

# Curing and Combustion Properties of a PU-Coating System with UV-Reactive Phosphazene

WOEI-KAE HUANG,<sup>1</sup> KWEI-JU CHEN,<sup>1</sup> JEN-TAUT YEH,<sup>2</sup> KAN-NAN CHEN<sup>1</sup>

<sup>1</sup> Department of Chemistry, Tamkang University, Tamsui 251, Taiwan

<sup>2</sup> Graduate Institute of Textile and Polymer Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan

Received 10 April 2000; accepted 8 October 2001

**ABSTRACT:** A UV-curable polyurethane (PU)-coating system containing phosphorus is formulated by the combination of photoinitiator, PU acrylate oligomer, and UV-reactive phosphazene monomer. PU acrylate oligomer is prepared by the addition of 2-hydroxyethylmethacrylate (HEMA) to NCO-terminated PU prepolymer. UV-reactive phosphazene monomer is derived from the HEMA substitution reaction to hexachlorocyclotriphosphazene (N<sub>3</sub>PCl<sub>2</sub>)<sub>3</sub>. The curing reaction of this PU-coating system is carried out by UV irradiation. The resultant UV-cured PU-coated films demonstrated better performance properties than those of original UV-cured PU acrylate (UV-PU) without UV-reactive phosphazene monomer. Furthermore, their thermal properties are investigated by a thermogravimetric analyzer and a dynamic mechanical thermal analyzer, respectively. The combustion behaviors of these UV-cured PU-coated films are evaluated by the measurements of a limiting oxygen index and a cone calorimeter. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1980–1991, 2002

**Key words:** PU; UV-reactive phosphazene; UV curing; combustion; cone calorimetry

## INTRODUCTION

Polyurethanes (PUs) have wide applications, such as coating, adhesive, sealant, elastomer, because of certain properties, which can be adjusted with various ingredients, materials, and processes.

PU is one of the best choices for coating applications. Although the coating technology for solvent-based PU resin was well established during last three decades, the restriction from both environmental and safety regulations are becoming tighter than ever. Therefore, aqueous-based and other nonsolvent-based PU resins have become

increasingly important.<sup>1–4</sup> Among those solvent-free PU resins, UV-curable PU resin is one of the substitutes for conventional solvent-based PU-coating applications. Because polymer drying is performed simply by UV irradiation with no volatile solvent emission, UV curing is considered an environmentally friendly process.

The polymer containing phosphorus is accepted for nonflammable coating applications.<sup>5</sup> Nonflammable polymer with organic phosphorus flame retardant is required for clear-coating applications. There are two methods to bring organic phosphorus composition into polymeric materials: physical blending<sup>5,6</sup> and chemical reaction.<sup>7–15</sup> The former is limited by the blending compatibility<sup>5</sup> and the latter has been reported in the literature.<sup>13</sup> In recent years, we utilized an aziridine and phosphorus-containing compound

Correspondence to: K.-N. Chen (knchen@mail.tku.edu.tw).  
Contract grant sponsor: National Science Council of the Republic of China.

*Journal of Applied Polymer Science*, Vol. 85, 1980–1991 (2002)  
© 2002 Wiley Periodicals, Inc.

to serve both as a curing agent<sup>7-9</sup> and as a flame retardant<sup>16</sup> for aqueous-based PU resin. The resultant PU resins exhibit higher thermal stability and better flame-retardation properties than those of the plain PU resin because of the phosphorus-containing crosslinkages formation among PU backbones. Aziridinyl phosphazene, which comprises phosphorus and multi-aziridinyl group for aqueous-based PU-curing system, is a good example.<sup>16</sup> This PU-curing system needs only a small phosphazene-curing dosage to achieve its improved performance.

UV-curing reaction with a UV-reactive monomer containing phosphorus is a convenient process of introducing covalent-bonded phosphorus into polymer. This UV-curable PU-coating system comprised a photoinitiator, PU acrylate oligomer, and UV-reactive phosphazene acrylate (NPHE) monomer. PU acrylate oligomer is a UV-curable PU resin containing acrylate-terminal groups. It is synthesized by the addition reaction of 2-hydroxyethyl-methacrylate (HEMA) to a conventional NCO-terminated PU prepolymer. NPHE monomer consists of multiacrylate and a high content (10.2%) of phosphorus. It is employed as a flame retardant, a UV-reactive diluent, and a crosslinker, simultaneously in this PU-coating system. NPHE is prepared by HEMA-substitution reaction to hexachlorocyclotriphosphazene ( $\text{NPCl}_2)_3$ . These UV-cured PU (NPHE-PU) films are obtained from PU acrylate oligomer, photoinitiator, and various dosages of NPHE by UV irradiation. The curing properties and the combustion behaviors of these NPHE-PU films will be discussed in this article.

## EXPERIMENTAL

### Materials

HEMA was supplied from Aldrich Chemical Co.  $(\text{NPCl}_2)_3$  was obtained as a gift from Dr. Y.-S. Chu's Laboratory, Chung-Shan Science Research Institute, Long-tan, Taiwan; THF and photoinitiator, Merck 1173, were supplied from Merck Co. Propylene glycol-2000 (PPG-2000) was obtained from Arco Chemical Co. These materials were dried and distilled or recrystallized before using. Isophorone diisocyanate (IPDI) was supplied from Huls Co. and used as received without further purification.

### Preparation of UV-Curable PU Acrylate Oligomer<sup>1</sup>

PPG-2000 (0.1 mol) was dried overnight at 110°C before mixing with IPDI (0.15 mol) in a 500-mL

four-necked resin flask. The reaction was carried out and kept at 90°C for 4 h with agitation under nitrogen atmosphere until the NCO content dropped below 3.0%. It became a NCO-terminated PU prepolymer at this stage. Then, a known weight of HEMA was added into it, which was based on the equivalent ratio (HEMA/NCO = 1.1/1.0). The reaction took place at 90°C until the NCO absorption peak ( $2230\text{ cm}^{-1}$ ) disappeared on the IR spectrum of the reaction mixture. The obtained material was a HEMA-terminated PU oligomer or was called UV-curable PU acrylate oligomer hereafter (Scheme I).

### Preparation of 2,2,4,4,6,6-Hexakis(2-oxethylmethacrylato)cyclotriphosphazene

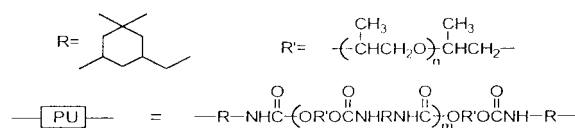
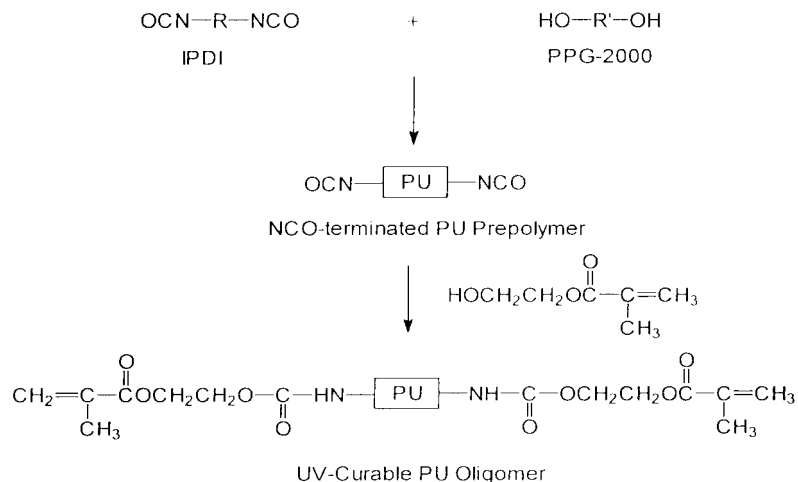
A 100-mL THF solution consisting of freshly distilled HEMA (0.18 mol), triethylamine (0.18 mol), and cuprous chloride (0.1 g) was placed into a 500-mL three-necked flask in an ice bath. A 100-mL THF solution of  $(\text{NPCl}_2)_3$  (0.02 mol) was added slowly through a dropping funnel. The reaction mixture was kept agitated in an ice bath and then at ambient temperature for 3 h under nitrogen atmosphere. The white triethylamine hydrochloride salt was filtered out from the reaction mixture. The residue was collected after THF was removed from the filtrate and then was chromatographed with a silica gel column by THF as an eluant. NPHE was isolated with 83% yield (Scheme II).

### UV-Cured PU Film (NPHE)

The UV-curable PU system was formulated by a photoinitiator (Merck 1173) (1 phr), PU acrylate oligomer (100 phr), and NPHE monomer in various dosages (10, 20, and 40 phr, respectively). The UV-curable PU-coating system was cast on a glass plate with  $1.4 \pm 0.2$  mm thickness and then UV irradiated (by a medium-pressure mercury lamp with 1000 W power output) for 15 s. The resulted UV-cured PU films (NPHE) were conditioned in a 75% relative humidity chamber at 25°C for 72 h before measurements.

### Mechanical and Physical Properties of NPHE Film

Dumbbell-shaped specimens with 1.0 mm thickness were used to determine the tensile properties of the NPHE films. The tensile experiments were performed on a Shimadzu Universal Testing Machine model Autograph S-100-C. The test was performed at a crosshead speed of 40 mm/min and



**Scheme 1** Preparation of UV-curable PU oligomer.

a gauge length of 40 mm. Six results of each PU sample were taken, and the three measurements that showed the highest tensile strength for calculating the mean value were selected.

### Gel Content

A known weight of UV-cured PU film was put into a Soxhlet extractor for a continuous 24-h extraction with THF. The polymer gel remaining after extraction was dried and calculated on the basis of the test results. Gel contents of the cured PU films are shown in Table I.

### Ethanol Swollen

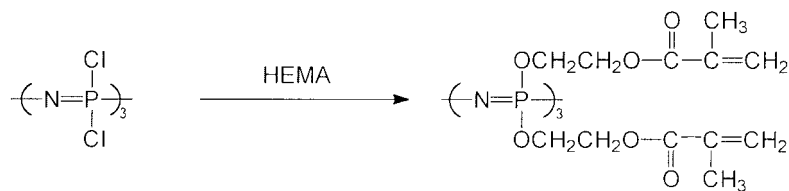
A known weight ( $W_0$ ) of UV-cured PU film with a dimension of  $60 \times 60 \times 1$  mm was immersed in

ethanol (95%) bath for 48 h. The towel-wiped dry sample weight ( $W_1$ ) and the oven-dried PU film weight ( $W_2$ ) were obtained. Ethanol absorption ( $W_e\%$ ) and weight loss ( $W_y\%$ ) of PU film in ethanol were calculated according to the following equations, respectively:

$$W_e\% = \frac{W_1 - W_2}{W_2} \times 100\%$$

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

where  $W_e$  is the amount of ethanol absorption by PU film and  $W_y$  is the amount of PU dissolved in ethanol.



Hexachlorocyclotriphosphazene

NPHE

**Scheme 2** Preparation of NPHE.

**Table I Performance Properties of NPHE-PU Films**

Properties	UV-PU <sup>b</sup>	NPHE-PU <sup>a</sup>		
		10	20	40
		NPHE (phr)		
Tensile strength and elongation at break (kg cm <sup>-2</sup> /%)	3.6/295	6.5/220	7.8/165	7.5/70
Gel content (%)	89.5	90.0	91.4	90.2
Ethanol uptake ( $W_e$ %)	297.2	198.2	127.7	60.8
Polymer wt. loss in ethanol ( $w_s$ %)	9.8	7.5	7.9	9.4
L. O. I.	22	24	25	27

<sup>a</sup> NPHE-PU represents UV-curable PU oligomer (100 phr) with 10.200 and 40 phr of UV-reactive NPHE, respectively, and is cured by UV irradiation.

<sup>b</sup> UV-PU indicates UV-curable PU is cured by UV irradiation without NPHE.

### Energy Dispersion Spectroscopy

A smooth cross section of PU film was conditioned in an oven at 50°C overnight. Each NPHE-PU film was irradiated with a 20-kV electron beam and phosphorus composition on the film was excited and emitted X-ray fluorescence. This X-ray fluorescence was detected and assigned to the location of phosphorus on NPHE-PU film.

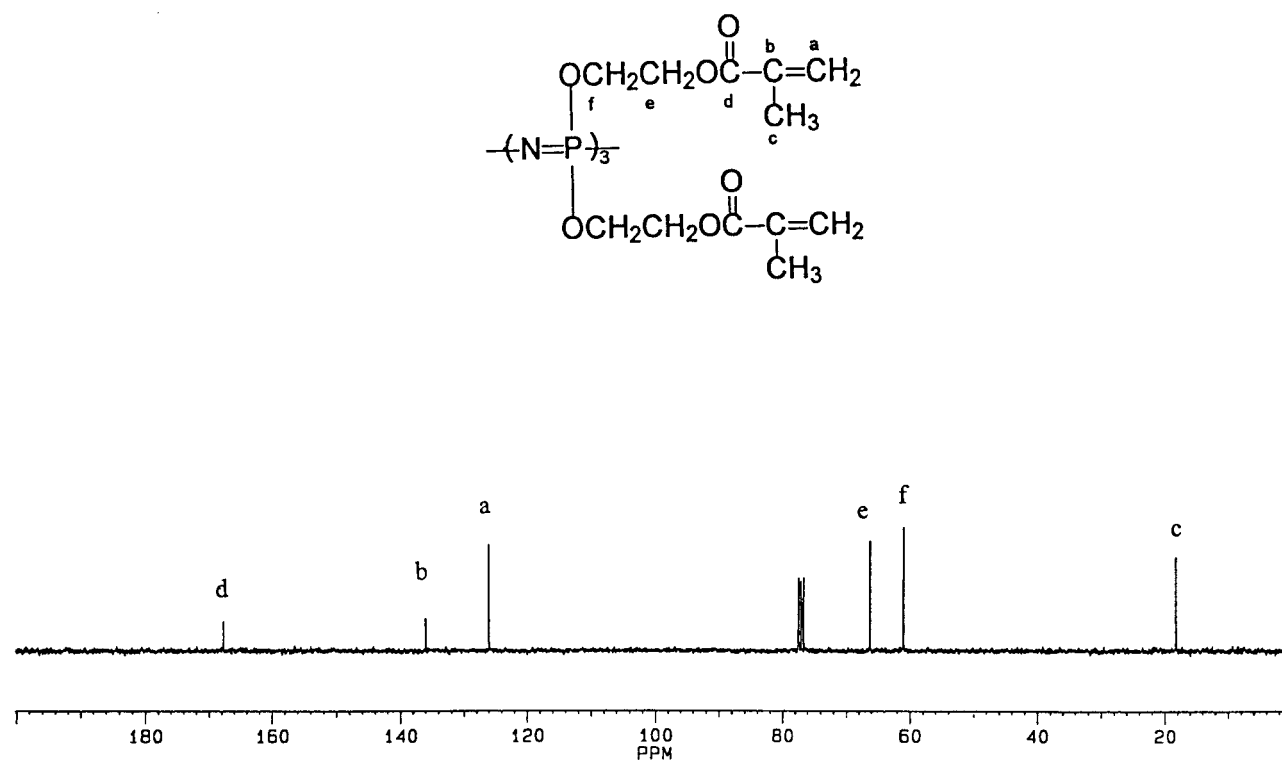
### Dynamic Mechanical Thermal Behavior

Each PU film was performed on a Polymer Laboratories dynamic mechanical thermal analyzer

(DMTA) instrument model MK-II. All the measurements were tested in bending mode at temperatures ranging from -80 to 150°C, 1.0 Hz frequency, and a heating rate of 3°C/min.

### Thermogravimetric Analysis

Each UV-cured PU sample (~ 10 mg) was taken and measured by a TA thermogravimetric analyzer model Hi-Resolution 2950 with a heating rate of 10°C/min from ambient temperature to 500°C under air and nitrogen atmosphere, respectively.


**Figure 1** <sup>13</sup>C-NMR spectrum of NPHE

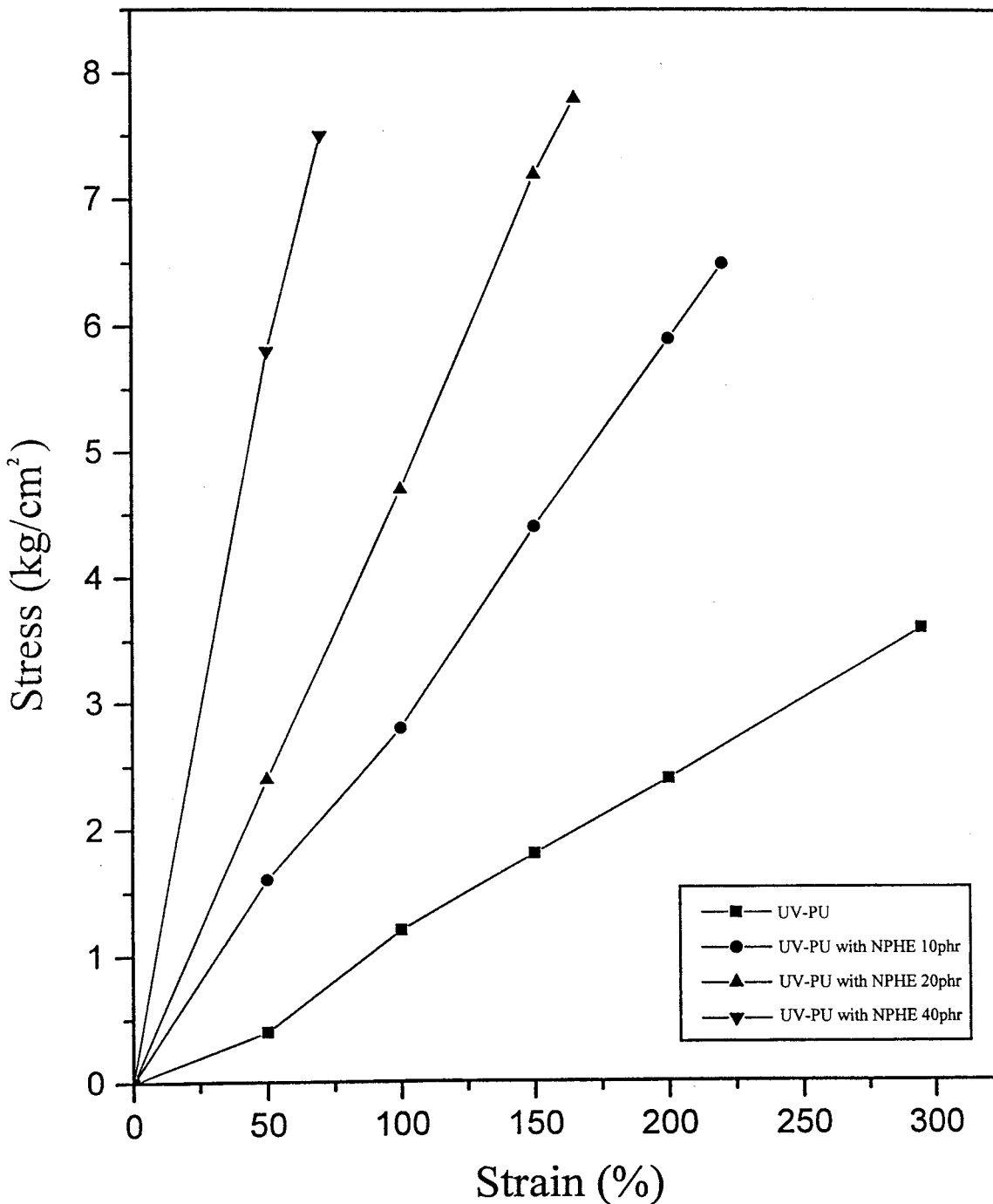


Figure 2 Stress-strain curves of UV-PU and NPHE-PU films.

**Limiting Oxygen Index**

The measurements of limiting oxygen index (L.O.I.) of PU films were performed on a Fire Testing Laboratories instrument. The specimen dimension was 15 × 50 cm and 1.2 mm thick. The values were determined as suggested by ASTM D 2863-74 by the following equation:

$$L. O. I. = \frac{[O_2]}{[N_2] + [O_2]} \times 100\%$$

where [N<sub>2</sub>] and [O<sub>2</sub>] are the concentration of nitrogen and oxygen in the gas mixture, respectively.

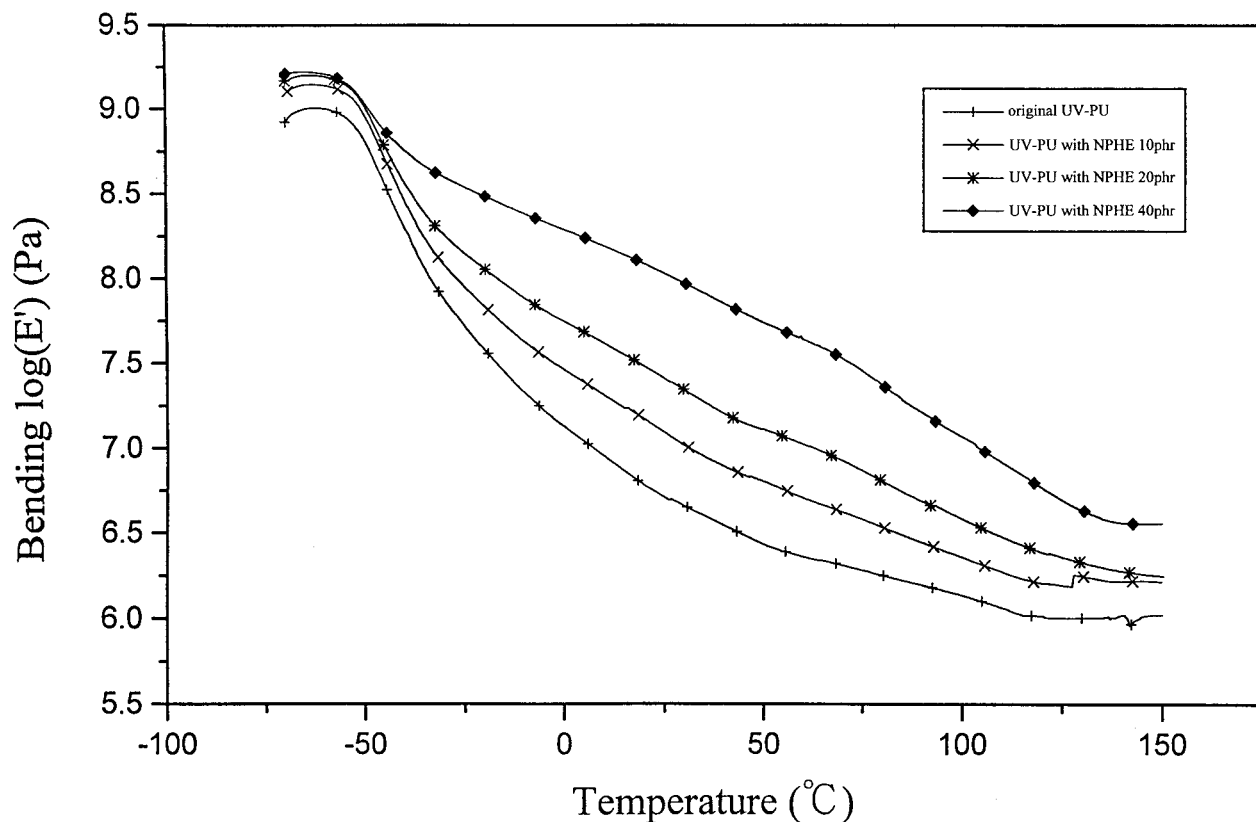


Figure 3 Storage moduli of NPHE-PU on DMTA.

### Cone Calorimeter Measurement

The combustion measurements were carried out according to ISO 5660 on a cone calorimeter from Fire Testing Laboratories Ltd. The specimen dimension was  $10 \times 10$  cm and 1.2 mm thickness. Triplicate tests were performed for the measurement of the heat release rate and a time to ignition at a heat flux of  $30 \text{ kW/m}^2$ .

## RESULTS AND DISCUSSION

UV-curable PU-coating system consists of PU acrylate oligomer, photoinitiator, and UV-reactive phosphazene acrylate monomer. PU acrylate oligomer was obtained from the addition of HEMA to NCO-terminated PU prepolymer (Scheme I). Another important ingredient of this coating system was UV-reactive phosphazene acrylate monomer, NPHE. It was prepared by the substitution to  $(\text{NPCl}_2)_3$  with HEMA (Scheme II). NPHE was a multifunctional monomer simultaneously serving as the flame retardant, the UV-reactive diluent, and the crosslinker for this coating system. UV-

cured PU (NPHE-PU) films were obtained from this PU-coating system with various curing dosages of NPHE by the UV irradiation. The curing properties and the combustion behaviors of these NPHE-PU and UV-cured PU without NPHE (UV-PU) films were evaluated in this article.

### Characterization of NPHE

The absorption peaks in the FTIR spectrum of NPHE indicated the presence of acrylic ester  $\text{C}=\text{O}$  stretching at  $1719 \text{ cm}^{-1}$  and acrylic  $\text{C}=\text{C}$  stretching at  $1637 \text{ cm}^{-1}$ . The HEMA-substituted  $\text{P}=\text{N}$  absorption frequency of phosphazene shifted to  $1244 \text{ cm}^{-1}$  from  $1172 \text{ cm}^{-1}$  of original phosphazene on FTIR spectrum.

The chemical shifts of  $^1\text{H-NMR}$  spectrum for methyl and methylene of HEMA in NPHE were 1.8, 3.7, and 4.2 ppm, respectively, whereas its  $^{13}\text{C-NMR}$  spectrum of NPHE (Fig. 1) exhibited the chemical shifts of methyl carbon at 18.5 ppm, two methylene carbons at 61.0 and 66.5 ppm, two vinyl carbons at 126.1 and 156.0 ppm, and carbonyl carbon at 168.0 ppm.

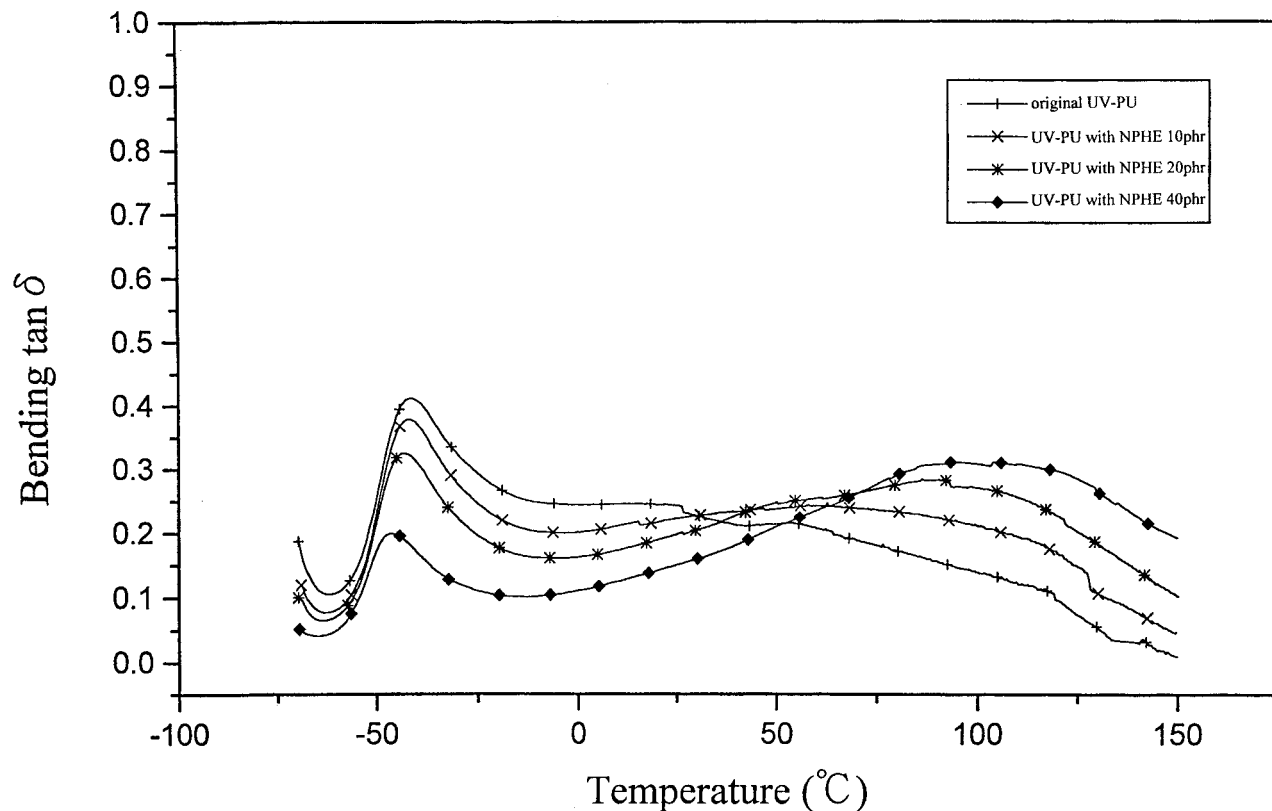


Figure 4  $\tan \delta$  of NPHE-PU on DMTA.

### Physical and Mechanical Properties

NPHE-PU film consisting of 10, 20, or 40 phr NPHE dosage had a gel content from 90.0 to 91.4%, whereas the original UV-PU (without NPHE) was 89.5%. These gel contents indicated that the NPHE was incorporated into the PU-coated film in the process of UV-curing reaction. Ethanol swollen of the PU-coated film decreased from 297.2% of the original UV-PU to 198.2, 127.7, and 60.8% of NPHE-PU films with 10, 20, and 40 phr NPHE, respectively (Table I). These changes in swollen ethanol were caused by the increment of the crosslinking density of NPHE-PU film, which was built by increasing NPHE crosslinker dosage.

The distribution of phosphorus in NPHE-PU film was observed on the energy dispersion spectra (EDS) by phosphorus mapping. The phosphorus composition was distributed evenly to NPHE-PU film of a dosage of 10, 20, or 40 phr NPHE. This phenomenon indicated that NPHE was compatible with the UV-curable PU-coating system in various dosages upon UV curing.

The tensile stress was  $1.2 \text{ kg cm}^{-2}$  at 100% elongation of the original UV-PU film. The tensile

stress can be increased to 2.8 or  $4.7 \text{ kg cm}^{-2}$  in NPHE-PU film, depending on a dosage of 10 or 20 phr NPHE. Furthermore, the tensile strength at break changed from  $3.6 \text{ kg cm}^{-2}$  at 295% elongation of UV-PU to 6.5, 7.8, or  $7.5 \text{ kg cm}^{-2}$ , respectively, at 220, 165, or 70% elongation in NPHE-PU film on the dosage of 10, 20, or 40 phr NPHE (Fig. 2). The tensile stress increased because of the increase in polymeric network formation in NPHE-PU film upon UV irradiation with an increase in NPHE-curing dosage.

### Thermal Properties

The storage modulus of original UV-PU film was lower than that of NPHE-PU film, as testified by a DMTA. The intensity of  $\tan \delta$  value of original UV-PU was higher than that of NPHE-PU films. The storage modulus was increased and its  $\tan \delta$  value was decreased with increase in NPHE-curing dosage (Figs. 3 and 4). This phenomenon resulted from the restricted polymer mobility with the smaller free volume on the NPHE-PU films.

The initial decomposition temperature (with 5% weight loss) of UV-PU was  $270^\circ\text{C}$ , as shown by

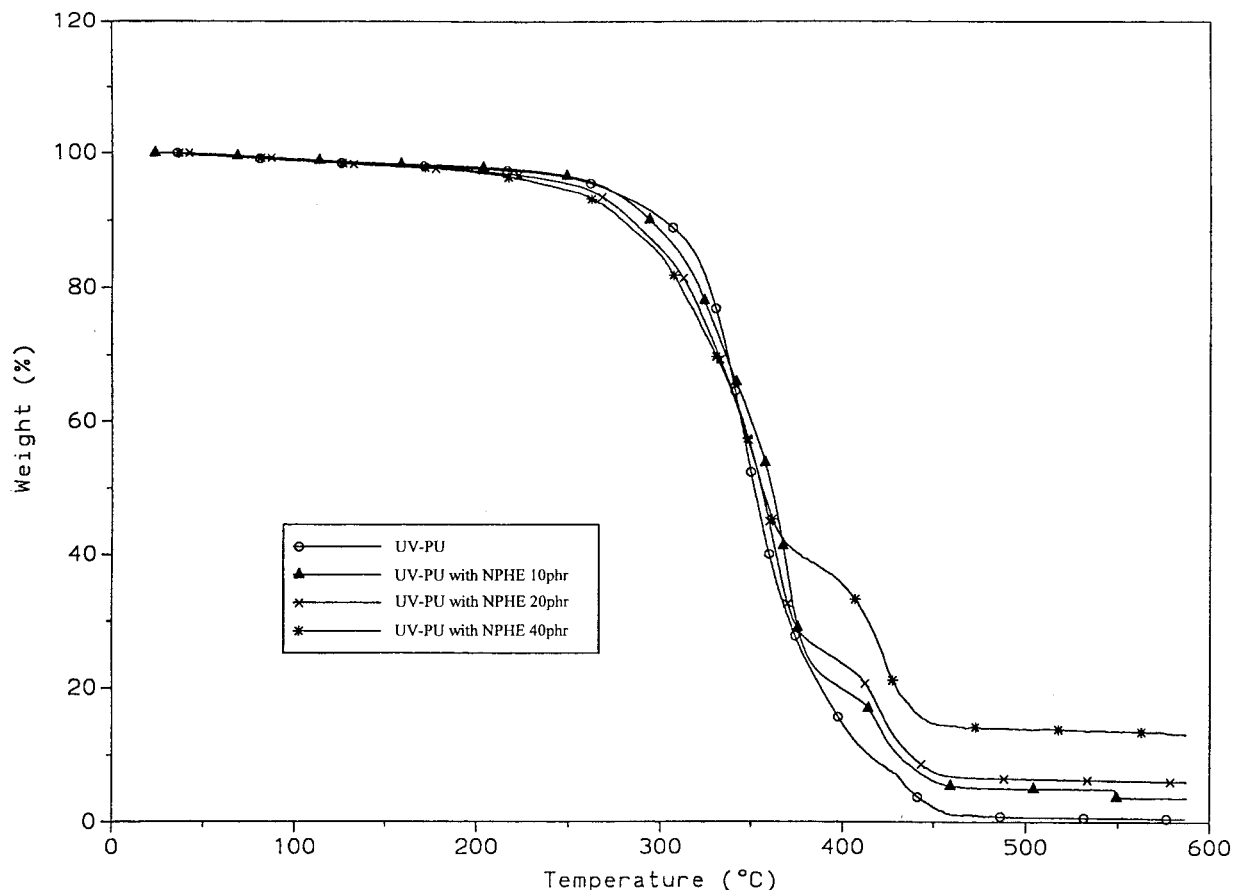


Figure 5 TGA thermogram of NPHE-PU under nitrogen.

thermogravimetric analysis (TGA), whereas that of NPHE-PU film was as low as 268, 255, or 241°C depending on 10, 20, or 40 phr curing dosages in the nitrogen atmosphere (Fig. 5). The decrease in initial decomposition temperature was caused by the lower bonding energy of P—O linkage (149 kcal/mol) in NPHE fraction of NPHE-PU, which decomposed at a temperature lower than that of C—O bond (257 kcal/mol) on PU backbones.

However, as observed by the differential thermogravimetric analysis (DTG), the first major decomposition temperature was 347°C of UV-PU and the decomposition temperature of NPHE-PU increased to 367 or 369°C due to 10 or 20 phr NPHE-curing dosage. The slight increase in thermal stability was caused by the crosslinking density increment of NPHE-PU. When NPHE dosage increased further to 40 phr, the NPHE major decomposition temperature dropped to 351°C. This finding showed that the crosslinking density of NPHE-PU did not increase with further increasing NPHE dosage to 40 phr. These observa-

tions coincided with the results of the gel content on Table I. The char yields of NPHE-PU films were 4.4, 9.2, and 14.7%, whereas the original UV-PU showed none of char yield when these samples were heated to 600°C on TGA under air atmosphere (Fig. 6). These char yields resulted from the incorporation into NPHE-PU of phosphorus and nitrogen compositions, which were derived from NPHE. The phosphorus and nitrogen contents of NPHE-PU film generated non-flammable phosphorus and nitrogen oxides blocking air supply at high temperature.

#### Combustion Behavior

The L.O.I. value of the original UV-PU was 22 and was increased to 24, 25, and 27 of NPHE-PU, respectively, with 10, 20, or 40 phr NPHE-curing dosage (Table I). This increase in L.O.I. value was caused by the phosphorus and nitrogen contents increment in NPHE-PU films.



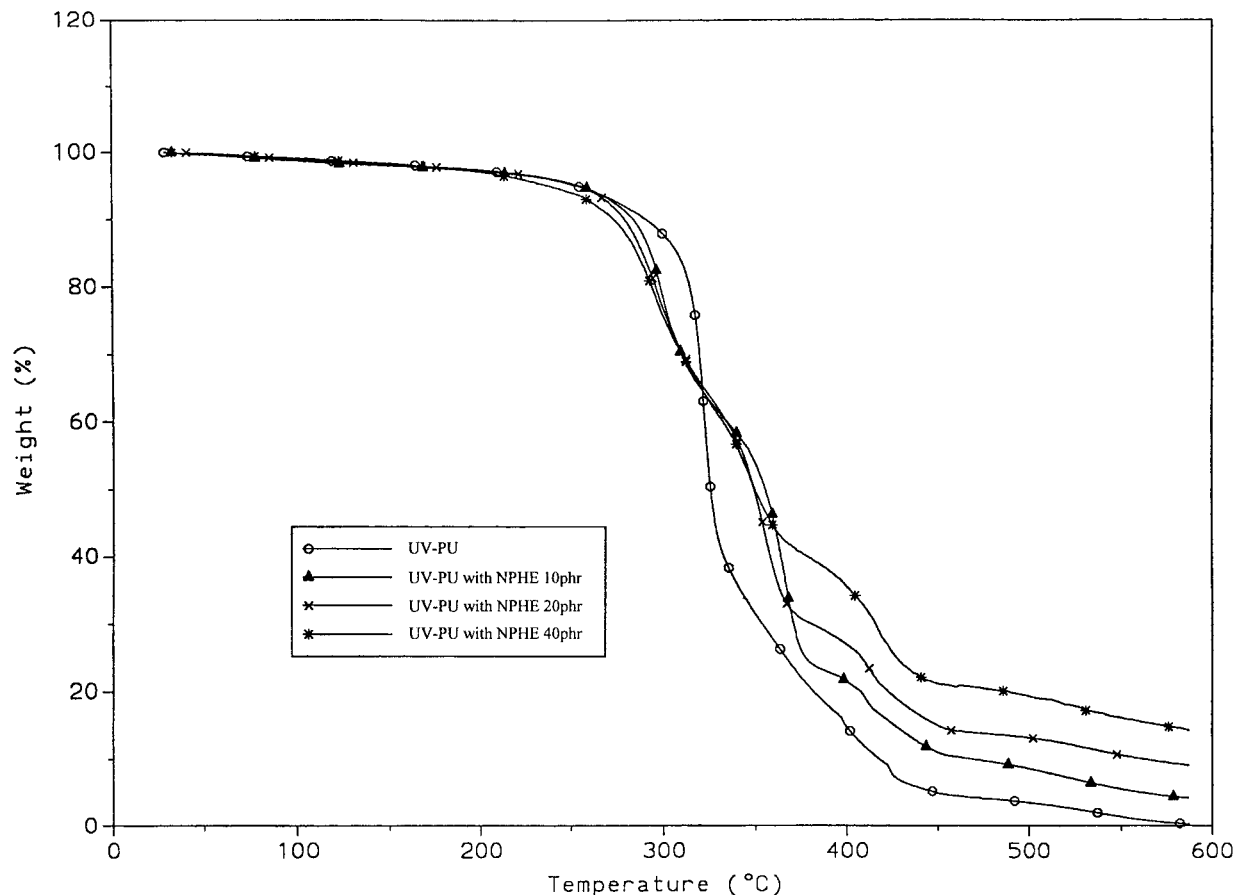


Figure 6 TGA thermogram of NPHE-PU under air.

The ignition time of UV-PU was 72 s under 30 kW/m<sup>2</sup> constant heat flux on the cone calorimeter. However, it decreased to 59, 45, and 37 s in NPHE-PU films with 10, 20, and 40 phr NPHE, respectively (Table II). These results indicate that

P—O bond linkages among PU main chains are less stable thermally. The NPHE-PU film was decomposed into small molecules and ignited more easily than UV-PU under a constant heat flux.

Table II Combustion Behaviors of NPHE-PU on Cone Calorimeter

	UV-PU	NPHE-PU		
		10	20	40
		NPHE (phr) <sup>a</sup>		
Ignition time (s) <sup>b</sup>	72	53	45	37
Char residue (%)	5	11.1	12.5	19.4
Maximum heat release (KW/m <sup>2</sup> )	297.2	353.3	369.2	275
Total heat release (MJ/m <sup>2</sup> )	36.6	30.3	27.5	19.5
Max smoke (l/s)	2.98	9.16	10.64	10.81
Average smoke (l/s)	1.53	3.99	3.29	2.41
Total smoke	346.5	698.7	717.9	714.3

<sup>a</sup> NPHE dosages of 10,20, or 40 phr indicate the addition of 10,20, or 40 gm per 100 gm of UV-curable PU oligomer.

<sup>b</sup> A constant heat flux 30 kW/m<sup>2</sup> is applied on cone calorimeter.

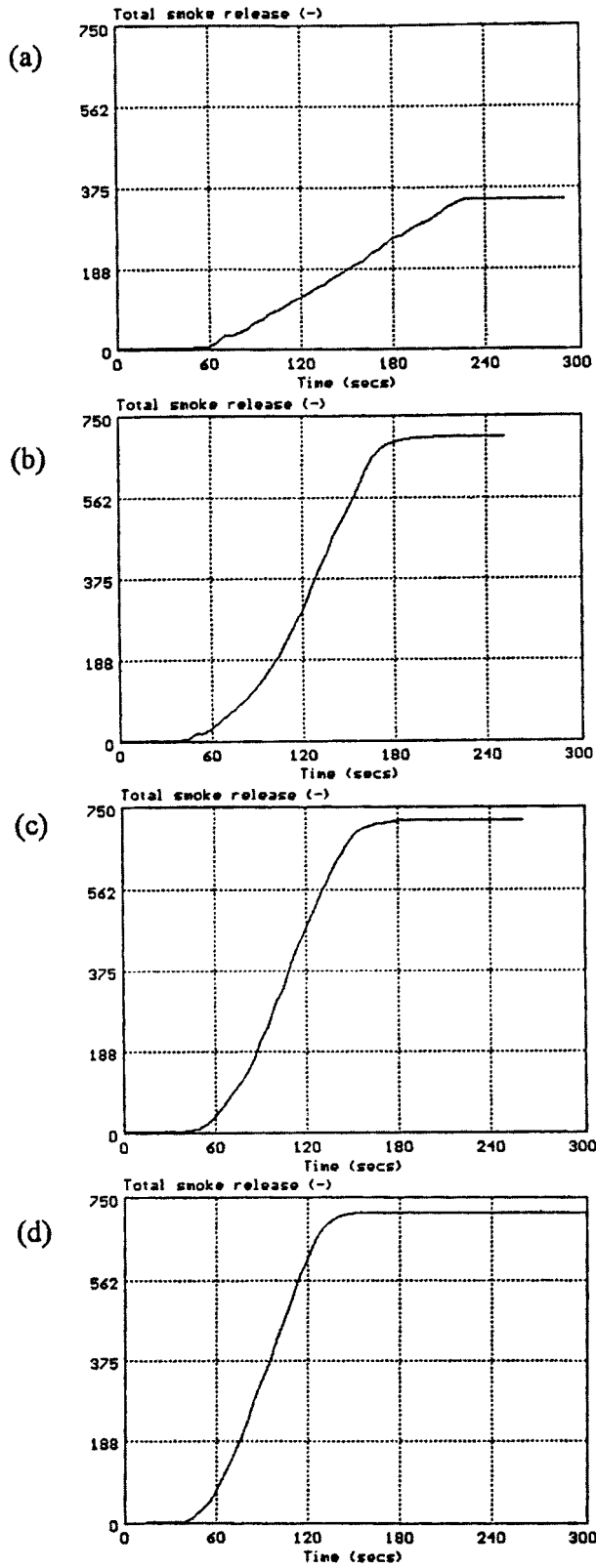


Figure 7 Total heat release profile of NPHE-PU.

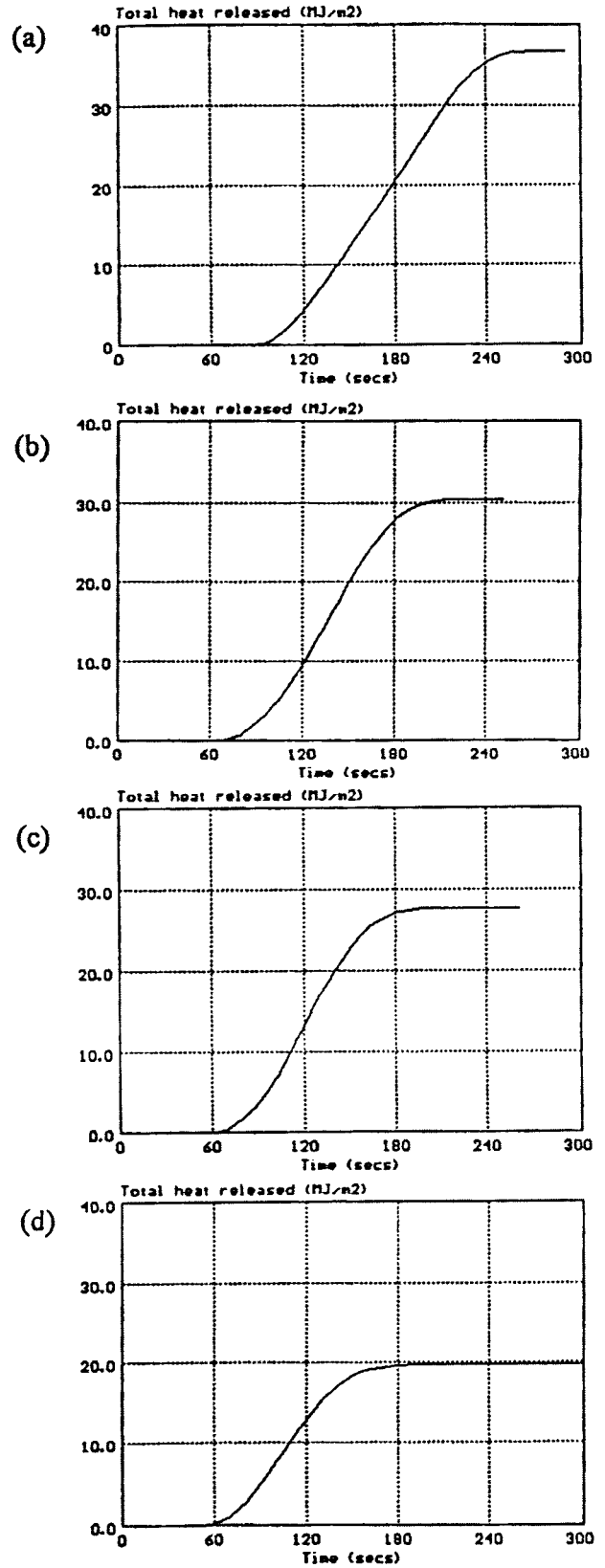


Figure 8 Heat release rate of NPHE-PU.

The total heat release of UV-PU was higher ( $36.6 \text{ MJ/m}^2$ ) than that of NPHE-PU films, which is 30.3, 27.5, or  $19.5 \text{ MJ/m}^2$  (Fig. 7 and Table II). The heat release of UV-PU started slowly but the heat release rate remained at  $200 \text{ MJ/m}^2$  or above for about 100 s, whereas those of NPHE-PU films remained at the same heat release rate for about 80 s or less (Fig. 8). The higher the phosphorus content of NPHE-PU, the less heat was released in combustion. The lower heat release of NPHE-PU films resulted from the nonflammable phosphorus and nitrogen oxides formation in combustion, which inhibited material from further burning at high temperature.

Furthermore, the char residue was 5.0% in original UV-PU, as shown on cone calorimeter, and it can be increased to 11.1, 12.5, and 19.4% in NPHE-PU with various NPHE dosages. Those results coincide with the char yields of NPHE-PU films, as shown on TGA measurements.

Total smoke generation of the NPHE-PU system was almost two times as much as that of UV-PU (Fig. 9 and Table II). Those results were caused by the presence of phosphorus and nitrogen compositions, which produced condensed-phase phosphorus oxides and gas-phase phosphorus oxides at high temperature. Both nonflammable phases blocked air supply on the material surface and produced the carbonaceous residue and smoke.

## CONCLUSION

The resultant UV-cured NPHE-PU film produced better mechanical, physical, and thermal properties. Because of the crosslinkage formation among the PU polymer main chains and the UV-reactive phosphazene (NPHE), monomer was incorporated into the final PU films by the UV irradiation. NPHE was compatible with this UV-curable PU-coating system as evidenced by the EDS shown by phosphorus mapping. The final NPHE-PU films demonstrated the flame-inhibition character on L.O.I. value (which increased from 22 to 27 with various NPHE dosages). Besides, the initial decomposition temperature and ignition time of NPHE-PU films were lower and shorter, respectively, than those of original UV-PU also observed in TGA and the cone calorimeter measurements, respectively. The result of lower heat release, higher carbonaceous residue, and higher smoke density of NPHE-PU films in cone calorimeter was caused perhaps by nonflammable phos-

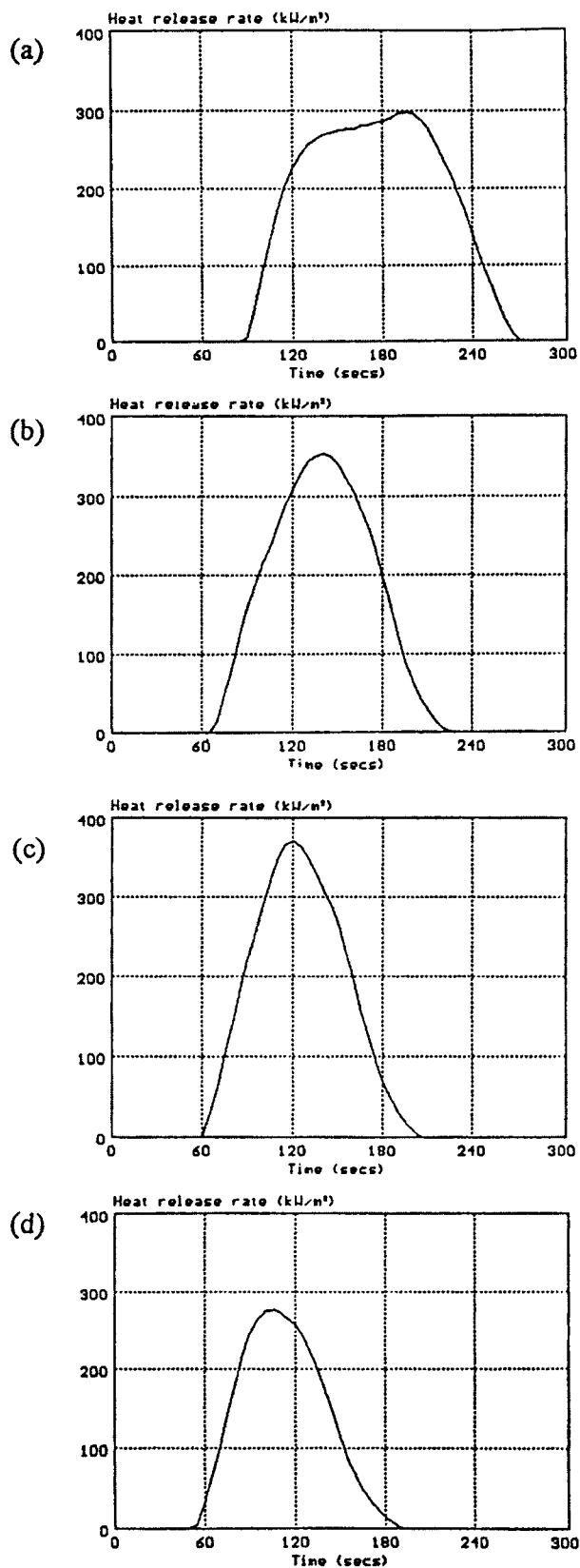


Figure 9 Total smoke release of NPHE-PU.

phorus and nitrogen oxide formation at high temperature. However, UV curing with NPHE was a convenient way to introduce high phosphorus and nitrogen contents simultaneously into the PU-coating system and to effectively improve PU performance properties. This multifunctional UV-reactive phosphazene (NPHE) monomer can serve three purposes simultaneously in this UV-curable PU-coating system: as a flame retardant, a UV-reactive diluent, and a crosslinker.

One of authors (K.-N. C.) is indebted to the National Science Council of the Republic of China for financial support.

## REFERENCES

1. Paul, S. *Surface Coatings—Science and Technology*; Wiley: Chichester, 1985; Chapter 8, p 601.
2. Chen, G.-N.; Chen, K.-N. *J Appl Polym Sci* 1997, 63, 1609.
3. Chen, G.-N.; Liu, P.-H.; Chen, M.-S.; Chen, K.-N. *J Polym Res* 1997, 4, 165.
4. Chen, G.-N.; Chen, K.-N. *J Appl Polym Sci* 1998, 67, 1661.
5. Hilado, C. J. in *Flammability Handbook for Plastics*, 4th ed.; Technomic Publishing Co.: Lancaster, PA, 1990; Chapter 5, p 167.
6. Green, J. in *Thermoplastic Polymer Additives*; Lutz, J. T., Jr., Ed.; Marcel Dekker: New York, 1989; Chapter 4, p 93.
7. Shao, C.-H.; Wang, T.-Z.; Chen, G.-N.; Chen, K.-J.; Chen, K.-N. *J Polym Res* 2000, 7, 41.
8. Wang, T.-Z.; Chen, K.-N. *J Appl Polym Sci* 1999, 74, 2499.
9. Shao, C.-H.; Huang, R. J.; Chen, G.-N.; Yeh, J.-T.; Chen, K.-N. *Polym Degrad Stab* 1999, 65, 359.
10. Banks, M.; Ebdon, J. R.; Johnson, M. *Polymer* 1994, 35, 3470.
11. Liu, Y.-L.; Hsiue, G.-H.; Lee, R.-H.; Chiu, Y.-S. *J Appl Polym Sci* 1997, 63, 895.
12. Yeh, J.-T.; Hsieh, S.-H.; Cheng, Y.-C.; Yang, M.-J.; Chen, K. N. *Polym Degrad Stab* 1998, 61, 339.
13. Cheng, T.-C.; Chiu, Y.-S.; Chen, H.-B.; Ho, S. Y. *Polym Degrad Stab* 1995, 47, 375.
14. Ratz, R.; Kober, E.; Grundmann, C.; Ottmann, G. *Inorg Chem* 1964, 3, 757.
15. Troev, K.; Kisiova, T.; Grozeva, A.; Borisov, G. *Eur Polym J* 1993, 29, 1211.
16. Huang, W.-K.; Chen, K.-J.; Yeh, J.-T.; Chen, K.-N. *J Appl Polym Sci* 2001, 79, 662.