

Introduction of Covalently Bonded Phosphorus into Aqueous-Based Polyurethane System via Postcuring Reaction

TA-ZEN WANG, KAN-NAN CHEN

Department of Chemistry, Tamkang University, Tamsui, Taiwan 251, Republic of China

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ABSTRACT: Anionic aqueous-based polyurethane (PU) dispersions were derived from a water dispersion process of carboxylic groups containing PU prepolymers together with a neutralization and a chain extension. These PU prepolymers were prepared from a conventional polyaddition of isophorone diisocyanate, polypropylene glycol-1000, and dimethylolpropanic acid. A covalently bonded phosphorus was introduced into PU by a phosphorus-containing curing agent. A series of phosphorus and multi-aziridinyl groups containing curing agents were synthesized for this purpose. Each of them served in a dual-function capacity as a postcuring agent for the anionic aqueous-based PU system. The resulting postcured PU exhibited improvements in its mechanical, physical, and thermal properties; furthermore, postcured PU synergistic flame inhibition was also observed due to the presence of nitrogen and phosphorus content in the process. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2499–2509, 1999

Key words: aqueous-based PU; reactive phosphorus flame retardant; dual-function curing

INTRODUCTION

Although the application technology of conventional solvent-based polyurethane (PU) is well developed, aqueous-based PU has recently assumed greater importance because of its desirable solvent-free characteristic, which makes it an environmentally friendly product.

The currently developed aqueous-based PU is inferior to the conventional PU in its performance properties, however, because of its low molecular weight with less crosslinking density. The postcuring reaction is the method used to improve on these shortcomings.^{1–6}

The aqueous-based PU dispersions were prepared from isophorone diisocyanate, polypropylene glycol-1000, and dimethylolpropanic acid (DMPA). The carboxylic group on the PU molecule is an ionic center for a self-emulsified aqueous-based PU system and it is the group that is reactive toward the compound containing the aziridinyl group. Multi-aziridinyl compound serves as a PU latent curing agent and its curing reaction took place either on drying or when its pH value dropped below 6.0.^{2,4}

A phosphorus-containing compound could be a flame retardant for polymeric material.^{7–15} Furthermore, when a compound contains both phosphorus and nitrogen, it performs a synergistic flame-inhibition function.^{7,8} A phosphorus-containing PU was prepared from the reaction of phosphorus-containing polyols with polyisocyanates; the resulting PU not only had a high phosphorus content but it also exhibited a lower deg-

Correspondence to: K.-N. Chen (knchen@mail.tku.edu.tw).
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radiation temperature, a lower activation energy, and a higher char yield.¹⁵

The chemically bonded phosphorus PU system could also be obtained by introducing a phosphorus-containing curing agent into an aqueous-based PU system by means of a postcuring reaction. This type of diaziridinyl or tetraaziridinyl curing agents—PEGAs and PHAs—was prepared from a substitution reaction of phosphorus oxychloride, first with ethylene glycol or phenol and then with nitrogen-containing aziridines [PEGA = phosphorus oxychloride + ethylene glycol + aziridine (or 2,2-dimethyl aziridine) for PEGA-0 or PEGA-2, respectively; PHA = phosphorus oxychloride + phenol + aziridine (or 2,2-dimethyl aziridine) for PHA-0 or PHA-2, respectively]. The resulting compounds (with either di- or tetra-functional aziridinyl groups) were characterized by a high content of phosphorus as well as nitrogen. In addition, these compounds served two functions as both a curing agent and a flame retardant, simultaneously. Syntheses of these dual-function curing agents and their curing behaviors for the aqueous-based PU system were evaluated. The performance properties as well as the flame retardation of the final cured PU system are reported in this study.

EXPERIMENTAL

Materials

Triethylamine (TEA), ethylenediamine (EDA), phosphorus oxychloride (POCl_3), and phenol were supplied by Junsei Chemical Co. (Japan). Isophorone diisocyanate (IPDI) was supplied by Dow Chemical Co. (USA). Polypropylene glycol-1000 (PPG-1000) was supplied by Arco Chemical Co. (Taiwan). Diepoxide, NPEW-254 (eew 205) was obtained from Nan-Ya Plastics Co. (Taiwan). They were used as received without further purification. Ethylene glycol was dried under vacuum at 110°C overnight before use. Acetone, tetrahydrofuran, ethyl ether, and other solvents were dried and distilled over anhydrous calcium chloride before use.

Instruments

Dynamic mechanical behaviors of PU films were performed by a dynamic mechanical thermal analyzer (DMTA), MK-II, Polymer Laboratories (United Kingdom). Thermogravimetric data were

obtained from a Perkin–Elmer TGA 7 Thermogravimetric Analyzer (USA). Infrared spectra were measured by FTS-40 FTIR, Biorad (USA). ^1H -, ^{31}P -, and ^{13}C -NMR spectra were taken by AC-300 FT-NMR, Bruker Co. (Germany). The tensile stress of the PU films was measured by Autograph S-100-C Universal Testing Machine, Shimadzu Co. (Japan). Contact angles of pure water droplets on a dried PU film were taken by a FACE contact angle meter, model CA-A, Kyowa Kaimenkagaku Co., Ltd. (Japan). Particle size distributions and average particle size of PU dispersions were measured by a Zetamaster and ZetaSizer ZEM 5002, Malvern Instruments Ltd. (United Kingdom). The limiting oxygen index was performed by Oxygen Index, model HFTA 11, Polymer Laboratories.

Preparations of Anionic Aqueous-Based PU Dispersions

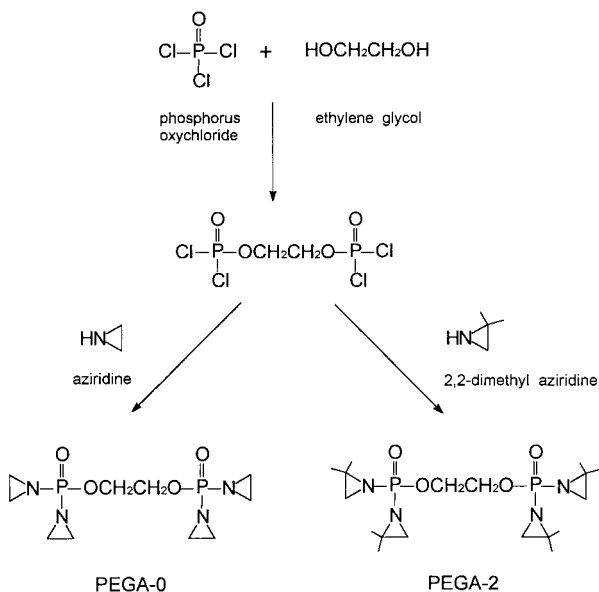
PPG-1000 (0.1 mol) and DMPA (0.1 mol) were dried at 110°C overnight before they were mixed with IPDI (0.3 mol) in a 500-mL four-necked resin flask. The preparation processes were followed according to a previous study.²

Preparations of Tetraaziridinyl Curing Agents: PEGA-0 and PEGA-2

A 200-mL solution of toluene and ethyl ether (1/1, v/v) containing POCl_3 (1.0 mol) was put into a 500-mL round-bottomed flask with a calcium chloride drying tube. A mixture of freshly dried ethylene glycol (0.5 mol) and triethylamine (3.5 mol) was added dropwise into the reaction flask. The reaction mixture was kept at ambient temperature for 8 h with constant agitation under nitrogen. The triethylamine hydrochloride salt generated by the reaction was removed by filtration; the filtrate was treated further with 2,2-dimethyl aziridine² (for PEGA-2) or aziridine⁹ (for PEGA-0) (2.0 mol) at -10°C under nitrogen for an additional 4 h. The reaction residue was collected after its triethylamine hydrochloride salt was removed and solvents were distilled off under vacuum (Scheme 1). The prepared PEGA-0 and PEGA-2 (Table I) were isolated and identified by NMR and FTIR spectra, respectively.

Preparations of Diaziridinyl Curing Agents: PHA-0 and PHA-2

A 200-mL ethyl ether solution containing POCl_3 (1.0 mol) was put into a 500-mL three-necked



flask with a calcium chloride drying tube. The reaction flask was kept in an ice-salt bath (-10°C), and freshly dried phenol (1.0 mol) and triethylamine (3.1 mol) were added through an additional funnel for 3 h. A mixture of freshly prepared aziridine (for PHA-0) or 2,2-dimethylaziridine (for PHA-2) (2.0 mol) and triethylamine (3.5 mol) was then added dropwise. The final reaction mixture was kept at constant agitation for 5 h before the resulting triethylamine hydrochloride salt was removed by filtration and distilla-

Table I Properties of PHA and PEGA Curing Agents

Properties	Curing Agents			
	PHA-0	PHA-2	PEGA-0	PEGA-2
Phosphorus %	13.8	11.9	19.3	14.3
Nitrogen %	12.5	10.8	17.4	12.9
Molecular weight	224	260	322	434
Aziridinyl functionality	2	2	4	4
Equivalent weight	112	130	80.5	108.5

tion, respectively (Scheme 2). The residue was purified by a silica gel column by a solvent pair (acetone/chloroform = 1/13). The resulting product, either PHA-0 or PHA-2 (Table I), was isolated and identified by NMR and FTIR spectra, respectively.

Aqueous-Based PU System with a Phosphorus-Containing Curing Agent

The treatment of aqueous-based PU dispersions with either tetraaziridinyl agent (PEGA-0 or PEGA-2) or diaziridinyl curing agent (PHA-0 or PHA-2) was based on the equivalent ratio of aziridinyl and carboxyl groups of the curing agent and aqueous-based PU, respectively. The usage of the

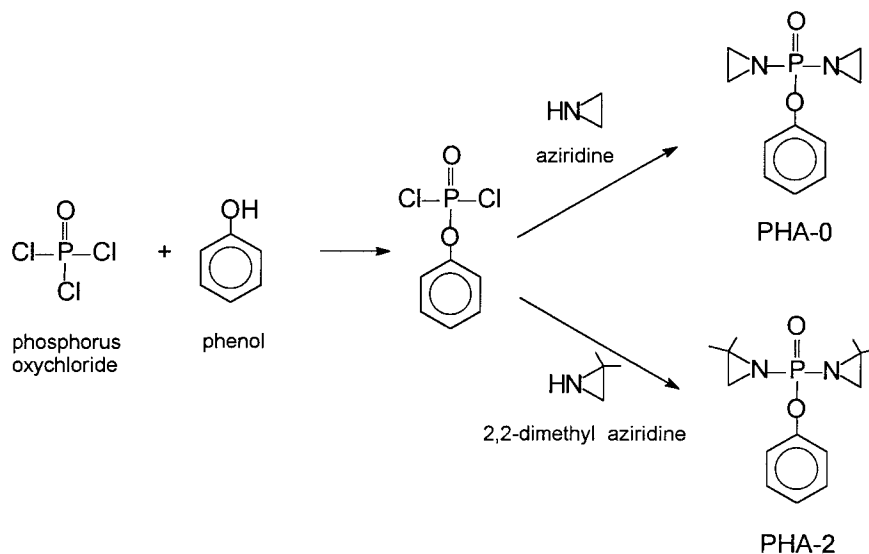


Table II Properties of PU with Various Dosages of PHA Curing Agents

Properties	PU with PHA-0 (phr)					PU with PHA-2 (phr)					
	Original PU	2.5	5.7	8.2	11.5	14.8	2.9	6.7	9.6	13.4	17.3
Elongation (%)											
100.0	4.4	5.4	6.6	6.8	7.4	7.7	4.1	4.4	4.6	5.6	5.8
200.0	6.9	9.4	10.8	11.3	12.3	13.1	6.5	6.9	7.3	8.6	9.1
300.0	10.0	14.1	16.7	17.9	19.5	20.8	9.4	10.0	10.6	12.5	13.3
400.0	14.5	20.9	24.6	—	—	—	13.4	14.1	15.3	17.6	18.9
500.0	—	—	—	—	—	—	18.7	19.4	21.2	24.7	26.1
Tensile strength at break (kg cm ⁻² %)	18.6/453	25.5/468	27.3/434	22.2/850	25.0/858	22.5/319	25.0/594	23.2/558	23.6/534	30.9/575	28.7/531
Gel content (%)	85.4	91.8	93.5	94.8	95.0	95.7	94.5	94.5	94.5	95.9	95.6
Contact angle (°)	76.0	91.0	94.5	92.5	92.0	89.8	81.8	82.4	87.0	88.6	81.7
Water uptake, W _a (%)	10.2	9.2	8.1	8.2	8.5	9.0	13.6	20.9	25.3	28.2	31.7
Polymer wt. loss in H ₂ O, W _x (%)	0.7	0.2	0.2	0.2	0.2	0.2	0.2	0.4	0.4	0.4	0.6

curing agent for each PU system is reported in Table II.

Mechanical and Physical Properties of Postcured PU Films

Stress and Strain

PU films were cast and air-dried from these prepared PU dispersions at room temperature and then dried at 50°C for 24 h. These PU films were conditioned in a 75% relative humidity (RH) chamber at 25°C for 72 h before the measurement. Each test specimen was formed in a dumb-bell shape with 1.0-mm thickness. The gauge length was 40 mm, and the test was performed at a crosshead speed of 40 mm/min. Six tests of each PU sample were taken, and the three measurements that showed the highest tensile stress for calculating the mean value were selected (Table II).

Gel Content

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

Contact Angle

PU film was cast on a glass plate from the PU dispersions and dried at room temperature. Distilled water droplets on the film surface were used for contact angle measurements at 25°C. The dimensions of the water droplets were measured about 10 s after placing the water droplet. Five measurements of each sample were performed and the three closest results were chosen and averaged for a mean value. Each contact angle value was calculated by the following equation:

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

where h is a 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) dried PU film with a dimension of 60 × 60 × 1 mm was immersed in distilled water bath for 8 days. The towel-wiped dry sample weight (W_1) and oven-dried PU film weight

(W_2) were obtained. Water uptake [W_a (%)] and the weight loss [W_x (%)] of PU film 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 PU film; and

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

where W_x is the amount of PU dissolved in water.

Dynamic Mechanical Thermal Behavior

The PU films were dried at 50°C for 24 h and conditioned in a 75% RH chamber at 25°C for 72 h before testing. Dynamic mechanical analysis (DMA) measurement in bending mode was used for the PU film at a heating rate of 3°C/min from -80 to 150°C at a 1.0-Hz frequency.

Thermogravimetric Analysis

Each dried PU sample (~10 mg) was taken and measured by a thermogravimetric analyzer at a heating rate of 20°C/min from ambient temperature to 500°C under air atmosphere.

Limiting Oxygen Index

ASTM D2863-74 testing procedures for the measurements of limiting oxygen index (L.O.I.) of polymer films were followed and the results were calculated according to the following equation:

$$\text{L.O.I.} = \frac{[\text{O}_2]}{[\text{N}_2] + [\text{O}_2]} \times 100$$

where $[\text{N}_2]$ and $[\text{O}_2]$ are the concentration of nitrogen and oxygen in a mixture of nitrogen and oxygen, respectively.

RESULTS AND DISCUSSION

An anionic aqueous-based PU dispersion was prepared by the water dispersion of an NCO-terminated PU prepolymer by simultaneous neutralization and chain-extension processes. The result was an amino-terminated, aqueous-based PU dispersion with 100 ± 10 nm average particle size,

50 ± 5 mV average zeta potential, and a 30% solid content. PU terminal amino groups were generated by a partial ethylenediamine chain extension and a fractional hydrolysis of NCO-terminated PU prepolymer on the water dispersion stage. Each 100 g of PU dispersion contained 3.8×10^{-3} equivalent amino groups, which were determined by a styrene oxide titration method.³ Since the amino group is reacted with epoxide compound at ambient temperature, a diepoxide compound, therefore, could also work as a separate curing agent for the amino-terminated aqueous-based PU system.⁴⁻⁶

There were 2.2×10^{-2} equivalents of carboxylic ion per 100 g of aqueous-based PU dispersions that were derived from one of the ingredients, that is, dimethylolpropanic acid (DMPA). The carboxylic ion is hydrophilic and resided on the PU particle surface toward the water phase of PU dispersions. Besides, these ionic groups provided surface charges and stabilized aqueous PU dispersions; the carboxylic ions are also the curing sites that reacted with a multi-aziridinyl compound for the aqueous-based PU curing system.^{2,4}

A compound with high phosphorus and nitrogen content could produce a synergistic effect on the flame retardation for polymeric materials,⁷⁻⁹ due to the formation of a condensed phase and a nonflammable gas phase, which are formed, respectively, by their phosphorus and nitrogen compositions and which, in turn, promote the char formation.¹⁶

A series of aziridinyl and phosphorus-containing compounds were synthesized from the substitution reactions of POCl_3 with phenol or ethylene glycol and aziridine, respectively. The resulting compounds had high phosphorus (11.9–19.3%) and nitrogen (10.8–17.4%) contents. The aziridinyl group of these curing agents reacted with PU carboxylic group at ambient temperature.²⁻⁴ This type of phosphorus-containing compounds was introduced into an aqueous-based PU system via a postcuring reaction. Any of these compounds can serve as both a crosslinker and a flame retardant for the PU system. The preparations and the curing behaviors of these dual-function curing agents are discussed in this study.

Syntheses and Characterizations of Tetraaziridinyl Curing Agents: PEGAs

The tetraaziridinyl group and phosphorus-containing curing agents, PEGA-0 and PEGA-2, were synthesized by the substitution reactions of POCl_3 with

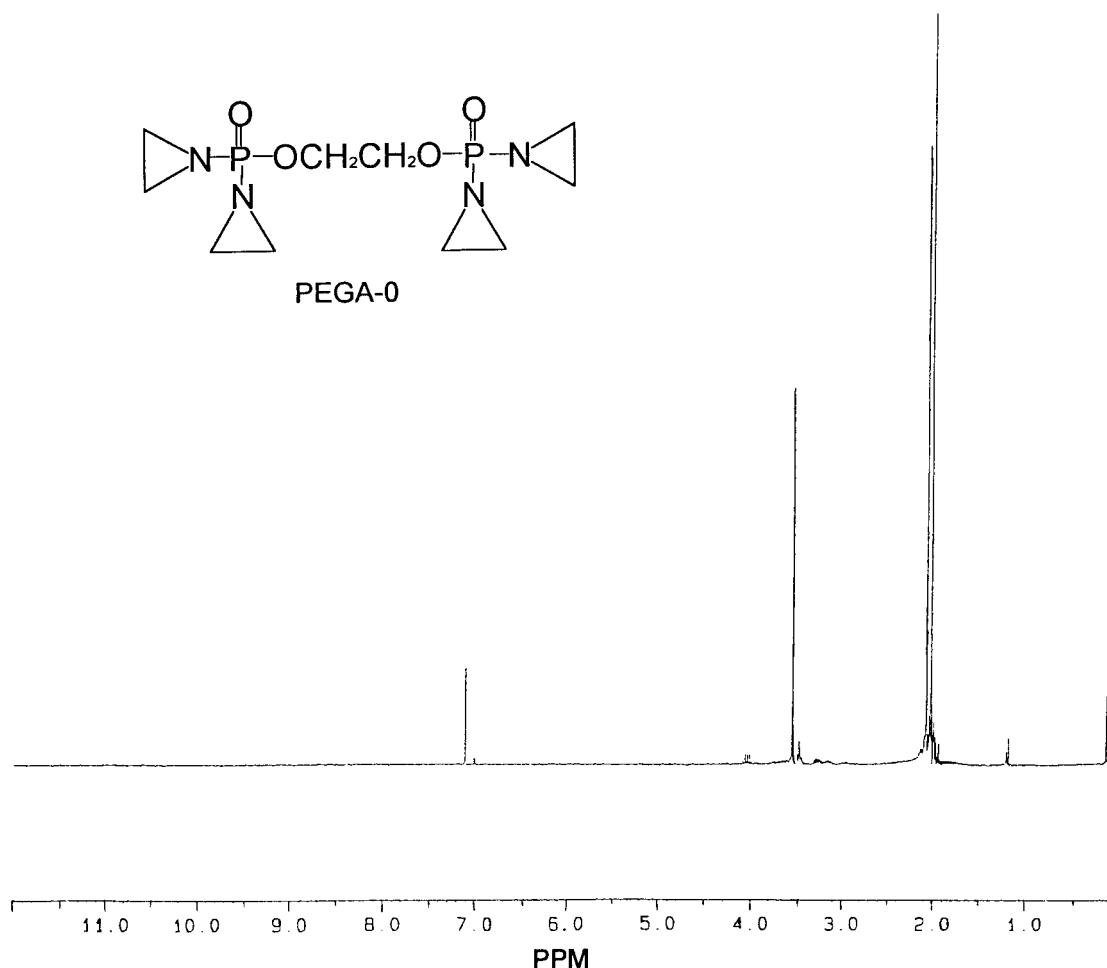


Figure 1 ^1H -NMR spectrum of PEGA-0.

ethylene glycol and then with aziridine and 2,2-dimethylaziridine, respectively (Scheme 1).

From the ^1H -NMR spectrum of PEGA-0 (Fig. 1), the aziridinyl methylene protons shifted from 1.5 to 2.1 ppm and split into two peaks; the methylene protons of ethylene glycol shifted to 3.7 ppm after aziridine and ethylene glycol bonded to phosphorus, respectively. However, 2,2-dimethylaziridinyl methylene protons shifted to 2.0 ppm on PEGA-2. From the ^{13}C -NMR spectrum of PEGA-0, both of the aziridinyl carbons were shifted to 23.8 and 28.9 ppm from 17.9 ppm after aziridine was bonded to a phosphorus-containing compound.

From FTIR spectra of PEGA-0 (Fig. 2) and PEGA-2, it was determined that both had absorption peaks on 1110, 1150, and 1240 cm^{-1} that indicated the existence of P—N, P—O—R, and P=O bond-stretching frequencies, respectively.

The resulting PEGA-0 contained 19.3% phosphorus and 17.4% nitrogen, whereas PEGA-2 contained 14.3% phosphorus and 12.9% nitrogen (Table I).

Syntheses and Characterizations of Diaziridinyl Curing Agents: PHAs

The diaziridinyl group and phosphorus-containing curing agents, PHA-0 and PHA-2, were synthesized by the sequential substitution reactions first with phenol and then with aziridine and 2,2-dimethylaziridine, respectively (Scheme 2).

^1H -NMR spectra of PHA-0 (Fig. 3) indicate that its aziridinyl methylene protons shifted from 1.5 to 2.2 ppm and split into two peaks after aziridine was bonded to phosphorus, whereas 2,2-dimethylaziridinyl methyl protons of PHA-2 shifted from 1.2 to 1.4 ppm.

On the ^{13}C -NMR spectrum of PHA-0, the aziridinyl methylene carbons shifted to 24.3 and 24.4 from 17.9 ppm. There were three sets of phenolic carbons that shifted, respectively, from 115.3, 120.7, and 129.6 ppm to 120.5, 124.2, and 129.3 ppm after POCl_3 was substi-

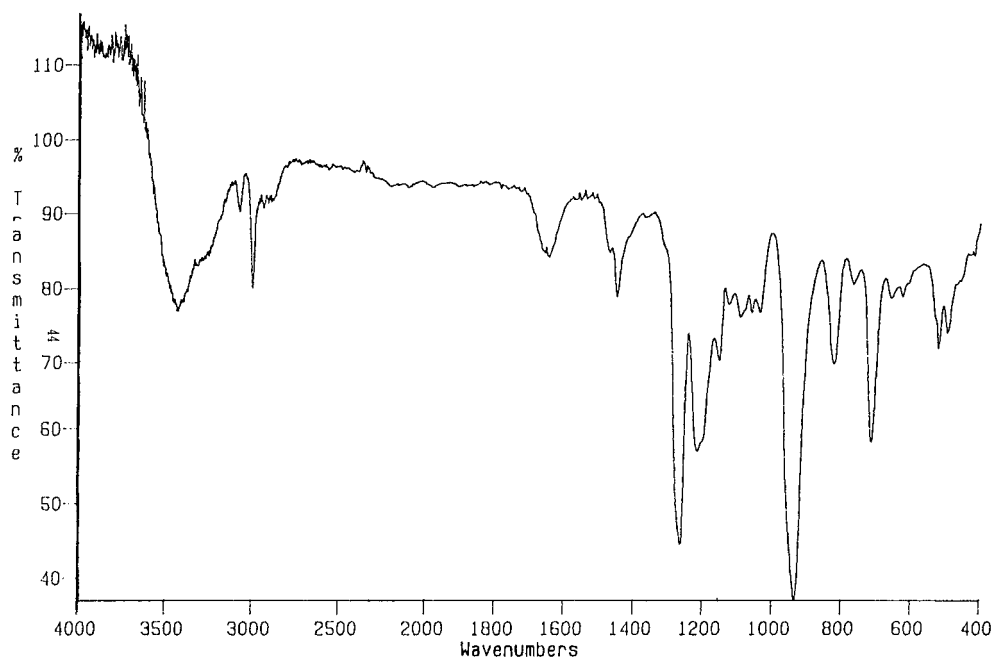
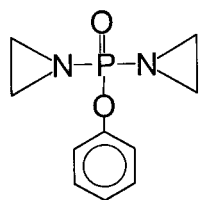


Figure 2 FTIR spectrum of PEGA-0.

tuted by phenol. Both PHA-0 and PHA-2 had a single peak on -0.4 ppm on each individual ^{31}P -NMR spectrum.

The resulting PHA-0 contains 13.8% phosphorus and 12.5% nitrogen, whereas PHA-2 contains 11.9% phosphorus and 10.8% nitrogen.



PHA-0

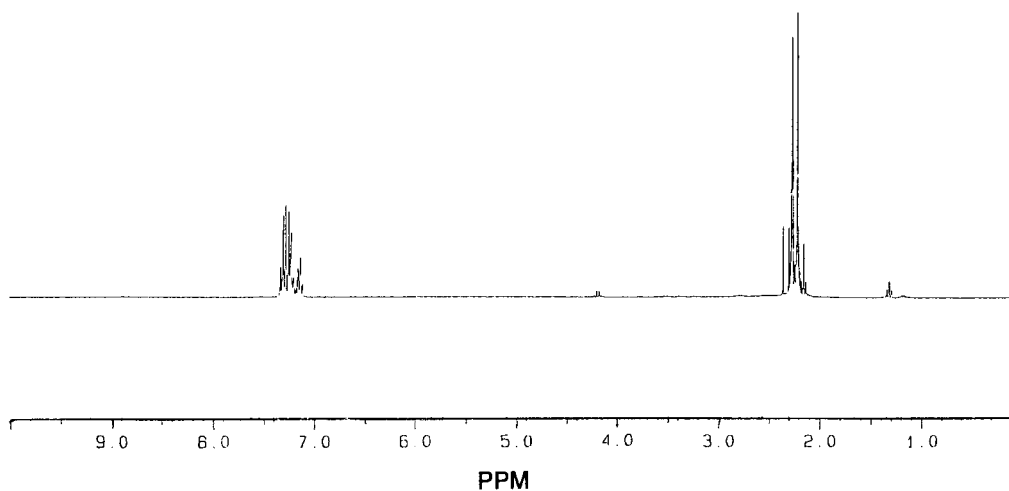


Figure 3 ^1H -NMR spectrum of PHA-0.

Properties of Postcured PU System

Gel Content

For the PU curing system with tetra-functional PEGAs, the cured PU gel content increased from the original 85.4% to 95.6% after PU was treated with 5.9 phr PEGA-0; it had an equal equivalent number of aziridinyl and carboxyl groups ($[\text{aziridinyl}]/[\text{carboxyl}] = 1.0$). Whereas PU gel content was 93.0% with 8.0 phr PEGA-2, the PU curing system also had an equal equivalent number of 2,2-dimethylaziridinyl and carboxyl groups; the 2,2-dimethylaziridinyl group nonetheless had more steric hindrance and less reactivity toward the PU carboxyl group than the aziridinyl group on PEGA-0.

For the PU curing system with di-functional PHAs, the cured PU gel content was 94.8% after aqueous-based PU was treated with 8.0 phr PHA-0. This curing system had an equal equivalent number of aziridinyl and carboxyl groups ($[\text{aziridinyl}]/[\text{carboxyl}] = 1.0$). In a similar case, 9.6 phr PHA-2 curing agent was applied and the resulting PU had 94.1% gel content (Table II). There was about a 10% increment on the polymer gel content that was due to the crosslinking reaction that took place between this curing agent and the aqueous-based PU system.

Contact Angle

A higher contact angle on the PU film surface indicated a more hydrophobic polymer character, which was the result of a higher crosslinking polymer density. The contact angle of the original PU was 76.0°, which increased to 87.7 and 82.8° after PU was treated with 5.9 and 8.0 phr (an equal equivalent number of aziridinyl and PU carboxyl groups) of PEGA-0 and PEGA-2, respectively. Its contact angle reached 92.9° after PU was treated with 8.9 phr PEGA-0.

The curing pattern for PHA-0 and PHA-2 was similar, in that after aqueous-based PU was cured by 8.2 phr PHA-0 or 9.6 phr PHA-2, its contact angle increased to 92.5 and 87.0°, respectively. Because of the hydrophilic homopolymer formation from an excess amount of curing agent, the contact angle on cured PU reached a maximum value and then dropped by further increasing the curing dosage (Table II).

Water Uptake

A polymer with a higher water uptake indicated a higher hydrophilic character with a less molecu-

lar network. The original PU had 10.2% water uptake, which changed to 8.2% after PU was treated with 8.2 phr PHA-0; the cured PU, however, had 25.3% water uptake after it was cured with 9.6 phr PHA-2. The curing system with the di-functional aziridinyl group (i.e., the 2,2-dimethylaziridinyl group) on PHA-2, however, is less reactive than the aziridinyl group on PHA-0, due to its steric hindrance. A hydrophilic homopolymer formation resulted from the remaining unreacted 2,2-dimethylaziridinyl groups² on PHA-2. Therefore, the PU curing system with PHA-2 had a higher water uptake than the PU curing system with PHA-0 (Table II). These phenomena were also observed on the PU curing system with PEGA-2. For example, the PU cured with 8.0 phr PEGA-0 and PEGA-2 produced, respectively, 13.3 and 26.9% water uptake.

Mechanical Properties

The tensile strength of an aqueous-based PU system was 24.6 kg/cm² at 452% elongation, and it increased to 34.3 kg/cm² at 509% elongation after the PU was treated with 8.0 phr PEGA-2. The PU tensile strength decreased with a further increase of PEGA-2 curing dosage. For example, the tensile strength of PU cured with 16.0 phr of PEGA-2 decreased to 21.8 kg/cm² at 451% elongation.

The resulting PU curing system with di-functional PHA-0 or PHA-2 had a slight change on its tensile stress. For example, the tensile stress of the original PU was 10.0 kg/cm² at 300% elongation, which increased to 17.9 kg/cm² after PU was cured by 8.2 phr PHA-0. The tensile stress of the PHA-2-cured PU system decreased to 10.6 kg/cm² at 300% after PU was treated with 9.6 phr PHA-2 (with an equal equivalent number of PHA-0). Because of the less reactive 2,2-dimethylaziridinyl groups of PEGA-2 and PHA-2, curing agents in the PU curing system could form homopolymers, resulting in a less polymeric crosslinking density.

Flammability and Thermal Behavior

The limiting oxygen index (L.O.I.) test determines the relative flammability of polymer by measuring the minimum oxygen concentration that just supports combustion of a sample. The sample with a higher L.O.I. value indicates a lesser flammability of the material. A phosphorus-containing curing agent was introduced into the aqueous-based PU as a reactive flame retardant via a postcuring reaction. The original aque-

Table III Flame Retardancy of PU with Dual-Function Curing Agents

Properties	PU with Curing Agent				
	PU	PHA-0	PHA-2	PEGA-0	PEGA-2
Dosage (phr) ^a	—	8.2	9.6	5.9	8.0
Phosphorus %	—	1.13	1.14	1.14	1.14
Nitrogen %	4.67	5.70 ^b	5.71 ^b	5.71 ^b	5.71
L.O.I.	22.0	26.6	26.8	27.2	27.0
Char yield (%) ^c	1.0	8.1	8.2	8.0	8.2

^a Dosage of curing agent based on the same equivalent ratio of two reactive groups ([aziridinyl]/[carboxylic] = 1) per 100 g of PU.

^b Nitrogen contents in cured PU indicated the total nitrogen of PU with curing agent.

^c Char yield of polymer on 500°C under air atmosphere.

ous-based PU contained 4.67% nitrogen and its L.O.I. was 22.0, which increased to 27.2 after PU was cured by 5.9 phr PEGA-0; the L.O.I. increased to 27.0 after PU was treated with 8.0 phr PEGA-2. Both PU curing systems contained 1.13% phosphorus and 1.03% nitrogen, introduced into PU by the postcuring reaction. The L.O.I. of PU curing systems with 8.2 phr PHA-0 and 9.6 phr PHA-2 were 26.6 and 26.8, respectively (Table III). When this final cured PU sample was burned at high temperature, its phosphorus content could form a condensed phase,

whereas its nitrogen content could generate a nonflammable gas phase. There was a synergy between phosphorus and nitrogen on the flame inhibition for this postcured PU sample.

An increase in the use of PEGA-0 or PEGA-2 resulted in a higher storage modulus of the cured PU than the original PU (Fig. 4). Aqueous-based PU was cured with various dosages of PHA-0 or PHA-2, which resulted in a lower damping peak intensity than the original PU because of the the increase of PU crosslinking density. When PU was treated with 1.0 phr diepoxide compound

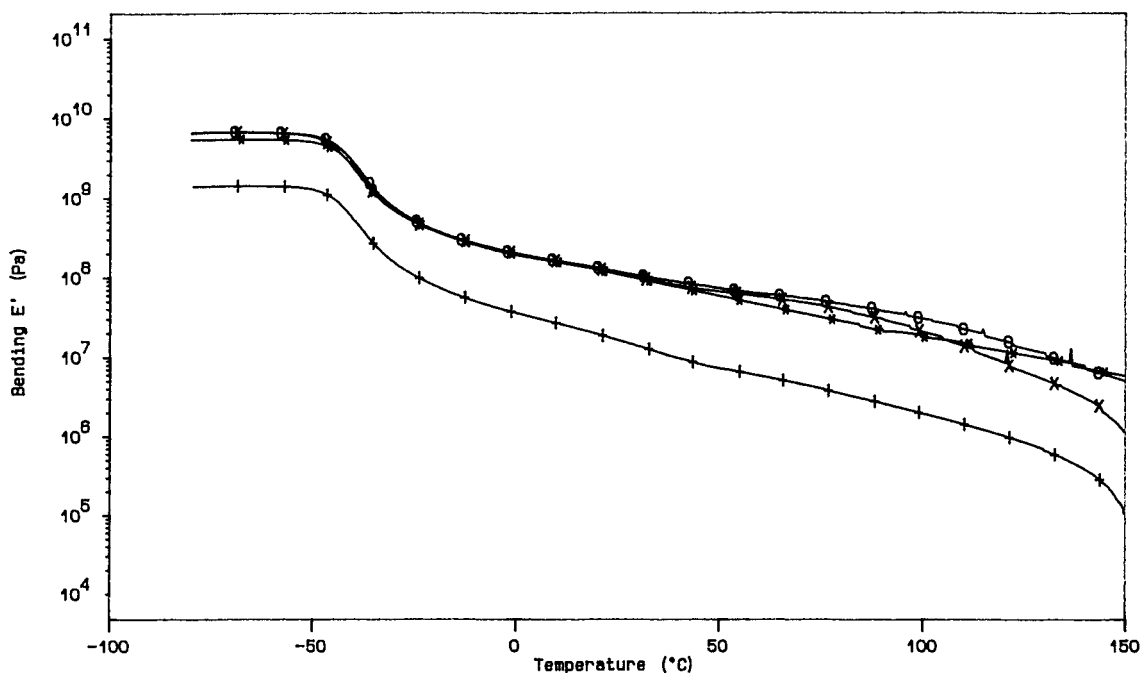


Figure 4 Storage moduli of PU with various dosages of PEGA-2: (a) original PU (+); (b) with 1.2 phr PEGA-2 (x); (c) with 8.0 phr PEGA-2 (o); and (d) with 14.8 phr PEGA-2 (*).

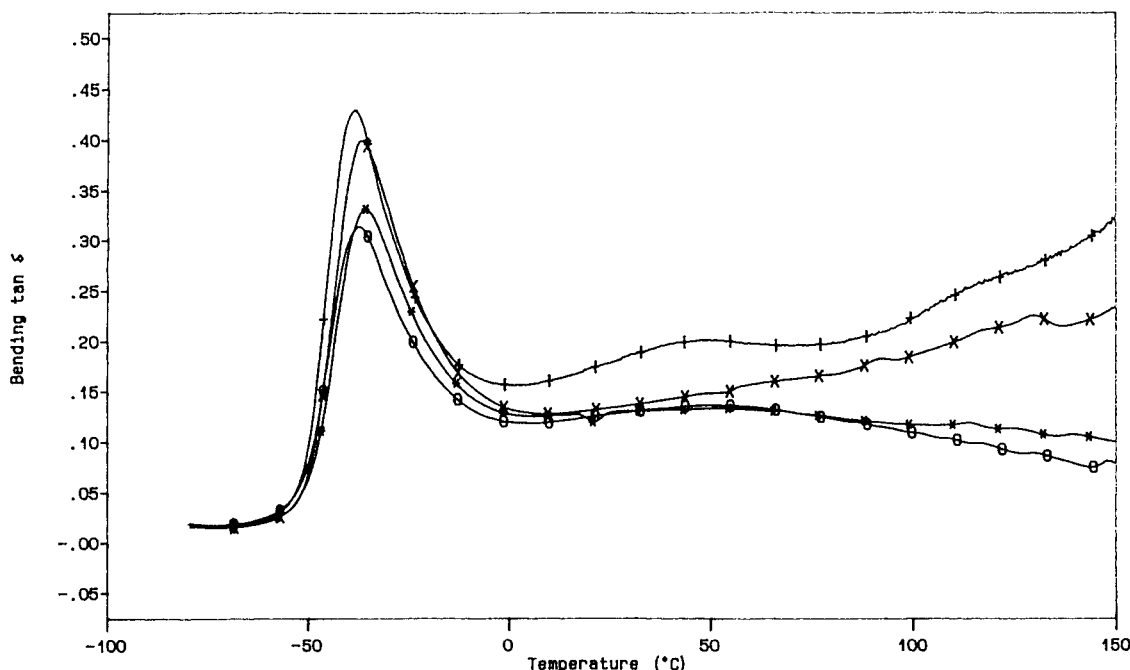


Figure 5 Damping curves of PU with PHA-0 and/or with diepoxide compound: (a) original PU (+); (b) with 8.2 phr PHA-0 (×); (c) with 1.0 phr diepoxide (*); and (d) with 8.2 phr PHA-0 and 1.0 phr diepoxide (○).

(NPEW-254) and then with 8.2 PHA-0 as a dual-curing agent, the resulting PU exhibited a lower damping peak intensity among the respective DMA damping curves (Fig. 5), because this type of dual-cured PU had a higher crosslinking density with a lower molecular mobility than the original PU or the others.

Original aqueous-based PU exhibited a weight loss of 45% at 350°C on its thermogravi-

metric analysis (TGA). The final cured PU exhibited weight losses of 26.0, 24.0, and 26.0% at 350°C on their TGA thermograms after it was cured with PHA-0, PHA-2, and PEGA-2 (8.2, 9.6, and 8.0 phr), respectively. These TGA data indicated that the better polymer thermal stability resulted from the higher polymeric crosslinking density by this type of postcuring. Furthermore, the char yields of the cured PU increased to 8.0–8.2% (Table IV), and these higher char yields correlated to the higher L.O.I. value of the polymer material.^{16,17}

Table IV PU Weight Loss on Thermogravimetric Analysis^a

Temperature (°C) ^b	Weight Loss (%)			
	PU with Curing Agent			
	PU	PHA-0	PHA-2	PEGA-2
250	3.0	1.5	2.0	2.5
300	11.0	6.0	8.0	8.5
350	45.0	26.0	24.0	26.0
400	92.0	89.5	88.5	88.0
450	97.5	91.0	91.8	92.0

^a PU were cured with 8.2, 9.6, and 8.0 phr of PHA-0, PHA-2, and PEGA-2, respectively.

^b Polymer was heated under air atmosphere.

CONCLUSIONS

A series of multi-aziridinyl and phosphorus-containing dual-function curing agents were synthesized by the substitution reactions of POCl_3 , first with ethylene glycol or phenol and then with aziridines. Each of them was added to serve as a latent curing agent and its aziridinyl group was reactive toward the aqueous PU carboxyl group at ambient temperature. The covalently bonded phosphorus PU system was introduced in order to promote its flame-inhibition property via this type of postcuring reaction.

The PU curing system was carried out with two equal equivalent numbers of two reactive groups ([aziridinyl]/[carboxyl] = 1), which improved its physical, mechanical, and thermal properties. The limiting oxygen index (L.O.I.) of PU was also increased to 26.6 or higher. This result is realized by the introduction of aziridinyl groups and a phosphorus-containing curing agent via this type of postcuring reaction. Each of these prepared compounds simultaneously served a dual-function, as both a curing agent and a reactive flame retardant for the aqueous-based PU system.

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