

Synergistic Effect of a Phosphorus–Nitrogen Flame Retardant on Engineering Plastics

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ABSTRACT: The novel flame retardant tris(3,5-dimethyl-4-diphenyl phenoxy phosphate)isocyanurate (TDPI) was synthesized from the reaction of diphenyl chlorophosphate and tris(3,5-dimethyl-4-hydroxybenzyl)isocyanurate. The compound was characterized with Fourier transform infrared spectroscopy, elemental analysis, mass spectrometry, ¹H-NMR, and ³¹P-NMR. Furthermore, blends of the flame retardant with engineering plastics in various weight ratios were made, and their thermal stability and flame retardancy were determined by thermogravimetric analysis (TGA), UL-94 vertical testing, and limiting oxygen index (LOI) measurements. The phosphorus–nitrogen synergistic effect on flame retardancy was compared with the effects of com-

monly used tetraphenyl resorcinol diphosphate and tetrabromobisphenol A. TGA indicated that the TDPI/engineering plastics systems were stable up to 397–503°C at a 5% weight loss in a nitrogen atmosphere with a relatively high char yield (21.0–42.1% at 700°C) and that they achieved UL-94 V-0 rating (with a low flame-retardant content: P, 0.76 wt %, and N, 0.34 wt %). No fume and toxic gas emissions were observed during the burning test for this system. The LOI values were 31.6–42.2. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 410–417, 2004

Key words: flame retardance; plastics; blends

INTRODUCTION

Engineering plastics (EPs), such as poly(ethylene terephthalate) (PET), polycarbonate (PC), polyamide (PA), and poly(phenylene oxide) (PPO), have found widespread applications in automobiles, precision instruments, electronics, electrical devices, and communications. Each resin has its own outstanding properties and specific applications.¹ The main drawback of organic polymers is their flammability. Flame retardants (FRs), such as phosphorus–halogen mixtures, ammonium phosphate, and organophosphorous compounds, either alone or in conjunction with nitrogen and/or silicon,² have been used to impart flame retardancy to polymers.^{3–6} Commercial fire-retardant polymers generally contain elements such as phosphorus, nitrogen, and halogen. These elements may be added in the form of an additive to the substrate polymers or incorporated into the structure of the polymer itself. As phosphorus-containing polymers give off nontoxic combustion products, they are becoming more popular^{7–14} than halogen-containing polymers.

In a fire, the halogens of bromine and chlorine produce smoke, toxicity, and corrosion. Organic phosphates do not cause any of these problems. Organophosphorous compounds have been demonstrated to be better as FRs for polymeric materials than halogen-containing compounds because they form a carbonaceous char, which acts as a physical barrier to heat transfer from the flame to the polymer and the diffusion of combustible gas and smoke.^{15–22} Generally, FR polymers are obtained through the physical blending of an FR additive with a polymer; it has been found that the introduction of phosphorus into a polymer can improve the flame retardancy and reduce contamination upon pyrolysis. The phosphorus moiety decomposes at low temperatures with respect to the polymer matrix. However, the oxidation of the phosphorus char can be observed at high temperatures. Thus, a phosphorus-rich char is formed to reduce the production of combustible gas during a fire.^{23–25} The main drawbacks of the most commonly used organophosphate FR, triphenylphosphate (TPP), are its volatility and mobility, which cause environmental contamination during processing and the migration of TPP to the surfaces of finished products. To alleviate these problems, tetraphenyl resorcinol diphosphate (RDP) has been developed to replace TPP.

In this study, we have attempted to prepare a novel nitrogen/phosphorus-containing FR with very low volatility and mobility to overcome the aforemen-

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tioned problems. The nitrogen-phosphorus synergistic effect on flame retardancy has been investigated through the blending of the FR with PET, PC, PA, and PPO, and we have compared the results with those of RDP and tetrabromobisphenol A (TBBA).

EXPERIMENTAL

Materials

All the reaction chemicals and solvents were reagent-grade or were purified by standard methods before use. Phosphoryl chloride, isocyanuric acid, paraformaldehyde, 2,6-dimethylphenol, and resorcinol were purchased from Acros Co. (Geel, Belgium). Xylene, *N,N*-dimethylformamide, and *N,N*-dimethylacetamide (Tedia, United States) and 1,1,2,2-tetrachloroethane, phenol, dichloromethane, formic acid, and toluene (TCI, Tokyo, Japan) were used as the reaction and blend solvents, respectively. The EPs were obtained from Chang Chun Plastic Co. (Kaohsiung, Taiwan) and Shinkong Synthetic Fibers Co. (Taiwan). 4-Dimethylaminopyridine, hexamethylenetetramine, triethylamine, and aluminum chloride from Aldrich (Milwaukee, WI) were used as catalysts. All the reagents were used as received and then stored in a dry box under reduced pressure.

Measurements

Fourier transform infrared spectra were recorded on a Nicolet Magna 520 spectrometer with KBr pellets or with 10- μm film. Spectra in the optical range of 400–4000 cm^{-1} were obtained through the averaging of 32 scans at a resolution of 4 cm^{-1} . Mass spectrometry analyses were performed on a VG 70-250S chromatography/mass spectrometry spectrometer with a solid inlet. Elemental analyses were carried out with a Heraeus CHN rapid elemental analyzer. $^1\text{H-NMR}$ and $^{31}\text{P-NMR}$ spectra were registered with Bruker Avance 600 and 300 spectrometers, with dimethyl sulfoxide- d_6 (DMSO- d_6) as a solvent. The chemical shifts were calibrated with tetramethylsilane. Thermogravimetric analyses (TGAs) were performed on a PerkinElmer TGA-7 thermal analyzer (7–10-mg samples) at a heating rate of 20°C/min in N_2 at a purge pressure of 25 psi within the temperature range of 50–800°C. The UL-94 vertical test was performed according to the testing procedure FMVSS 302/ZSO 3975 with a test specimen bar 127 mm long, 12.7 mm wide, and about 1.27 mm thick. The limiting oxygen index (LOI) was determined with an Atlas LOI chamber according to the standard procedure (ASTM D 2863-77) with a test specimen bar 7–15 cm long, 6.5 \pm 0.5 mm wide, and 3.0 \pm 0.5 mm thick.

Synthesis of diphenyl chlorophosphate (DPCP)

To a 250-mL reactor equipped with a stirrer, a reflux condenser, a thermometer, a Dean-Stark water sepa-

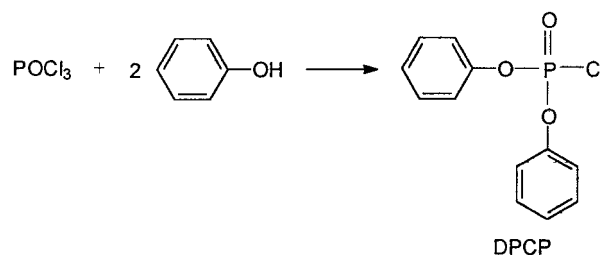


Figure 1 Synthesis of DPCP.

rator, and a nitrogen inlet were charged 18.80 g (0.2 mol) of phenol in 20 mL of xylene and 4-dimethylaminopyridine (0.18 g) as a catalyst. The mixture was heated to 140°C with stirring under a nitrogen atmosphere, and then the phosphoryl chloride (16.1 g, 0.105 mol) in 12 mL of xylene was added incrementally over 1 h. Upon the completion of the addition, the reaction mixture was allowed to reflux for 7 h. Xylene and excess phosphoryl chloride were removed by vacuum distillation to yield DPCP (90% yield).

IR (KBr, cm^{-1}): 1297 (P=O), 1180, 973 (P—O—Ph), 1486, 1580 (aromatic C=C), 3027 (aromatic C—H). FB^+ mass spectrum intensity (%), m/z): 269 (100, M^+). $^1\text{H-NMR}$ (600 MHz, DMSO- d_6 , δ): 8.04 (d, 4H, phenyl H), 7.95 (t, 4H, phen. H), 7.88 (t, 2H, phenyl H). $^{31}\text{P-NMR}$ (300 MHz, DMSO- d_6 , δ): -11.27 ppm (singlet peak). ELEM. ANAL. Calcd. for $\text{C}_{12}\text{H}_{10}\text{ClO}_3\text{P}$: C, 53.63%; H, 3.72%; Cl, 17.88%. Found: C, 53.67%; H, 3.74%; Cl, 17.85%. The reaction scheme is shown in Figure 1.

Synthesis of RDP

DPCP (56.4 g, 0.21 mol) with 0.56 g of AlCl_3 was added to a 250-mL reaction vessel equipped with a temperature controller, an overhead stirrer, and a reflux condenser with a Dean-Stark trap. Resorcinol (11 g, 0.1 mol), dissolved in 25 mL of xylene, was added and heated to 160°C for 1 h with stirring under a nitrogen atmosphere. The system was slowly reduced to a 350 mmHg atmosphere and then was reacted another 4 h at 160°C. After the completion of the reaction, 25 g of a 2.5% HCl solution was added, and the mixture was stirred for 1 h at 80°C. The organic phase was separated, 0.6 g of Na_2CO_3 was added, and the mixture was stirred for 1 h at 85°C and then filtered. After the removal of the solvent by vacuum distillation, the product was a pale yellow, viscous liquid of RDP (87% yield).

IR (KBr, cm^{-1}): 1297 (P=O), 1186, 968 (P—O—Ph), 1482, 1578 (aromatic C=C), 3074 (aromatic C—H). FB^+ mass spectrum intensity (%), m/z): 575 (100, M^+). $^1\text{H-NMR}$ (600 MHz, DMSO- d_6 , δ): 7.24–7.56 (m, 24H, phenyl H). $^{31}\text{P-NMR}$ (300 MHz, DMSO- d_6 , δ): -17.71 ppm (singlet peak). ELEM. ANAL. Calcd. for $\text{C}_{30}\text{H}_{24}\text{O}_8\text{P}_2$: C, 62.72%; H, 4.18%; O, 22.30%; P, 10.80%.

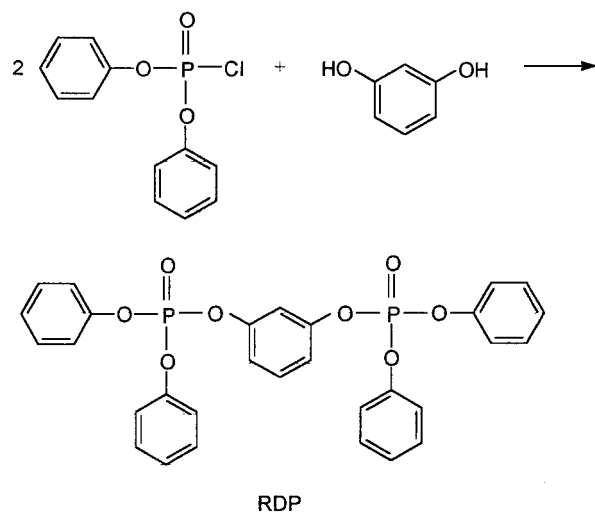


Figure 2 Synthesis of the phosphorus-containing FR RDP.

11.25%. Found: C, 62.77%; H, 4.11%; P, 10.74%. The reaction scheme is shown in Figure 2.

Synthesis of tris(3,5-dimethyl-4-hydroxybenzyl)isocyanurate (TDHI)

Into a 500-mL, four-necked, flat-bottomed flask equipped with a heating mantle, a thermocouple, a

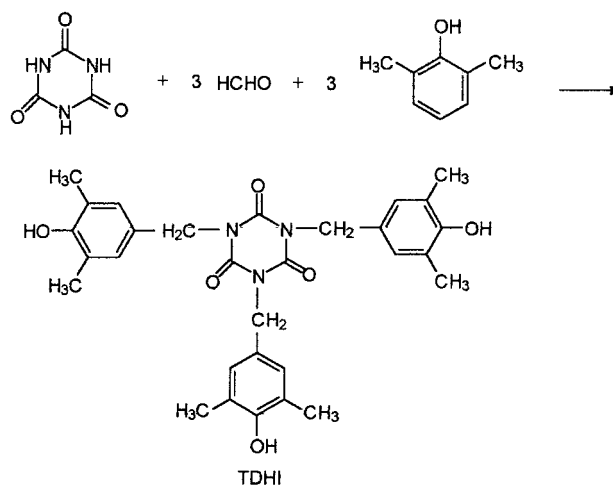


Figure 3 Synthesis of TDHI.

temperature controller, an overhead stirrer, and a Dean-Stark trap with a reflux condenser were added isocyanuric acid (12.9 g, 0.1 mol), paraformaldehyde (9.45 g, 0.315 mol), and 2,6-dimethylphenol (38.43 g, 0.315 mol) in 200 mL of *N,N*-dimethylformamide and 50 mL of H₂O. Hexamethylenetetramine (1.5 g) as a catalyst was added to this solution at room temperature, and the mixture was allowed to react with stirring at 100°C for 6 h; this resulted in the precipitation

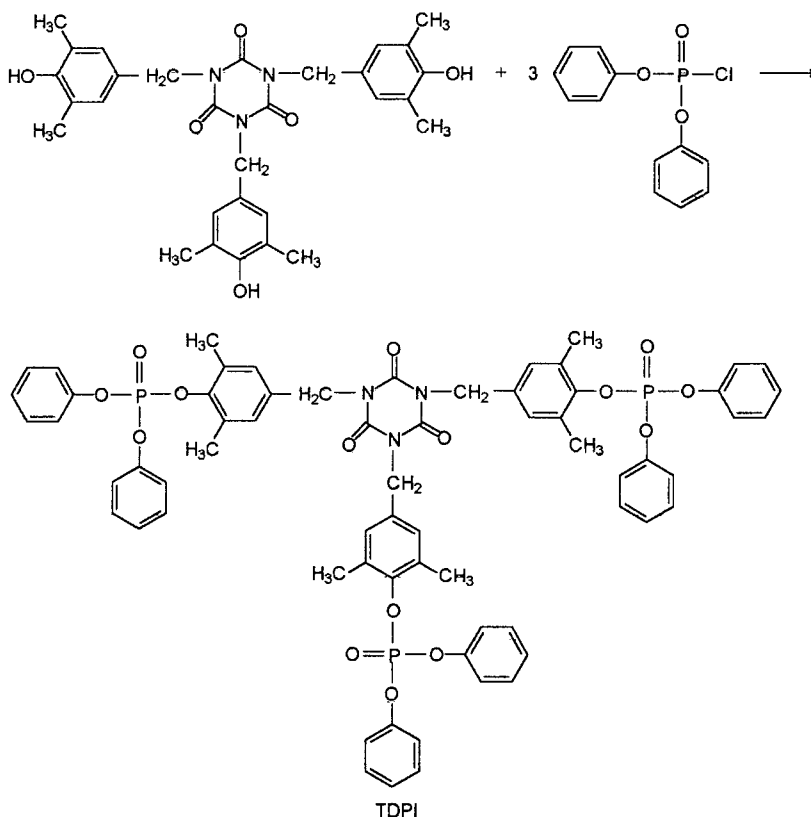


Figure 4 Synthesis of the phosphorus- and nitrogen-containing FR TDPI.

of the product. The precipitated crude solid was filtered and washed thoroughly with methanol to yield white, powdered TDHI (84% yield).

IR (KBr, cm^{-1}): 1354 (isocyanurate structure), 3244–3645 (aromatic, C—OH), 1490, 1606 (aromatic C=C). FB^+ mass spectrum intensity (% m/z): 532 (20, M^+). $^1\text{H-NMR}$ (600 MHz, $\text{DMSO-}d_6$, δ): 8.16 (s, 3H, —OH), 6.84 (s, 6H, phenyl H), 4.77 (s, 6H, — CH_2), 2.09 (s, 18H, — CH_3). ELEM. ANAL. Calcd. for $\text{C}_{30}\text{H}_{33}\text{O}_6\text{N}_3$: C, 67.80%; H, 6.21; N, 7.91%; H, 18.08%. Found: C, 67.76%; H, 6.28; N, 7.93%. The reaction scheme is shown in Figure 3.

Synthesis of tris(3,5-dimethyl-4-diphenyl phenoxy phosphate)isocyanurate (TDPI)

DPCP (84.60 g, 0.315 mol) and triethylamine (31.8 g, 0.315 mol) as an acid scavenger were added to a 500-mL reaction vessel equipped with a temperature controller and an overhead stirrer and were heated to 80°C with stirring under a nitrogen atmosphere. To the stirring mixture, TDHI (53.2 g, 0.1 mol) in 120 mL of *p*-xylene was added incrementally over 30 min and then maintained at that temperature for 4 h. Finally, methanol was added to the reaction mixture to precipitate the product. The precipitated crude solid was filtered and washed thoroughly with methanol to yield a yellow powder of TDPI (85% yield).

IR (KBr, cm^{-1}): 1357 (isocyanurate structure), 1296 (P=O), 1188, 957 (P—O—Ph), 1456, 1591 (aromatic C=C). FB^+ mass spectrum intensity (% m/z): 1227 (50, M^+). $^1\text{H-NMR}$ (600 MHz, $\text{DMSO-}d_6$, δ): 6.89–7.41 (m, 36H, phenyl H), 4.88 (d, 6H, — CH_2), 2.20 (t, 18H, — CH_3). $^{31}\text{P-NMR}$ (300 MHz, $\text{DMSO-}d_6$, δ): -16.38 ppm (singlet peak). ELEM. ANAL. Calcd. for $\text{C}_{66}\text{H}_{60}\text{O}_{15}\text{N}_3\text{P}_3$: C, 64.55%; H, 4.89; N, 3.42%; H, 19.56%; P, 7.58%. Found: C, 64.49%; H, 4.92; N, 3.46%; P, 7.65%. The reaction scheme is shown in figure 4.

Blend preparation

A series of FR/EP mixtures with designated FR weight percentages (5, 10, or 15%) were stirred and dissolved in various organic solvents: for PET, a 1,1,2,2-tetrachloroethane/phenol mixture (3:2 w/w); for PC, dichloromethane; for PA, formic acid; and for PPO, toluene. The blends were thoroughly mixed, and the solvent was vaporized in a circulation oven with an exhaust fan at 70°C.

UL-94V and LOI flame-retardancy tests

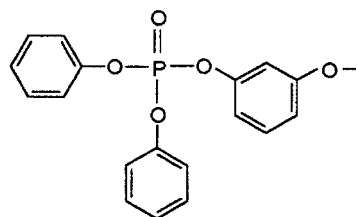
The UL-94V test determines the upward-burning characteristics of a solid. Five sample bars were suspended vertically over surgical cotton ignited by a Bunsen burner; two ignitions with a 10-s burning time were applied to each sample bar. The LOI value can be used as an indicator to evaluate the flame retardancy of polymers. The LOI is defined as the minimum fraction

of oxygen in an oxygen–nitrogen mixture that is sufficient to sustain combustion of the specimen after ignition. Thus, the FR properties of these polymers were further confirmed by the LOI measurement.

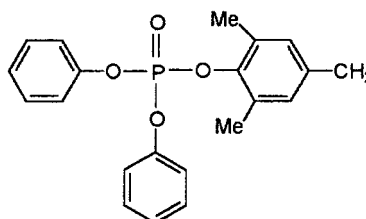
RESULTS AND DISCUSSION

Synthesis of the FR compounds and analysis

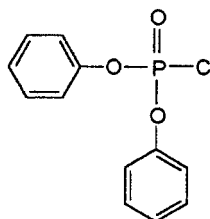
Figures 2 and 4 show the synthetic routes to RDP and TDPI. They were prepared through the reactions between DPCP and TDHI or resorcinol, respectively. The typical IR spectra of TDHI and corresponding TDPI exhibited several differences. TDHI showed strong absorption at 3244–3645 cm^{-1} for the characteristic aromatic hydroxyl group. TDPI showed strong absorption around 1296 cm^{-1} corresponding to the vibration with P=O, which is characteristic of phosphoric compounds, peaks at 1188 and 957 cm^{-1} corresponding to P—O—C (aromatic group) stretching absorptions, and absorption at 1695 cm^{-1} associated with the C=O group and at 1456 cm^{-1} for the amide group. The P=O group is electron-withdrawing by a mesomeric effect. The mesomeric effect of the phenoxy group for RDP and TDPI can be shown as follows:



RDP ($\delta = -17.7$)



TDPI ($\delta = -16.4$)



DPCP ($\delta = -11.3$)

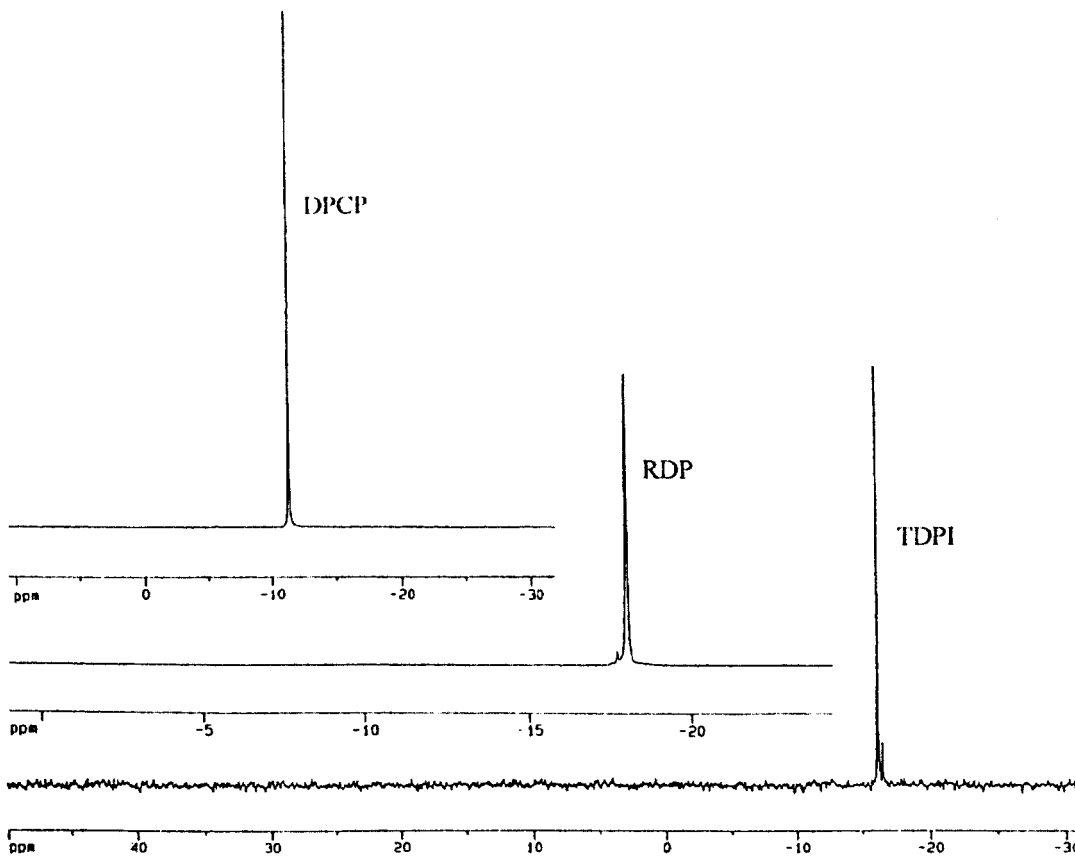


Figure 5 ³¹P NMR spectra of DPCP, RDP, and TDPI.

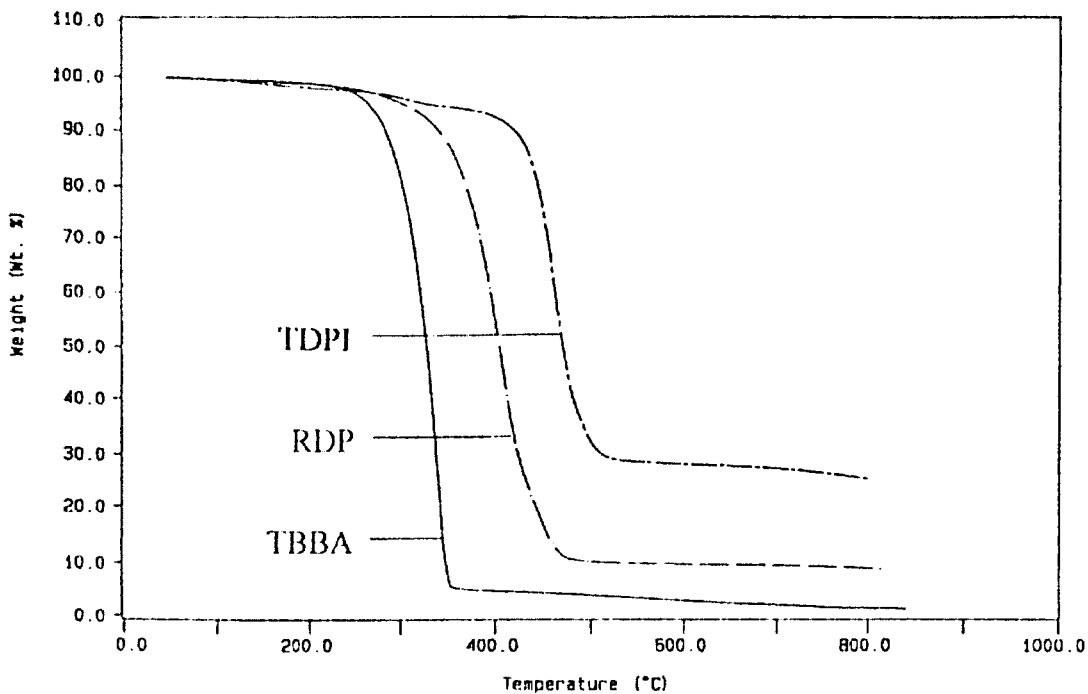


Figure 6 TGA thermograms of FRs TBBA, RDP, and TDPI.

TABLE I
Compositions and Properties of Blends Based on PET and FRs

Sample	PET/FR	Br (wt %)	P (wt %)	N (wt %)	Weight-loss temperature		Char yield at 700°C (%)	Drip	Fume	UL-94V	LOI
					5%	10%					
PET	100/0	0			418	429	9.7	Yes	Heavy	V-2	24.1
Br-1	95/5	2.94			385	408	13.4	Yes	Heavy	V-2	26.2
Br-2	90/10	5.88			358	400	15.0	Yes	Heavy	V-2	27.2
Br-3	85/15	8.82			308	360	16.0	Yes	Heavy	V-2	27.7
P-1	95/5		0.54		394	419	15.9	Yes	Slight	V-1	28.0
P-2	90/10		1.08		385	413	17.8	No	No	V-1	28.8
P-3	85/15		1.62		350	400	20.5	No	No	V-0	29.7
N/P-1	95/5		0.38	0.17	406	425	19.5	No	Slight	V-1	30.2
N/P-2	90/10		0.76	0.34	397	421	21.0	No	No	V-0	31.6
N/P-3	85/15		1.14	0.51	394	421	24.8	No	No	V-0	33.7

Br = TBBA; P = RDP; N/P = TDPI.

The mesomeric effect is weaker for RDP than for TDPI because of the phenoxy group in the meta position; however, two phenoxy groups ($-\text{O}-\text{C}_6\text{H}_4-\text{O}-$) compensate for each other and result in magnetism similar to that of TDPI. DPCP has lower magnetism because the structure cannot resonate with the $\text{P}=\text{O}$ group, and the electron-donating properties of chlorine are less than those of the phenoxy group. Therefore, the chemical-shift parameter tends to shift downfield (Fig. 5). The elemental analyses, mass and NMR (^1H and ^{31}P) spectra, and characteristic bands in the IR spectra correlate sufficiently well with the proposed structures of the compounds.

Thermal properties of the FR/EP blends

TGA is the most favored technique for rapid evaluation in comparing and ranking the thermal stabilities of various polymers. The thermal stabilities of FRs are in the order TDPI > RDP > TBBA (Fig. 6), and the char yields at 700°C under nitrogen are 27, 10, and 3%

for TDPI, RDP, and TBBA, respectively. The TGA results for PET blended with various weight ratios of TBBA, RDP, and TDPI in nitrogen are shown in Table I. The weight-loss temperature gradually decreased with the FR content in the blend. The reductions in the 5% weight-loss temperature and 10% weight-loss temperature are in the order TBBA > RDP > TDPI. TDPI achieved a UL-94 V-0 rating with the least amount of the FR element (N/P-2: 0.76% P and 0.34% N), whereas RDP required a P content of 1.62% (15 wt % RDP) in the blend. TBBA was the worst; even with 8.82% Br (15 wt % TBBA) in the blend, it was still quite flammable (V-2). To achieve nonflammability (V-0 rating), the 5% weight-loss temperatures of the FR/PET systems were 397 and 350°C for TDPI and RDP, respectively, whereas for TBBA, it was well below 300°C. TDPI also exhibited the highest char yields among the blended polymers because of its rigid isocyanurate structure and nitrogen-phosphorus synergistic effect. All other blended systems (PC, PA, and PPO; see Tables II-IV) exhibited characteristics analo-

TABLE II
Compositions and Properties of Blends Based on PC and FRs

Sample	PC/FR	Br (wt %)	P (wt %)	N (wt %)	Weight-loss temperature		Char yield at 700°C (%)	Drip	Fume	UL-94V	LOI
					5%	10%					
PC	100/0	0			519	531	20.0	Yes	Slight	V-2	30.0
Br-1	95/5	2.94			489	512	23.1	Yes	Slight	V-2	31.8
Br-2	90/10	5.88			443	494	24.9	Yes	Slight	V-2	32.7
Br-3	85/15	8.82			430	489	25.1	Yes	Slight	V-1	32.9
P-1	95/5		0.54		502	531	25.1	No	No	V-1	33.0
P-2	90/10		1.08		467	507	25.8	No	No	V-0	33.3
P-3	85/15		1.62		435	484	26.5	No	No	V-0	33.7
N/P-1	95/5		0.38	0.17	512	530	26.0	No	No	V-1	33.4
N/P-2	90/10		0.76	0.34	503	526	26.8	No	No	V-0	33.9
N/P-3	85/15		1.14	0.51	479	506	29.4	No	No	V-0	35.4

Br = TBBA; P = RDP; N/P = TDPI.

TABLE III
Compositions and Properties of Blends Based on PA and FRs

Sample	PA/FR	Br (wt %)	P (wt %)	N (wt %)	Weight-loss temperature		Char yield at 700°C (%)	Drip	Fume	UL-94V	LOI
					5%	10%					
PA	100/0	0			408	423	1.2	Yes	Heavy	V-2	19.3
Br-1	95/5	2.94			340	377	1.7	Yes	Heavy	V-2	19.6
Br-2	90/10	5.88			322	353	2.5	Yes	Heavy	V-2	20.0
Br-3	85/15	8.82			310	335	5.7	Yes	Heavy	V-2	21.8
P-1	95/5		0.54		354	388	3.6	Yes	Slight	V-2	20.7
P-2	90/10		1.08		337	367	6.2	Yes	Slight	V-2	22.1
P-3	85/15		1.62		329	350	7.9	Yes	Slight	V-2	23.1
N/P-1	95/5		0.38	0.17	377	400	6.95	Yes	Slight	V-2	23.5
N/P-2	90/10		0.76	0.34	363	392	10.6	Yes	Slight	V-2	25.6
N/P-3	85/15		1.14	0.51	352	384	14.7	Yes	Slight	V-1	28.0

Br = TBBA; P = RDP; N/P = TDPI.

gous to those of PET. The flammability of the PA system was the worst of the polymers evaluated, whereas the PC and PPO blends were better than those of the other polymers; this may be attributed to the increased concentration of aromatic groups in the polymer chain.

UL-94V test and LOI measurement for blends

The FR properties of FR/EP blends were further examined with UL-94V and LOI testing. Tables I–IV summarize the results. Except for PA (nylon 66), the V-0 and V-1 ratings could be achieved for phosphorus/nitrogen- and phosphorus-containing blends. The LOI values of the blended polymers are shown in Tables I–IV. For the neat polymers, the LOI values were as follows: for PET, 24.1; for PC, 30.0; for PA, 19.3; and for PPO, 35.5. When 5 wt % TBBA was blended with a polymer, the LOI values were increased by 2.0–8.7% (PET, 26.2; PC, 31.8; PA, 19.6; and PPO, 37.1). However, when the same weight percent-

age of RDP was blended with a polymer, the LOI values were increased by 10.0–16.2% (PET, 28.0; PC, 33.0; PA, 20.7; and PPO, 39.6), indicating that phosphorus had higher FR efficiency than bromine. Furthermore, less fumes were observed for the phosphorus-containing blends. The increases in the LOI values through the addition of TDPI were much more significant. With 5 wt % TDPI, the LOI values increased by 13.5–25.3% (PET, 30.2; PC, 33.4; PA, 23.5; and PPO, 40.3); this was another demonstration of the phosphorus/nitrogen synergistic effect.

Figures 7–9 show the relationship between the content of the FR element and the LOI values. When bromine, phosphorus, and nitrogen (isocyanurate) were introduced into the blending compositions, the LOI values of the resultant blends increased with an increase in the element contents. However, the TDPI series exhibited a higher LOI increase than the other series (TBBA and RDP) with the same composition, and no fumes or drips were observed for nitrogen/phosphorus-containing systems.

TABLE IV
Compositions and Properties of Blends Based on PPO and FRs

Sample	PPO/FR	Br (wt %)	P (wt %)	N (wt %)	Weight-loss temperature		Char yield at 700°C (%)	Drip	Fume	UL-94V	LOI
					5%	10%					
PPO	100/0	0			466	473	29.6	Yes	Heavy	V-2	35.5
Br-1	95/5	2.94			436	459	32.5	Yes	Heavy	V-2	37.1
Br-2	90/10	5.88			421	459	35.8	Yes	Heavy	V-2	39.0
Br-3	85/15	8.82			394	448	37.8	No	Heavy	V-2	40.1
P-1	95/5		0.54		447	466	36.8	No	Slight	V-1	39.6
P-2	90/10		1.08		438	461	39.4	No	Slight	V-1	41.0
P-3	85/15		1.62		407	450	40.2	No	No	V-0	41.5
N/P-1	95/5		0.38	0.17	457	475	40.4	No	Slight	V-1	40.3
N/P-2	90/10		0.76	0.34	447	470	42.1	No	No	V-0	42.2
N/P-3	85/15		1.14	0.51	417	461	45.8	No	No	V-0	45.8

Br = TBBA; P = RDP; N/P = TDPI.

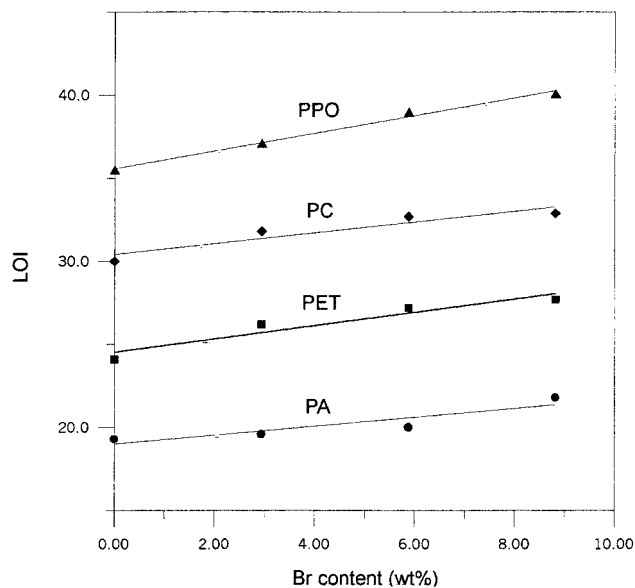


Figure 7 LOI values versus the bromine weight contents of the blended engineering polymers.

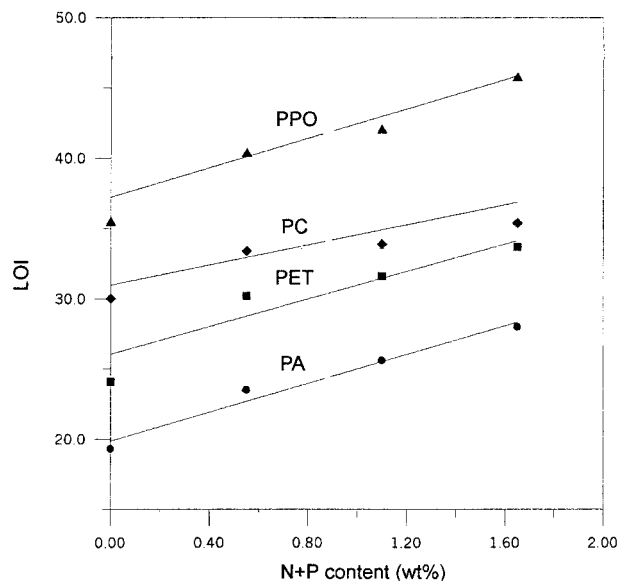


Figure 9 LOI values versus the total phosphorus and nitrogen weight contents of the blended engineering polymers.

CONCLUSIONS

The novel FR TDPI was successfully synthesized from DPCP and TDHI. The compounds were blended with EPs, and the flame retardancy of the final blends was examined by UL-94 vertical testing and LOI measurements. The combination of phosphorus and nitrogen (isocyanurate structure) had an excellent synergistic effect on the flame retardancy, and the UL-94 V-0 rating could be achieved with very low nitrogen and phosphorus contents (i.e., 0.76 wt % P and 0.34 wt % N).

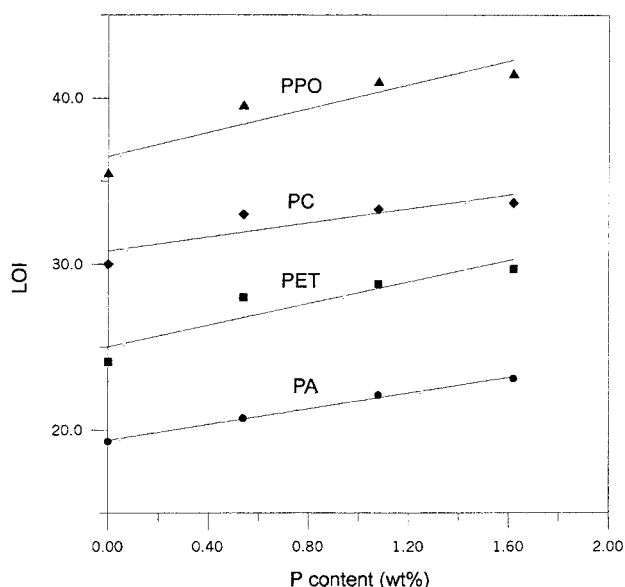


Figure 8 LOI values versus the phosphorus weight contents of the blended engineering polymers.

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