

Self-Curing Behaviors of Single Pack Aqueous-Based Polyurethane System

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ABSTRACT: A di- or triaziridinyl compound served as the latent curing agent for the prepared carboxylic groups containing aqueous-based polyurethane (PU) dispersions. It was formulated as a single pack self-curable aqueous-based PU system. This system was stable under an alkaline environment and its curing reaction could be initiated by a pH control. A model reaction between a monoaziridinyl compound and formic acid was demonstrated and identified by infrared spectrophotometry. The stabilities of this convenient one-package PU system with a different dosage of di- or triaziridinyl latent curing agent were monitored by a particle sizer and fluorescence spectroscopy. The PU films were cast and self-cured from these single pack PU dispersions at ambient temperature. The physical and mechanical properties as well as thermal behaviors of each self-cured PU were evaluated. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 1609–1623, 1997

Key words: anionic aqueous-based polyurethane; self-curing; aziridinyl latent curing agent

INTRODUCTION

Polyurethanes (PUs) have many applications because their versatile property patterns can be tailor-made. Although every PU product comes from a polyaddition of polyisocyanates and polyols, various raw materials, curing agents, and application processes could produce entirely different performance products.¹

Conventional solvent-based PU for adhesives, coatings, printing inks, etc., are regulated in some areas by safety, economic, and environmental requirements. Aqueous-based PUs have become increasingly important for these purposes in recent years.² There are two types of aqueous-based PUs: a PU emulsion system derived from a conventional PU with some external emulsifiers and co-solvents added,² and PU dispersion, which is a

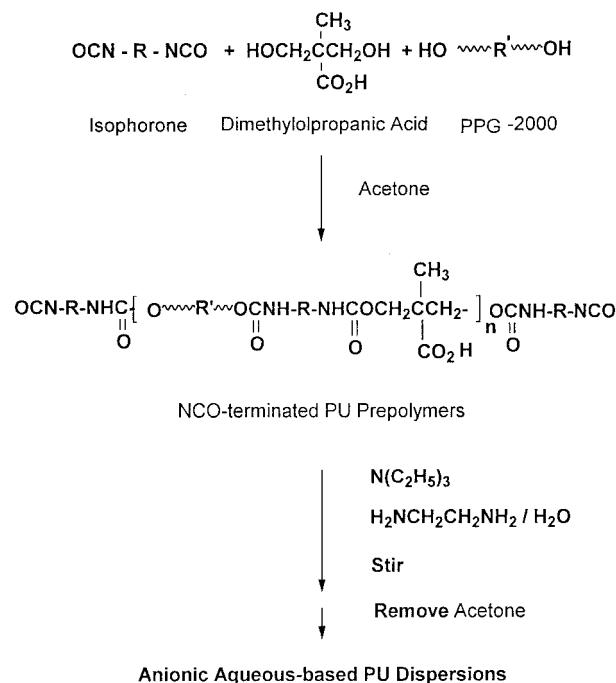
self-emulsified and solvent-free system.^{2,3} The latter is the main one in this category because it is an environmentally friendly product.

Self-emulsified anionic PU dispersions can be prepared from carboxylic ion containing and NCO-terminated PU prepolymers. These PU prepolymers can also result from a reaction of isophorone diisocyanate (IPDI), polypropylene glycol-2000 (PPG-2000), and dimethylolpropanic acid (DMPA). The carboxylic ion of DMPA in the polymers is a hydrophilic group and served as an internal emulsifier for PU dispersions. However, the existence and concentration of this ionic center could also affect the stability of PU dispersions as well as its final properties. This type of aqueous-based PU normally has poorer mechanical properties than the conventional solvent-based PU because of its lower average molecular weights with linear thermoplastic characteristics.

There were several different chemical modifications to improve aqueous-based PUs.² One of the best processes to compensate for this weak-

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Scheme 1 Preparations of anionic aqueous-based PU dispersions.

ness would be one-component PU system with a latent curing agent. The useful latent curing agent can react with the hydrophilic ionic centers of the polymers. Furthermore, it would have the curing reaction only in the application stage while not disturbing the dispersion stability. Ethyleneimine is one of the ideal reactive functional groups⁴ for this purpose.

Ethyleneimine, also called aziridine,⁵ was first prepared by S. Garbriel in 1888. Aziridine reacts not only with carboxylic or hydroxyl group^{2,6} containing compounds, but also reacts by itself to form its homopolymers under an acidic condition⁷ at ambient temperature. However, it remains stable in an alkaline solution system. The aziridinyl compounds have been used for several reported applications in coatings,² textiles,⁶ and medicines⁸ during the past years because of the unique properties of their aziridinyl functional groups.

Di- and triaziridinyl compounds were used as the latent curing agents in this study (Geilie Co. Ltd.). Di- or triaziridinyl compounds are water soluble and ready to mix with the anionic aqueous-based PU dispersions in various ratios. The resultant single pack anionic aqueous-based PU system was stable for more than 3 months without any sedimentation observed in a tightly sealed container.

A model reaction of a monoaziridinyl compound

with formic acid was demonstrated and identified by an infrared spectrophotometer. The curing behaviors of these single pack self-curable PU systems with di- or triaziridinyl compound were investigated by the measurements of contact angle, gel content, water uptake, tensile strength, elongation, dynamic mechanical behavior, and thermogravimetric analysis.

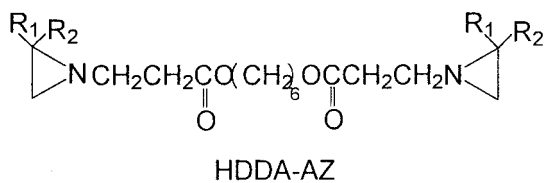
EXPERIMENTAL

Materials

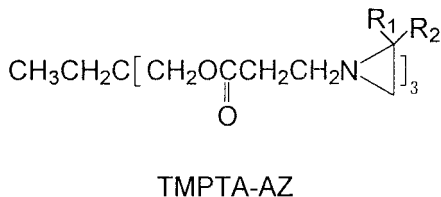
Pyrene and DMPA were supplied by Aldrich Chemical Co. Inc. Acetone, methanol, and other solvents were dried and distilled over anhydrous calcium chloride before use. Mono-, di-, and triaziridinyl compounds (MA-AZ; HDDA-AZ-0, HDDA-AZ-1, and HDDA-AZ-2; TMPTA-AZ-0, TMPTA-AZ-1, and TMPTA-AZ-2) were prepared by the research laboratory of Gelei Co. Ltd. IPDI was supplied by Olin Chemical Co. PPG-2000 was used as received without further purification.

Instruments

Dynamic mechanical behaviors of PU films were measured with a dynamic mechanical thermal an-



HDDA-AZ-0 (I)	$R_1=R_2=H$
HDDA-AZ-1 (II)	$R_1=CH_3, R_2=H$
HDDA-AZ-2 (III)	$R_1=R_2=CH_3$



TMPTA-AZ-0 (IV)	$R_1=R_2=H$
TMPTA-AZ-1 (V)	$R_1=CH_3, R_2=H$
TMPTA-AZ-2 (VI)	$R_1=R_2=CH_3$

Scheme 2 Di- and triaziridinyl curing agents.

alyzer (DMTA; Polymer Laboratories MK-2). Thermogravimetric data were attained on a Setaram TG-DTA 92-16. Infrared spectra were measured by a Biorad FTIR FTS-40. Proton and ^{13}C -NMR spectra were taken by a Bruker AC-300 FT-NMR. Stress and strain curves of the PU films were measured by a Shimadzu Autograph S-100-C. Average particle size and particle size distributions of PU dispersions were measured by a Coulter particle sizer (model N4 MD). Fluorescence spectra of PU dispersions with pyrene as a fluorescence probe were derived by a Aninco Bowman Series 2. Contact angles of pure water droplets on a dried PU film were measured by a FACE contact angle meter (model CA-A, Kyowa Kai-menkagaku Co., Ltd.).

Preparations of Anionic Aqueous-Based PU Dispersions

PPG-2000 (0.1 mol) and DMPA (0.1 mol) were dried overnight at 110°C before they were mixed

with IPDI (0.3 mol) in a 500-mL four-necked resin flask.^{2,9} The resin flask was equipped with a mechanical stirrer, thermometer, nitrogen inlet, and condenser with a $CaCl_2$ drying tube. The reaction mixture was kept at 110°C for about 4 h until the percent NCO dropped below 3.0 (ASTM D1638 NCO determination method) and remained at a constant value for another 0.5 h. Then freshly dried acetone (230 mL) was added into the reaction flask to adjust the viscosity of these PU prepolymers. The PU dispersions were obtained from an addition of these PU prepolymers into 450 mL aqueous amines solution that contained ethylenediamine (EDA 0.08 mol) and triethylamine (0.1 mol) with high shear rate agitation throughout the dispersion process. After acetone was removed from these PU dispersions, the final PU dispersions had 30% solid contents and their pH values were maintained at 8.0–9.0. The preparations of PU dispersions are shown in Scheme 1.

Preparations of Single Pack Self-Curable Aqueous-Based PU Dispersions

A quantity of 1.0, 2.5, or 5.0% (w/w of PU dispersions) of di- or triaziridinyl compound was used as a latent agent for this aqueous-based PU system. It was diluted with a fivefold amount of deionized water and acetone mixture before its addition to PU dispersions. The addition mixture was kept at constant agitation for 60 min under a nitrogen blanket. It was necessary to maintain its pH value at 8.0 or above before and after an addition of the latent curing agent. These resulting single pack self-curable aqueous-based PU dispersions were kept in a tightly closed container for testings or applications.

Model Reaction of MA-AZ Compound with Amine Formate

An aqueous solution of 1.0N formic acid (10 mL) was neutralized slowly with an excess amount of triethylamine with stirring until its pH value reached 8.5. The produced solution was treated with 0.8 g MA-AZ with stirring under nitrogen for 20 min. The final reaction mixture was air dried and readied for infrared spectrophotometric measurements.

Physical Properties of PU Dispersions

The physical properties of these single pack self-curable aqueous-based PU dispersions were moni-

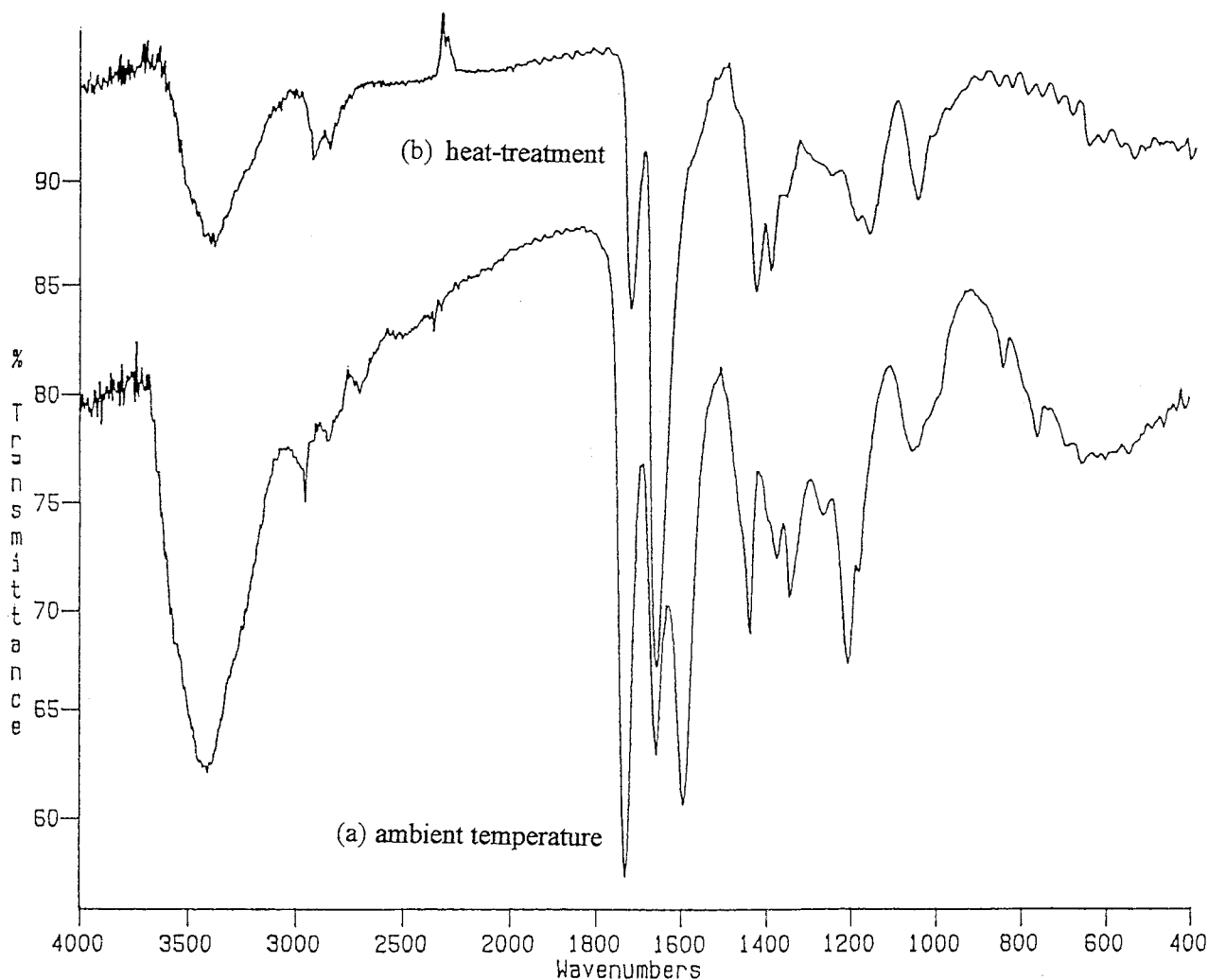


Figure 1 FTIR from a model reaction of MA-AZ with formic acid: (a) spectrum at ambient temperature and (b) spectrum heat treatment of sample (a) at 120°C for 3 h.

tored by a particle sizer and fluorescence spectroscopy.

Particle Size Analyses

A 200-fold deionized water diluted PU sample was measured by a Coulter particle sizer. The average particle size and particle size distributions of PU dispersions were recorded before and after the addition of a latent curing agent.

Fluorescence Spectra

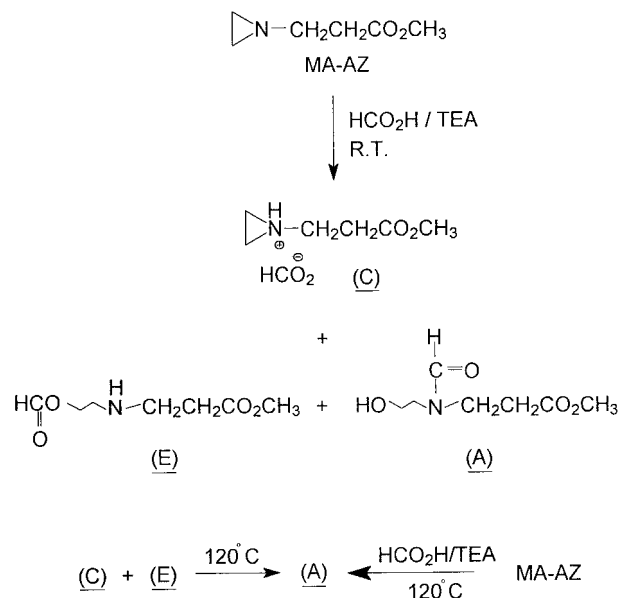
Pyrene was used as a fluorescence probe in PU dispersions. Pyrene was recrystallized twice from methanol before it was dissolved in acetone. Its acetone solution was added slowly into PU dispersions (ca. 10^{-6} M) and stirred for 3 h. Pyrene was

diffused into the hydrophobic PU particles after acetone was removed. The PU dispersions were bubbled with nitrogen to remove the dissolved oxygen before sampling for a fluorescence spectrum. The UV excitation wavelength for the I_3/I_1 value on the fluorescence spectrum of pyrene was 320 nm.

Mechanical and Physical Properties of PU Films

Tensile Strength and Elongation

PU films were cast and dried from these prepared single pack self-curable PU dispersions at ambient temperature and were kept in a 75% relative humidity chamber at 25°C for 72 h before the tests. Dumbbell-shaped specimens of 1.0 mm thickness were used. The gauge length was 40



Scheme 3 Model reaction of monoaziridiny compound MA-AZ with formic acid.

mm, and the test was performed at a crosshead speed of 40 mm/min. Six test specimens of each PU sample were taken for the measurement. We selected those three tests that showed the highest tensile strength for calculating the mean results.

Gel Contents

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

Contact Angles

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

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

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

Water Uptake

A known weight (W_0) of $60 \times 60 \times 1$ mm dried PU film sample was immersed in a distilled water bath for 8 days. The sample weight (W_1) of paper towel dried and the weight (W_2) of oven dried PU films were obtained. Three measurements were taken and averaged for each PU sample. Water uptake (W_A %) and weight loss (W_L %) of PU films 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 the PU film and

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

where W_L is the amount of PU dissolved in water.

Dynamic Mechanical Behaviors

Air-dried PU films were conditioned in a 75% relative humidity chamber at 25°C for 72 h before the tests. DMTA was performed with a bending mode with a heating rate of 3°C/min from -80 to 150°C at a 1.0-Hz frequency.

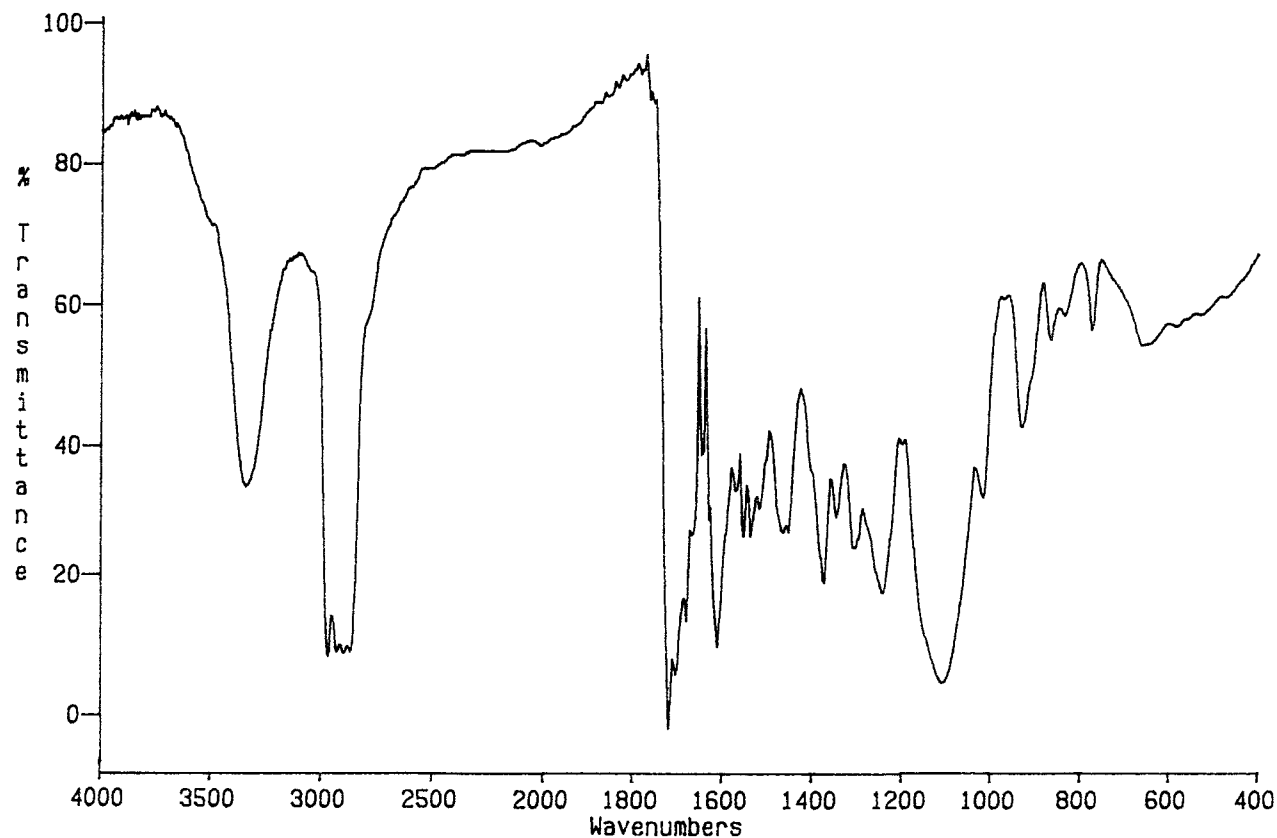


Figure 2 Infrared spectrum of original PU film before curing.

Thermogravimetric Analyses

The prepared PU samples were measured by a thermogravimetric analyzer with a heating rate of 20°C/min from ambient temperature to 500°C under an argon gas atmosphere.

RESULTS AND DISCUSSION

These self-emulsified anionic aqueous-based PU dispersions were prepared by an acetone process and chain extended with EDA during the water dispersion process (Scheme 1). The PU dispersions had 30% solid contents and an average particle size of 90 ± 5 nm. The stabilities of PU dispersions were aided by the electric repulsive force of PU particle surface charges in the aqueous dispersions.

The presence of carboxylic ions in this PU system were mainly for the stabilization of PU dispersion. However, the incorporation of these ionic groups in the polymers also brought about the deficiencies in water resistance and other physical or mechanical properties of PU films. Therefore,

the crosslinking reactions toward the ionic centers of the polymers were very important for the improvements of the final PU performances.

Aziridines could undergo a cation initiated homopolymerization reaction⁷ or an addition reaction with carboxylic acid² or a hydroxyl group⁶ under an acidic condition. Di- and triaziridinyl compounds, series TMPTA-AZ and HDDA-AZ, (compounds I–VI), are listed in Scheme 2. Their excellent stability under an inert gas atmosphere or in an alkaline solution was proven by infrared and nuclear magnetic resonance spectroscopic analyses. Either HDDA-AZ or TMPTA-AZ compound served as a latent curing agent for a single pack self-curable PU system. The self-curing behaviors of this kind of single pack PU dispersions are evaluated in this report.

Stable Single Pack PU Dispersions

Every HDDA-AZ or TMPTA-AZ series compound is water soluble and can be added as a latent curing agent for a single pack PU system. The average particle size remained in the 90 ± 5 nm range

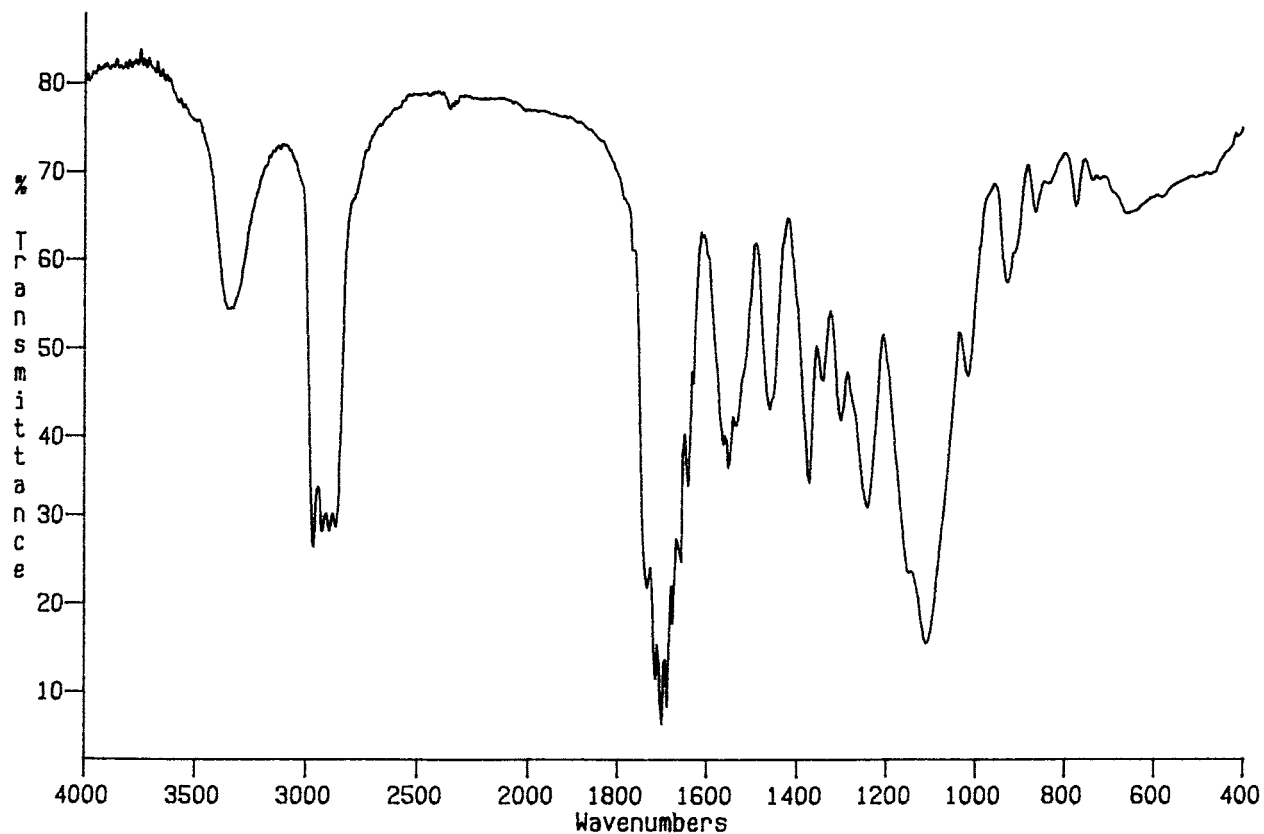


Figure 3 Infrared spectrum of an ambient temperature self-cured PU with 7.5% (w/w) TMPTA-AZ-0.

and the particle size distributions of the resulting PU dispersions did not change after 7-day storage in a closed container at ambient temperature.

Pyrene is the hydrophobic compound that functioned as a fluorescence probe¹⁰ in PU particles for this single pack aqueous PU system. A fluorescence spectrophotometer was utilized to monitor the polarity changes inside PU particles. The fluorescence spectrum of pyrene (ca. 10^{-6} M) in PU dispersions had an I_3/I_1 value of 0.86; the I_3/I_1 value of pyrene in pure water is 0.63.¹⁰ A TMPTA-AZ-1 curing agent was added and formed a single pack PU system. The I_3/I_1 value of its fluorescence spectrum was 0.90 and changed to 0.88 after 48-day storage in a closed container at ambient temperature. This indicates that this hydrophilic latent curing agent stayed in the aqueous phase, and did not interfere with the hydrophobic PU particles in the alkaline environment.

However, these single pack PU dispersions were bubbled with carbon dioxide and the pH value of the dispersions dropped to 5.9. Most of the PU particles agglomerated from the dispersion, due to the TMPTA-AZ-1 reaction with the

carboxylic acid groups on the surface of PU particles. The zeta potential of PU dispersions dropped immediately under this acidic condition. The I_3/I_1 value of its fluorescence spectrum changed to 0.58 at this stage, which is the fluorescence spectrum of pyrene in the aqueous phase, and no more PU particles with pyrene dispersed in the aqueous system.

Self-Curing Behaviors of Single Pack PU System

Infrared Spectra Evidence

Carboxylic pendants of this aqueous PU system were the reactive sites toward the aziridinyllatent curing agent. A model reaction of MA-AZ with triethylamine salt of formic acid took place after triethylamine was evaporated at ambient temperature.

From the infrared spectra (Fig. 1), it was suggested that the resulting products were a mixture of amine carboxylates (*C*; carboxylic ions carbonyl stretching at 1603 cm^{-1}), esters (*E*; ester carbonyl stretching at 1737 cm^{-1}), and amides (*A*;

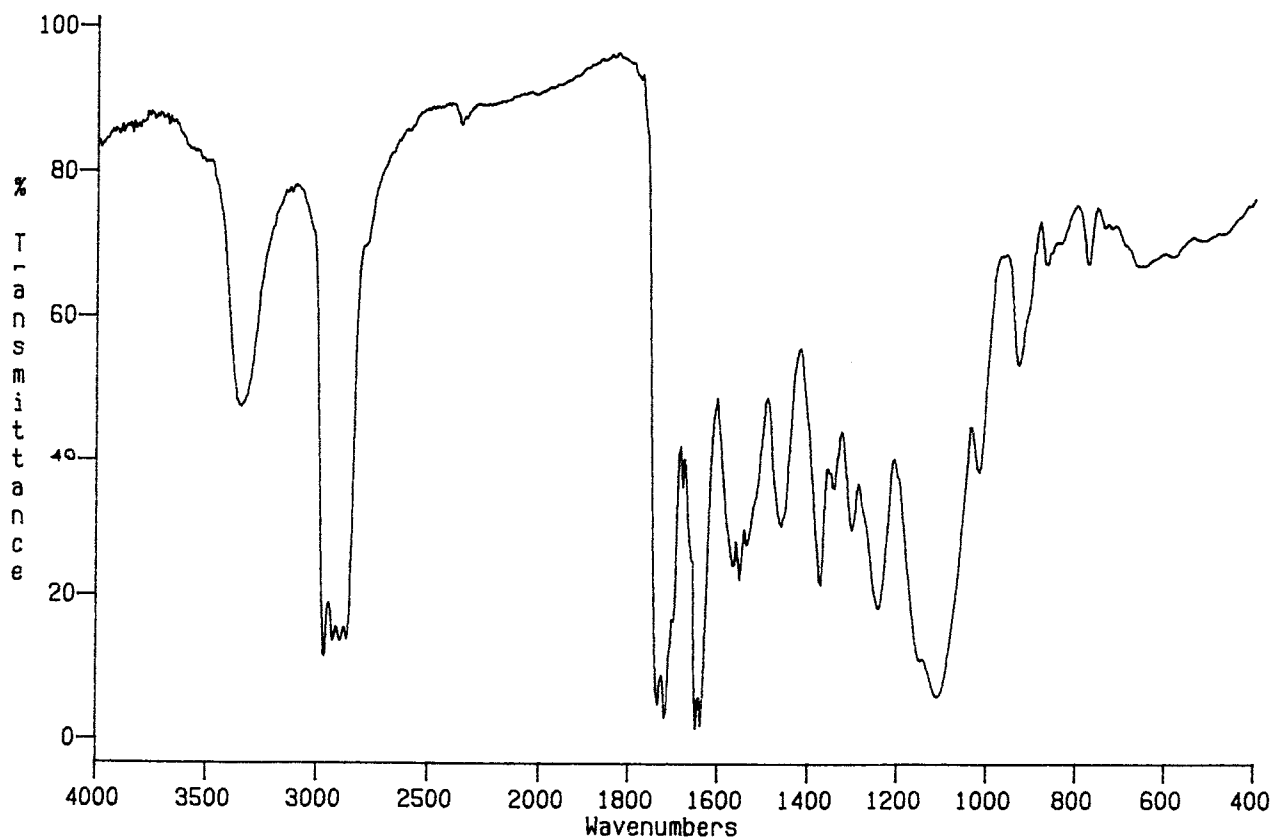


Figure 4 Infrared spectrum of a heat-treated PU film (from Fig. 3) at 120°C for 3 h.

amide I band at 1660 cm^{-1}) linkage formations. This air dried reaction mixture was heated at 120°C for 3 h. The infrared spectrum of the 1737 cm^{-1} ester carbonyl peak shrunk (the remains were the ester part of MA-AZ), its 1660 cm^{-1} amide I band increased, and the 1603 cm^{-1} carboxylic absorption peak disappeared. The peak of 1603 cm^{-1} absorption could be derived from a triethylamine formate or a neutralization of formic acid with aziridinyl amine after triethylamine was evaporated whereas the ester and amide linkages were from the ring opening reactions of the aziridinyl ring of MA-AZ with formic acid. When the reaction mixture was heated at an elevated temperature (ca. 120°C), some of the resultant ester groups changed to a more stable amide form (A) (Scheme 3).

The concentration of carboxylic ions in this PU system was 0.1 mol/kg of PU dispersions (that had 30% solid contents). The infrared spectrum of the original PU film had a 1612 cm^{-1} absorption peak, which indicated a carboxylic carbonyl stretching frequency, and 1680–1720 cm^{-1} for urethane and ureas carbonyl absorptions (Fig. 2). A single pack and self-curable PU system with

7.5% (w/w) TMPTA-AZ-0 was cast and self-cured at ambient temperature. Its infrared spectrum had absorption peaks at 1640–1737 cm^{-1} and there was no carboxylic peak; its ester carbonyl absorption frequency higher was than 1720 cm^{-1} (Fig. 3) and was contributed partially by the curing agent, TMPTA-AZ-0, and its own ester groups. The rest of peaks were from the ring-opening reactions of the aziridinyl rings with carboxylic pendants on the PU main chain and the homopolymers of an excess amount of TMPTA-AZ-0.

This ambient temperature dried PU film was heated at 120°C for 3 h. There was a 1737 cm^{-1} peak for an ester absorption frequency (from the curing agent its ester groups) and absorption peaks at 1795 and 1720 cm^{-1} for urethane and urea carbonyls. There were also two absorption peaks, amide I and amide II bands at 1639 and 1651 cm^{-1} , that appeared on its infrared spectrum (Fig. 4).

These results indicated that the curing phenomena of this PU system were similar to the model reaction of MA-AZ (Scheme 3). The curing reaction of a single pack PU system took place on air drying, even at ambient temperature. This

Table I Physical and Mechanical Properties of PU Films with Various Curing Agents

PU with Various Curing Agents	Curing Agent % (w/w) in PU Dispersions	AZ/CO ₂ ⁻ Equiv. Ratio ^a	Gel Contents ^b (%)	100% Modulus (kg/cm ²)	Tensile Strength (kg/cm ²)/			Contact Angle (°)
					Elongation at Break (%)	W _A (%)	W _L (%)	
PU	0	0	85.4	1.2	6.0/1000	16.1	3.1	79.7
TMPTA-AZ-0	1.0	0.7	90.5	4.3	12.4/442	10.4	2.9	84.7
	2.5	1.7	91.1	5.9	7.7/179	13.1	2.3	84.7
	5.0	3.5	90.6	12.5	13.3/121	20.8	4.3	79.7
TMPTA-AZ-1	1.0	0.6	88.8	4.5	7.6/250	9.3	1.8	84.3
	2.5	1.6	89.7	5.6	6.7/134	11.5	1.6	88.0
	5.0	3.2	89.2	7.2	9.0/139	17.1	1.9	82.3
TMPTA-AZ-2	1.0	0.6	87.8	4.9	8.5/255	10.3	1.9	78.0
	2.5	1.5	89.7	4.2	5.7/152	18.2	3.6	89.0
	5.0	2.9	88.0	3.2	5.1/188	20.7	4.8	79.6
HDDA-AZ-0	1.0	0.6	87.2	3.2	11.4/588	7.2	1.4	87.3
	2.5	1.2	88.9	5.3	7.5/183	6.3	1.8	82.7
	5.0	3.2	89.6	5.7	7.8/156	8.5	2.9	85.7
HDDA-AZ-1	1.0	0.6	86.8	3.1	6.9/328	5.7	1.3	85.5
	2.5	1.5	88.7	3.5	8.4/308	5.5	2.0	86.3
	5.0	2.9	89.4	3.7	7.4/225	5.5	2.2	79.3
HDDA-AZ-2	1.0	0.5	86.2	2.9	8.2/479	8.6	0.8	79.0
	2.5	1.3	87.3	3.8	10.2/438	7.8	1.5	78.7
	5.0	2.6	89.2	2.3	8.4/470	5.6	1.9	79.8

W_A, amount of water uptake by PU film; W_L, amount of PU dissolved into water.

^a AZ/CO₂⁻, aziridinyl/carboxylic groups equivalent ratio.

^b Soxhlet extraction with THF.

self-curing had a ring-opening reaction of the aziridinyl curing agent with the carboxylic group of PU and resulted in crosslinked polymeric network formation.

Mechanical Properties

A single pack PU dispersion system with 2.5% (w/w in PU dispersions) triaziridinyl curing agent (TMPTA-AZ-0, TMPTA-AZ-1, or TMPTA-AZ-2) had an AZ/CO₂⁻ equivalent ratio from 1.7 to 1.5. The self-cured PU films had a 100% modulus at 5.9, 5.6, and 4.2 kg/cm² and ultimate tensile strength at 7.7/179, 6.7/134, or 5.7/152 kg/cm²/ % (tensile strength/elongation) individually. The cured films had quite different mechanical properties from the original PU film that had a 100% modulus of 1.2 kg/cm² and ultimate tensile strength of 6.0 kg/cm² for about 1000% elongation (Table I).

A similar curing reaction was found with a diaziridinyl (HDDA-AZ) curing agent with this one-component PU system in various formulations. The tensile strength of HDDA-AZ cured PU film

had a higher modulus than the original PU (Table II). One of the diaziridinyl compounds, HDDA-AZ-2 (compound VI), had two methyl groups, and HDDA-AZ-1 (compound V) had one methyl group on the aziridinyl ring. The methyl group on the aziridinyl ring of the curing agent seemed to have a softening effect on the cured PU film (Table II). The ultimate strength of the cured PU films with 2.5% (w/w) HDDA-AZ-0, -1, and -2, were 7.5/183, 8.4/308, and 10.2/438 kg/cm²/%, respectively. From the stress–strain diagram of the cured PU films by HDDA-AZ-2 (Fig. 5), the curings had improvements in their tensile strength. But the tensile strength decreased as its dosage increased to 5.0% (w/w). This was due to the fact that an excess amount of HDDA-AZ-2 (its AZ/CO₂⁻ equivalent ratio is 2.6) formed the homopolymers by itself with less crosslinking density with the PU system than with the other two lower dosages.

Gel Contents

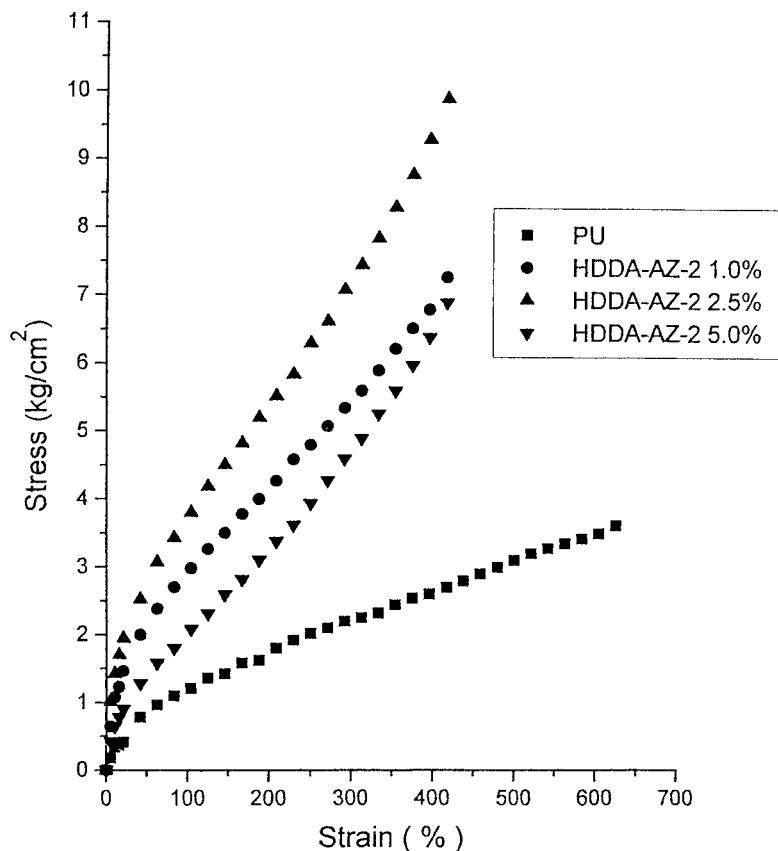
Each of these self-cured PU films had greater gel contents than the original PU (e.g., 85.4%) (Table

Table II Mechanical Strength of PU Cured Films with Diaziridinyl Curing Agent HDDA-AZ Series

Elongation (%)	Tensile Strength (kg/cm ²)									Original PU
	HDDA-AZ-0 (% w/w)			HDDA-AZ-1 (% w/w)			HDDA-AZ-2 (% w/w)			
	1.0	2.5	5.0	1.0	2.5	5.0	1.0	2.5	5.0	
100	3.2	5.3	5.7	3.1	3.5	3.7	2.9	3.8	2.3	1.2
200	4.1	—	—	4.6	5.4	6.5	4.2	5.7	3.6	1.7
300	5.9	—	—	6.4	8.1	—	5.5	7.2	5.5	2.2
400	7.5	—	—	—	—	—	7.0	9.6	6.8	2.6
500	9.9	—	—	—	—	—	—	—	—	3.1
600	—	—	—	—	—	—	—	—	—	3.5
700	—	—	—	—	—	—	—	—	—	4.1
800	—	—	—	—	—	—	—	—	—	4.7
900	—	—	—	—	—	—	—	—	—	5.3
1000	—	—	—	—	—	—	—	—	—	6.0

I). For example, for 5.0% (w/w in the dispersions) of TMPTA-AZ-0 in a single pack PU system, its AZ/CO₂ equivalent ratio was 3.5 and that added up to 16.7 phr of the curing agent in the final

cured PU system. The resulting PU had 90.6% gel contents. There were contributions from TMPTA-AZ-0 crosslinked PU networks and also from its partial homopolymers. These phenomena also

**Figure 5** Stress-strain diagram of PU films with HDDA-AZ-2 at various weight percents.

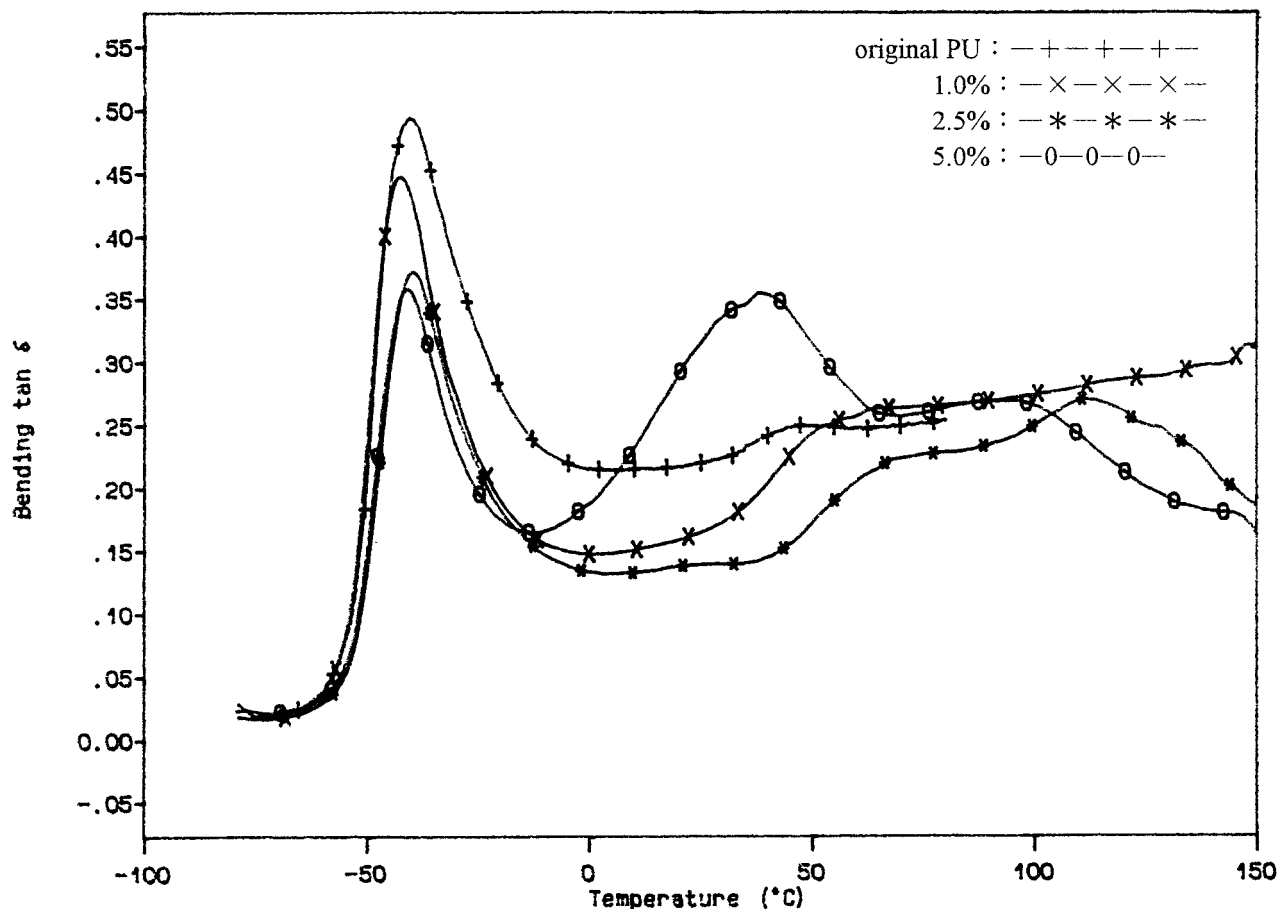


Figure 6 Damping factors of PU films with various weight percents of TMPTA-AZ-0.

happened with other different di- or triaziridinyl curing agents.

Water Uptake

Diaziridinyl curing agents, HDDA-AZ series compounds in PU dispersions, had AZ/CO₂⁻ equivalent ratios of 0.5–3.2. Each cured PU film by one of these diaziridinyl curing agents had water uptake from 5.5 to 8.6%; that is less than the original PU and triaziridinyl cured PU system (Table I). This might be due to the fact that the diaziridinyl curing agent HDDA-AZ has a better molecular mobility with less steric hindrance toward the carboxylic group of PU and also has a better affinity with PU dispersions on drying. In other words, triaziridinyl curing agents (TMPTA-AZ series compounds) have bulkier molecules than the HDDA-AZ series. In TMPTA-AZ-2, for instance, there were two methyl groups on each aziridinyl ring and it created not only the steric hindrance to-

ward the curing reactions but also a phase separation occurred in the PU film drying process. An excess amount or a phase separated free aziridinyl curing agent would eventually form the homopolymers by itself at ambient temperature. Homopolymers of TMPTA-AZ-2, for example, have better hydrophilicity and 33.3% water uptake. The observations of a greater water uptake for some of the TMPTA-AZ series cured PU films might have had their homopolymers involved.

Contact Angles

Contact angle measurement of water droplets on the surface is a convenient method to estimate the hydrophilic characteristics of a film surface. PU film cured by 1.0% (w/w) TMPTA-AZ-0 (AZ/CO₂⁻ equivalent ratio is 0.7) had contact angles of 84.7°, 5.0° higher than the original PU (79.7°) (Table I). If its dosage was increased to 5.0% (w/w), its contact angle decreased to 79.7°.

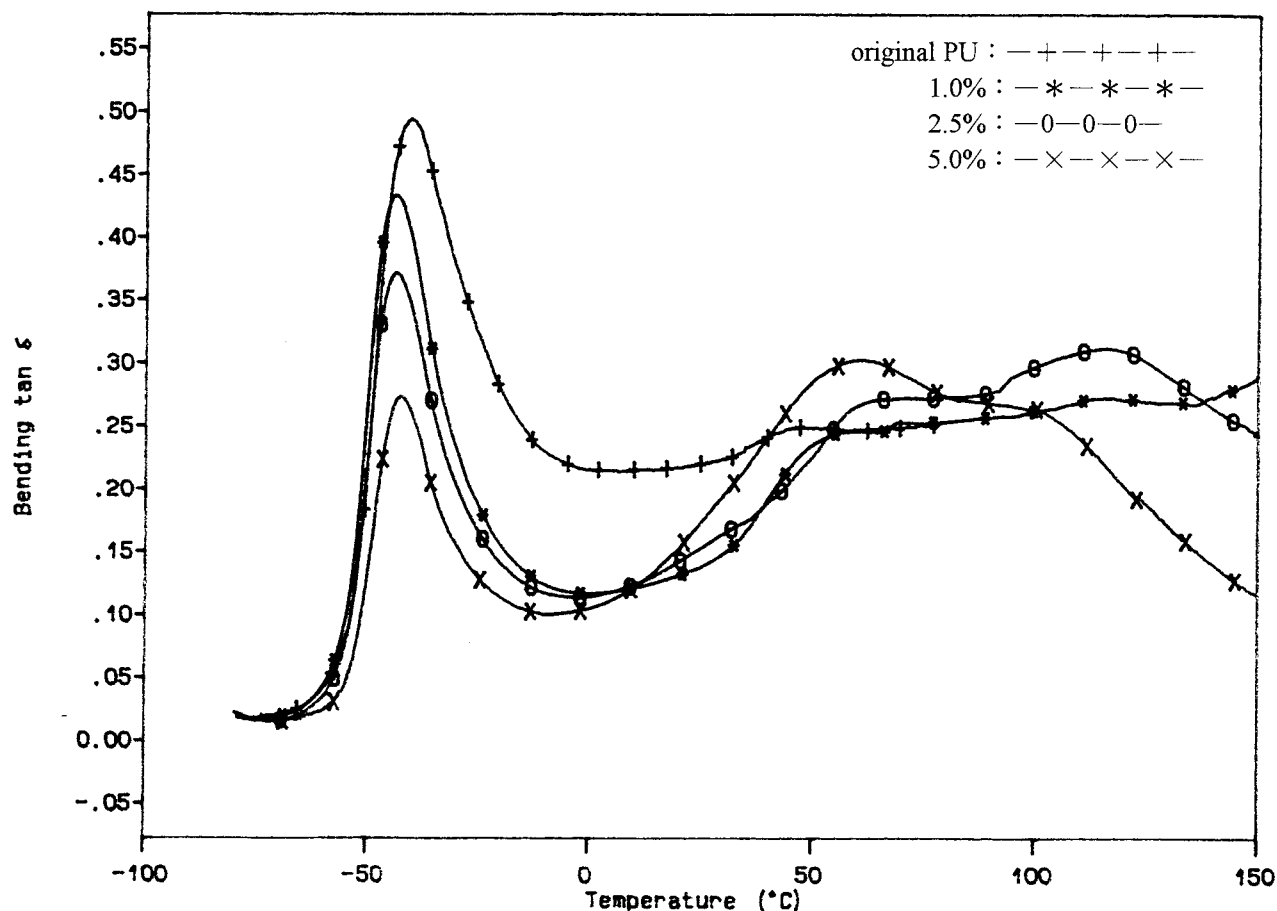


Figure 7 Damping factors of PU films with various weight percents of HDDA-AZ-0.

However, for the PU curing system with the di-aziridinyl curing agent HDDA-AZ-2, for example, its contact angle on cured PU film did not change with various dosages because it has two methyl substituents on each aziridinyl ring. These methyl groups on the aziridinyl ring may not only increase the steric hindrance toward the reaction with carboxylic groups of the polymer, but may also decrease its compatibility with the aqueous dispersion system. They could have a phase separation occurring in the drying process and further leading them to form their individual homopolymers. That could be the reason for the inconsistent contact angles for these cured PU films.

Dynamic Mechanical Properties of PU Films

The original PU film had a glass transition temperature of -40°C for the polymer soft segments, and its peak intensity decreased as the crosslink-

ing density increased after curing with either HDDA-AZ or TMPTA-AZ latent curing agent. This indicated that this curing reaction only occurred on the carboxylic pendants of the PU hard segments.

The original PU film had thermoplastic characteristics and it melted at around 80°C . For a single pack PU system with 1.0% (w/w) TMPTA-AZ-0, its AZ/CO_2 equivalent ratio was 0.7. The resulting PU film remained rubbery up to 150°C on its DMTA curve. If 2.5% (w/w) of TMPTA-AZ-0 was used, the cured PU had two damping relaxation peaks on its DMTA curve. A broad peak with higher intensity centered on 115°C could have been derived from the amide crosslinks on the polymer hard segments; a lower peak centered on 60°C had a little phase separation from the parent polymer that could have been caused by the ester crosslinks and the partial homopolymer formations of the triaziridinyl curing agent. Further-

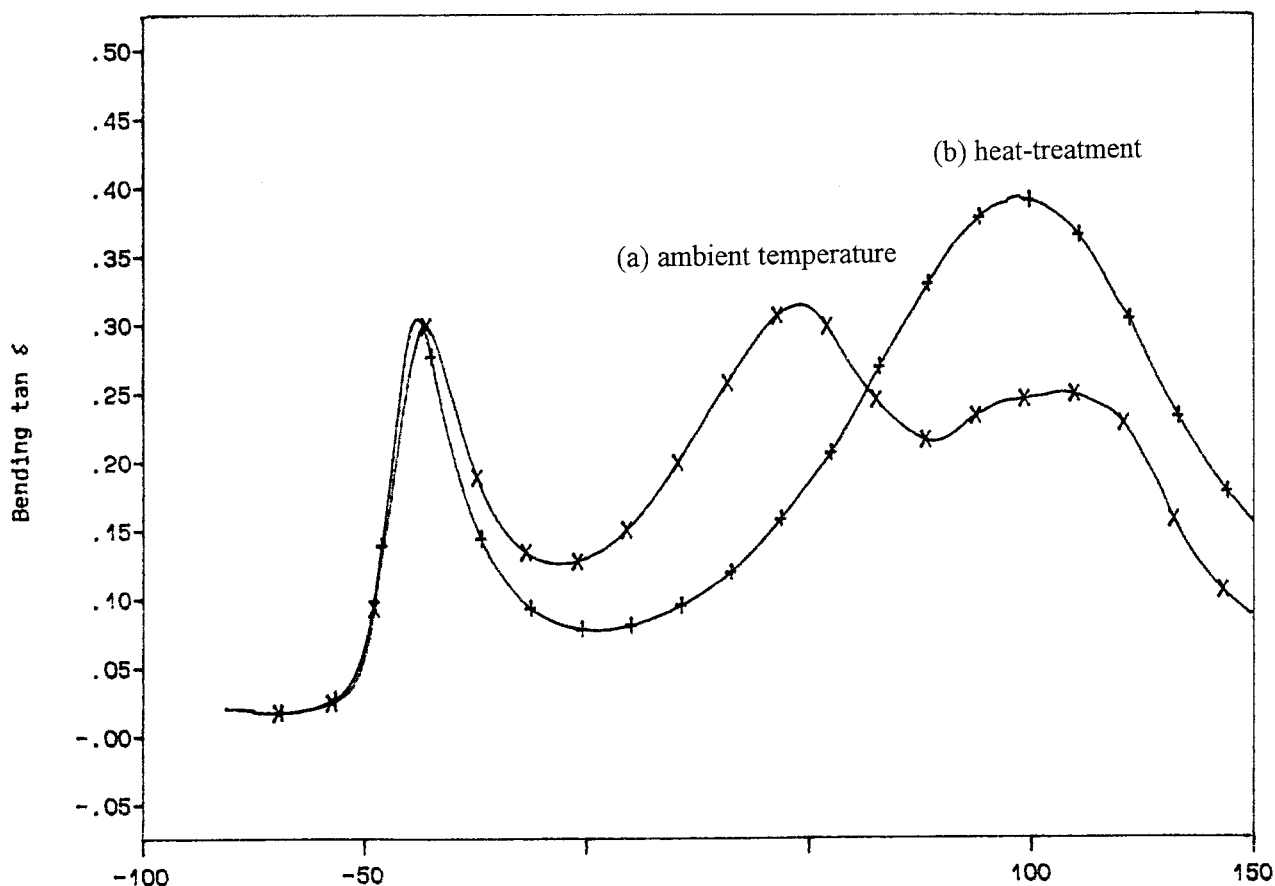


Figure 8 Damping factors of PU films with 5.0% (w/w) TMPTA-AZ-0: (a) spectrum at ambient temperature (×) and (b) spectrum heat treatment of (a) at 120°C for 3 h (+).

more, the PU system with 5.0% (w/w) TMPTA-AZ-0 also had two damping relaxation peaks around 60 and 103°C on its DMTA curve (Fig. 6). The higher intensity peak centered on 60°C was due to the homopolymer formation from an excess amount of TMPTA-AZ-0.

After a heat treatment (ca. 120°C for 3 h) of the cured PU film with 5.0% (w/w) TMPTA-AZ-0, both of the two damping peaks on the PU hard segments shifted and centered at 97°C on the DMTA curve (Fig. 7). This coincided with the infrared spectrophotometric evidence on the internal chemical bond transformations from amino esters to amide linkages upon heating the reaction mixture of a model reaction of MA-AZ with formic acid (Fig. 1) or on a cured PU film with 7.5% (w/w) TMPTA-AZ-0 (Figs. 3, 4). There was a similar observation for other PU systems cured with TMPTA-AZ-1 or TMPTA-AZ-2.

The HDDA-AZ-0 cured PU system had the

same pattern (Fig. 8). It had two damping relaxation peaks centered on 67 and 109°C for 2.5% (w/w) HDDA-AZ-0 and 37 and 95°C for 5.0% (w/w) HDDA-AZ-0. Their glass transition temperatures of the PU soft segment also stayed at -40°C, and their peak intensity decreased as the curing dosage increased because the molecular mobility decreased as the final PU crosslinking density increased.

Thermogravimetric Analyses of PU Films

This single pack PU system contains 1.0% (w/w) of any triaziridinyl latent curing agent, TMPTA-AZ-0, or TMPTA-AZ-2, and its AZ/CO₂ equivalent ratio is 0.7 or 0.6, but it has 3.3 phr curing agent added to its final PU compositions. For other two dosages, 2.5, and 5.0% (w/w) of this curing agent in PU dispersions and there are 8.3,

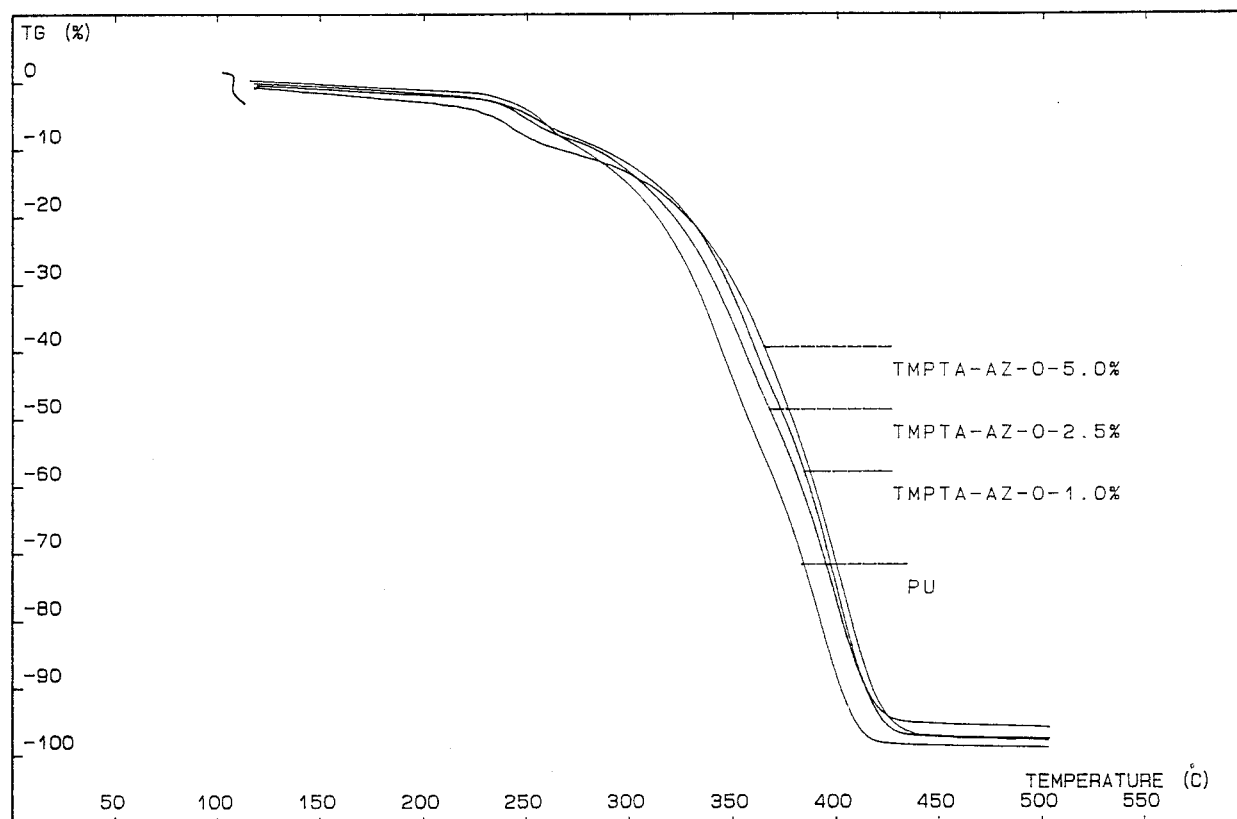


Figure 9 Thermogravimetric analyses of PU films with various weight percents TMPTA-AZ-0.

and 16.7 phr curing agent adds it into each individual PU system.

PU film cured with 3.3 phr of TMPTA-AZ-0 or TMPTA-AZ-2 has a better thermal stability than the original PU and the other cured PU systems with a higher dosage (Figs. 9, 10). But a self-cured PU system by 16.7 phr (5.0%, w/w) of TMPTA-AZ-0, or TMPTA-AZ-2, is thermally less stable than the original PU on its lower range thermogram (below 282 or 330°C). The homopolymers formation from an excess amount of the curing agent in this single pack PU system is a possible explanation.

CONCLUSION

Either di- or triaziridinyl compounds used in this study were hydrophilic and water soluble. They were added and served as latent curing agents for single pack self-curable PU systems. They were stable in aqueous-based PU dispersions with pH

values at 8.5 or above and were free of electrolytes. The stability of the single pack PU dispersions was confirmed by the measurements of their average particle size and particle size distributions as well as the fluorescence spectra.

The curing of this single pack self-curable aqueous-based PU system can be initiated by a pH control, and its reaction takes place via a ring opening of the aziridinyl latent curing agent with the carboxylic group of the polymer. In the meantime, these multiaziridinyl curing agents offered the crosslinked PU networks. The amino ester bonds of the ambient temperature cured PU could be transformed to the more stable amide linkages within the PU system upon heat treatment.

These single pack PU dispersions could provide improvements on the physical, mechanical, and thermal properties of the final PU film. The improvements depend on the availability of the carboxylic group on the polymer, the functionality of the multiaziridinyl latent curing agent, and the equivalent ratio of the curing system. They are

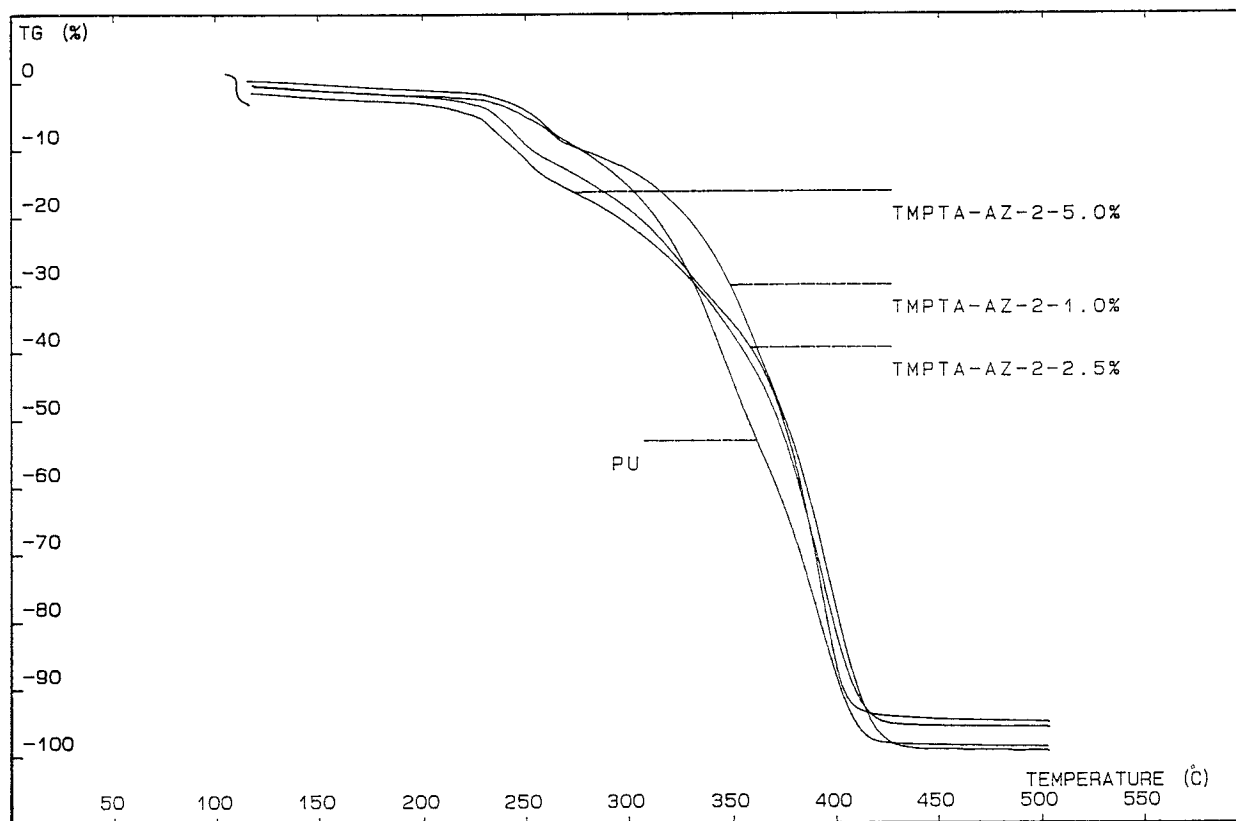


Figure 10 Thermogravimetric analyses of PU films with various weight percents TMPTA-AZ-2.

very useful and convenient for application oriented purposes.

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