Flame Retardation Improvement of Aqueous-Based Polyurethane with Aziridinyl Phosphazene Curing System

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ABSTRACT: Aziridinyl phosphazene (NPAZ) was introduced to aqueous-based polyurethane (PU) as a flame retardant and a postcuring agent, mainly because of the presence of phosphorus compositions, as well as the reactive aziridinyl groups on NPAZ. This dual-function NPAZ was prepared from the substitution reaction of hexachlorocyclotriphosphazene with aziridine. Aqueous-based PU was treated with NPAZ and its curing reaction took place upon drying. The performance properties of this NPAZ cured PU (NPAZ-PU) were improved and better than those of the original PU. The phosphorus composition from NPAZ was evenly distributed on this NPAZ-PU film, which was identified by the phosphorus mapping on the energy dispersion spectrum. The physical and mechanical properties of NPAZ-PU were evaluated by the measurements of the gel content, water uptake, ethanol swelling, and tensile stress. The thermal properties of NPAZ-PU were investigated by thermogravimetric analysis (TGA), TG analyzer-interfaced FTIR, and dynamic mechanical thermal analysis. Furthermore, its combustion behaviors were demonstrated with the data of a cone calorimeter measurement. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 662–673, 2001

Key words: aqueous-based polyurethane; aziridinyl phosphazene; curing; flame retardation; cone calorimetry

INTRODUCTION

Anionic aqueous-based polyurethane (PU) was prepared from isophorone diisocyanate (IPDI), poly(propylene glycol) 1000 (PPG-1000), and dimethylolpropanoic acid (DMPA) via a prepolymer process. The self-emulsified aqueous-based PU dispersion resulted from a water dispersion process of NCO terminated PU prepolymer.[1–3] Aqueous-based PU replaced the solvent-based PU and became increasingly important, because it is an environmental friendly product. However, some of the performance properties of the current aqueous-based PU were inferior to conventional solvent-based PU. Those inferior properties were usually caused by the presence of a hydrophilic group and the low crosslinking density in the polymer. The postcuring reaction[1–6] or polymer hybridization[7] was one of the best alternatives for improvement. PU carboxyl and amino groups were the reactive sites toward aziridinyl and epoxy curing agents, respectively, for those PU postcuring systems.[1–3]

Conventional flame retarded polymers can be formulated with phosphorus flame retardants.[8–13] For example, a phosphorus containing polyol was incorporated and became part of the polymeric backbone. The resulting polymer exhibited the
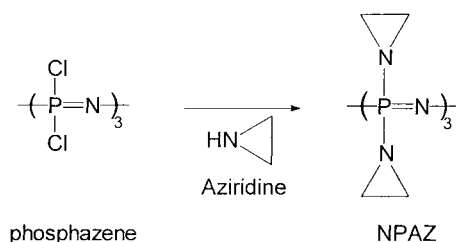
Scheme 1 The preparation of aziridinyl phosphazene (NPAZ).

flame retardation properties but with a lower thermal degradation temperature.[10–13] This flame retardant polymer with less thermal stability was due to the presence of a lower bonding energy P—O bond (149 kJ/mol) than a C—O bond (256 kJ/mol) on the polymer main chain.

Aziridinyl phosphonate derivatives were simultaneously introduced into the PU as a crosslinker and a reactive flame retardant.[6,7] Those cured PUs exhibited better thermal stability and a higher oxygen limiting index value. Because those curing agents had a phosphorus composition and a stable P—N bond (165 kJ/mol), they formed the polymeric networks between the polymer main chains as the crosslinker.

2,2,4,4,6,6-Hexakis(1-aziridinyl)cyclotriphosphaza-1,3,5-triene (NPAZ) consists of high phosphorus (24.03%) and nitrogen (32.56%) contents and six reactive aziridinyl groups, which were prepared from the substitution reaction of hexachlorocyclotriphosphazene with aziridine (Scheme 1). NPAZ served a dual-function role as a flame retardant and a crosslinker to the aqueous-based PU. The performance properties and the combustion behaviors of the NPAZ-PU curing system with various NPAZ dosages are discussed in this report.

EXPERIMENTAL

Materials

Triethylamine (TEA), monoethanol amine, and DMPA were supplied by Aldrich Chemical Co. Hexachlorocyclo-triphosphazene [(NPCl$_2$)$_3$] was obtained as a gift from Dr. Y.-S. Chu's Laboratory, Chung-Shan Science Research Institute, Lung-Tung, Taiwan. These materials were distilled or recrystallized before use. The IPDI and PPG-1000 were supplied by Huls and Arco Chemical Co., respectively. They were used as received without further purification.

Preparation of Anionic Aqueous-Based PU Dispersion

The PPG-1000 (0.1 mol) and DMPA (0.1 mol) were dried at 110°C overnight before they were mixed with the IPDI (0.3 mol) in a 500-mL four-necked resin flask. The reaction was carried out and kept at 90°C for 4 h until the percentage of NCO dropped below 3.0%. The freshly dried acetone was then added into the flask to adjust the viscosity of the PU prepolymer. The PU dispersion was then prepared by mixing this PU prepolymer with the aqueous solution of TEA (0.1 mol) at a high shear rate.[1] The prepared PU dispersion had 30% solid contents after acetone was removed from the dispersion, and its pH value remained at 8.0.

Preparation of NPAZ

A 100-mL solution of toluene with 7.74 g (0.18 mol) of the prepared aziridine[1] and 20.2 g (0.20 mol) of TEA was placed in a 250-mL three-necked flask that was kept in an ice bath and equipped with a calcium chloride drying tube. A 50-mL toluene solution with 6.96 g (0.02 mol) of hexachlorotriphosphazene (NPCl$_2$)$_3$ was then added into the reaction flask through an addition funnel. The reaction mixture was first agitated at 0°C for 3 h and then at ambient temperature for 24 h under nitrogen. The reaction mixture was heated at 45°C for 1 h before the reaction was completed, and white TEA hydrochloride salt was removed from the reaction mixture by filtration. Toluene was distilled off from the filtrate under a vacuum, and a white solid was collected. The white crystalline NPAZ product was recrystallized from a toluene and hexane mixture (1/1) and obtained in 55.4% yield (Scheme 1).[14]

Curing of Aqueous-Based PU with NPAZ

Various dosages (1.5, 2.5, and 3.0 g) of NPAZ were added into 333 g of an aqueous-based PU dispersion (which consisted of 100 g of PU solid) with agitation. NPAZ-cured PU (NPAZ-PU) films were obtained from the casting and air drying of those NPAZ treated PU dispersions at ambient temperature and then heated in a 50°C oven for 24 h.

Properties Measurements of NPAZ-PU Films

Stress and Strain

PU films were cast and air dried from the prepared PU dispersion at ambient temperature and then dried at 50°C for 24 h. These dried PU films

Table I   Properties of Aqueous-Based PU Cured with NPAZ

		NPAZ (phr)[a]		
Properties	Original PU	1.5	2.0	3.0
Tensile strength (kg/cm^2) and elongation at break (%)	8.1/713	4.3/81.3	5.3/52.1	5.6/41.6
Gel content (%)	0[b]	95.3	95.1	94.5
Water uptake (%)	25.8	6.9	8.2	14.2
PU wt. loss in H$_2$O (%)	1.2	2.0	2.0	2.0
Ethanol absorption (%)	Dissolved	162	176	169
PU wt. loss in ethanol[c] (%)	100	3.9	3.9	3.4

[a] The 1.5, 2.0, and 3.0 phr curing dosages respectively represent 1.5, 2.0, and 3.0 g of NPAZ added per 100 g of PU resin.
[b] Original aqueous-based PU was completely dissolved in THF during the Soxhlet extraction process.
[c] 95% (v/v) ethanol was used.

were conditioned in a 75% relative humidity chamber at 25°C for 72 h before measurements. The tensile experiments were performed on a Shimadzu universal testing machine (Autograph S-100-C). Dumbbell-shaped specimens with 1.00-mm thickness were used to determine the tensile properties of the postcured films. The test was performed at a crosshead speed of 40 mm/min and a gauge length of 40 mm. Six tests of each PU sample were taken, and the three measurements that showed the highest tensile strength for calculating the mean value were selected (Table I).

Gel Content

A known weight of dried PU film was put into a Soxhlet extractor for a continuous 24-h extraction with tetrahydrofuran (THF). The PU gel remaining after extraction was dried and calculated according to the test results. The gel contents of the cured PU films are shown in Table I.

Water Uptake and Ethanol Swelling

A known weight (W_0) of 60 × 60 × 1 mm dried PU 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 swelling. The towel-dried sample weight (W_1) and oven-dried PU film weight (W_2) were obtained. The percentage of water uptake (W_a), ethanol absorption (W_e), and weight losses (W_x, W_y) of PU films in water and 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 PU film and the amount of PU dissolved in 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 PU film and the amount of PU dissolved in ethanol, respectively.

Dynamic Mechanical Thermal Analysis (DMTA)

The PU films were dried at 50°C for 24 h and conditioned in a 75% relative humidity chamber at 25°C for 72 h before testing. The DMA measurement of the PU films was performed on a Polymer Laboratories DMTA instrument (model MK-II). All the measurements were tested in bending mode at temperatures ranging from −80 to 150°C at a 1.0-Hz frequency and a heating rate of 3°C/min.

Thermogravimetric Analysis (TGA)

Each dried PU sample (~10 mg) was taken and measured by a TA TG analyzer (Hi-Resolution 2950) with a heating rate of 10°C/min from ambient temperature to 500°C. These were carried out under air and a nitrogen atmosphere for the measurements of the polymer thermal oxidative
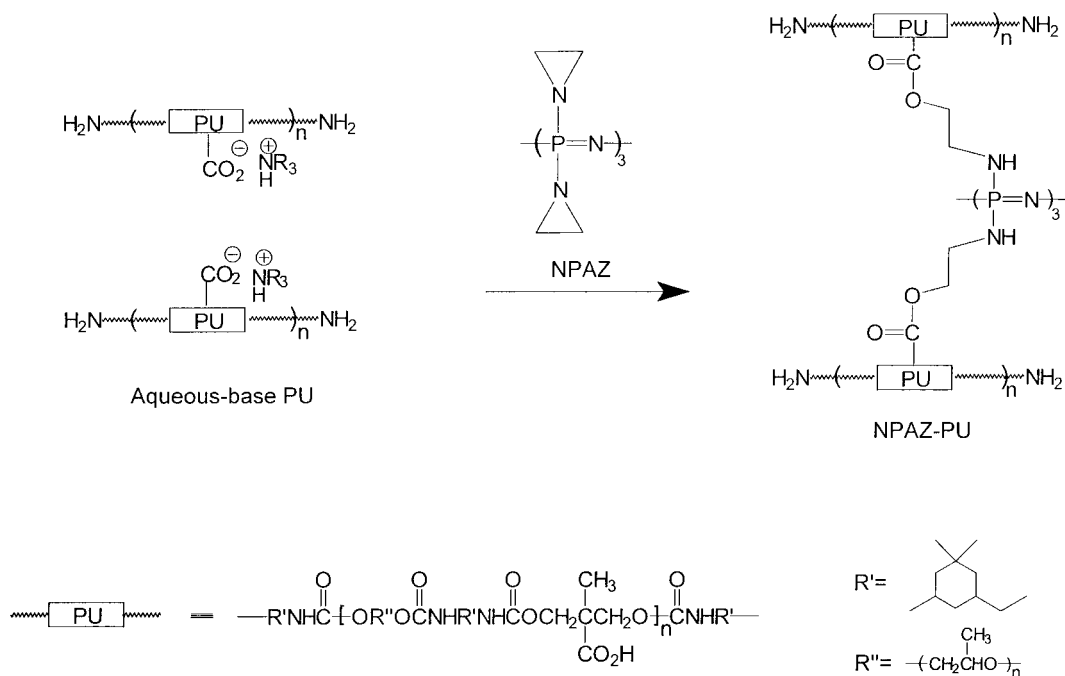
Scheme 2   The NPAZ-PU curing reaction.

and thermal stabilities, respectively. TGA-interfaced FTIR spectra (TGA/FTIR) were recorded according to the major polymer degradation temperature on the TGA.

Energy Dispersion Spectroscopy (EDS)

A smooth cross section of PU film was selected and mounted. An electron beam of 20 kV was applied for the PU sample bombardment. The phosphorus element on the film was excited and then it emitted X-ray fluorescence. This X-ray fluorescence was detected and identified as the location of each phosphorus element on the NPAZ-PU film.

Cone Calorimeter Measurement

The combustion measurements were carried out according to ISO 5660 on a cone calorimeter from Fire Testing Laboratories Ltd. The specimen dimensions were 10×10 cm and the thickness was 1.2 mm. Triplicate tests were performed for the measurements of the ignition time, char residue, heat release, and total smoke of the polymer at a heat flux of 20 kW/m^2.

RESULTS AND DISCUSSION

The resulting aqueous-based PU had 30% solid contents and 2.2×10^{-2} equivalents of carboxyl ions per 100 g of aqueous-based PU dispersion. The hydrophilic PU carboxyl ion stabilized the aqueous PU dispersion and also provided the reactive site toward the multi-aziridinyl curing agent. This PU curing pattern was applied for a single-pack aqueous-based PU self-curing system.[1]

The physically blended or chemically bonded phosphorus containing polymer demonstrated good flame retardation behaviors. Furthermore, the polymer was treated with a reactive flame retardant and the flame inhibition function became permanent. The resulting polymer had phosphorus and nitrogen contents and exhibited a synergistic effect on the flame inhibition characteristics.[6–10,13,15]

The NPAZ contained six aziridinyl groups, phosphorus (24.03%), and nitrogen (32.56%). Its aziridinyl groups reacted with the PU carboxyl pendant group and formed amino ester linkages between the PU main chains in this postcuring process (Scheme II). In the meantime, the phosphorus and nitrogen of NPAZ were covalent bonded on the PU, which exhibited flame inhibition behaviors. The NPAZ demonstrated dual-function crosslinking and flame retardation for this anionic aqueous-based PU curing system.

Synthesis and Characterizations of NPAZ

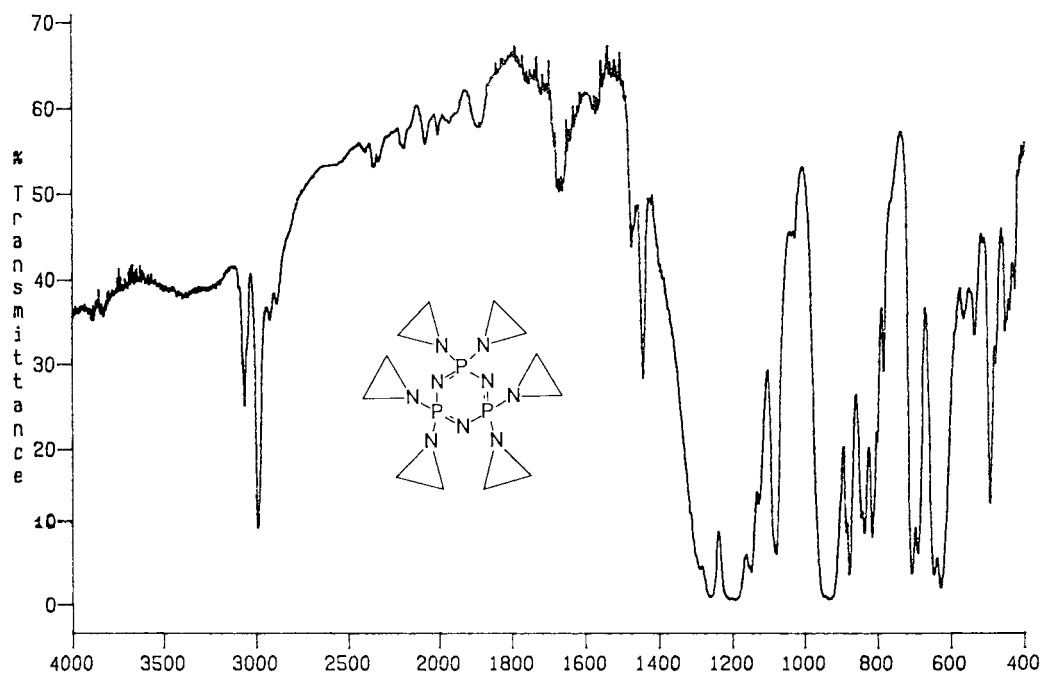NPAZ was obtained from a nucleophilic substitution reaction of (NPCl$_2$)$_3$ with aziridine[14] (Scheme

Figure 1 An FTIR spectrum of NPAZ.

1). The absorption peak of P=N stretching was shifted to 1200 cm^{-1} on the FTIR spectrum of NPAZ (Fig. 1) from the original 1219 cm^{-1} of (NPCl$_2$)$_3$. And the peaks of P—Cl stretching at 528 and 609 cm^{-1} disappeared and new peaks appeared at 3000 and 3100 cm^{-1} for C—H unsymmetric stretching. Furthermore, the aziridi-

nyl group of NPAZ had absorption peaks at 1260 and 939 cm^{-1}. These IR spectra data indicated the characteristic absorption peaks of NPAZ.

The aziridinyl protons of NPAZ were shifted to 2.1 ppm with a doublet on its ^{1}H-NMR spectrum and original pure aziridine was 1.5 ppm with a singlet. The ^{13}C-NMR spectrum of NPAZ showed
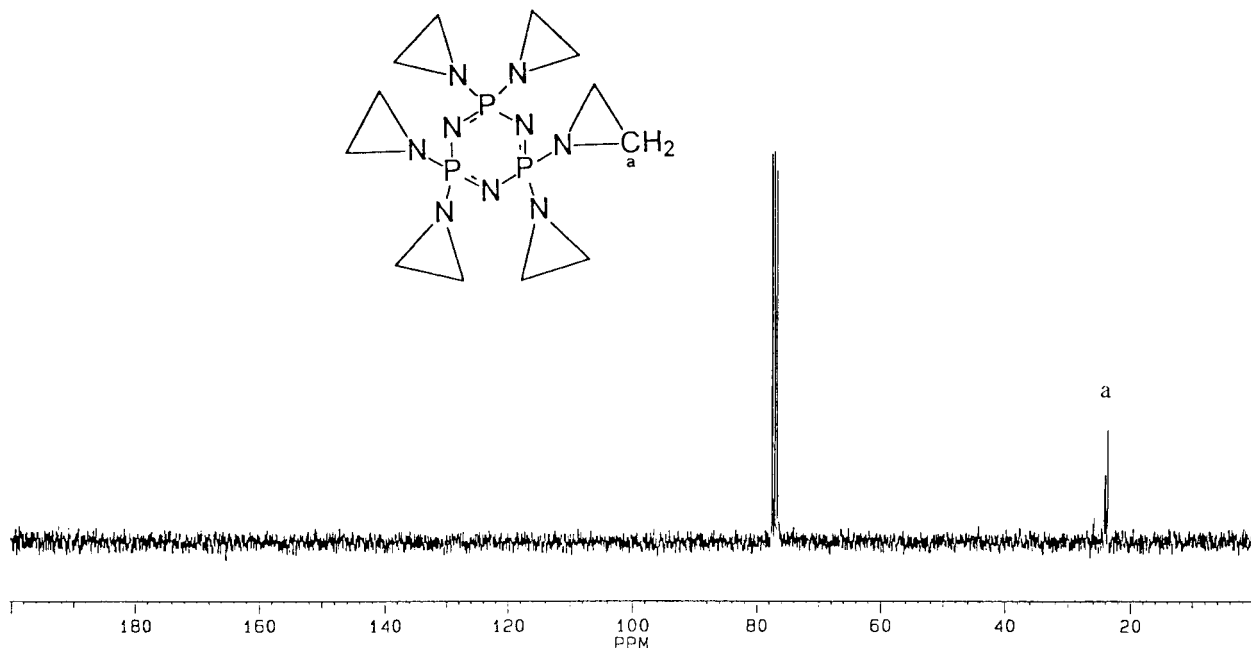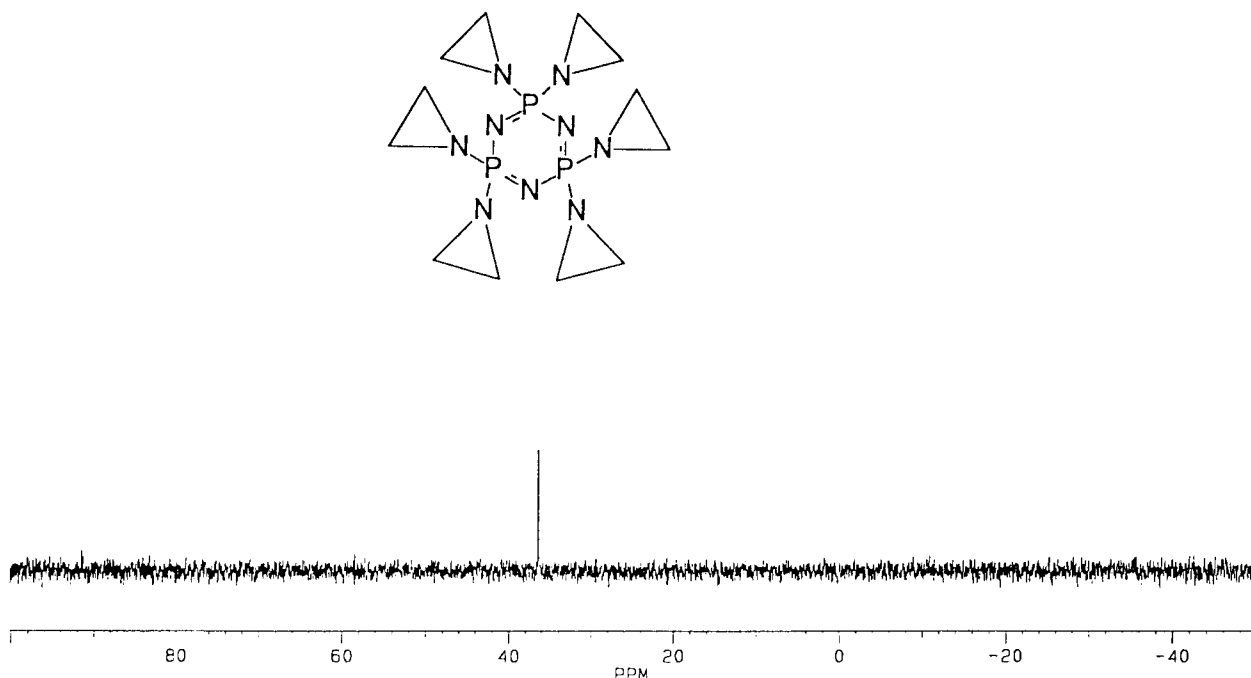

Figure 2 A ^{13}C-NMR spectrum of NPAZ.

Figure 3   A ^{31}P-NMR spectrum of NPAZ.

two peaks at 23.7 and 23.9 ppm of the aziridinyl carbon (Fig. 2), and the original aziridine had a single peak at 17.9 ppm. The NMR spectra of carbons or hydrogen on pure aziridine were identical. However, those aziridinyl carbons or hydrogen of NPAZ became nonsymmetric after aziridine attached to the phosphazene framework.

NPAZ had only one peak at 36.3 ppm (Fig. 3) compared to the original $(NPCl_2)_3$ at 19.1 ppm on those ^{31}P-NMR spectra. Those spectra demonstrated that a single phosphorus peak remained with a different chemical shift on the NPAZ, which was a single NPAZ product with three identical phosphorus elements.

These NMR spectroscopic data showed that there was a single NPAZ with identical phosphorus elements and aziridinyl groups.

Physical and Mechanical Properties

Aqueous-based PU was a thermoplastic polymer and was soluble in THF. However, the gel contents of NPAZ-PU reached 95.3, 95.1, and 94.5% after the curing with 1.5, 2.0, and 3.0 phr NPAZ dosages, respectively (Table I). These results indicated that the NPAZ-PU system was highly crosslinked, even with a small NPAZ dosage.

Furthermore, this aqueous-based PU completely dissolved in ethanol and the ethanol swelling of those NPAZ-PU films were 162, 176, and 169%, respectively (Table I). The NPAZ-PU cur-

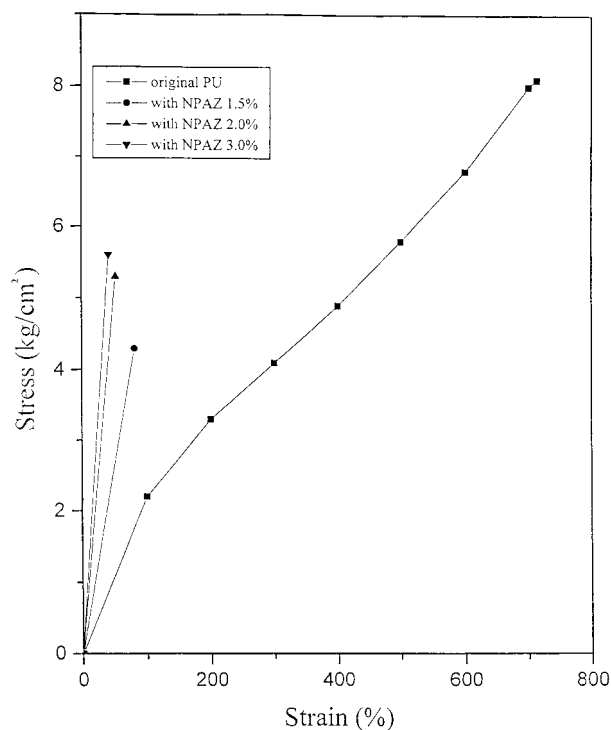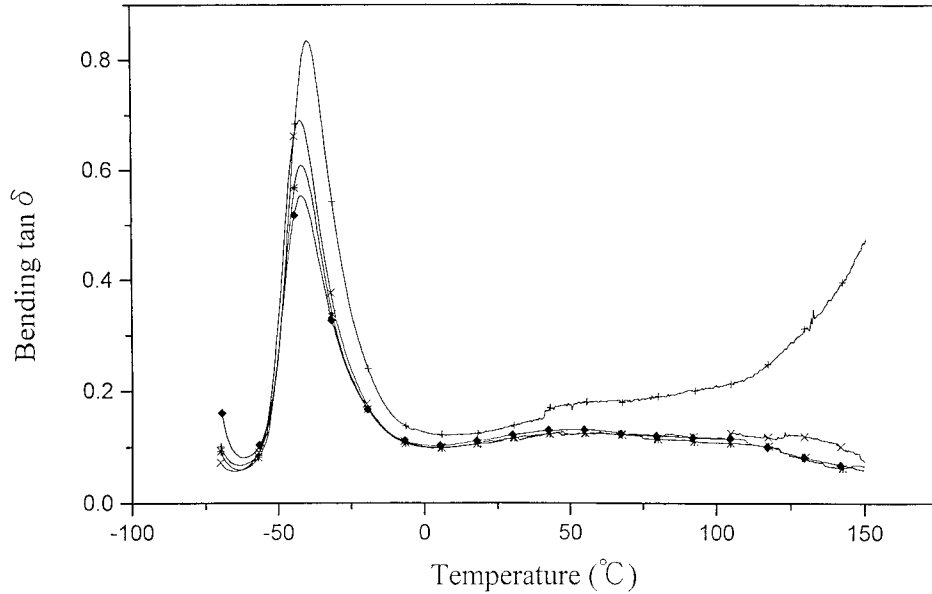ing system again demonstrated a high degree of polymeric network formation between the PU main chains.

Figure 4   Stress–strain curves of NPAZ-PU: (■) the original PU; (●) PU with 1.5 phr NPAZ, (▲) PU with 2.0 phr NPAZ, and (▼) Pu with 3.0 phr NPAZ.
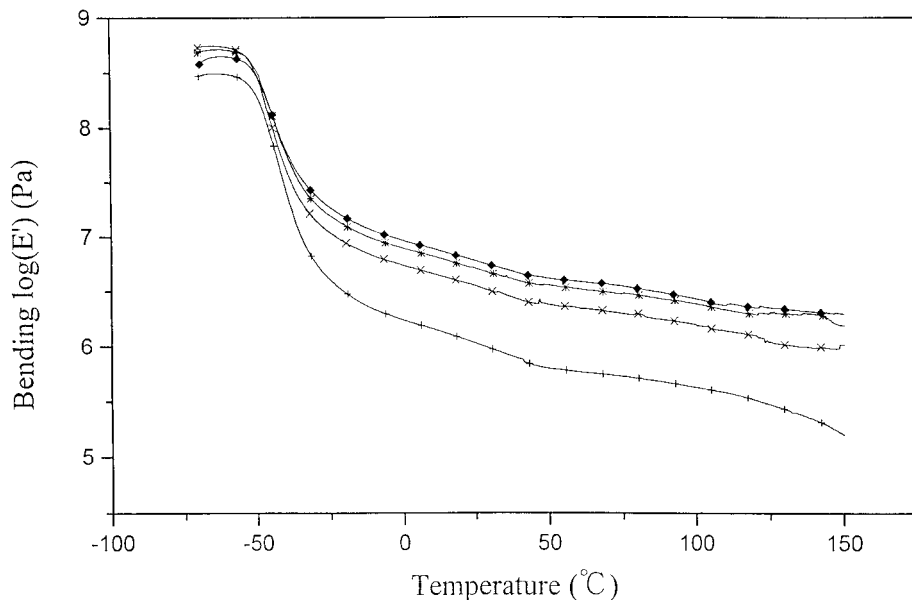
Figure 5   The tan δ curves of NPAZ-PU: (+) the original PU, (×) PU with 1.5 phr NPAZ, (*) PU with 2.0 phr NPAZ, and (♦) PU with 3.0 phr NPAZ.

The water uptake of the original aqueous-based PU resin was 25.8% and it decreased to 6.9% of the NPAZ-PU resin (with 1.5 phr NPAZ). This indicated that the hydrophilic PU carboxyl groups were consumed by the aziridinyl groups of the NPAZ and resulted in a crosslinked NPAZ-PU polymer simultaneously. The water uptake of NPAZ-PU did not decrease further with increasing NPAZ dosage, so it could be due to the influence on both the steric hindrance of NPAZ and the availability of the PU carboxyl group.

The phosphorus composition on NPAZ-PU film was identified with an EDS spectrum. The even distribution of the phosphorus content on the NPAZ-PU with various NPAZ dosages was proved by the phosphorus mapping measurement on the EDS spectrum.


Figure 6   Storage moduli of NPAZ-PU: (+) the original PU, (×) PU with 1.5 phr NPAZ, (*) PU with 2.0 phr NPAZ, and (♦) PU with 3.0 phr NPAZ.

Table II   TGA Weight Remains of Aqueous-Based PU with NPAZ

| Temp. (°C) | Wt. Remaining under N_2 (%) | | | | Wt. Remaining under Air (%) | | | |
| | PU with NPAZ (phr) | | | | PU with NPAZ (phr) | | | |
	PU	1.5	2.0	3.0	PU	1.5	2.0	3.0
250	97	> 99	> 99	> 99	86	> 99	> 99	> 99
300	83	96	97	98	21	76	76	83
350	53	59	63	70	9	19	23	28
400	0	5	8	14	7	16	18	23
450	0	5	7	10	5	14	16	21

The tensile strength and elongation at break of the original PU film were 8.1 kg cm^{-2} and 713%, respectively. The tensile strength and elongation at break were reduced significantly to 4.3 kg cm^{-2} and 81.3%, 5.3 kg cm^{-2} and 52.1%, and 5.6 kg cm^{-2} and 41.6% after PU was cured with 1.5, 2.0, and 3.0 phr NPAZ, respectively (Table I and Fig. 4).

Presumably, these significant changes in the tensile strength and elongation at break were due to the polymeric network formation by the hexaaziridinyl group of NPAZ in the postcured NPAZ-PU resins. Because of the "crosslinked" network the molecules were likely to distribute the stress along these crosslinked molecules and restrain the deformation of the postcured PU resins.
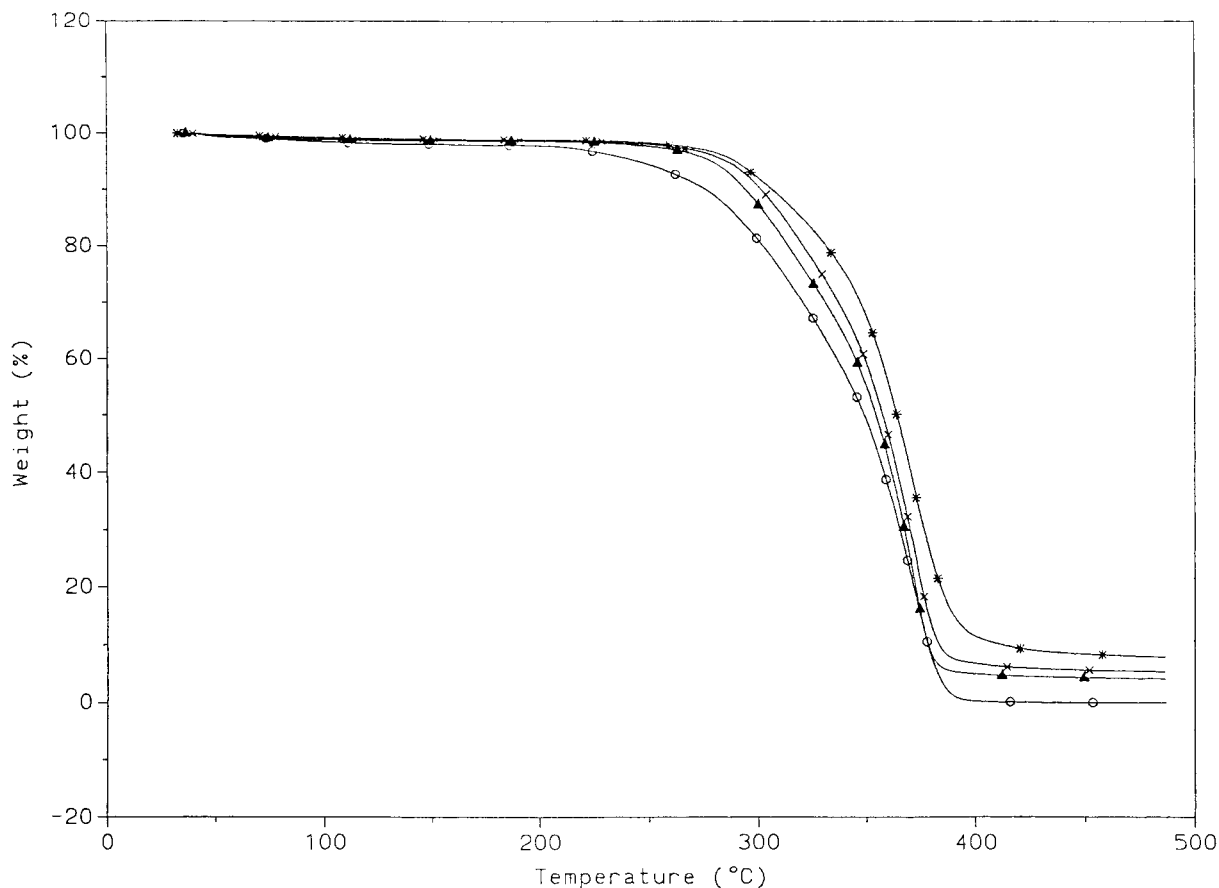
Figure 7   TGA of NPAZ-PU under a nitrogen atmosphere: (○) the original PU, (▲) PU with 1.5 phr NPAZ, (×) PU with 2.0 phr NPAZ, and (*) PU with 3.0 phr NPAZ.
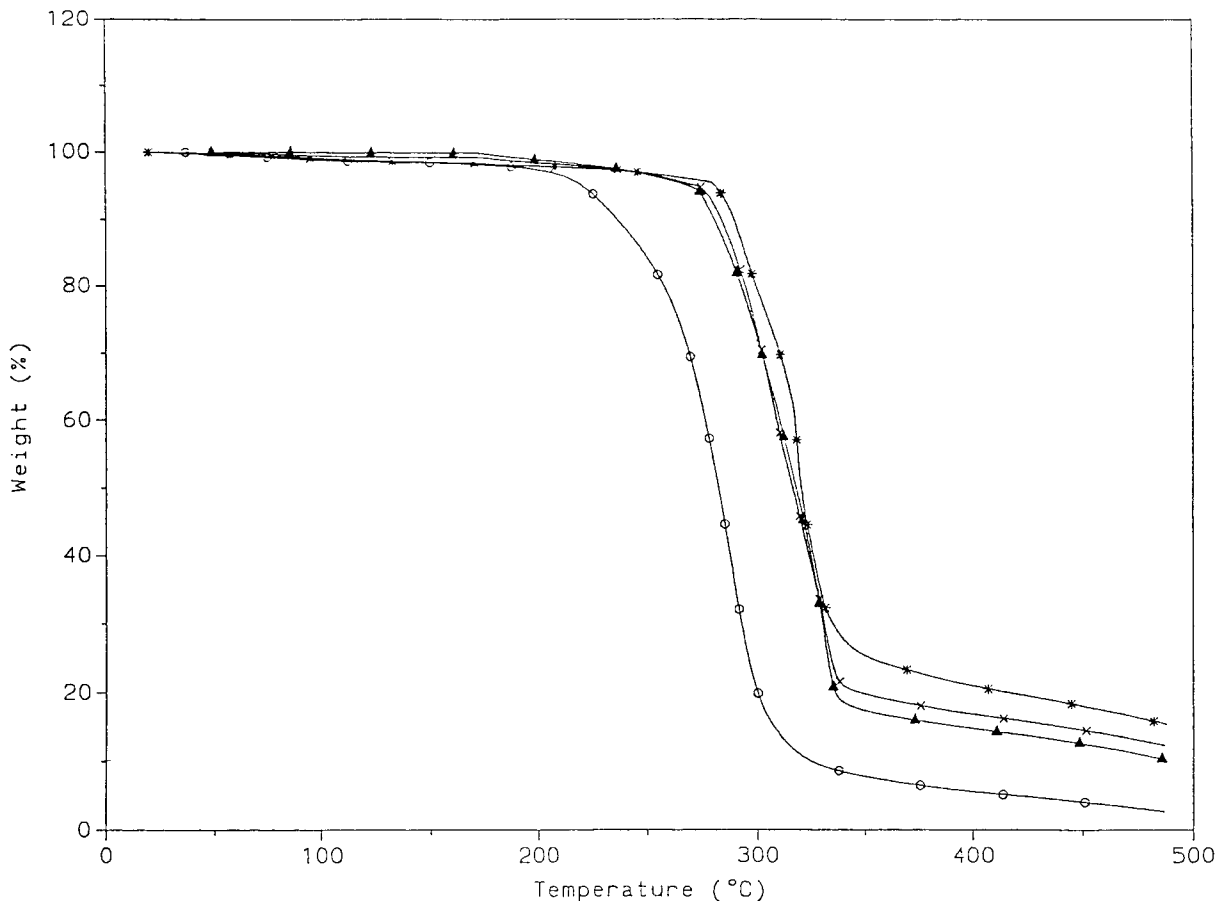
Figure 8 TGA of NPAZ-PU under an air atmosphere: (○) the original PU, (▲) PU with 1.5 phr NPAZ, (×) PU with 2.0 phr NPAZ, and (*) PU with 3.0 phr NPAZ.

DMTA

The original PU film had a damping peak (tan δ) at −38°C and its peak intensity decreased with increasing NPAZ curing dosage, which exhibited the curing behavior of NPAZ-PU on the DMTA curves (Fig. 5). Furthermore, the storage modulus curve of each NPAZ-PU was higher than the original PU (Fig. 6). Those phenomena on the DMTA were caused by less free volume of the NPAZ-PU curing system. It also demonstrated the polymeric network formation between NPAZ and PU carboxyl pendants on this NPAZ-PU resin.

TGA

The weight remaining of the original aqueous-based PU resin was 53% with the TGA under a nitrogen atmosphere at 350°C. The weights remaining of the NPAZ-PU were 59, 63, and 70% corresponding to 1.5, 2.0, and 3.0 phr NPAZ curing dosages, respectively, at the same temperature (Table II). This indicated the thermal stability of NPAZ-PU was improved with increasing NPAZ dosage (Fig. 7).

Furthermore, the thermal oxidative resistance of NPAZ-PU was also improved with increasing NPAZ dosage. There were 76–83% of the weight remaining at 350°C, which compared to 21% of the weight remaining of original PU under air at the same temperature (Table II, Fig. 8). The char yields (at 500°C) of NPAZ-PU were 10.9, 12.5, and 15.8% under air on the TGA, but the original PU was only 2.9% (Table II). These are due to the presence of high phosphorus and nitrogen compositions in the resulting NPAZ-PU resin. The phosphorus and nitrogen contents formed nonflammable oxides at high temperature under an air atmosphere; these retarded the flammability of the polymer and promoted char formation.

The large percentage of weight loss on the NPAZ-PU or PU started at around 370°C with the TGA under nitrogen. Those evolved gases showed absorption peaks at 1112, 1375, 1775, and 2820–2950 cm^{-1} on their TGA/FTIR spectrum (Fig. 9).
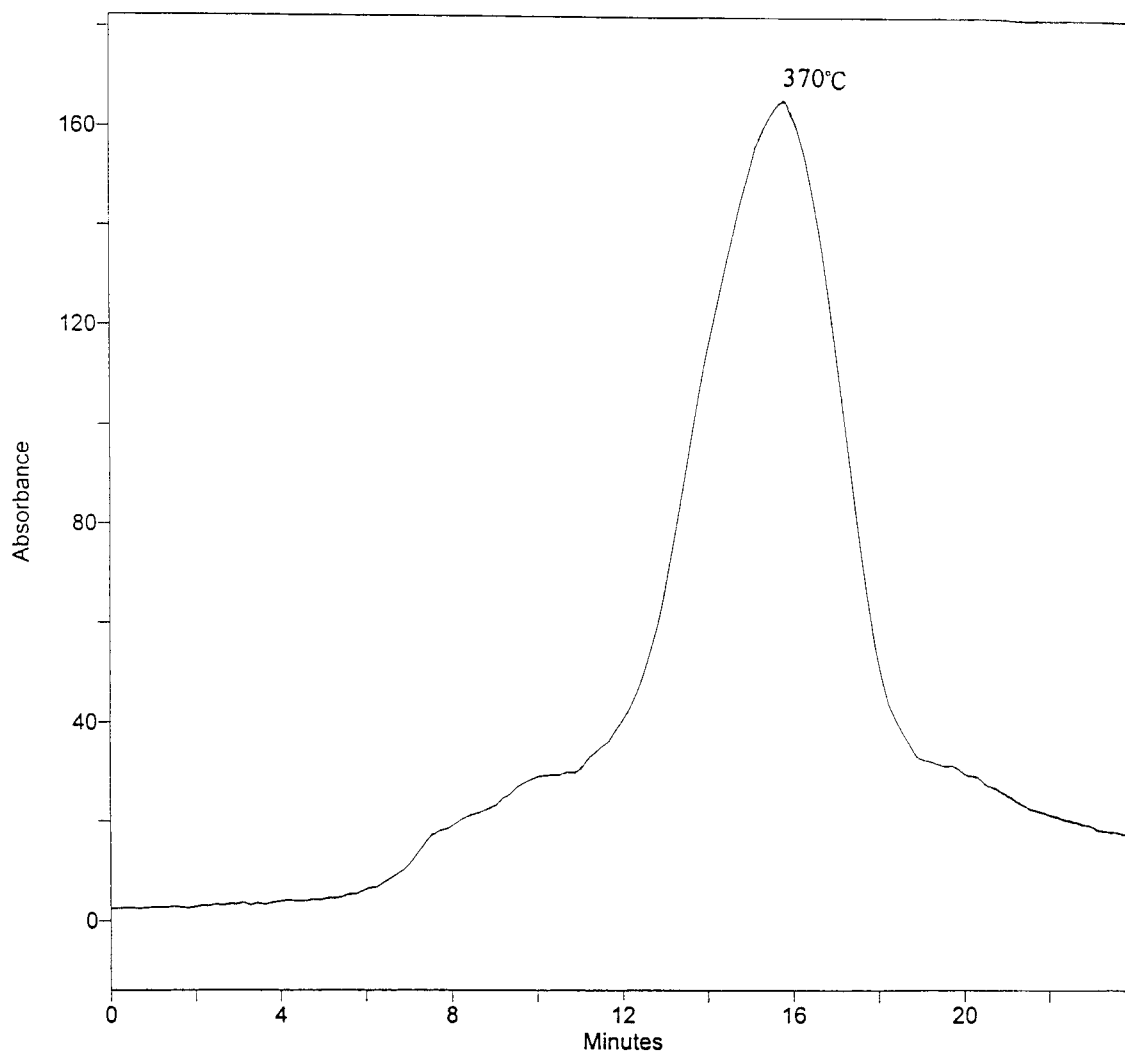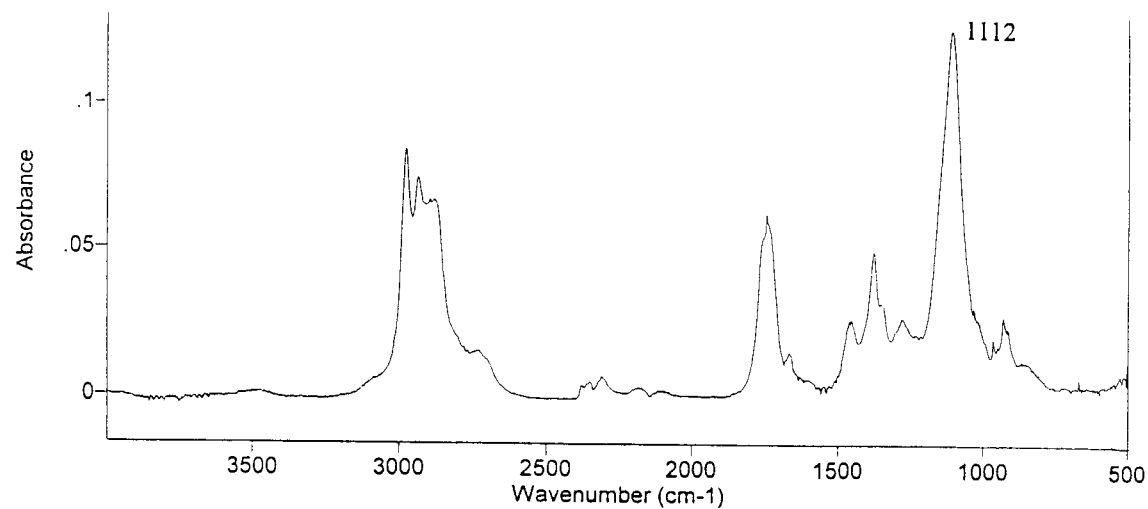
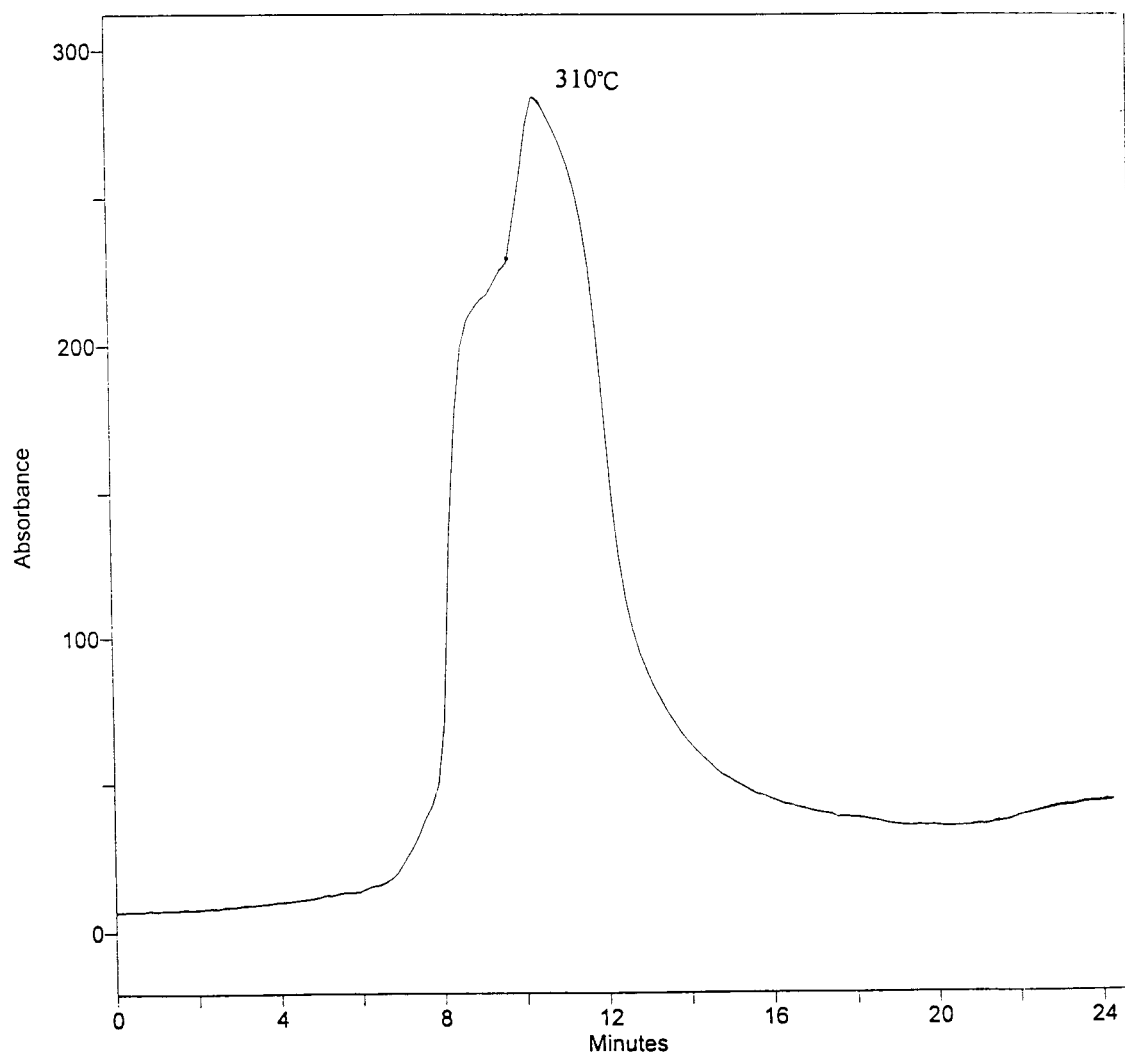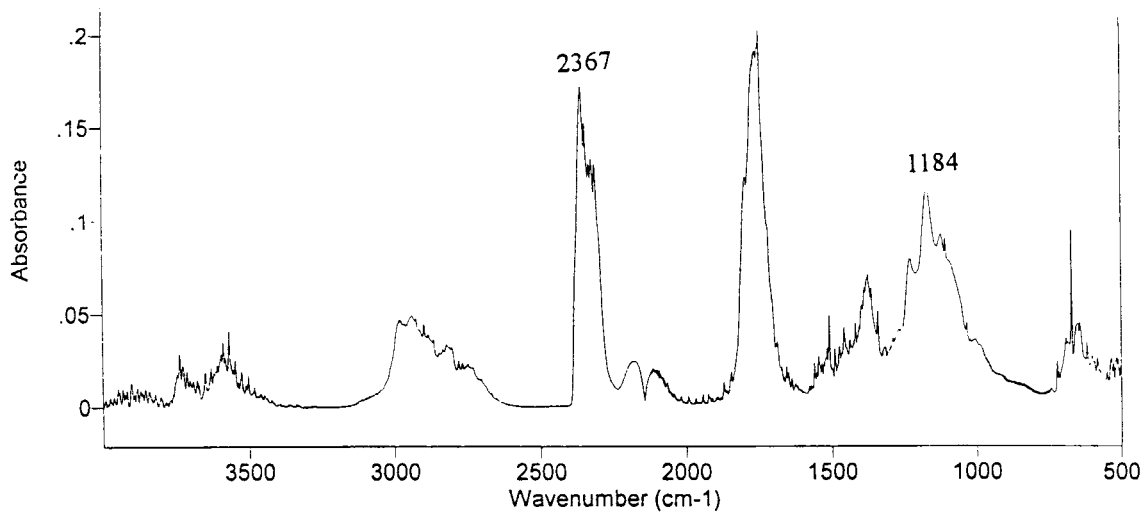**Figure 9**   TGA/FTIR of NPAZ-PU under a nitrogen atmosphere.

Figure 10   TGA/FTIR of NPAZ-PU under an air atmosphere.

Table III   Combustion Properties of Aqueous-Based PU Cured with NPAZ

	Original PU	NPAZ (phr)		
		1.5	2.0	3.0
Ignition time (s)	100	237	263	187
Char residue (%)	16.4	36.6	43.0	55.7
Heat release				
Maximum (kW/m^2)	150.3	136.3	132.5	210
Average (kW/m^2)	28.3	24.2	36.8	102.9
Total (MJ/m^2)	12.2	7.4	8.8	10.0
Total smoke	77.1	338.0	440.1	307.5

Those peaks were identified as low molecular weight poly(propylene glycols) from PU thermal decomposition. However, the large weight loss of NPAZ-PU and PU changed to around 280 and 310°C, respectivel,y under an air atmosphere. Those evolved gases revealed the absorption peaks at 1184, 1750, and 2367 cm^{-1} (Fig. 10), at which CO_2 and other degradation products are generated at that temperature. It indicated the thermal oxidative stability of NPAZ-PU was better than the original aqueous-based PU.

Cone Calorimetric Measurement

The ignition time of the original aqueous-based PU was 100 s under a 20 kW/m^2 heat flux on a cone calorimeter. However, the ignition time of NPAZ-PU resins was delayed to 237, 263, and 287 s (Table III). Those results exhibited that NPAZ-PU resins were more thermally stable and less flammable than the original PU. Although the combustion residue of the original PU was 16.4%, the NPAZ-PU resins were increased to 36.6, 43.0, and 55.7% (Table III). The higher phosphorus contents resulted in a higher combustion residue on the cone calorimetric measurements. Those results coincided with the char yield from the TGA.

Even though the total heat release of NPAZ-PU resins (7.4–10.0 mJ/m^2) was lower than the original PU (12.2mJ/m^2), the maximum smoke release and total smoke of the NPAZ-PU resins (2.3–4.56 L/s and 307.5–338.0) were much higher than the original PU (1.6 L/s and 77.1) during combustion (Table III). These phenomena were due to the generation of a condensed phase and noncombustible gases from NPAZ-PU; those nonflammable phases blocked the air supply. It could also be the reason for the higher char yield and larger smoke formation of NPAZ-PU than the original PU on combustion.

CONCLUSIONS

The thermal stability and the physical and mechanical properties of aqueous-based PU were improved with a small dosage of NPAZ curing agent. These were caused by the polymeric network formation from the crosslinking reaction between the NPAZ and PU main chains. The flame inhibition characteristics of the NPAZ-PU were due to the presence of both phosphorus and nitrogen compositions. NPAZ served a dual function as the crosslinker and the reactive flame retardant for the curing of aqueous-based PU.

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