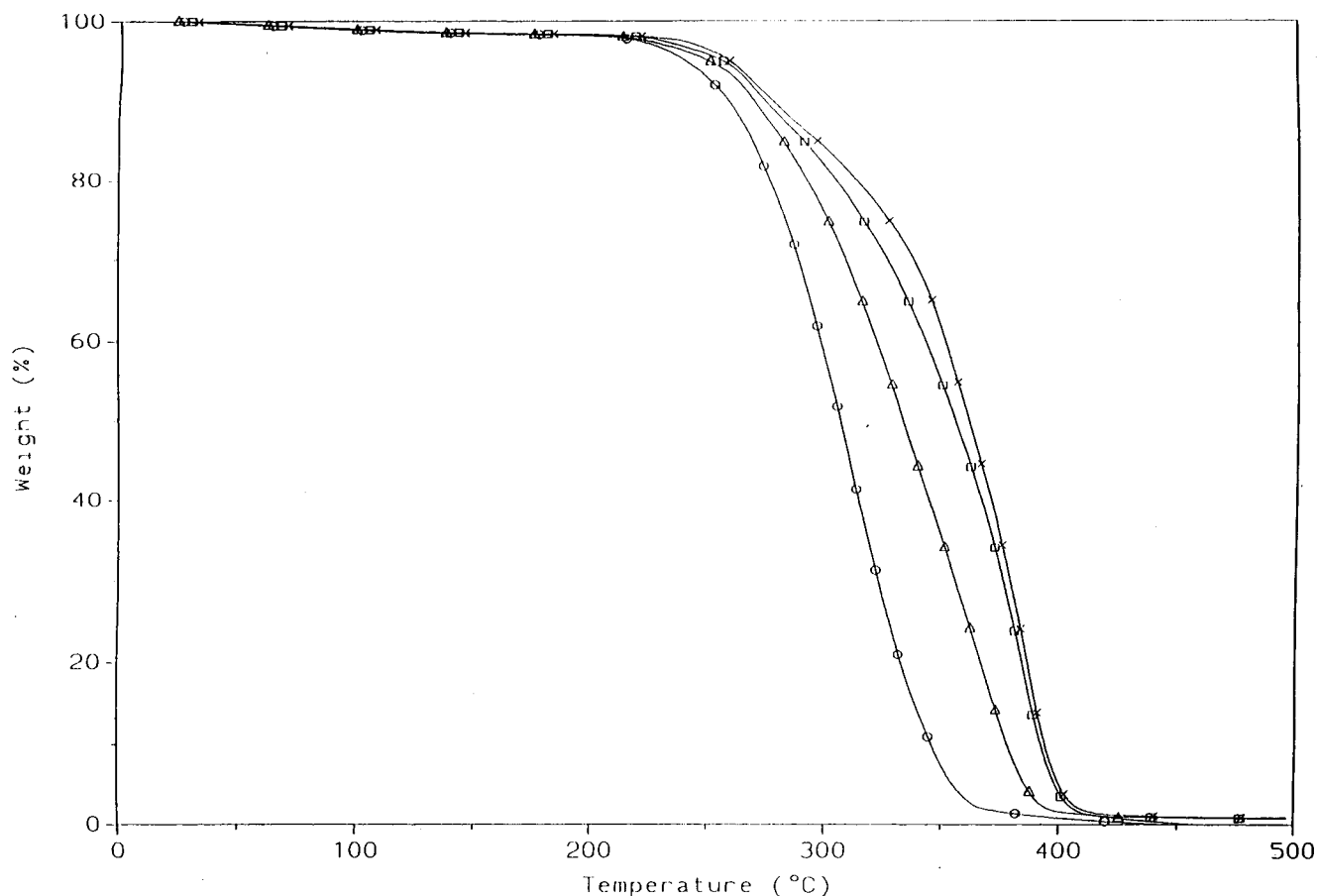


Figure 8 Thermogravimetric analyses of Aqueous-based PU with various dosages of HDI-AZ under nitrogen atmosphere. Original PU (○); with 2.0 phr (△); with 4.0 phr (□) and with 8.0 phr (×) HDI-AZ curing agent.

cm^{-1} of this reaction adduct (Fig. 6). This model reaction of ADA-AZ proves the ring opening reaction of aziridinyl moiety of this new curing agent by acetic acid on drying at ambient temperature.

Monitoring the air exposure of ADA-AZ curing agent by infrared spectra

The hydrophilic ADA-AZ is exposed in the air for 1, 4 and 7 days at ambient temperature. There are three new absorption peaks appear at 1740, 1640 and 1550 cm^{-1} for ester carbonyl stretching, amide I, and amide II bands, respectively, (Figs. 7a to 7c). The FT-IR spectrum of final air exposure product (Fig. 7c) is similar to that of the model reaction adduct (Fig. 6); it demonstrates the aziridinyl ring opening reaction of ADA-AZ can take place at lower pH which caused by the presence of carbon dioxide in air.

Physical and mechanical properties

The gel content and ethanol uptake of PU indicate the relative degree of polymer crosslinking density.

The gel content of cured PU increases with increasing HDI-AZ or ADA-AZ curing dosage comparing to 84.4% of original PU. For examples, their gel contents are 95.4 and 96.8% cured with 1.0 and 4.0 phr HDI-AZ, respectively; their aziridinyl group and carboxyl group ratios (AZ/COOH) are 0.8 and 3.1. Their respective ethanol uptakes are 334.0 and 241.0%. In ADA-AZ curing system, their gel contents are 93.1 and 93.6% with 1.0 and 4.0 phr ADA-AZ (Tables I); their AZ/COOH ratios are 1.0 and 4.0. The increasing gel content and decreasing ethanol uptake of cured PU, these are the evidence of crosslinking reaction occurred within these self-curing PU systems (Scheme V).

The tensile stress at 4.4 kg/cm^2 with 100% elongation of original PU and its value of cured PU increases with the increasing curing dosage. The tensile strength changes from original 18.6 kg/cm^2 at 453% elongation to 13.6 kg/cm^2 at 176.5% elongation of 4.0 phr HDI-AZ curing system. However, the final PU with 4.0 phr ADA-AZ becomes 13.1 $\text{kg}/\text{cm}^2/250\%$. And the tensile stress at 5.7, 6.3, 6.5 and 8.9 kg/cm^2 with 100% elongation of cured PU

TABLE I
Properties of Cured PU with HDI-AZ and ADA-AZ Curing Agent

Properties	Original PU	PU with HDI-AZ (phr)				PU with ADA-AZ (phr)			
		0.5	1.0	2.0	4.0	0.5	1.0	2.0	4.0
Tensile Stress (kg/cm ²)									
Elongation (%)									
100	4.4	5.7	6.3	6.5	8.9	4.4	5.0	5.8	5.6
200	6.9	9.2	10.3	—	—	7.1	8.1	9.9	10.2
300	10.0	13.1	15.8	—	—	9.9	12.1	15.4	—
400	14.5	18.2	—	—	—	15.1	—	—	—
Tensile strength at break (kg/cm ²)	18.6	25.3	16.7	11.5	13.6	19.5	17.1	16.5	13.1
Elongation at break (%)	453.0	494.0	313.5	188.5	176.5	473.0	394.0	320.0	250.0
Gel content (%)	84.4	93.1	95.4	97.2	96.8	93.1	93.1	93.8	93.6
Contact angle (°)	78.0	87.3	86.9	83.6	85.0	89.3	88.9	91.8	94.6
Ethanol uptake (%)	3128.6	535.2	334.0	244.8	241.0	740.1	523.9	366.5	322.1

with 0.5, 1.0, 2.0 and 4.0 phr HDI-AZ dosages, respectively. And the similar results are obtained from the ADA-AZ curing system (Table I).

Thermal behaviors

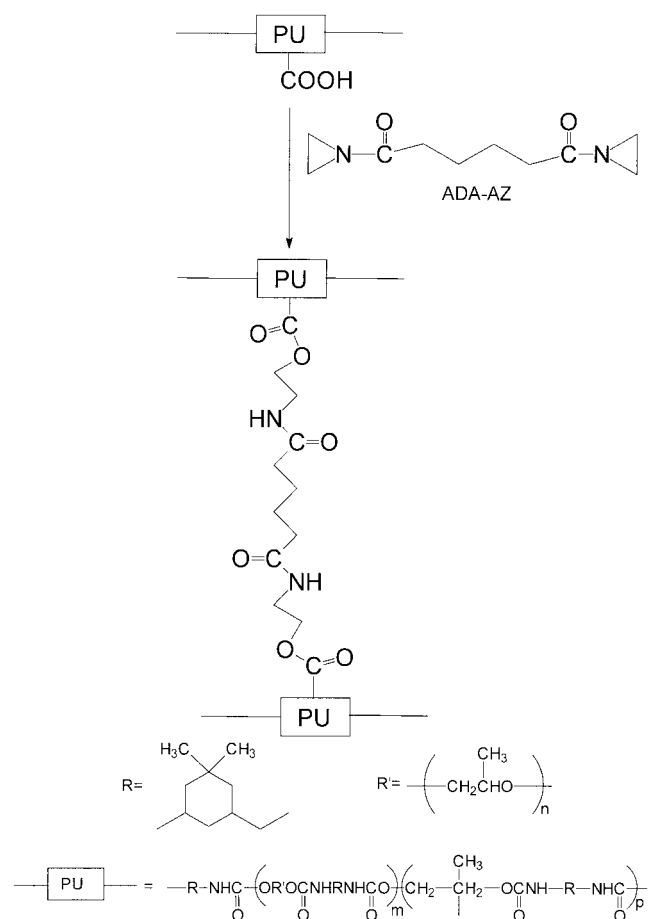
The thermal decomposition temperature under nitrogen of original aqueous-based PU (without curing) has a major decomposition temperature at 310°C and it increases to 385°C of the cured PU with 4.0 and 8.0 phr HDI-AZ. This increasing PU thermal stability due to the self-curing reaction takes place within this single component HDI-AZ cured PU system (Fig. 8).

The dynamic mechanical thermal analysis (DMTA) curve of original PU has a low temperature damping peak at -40°C, and its peak intensity decreases with an increasing HDI-AZ and ADA-AZ curing dosage. The original PU softens around 120°C and the cured PU remains rubbery up to 150°C on their DMTA curves. A broad damping peak centered at 70°C and its intensity increases as the increasing curing dosage, it could be due to the amino ester bond formation between polymers. This peak intensity sharply increases with 4.0 phr HDI-AZ or ADA-AZ, it may be also caused partially by the homopolymer formation from excess curing agent (Fig. 9).

CONCLUSION

Self-emulsified aqueous-based PU dispersion with various curing dosages of HDI-AZ and ADA-AZ, respectively, and becomes a single component self-curable PU system. These PU resins are cured automatically after air dry at ambient temperature, due to its curing reaction takes place between carboxyl groups of PU and aziridiny moiety of HDI-AZ or ADA-AZ. Properties of cured polymers are improved depending on their curing dosages. For examples, the gel content increases from 84.4% of

original PU to 97.2 and 93.8% of final PU with 2.0 phr of HDI-AZ and ADA-AZ, respectively; the ethanol uptake decreases from 453% of original PU and down to 188.5 and 320% of these cured PU. And their mechanical and thermal properties of self-



Scheme 5 Reaction of Self-cured Aqueous-based PU with HDI-AZ.

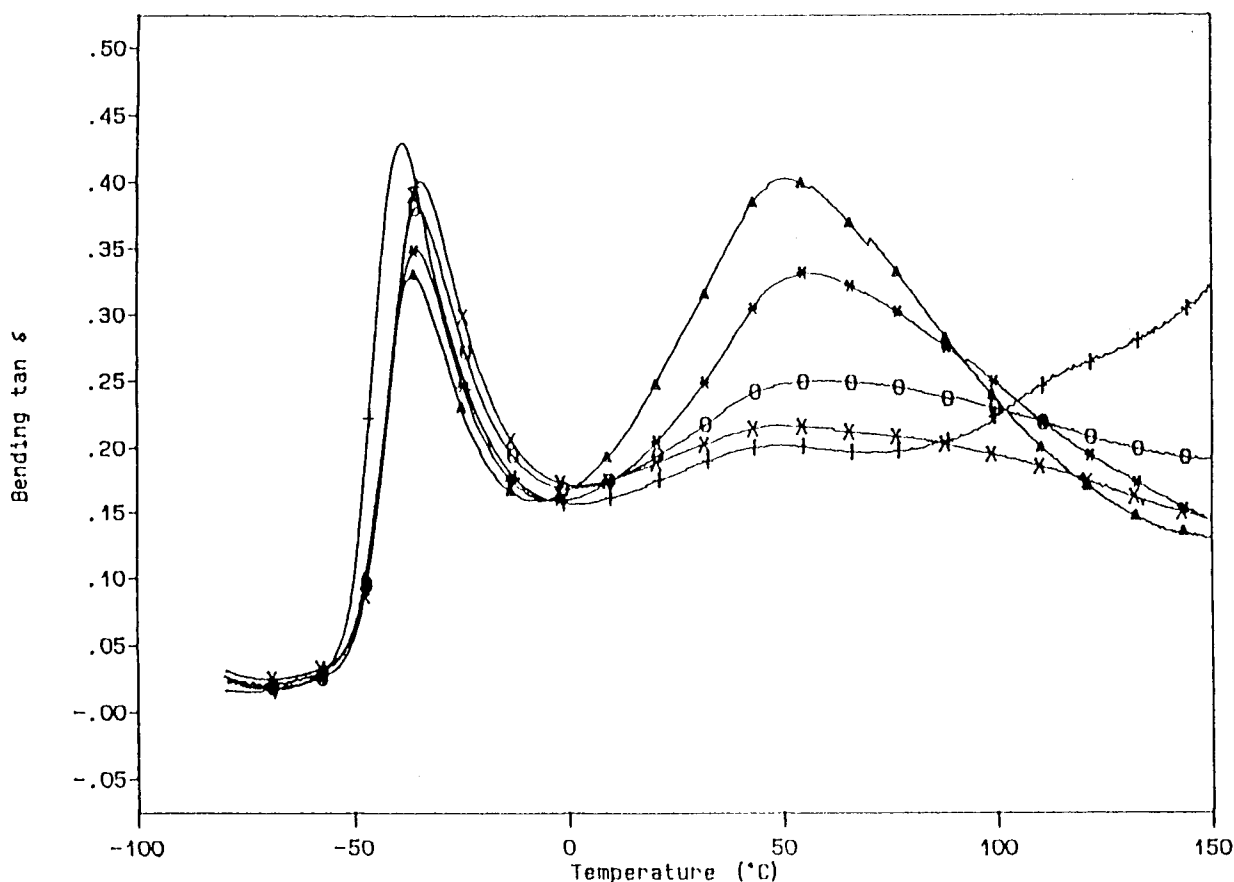


Figure 9 Dynamic mechanical thermal analyses of Aqueous-based PU with various dosages of ADA-AZ. Original PU (+); with 0.5 phr (x); with 1.0 phr (o); with 2.0 phr (•) and with 4.0 phr (Δ) DA-AZ curing agent.

cured PU systems are better than that of original PU. These property improvements are the benefit of this convenient single component self-curable aqueous-based PU system.

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