

# Characterizations for Blends of Phosphorus-Containing Copolyester With Poly(Ethylene Terephthalate)

SHINN-JEN CHANG<sup>1,2</sup> and FENG-CHIH CHANG<sup>\*1</sup>

<sup>1</sup>*Institute of Applied Chemistry  
National Chiao-Tung University  
Hsinchu, Taiwan*

<sup>2</sup>*Union Chemical Laboratories  
Industrial Technology Research Institute  
Hsinchu, Taiwan*

High molecular weight phosphorus-containing copolyesters, poly(ethylene terephthalate)-co-poly(ethylene DDP) (PET-co-PEDDP)s, were prepared and characterized with the objective of producing a non-halogen flame retardant system for practical applications. The phosphorus-containing copolyester with 30 wt% phosphorus (P30 copolyester) was blended with PET to evaluate their characteristics and flame retardancy. Higher phosphorus content results in lower crystallinity and higher char formation after thermal degradation. The rheological behavior remains similar to that of PET. The P30/PET blend possesses higher crystallization rate than the corresponding phosphorus-containing copolyester containing equal phosphorus content. Thermal and rheological behaviors of P30/PET blends are similar to PET or the phosphorus-containing copolyesters. The P30/PET blends are miscible or compatible base on single  $T_g$ s detected by DSC or DMA. The SEM/EDX phosphorus mapping image of the P30/PET blend shows uniform distribution of the phosphorus moieties within the P30/PET matrix, another indication of a compatible or miscible blend between the phosphorus-containing copolyester P30 and PET. Flame retardancy of the P30/PET blend is identical to that of the phosphorus-containing copolyester with identical phosphorus content. Blending of high phosphorus content copolyester with virgin PET provides a feasible method to obtain a flame resistant PET with LOI greater than 28.

## INTRODUCTION

In recent years, emphasis has been placed on the necessity for rendering flame retardant products from the standpoint of human importance, and much effort has been directed to this purpose (1–4). Flame retardant polyesters can be obtained by blending flame retardants before they are fabricated into shaped articles (2). This method has the advantages of convenience and low manufacturing cost. However, organic flame retardants usually cannot endure normal processing conditions at elevated temperatures, and therefore a great portion of the organic flame retardants in the blend may eventually be lost as a result of vaporization or decomposition. In addition, poor compatibility between polymers and flame retardants often causes the migration of flame retardants when the blend is in processing or use.

Polyesters are usually extruded into filaments at a temperature higher than 290°C and thus often cause degradation of the organic flame retardant and result in breakage of filaments. If the polyesters are blended with inorganic flame retardants, the spinnerets will be blocked during spinning and affect the pack pressure in spinning. In addition, the presence of a flame retardant is usually detrimental to the physical properties of the polyester and the flame retardant migrating to surface of the fabricated products also results in reduced flame-retarding efficiency (5–8).

Recently, flame retardants of phosphorus-containing large molecules have been developed to replace conventional halogen-containing flame retardants to meet the requirements of low toxicity, low smoke, and low migration in view of environmental and health considerations. These phosphorus-containing flame retardants usually possess degree of polymerization of around 15 and molar mass of about 2000. However, the heat stability of these phosphorus-containing flame

\*To whom correspondence should be addressed.

retardants is still unsatisfactory, only suitable to be processed at relatively lower temperatures.

In order to improve the poor heat resistance, low compatibility, and migration problems of conventional retardants, we have developed a high molecular weight copolyester flame retardant by importing a phosphorus-containing diacid into the main chain of the copolyester. When the flame retardant comonomer is chemically incorporated into the polyester backbone with high molar ratio, it functions as a compatible high molecular flame retardant. When this compatible high molecular flame retardant is blended with polyester, it will not migrate to the surface during melt processing such as extruding, injection molding, and spinning, and thus the efficiency of the flame retardancy can be retained. Therefore, the blended polyesters are expected to possess better physical properties and permanent flame retardancy than those conventional flame retardants.

For this study, phosphorus-containing copolyesters, poly(ethylene terephthalate)-co-poly(ethylene DDP)s (PET-co-PEDDPs), with phosphorus contents of 0.7, 2.0 and 3.0 wt% were synthesized by polycondensation of terephthalic acid, ethylene glycol and phosphorus-containing comonomer (9,10-dihydro-10-[2,3-di(hydroxycarbonyl) propyl]-9-oxa-10-phosphaphenanthrene-10-oxide, hereinafter referred to as DDP). The purpose of this study is to identify and characterize

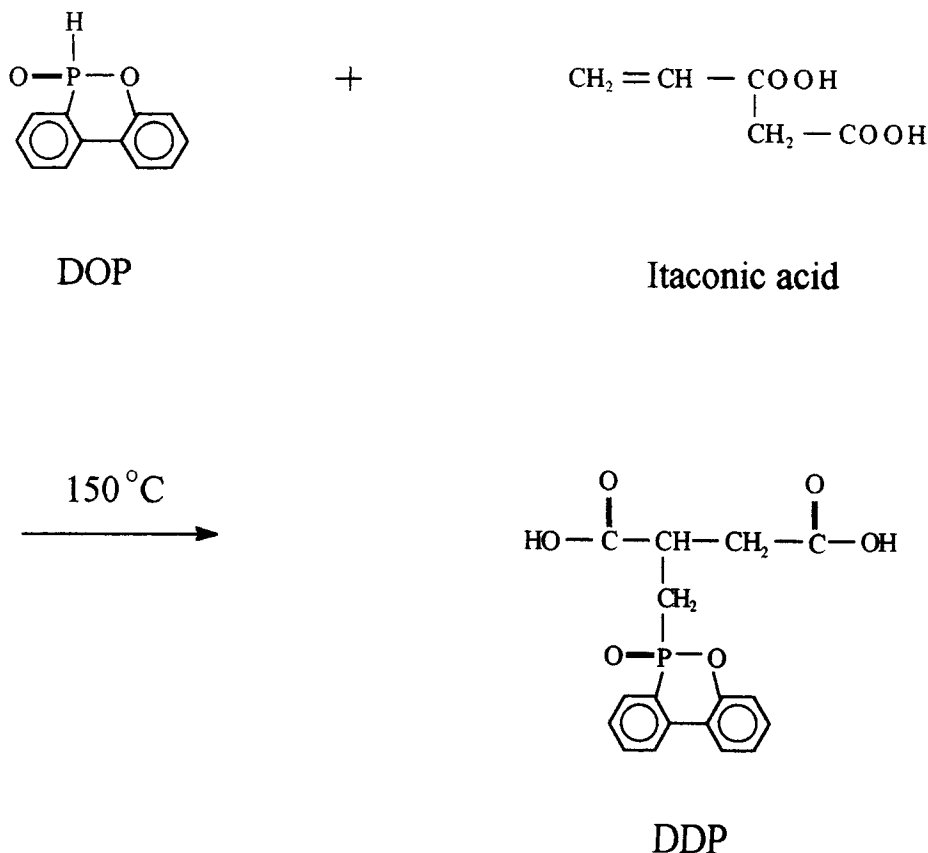
these phosphorus-containing copolyesters and P30/PET blends. Furthermore, we also want to compare the performance of the phosphorus-containing copolyester with P30/PET blends and PET in terms of its thermal, flammable, morphological, rheological, and mechanical properties.

## EXPERIMENTAL

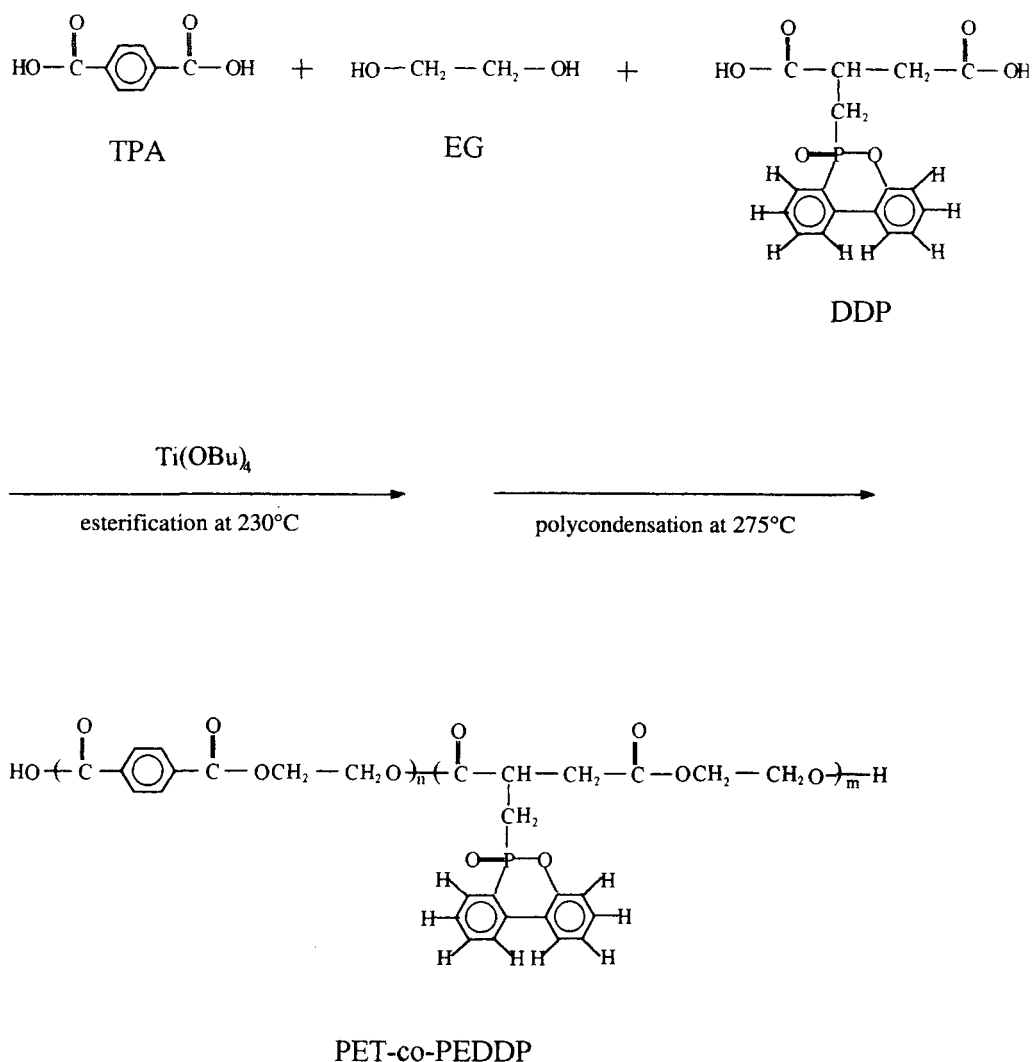
### Materials

Terephthalic acid (TPA) and ethylene glycol (EG) were obtained from Tuntex Distinct Corp. of Taiwan. The compound 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOP) and itaconic acid were purchased from the Sanko Ltd. of Japan. Tetrabutyl orthotitanate was purchased from Merck Schuchardt Ltd. The compound 9,10-dihydro-10-[2,3-di(hydroxycarbonyl) propyl]-10-phosphaphenanthrene-10-oxide (DDP) was prepared by an addition reaction of DOP with itaconic acid (9) as shown in *Scheme 1*.

The phosphorus-containing copolyesters of phosphorus contents of 0.7, 2.0, and 3.0 wt% were synthesized through co-condensation of DDP with TPA and EG catalyzed by tetrabutyl orthotitanate. The preparations were made according to a method previously described by Chang *et al.* (10) (as shown in *Scheme 2*). The copolyester with phosphorus content of 0.7 wt% is denoted as P07, 2.0 wt% is denoted as P20 and 3.0



*Scheme 1. Preparation of DDP.*



Scheme 2. Preparation of PET-co-PEDDP polymer.

wt% is denoted as P30. Nature grade PET (IV = 0.635) was obtained from Shin-Kong Synthetic Fibers Corporation of Taiwan.

### Melt Blending and Sample Preparation

The blends of the copolyester P30 with PET were prepared by using a counter-rotating 20 mm twin-screw extruder (L/D = 48, Welding Engineers Instruments Model 8 HT) with a rotational speed of 250 rpm. Vacuum was applied in the decompression zone. The barrel temperatures were set from 150 to 250°C. All materials were vacuum dried at 65°C for 15 hours prior to the extruder blending. The P30/PET blend with phosphorus content of 0.3 wt% is denoted as BP03, 0.4 wt% is denoted as BP04, and so on. The detailed processing conditions for extrusion and injection molding are listed in *Table 1* and *Table 2*.

### Characterizations

The intrinsic viscosities of copolyesters were determined by an Ubbelohde viscometer at 30°C in the phenol/1,1',2,2'-tetrachloroethane (60/40 wt%/wt%)

solution. The melting temperature ( $T_m$ ), heating crystallization temperature ( $T_{hc}$ ) and glass transition temperature ( $T_g$ ) of the phosphorus-containing copolyesters and their blends were determined on a DuPont 910 DSC at a heating rate of 10°C/min under nitrogen atmosphere. The cooling crystallization temperature ( $T_{cc}$ ) was obtained by cooling the sample from 300°C also at a cooling rate of 10°C/min. The thermogravimetric analysis was carried out using a DuPont Model 951 TGA with a heating rate of 20°C/min under oxygen and nitrogen atmospheres, respectively. Rheological characterizations were performed using a Goettfert 2001 Capillary Rheometer at 270°C. The flammability test was based on the limiting oxygen index (LOI) measurement by following the ASTM D2863-87 method. The crystallinity was determined by a Rigaku D/MAX-RC X-ray diffractometer using the Ni-filtered Cu K $\alpha$  radiation at 100 A, 40 kV, and 2 $\theta$  ranging from 5° to 45°.

Dynamic mechanical analysis (DMA) was carried out on a DuPont DMA Model 983 at temperatures ranging from -150 to 150°C under nitrogen atmos-

Table 1. Processing Conditions for Extrusion.

Sample <sup>a</sup>	P <sup>b</sup> (wt%)	P30/PET <sup>c</sup> (wt% / wt%)	stage:	Barrel Temperature (°C)					
				1	2	3	4	5	6
BP03	0.30	10 / 90		150	250	250	250	245	245
BP035	0.35	12 / 88		150	245	245	245	240	230
BP04	0.40	13.3 / 86.7		150	250	250	250	245	250
BP05	0.50	16.6 / 83.4		150	250	250	250	245	250
BP06	0.60	20 / 80		150	245	245	245	240	245
BP07	0.70	23 / 77		150	245	245	245	240	245
BP12	1.20	40 / 60		150	245	245	245	240	245

<sup>a</sup>BP03 is the P30/PET blended polyester with 0.3 wt% phosphorus content, BP035 is the P30/PET blended polyester with 0.35 wt% of phosphorus content, BP04 is the P30/PET blended polyester with 0.4 wt% phosphorus content, BP05 is the P30/PET blended polyester with 0.5 wt% phosphorus content, BP06 is the P30/PET blended polyester with 0.6 wt% phosphorus content, BP07 is the P30/PET blended polyester with 0.7 wt% phosphorus content, BP12 is the P30/PET blended polyester with 1.2 wt% phosphorus content.

<sup>b</sup>wt% phosphorus content base on total polymer.

<sup>c</sup>PET is poly(ethylene terephthalate), P30 is phosphorus-containing copolyester with 3.0 wt% phosphorus content.

phere. The dimension of the DMA specimen was 50 mm × 12.7 mm × 3.2 mm. The morphologies of the injection-molded specimens were examined by scanning electron microscopy (SEM) using a CAMSCAN SEM Series 4 microscopy at an accelerating voltage of 20 kV and 0° tilt angle. The specimen was prepared by fracturing under liquid nitrogen, followed by sputter coating with gold on the fractured surface before observation. The spatial dispersion of the phosphorus moieties in the blended polyester was examined by means of energy dispersive X-ray analysis (EDX) (CAMSCAN EDX PV9100/C10) using an elemental mapping technique based on phosphorus element. The phosphorus dispersion of the blended polyester fiber cross section was analyzed by the EDX using phosphorus elemental line scanning technique. The specimen was prepared by embedding with epoxy, followed by cross section and sputter-coating with gold on the surface before observation.

The tenacities of the polyester fibers were measured at a crosshead speed of 30 cm/min according to the JIS Standard, L1070-1964. The fiber was obtained by melt spinning from a single screw extruder equipped with a spinneret, an air cooling system and a pair of

take-up rollers. The temperature profile in the extruder along with the spinneret was set around 285–292°C. The as-spun fibers were then subjected to hot-drawing to various extent at 100°C.

Tensile properties were performed by using an Instron universal testing machine Model 4201 according to the ASTM D638 with a crosshead speed of 5 mm/min. Impact properties are performed by using TMI impact tester according to the ASTM D256 method. The testing specimens were prepared on a Toshiba Is 55 EPN injection molding machine. The temperature profile was set to range from 150 to 250°C.

## RESULTS AND DISCUSSION

The phosphorus-containing copolyesters of P07, P20, and P30 were obtained through co-condensation of DDP with TPA and EG as shown in Scheme 2. The charged monomer fraction of DDP is 4.5 mol%, 13.0 mol% and 22.6 mol%, respectively. P30 copolyester with high DDP molar ratio is a high molar mass polyester type flame retardant. We intend to use the P30 copolyester as a high molar mass flame retardant to blend with PET to give various phosphorus content P30/PET blends.

Table 2. Processing Conditions for Injection Molding.

Sample <sup>a</sup>	P <sup>b</sup> wt%	P30/PET <sup>c</sup> (wt% / wt%)	stage:	Barrel Temperature (°C)				Mold Temperature (°C)
				1	2	3	Nozzle	
PET	0.00	0 / 100		245	250	245	245	50
P07	0.70	—		235	245	240	245	50
P20	2.00	—		210	210	205	205	50
P30	3.00	—		200	180	180	150	50
BP03	0.30	10 / 90		235	245	240	245	50
BP035	0.35	12 / 88		235	245	240	245	50
BP04	0.40	13.3 / 86.7		235	245	240	245	50
BP05	0.50	16.6 / 83.4		235	245	240	245	50
BP06	0.60	20 / 80		235	245	240	245	50
BP07	0.70	23 / 77		235	245	240	245	50
BP12	1.20	40 / 60		235	245	240	245	50

<sup>a</sup>P07 is phosphorus-containing copolyester with 0.7 wt% phosphorus content, P20 is phosphorus-containing copolyester with 2.0 wt% phosphorus content.

<sup>b</sup>wt% of phosphorus content based on total polymer.

<sup>c</sup>The ratio of P30 blend with PET.

**Table 3. The Phosphorus Content, Phosphorus Comonomer Molar Fraction, Thermal Properties and Intrinsic Viscosity of PET and Phosphorus-Containing Copolyesters.**

Sample	p <sup>a</sup> (wt%)	DDP <sup>b</sup> (mol%)	T <sub>cc</sub> <sup>c</sup> (°C)	T <sub>hc</sub> <sup>d</sup> (°C)	T <sub>m</sub> <sup>e</sup> (°C)	T <sub>g</sub> (DSC) <sup>f</sup> (°C)	IV <sup>g</sup> (dl/g)
PET	0	0	188	158	257	81.7	0.635
P07	0.7	4.5	176	165	236	77.2	0.633
P20	2.0	15.0	148	—	188	77.0	0.640
P30	3.0	22.6	—	—	—	76.8	0.638

<sup>a</sup> wt% of phosphorus content based on total polymer.

<sup>b</sup> DDP is the phosphorus-containing diacid, mol% of DDP is based on diacid.

<sup>c</sup> T<sub>cc</sub> is the cooling crystallization temperature.

<sup>d</sup> T<sub>hc</sub> is the heating crystallization temperature.

<sup>e</sup> T<sub>m</sub> is the melting temperature.

<sup>f</sup> T<sub>g</sub> is the glass transition temperature measured by DSC.

<sup>g</sup> IV is the intrinsic viscosity.

### Characterizations of Phosphorus-Containing Copolyesters

The charged monomer fraction of the phosphorus-containing diacid (DDP), intrinsic viscosity (IV), melting temperature (T<sub>m</sub>), glass transition temperature (T<sub>g</sub>), heating crystallization temperature (T<sub>hc</sub>) and cooling crystallization temperature (T<sub>cc</sub>) of the synthesized phosphorus-containing copolyester P07 and P30 are summarized in Table 3. All the intrinsic viscosities are around 0.633 to 0.640 as shown in Table 3. These intrinsic viscosities indicate that the molecular weights of those phosphorus-containing copolyesters are comparable, so that the effect of molecular weight on the characteristic can be neglected. The DSC thermograms of PET, phosphorus-containing copolyesters (P07 and P30) and blends (BP04 and BP07) are shown in Fig. 1. The P07 copolyester exhibits a similar thermal behavior to that of the PET with a relatively lower T<sub>m</sub> (236°C vs. 257°C) but a higher T<sub>hc</sub> (165°C vs. 158°C), an indication of slower rate of crystallization. As can be seen

from Fig. 1, the P30 copolyester possesses only the glass transition while the crystallization does not occur under this scanning. The presence of the bulky pendent phosphorus side groups in this copolyester tends to decrease structural regularity and retard its crystallization. The X-ray diffraction patterns of PET and copolyesters (P07 and P30) are shown in Fig. 2. The intensity of scattering is plotted as a function of 2θ. The relatively sharp peaks are due to scattering from the crystalline regions and the broad regions are due to scattering from non-crystalline areas. The results of WAXD also demonstrate that the crystalline region of copolyester decreases qualitatively with the increase of the phosphorus content. However, all copolyesters demonstrate similar diffraction patterns. The sharp peaks of all copolyesters are at the same 2θ, implying that the crystal lattices of all copolyesters do not change with the incorporation of the phosphorus-containing comonomer in the polyester backbone.

The thermogravimetric curves of PET and the phosphorus-containing copolyesters under nitrogen atmos-

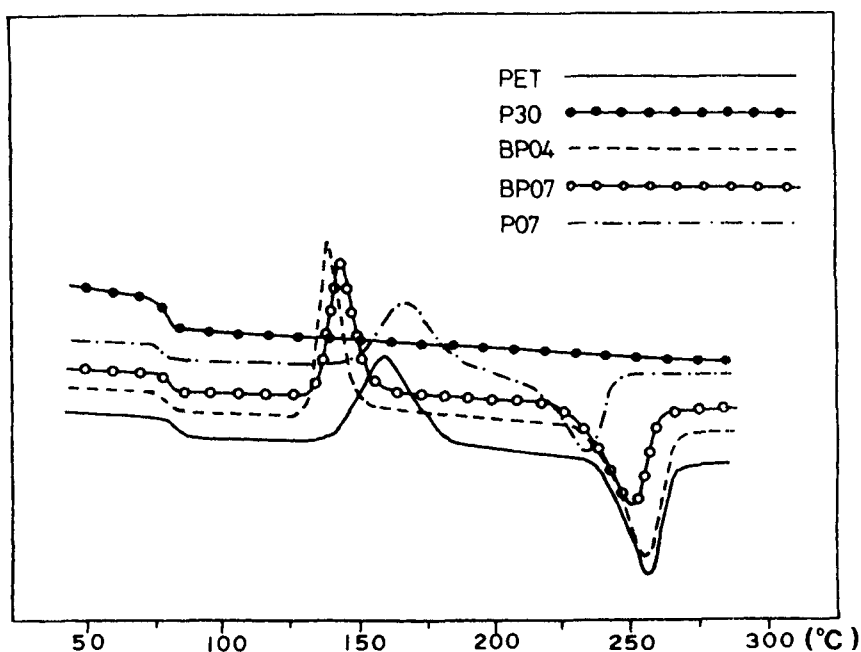


Fig. 1. DSC heating scans thermograms of various phosphorus-containing polyesters.

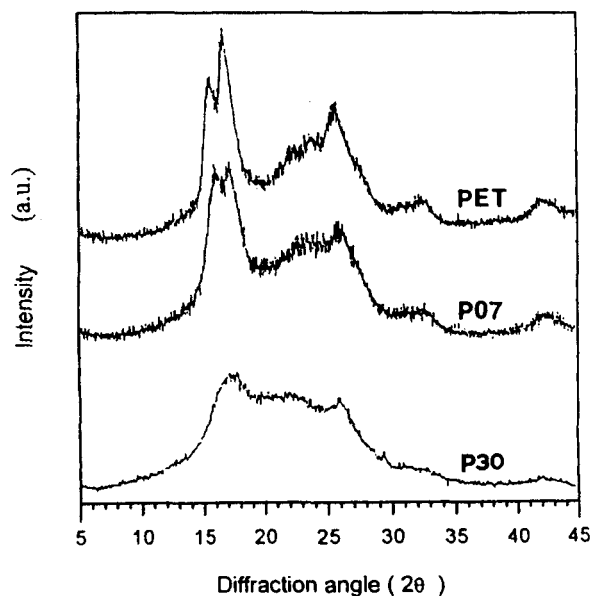


Fig. 2. X-ray diffraction patterns of P07, P30, and PET.

here are shown in Fig. 3. It is clearly shown that an increase in the phosphorus content results in a lowering of the initial degradation temperature but an increase in the residual char. The flame retardancy of a phosphorus-containing polymer and the correlation with its phosphorus content have been previously studied (11-13). Table 4 shows LOI values and the corresponding char residuals of the PET and phosphorus-containing copolyesters. Both LOI value and residual char increase as the phosphorus content is increased. Table 5 reveals that PET has the highest thermal decomposition temperature ( $T_d = 442^\circ\text{C}$ ) under nitrogen atmosphere, followed by P07 copolyester ( $T_d = 431^\circ\text{C}$ ),

Table 4. The Residual Char and Limiting Oxygen Index (LOI) Values of PET and Phosphorus-Containing Polyesters.

Sample	P (wt%)	Residual Char <sup>a</sup> (wt%)	LOI
PET	0	4.2	23.7
P07	0.7	10.0	33.3
P20	2.0	12.4	35.0
P30	3.0	12.5	35.2

<sup>a</sup>wt% of residual char at  $850^\circ\text{C}$ .

P20 copolyester ( $T_d = 419^\circ\text{C}$ ) and P30 copolyester ( $T_d = 413^\circ\text{C}$ ). Lower thermal stability with higher phosphorus content is due to more P-O bond cleavage of the phosphorus-containing copolyester. However, under oxygen atmosphere, the trend of thermal decomposition temperatures has been reversed, as shown in Table 5. The formation of a protected char layer (3, 14) for the copolyester (P07, P20 and P30) raises the decomposition temperature of the copolyester under oxygen atmosphere higher than that of the PET.

The melt viscosity as a function of shear rate for PET and phosphorus-containing copolyesters at  $270^\circ\text{C}$  is delineated in Fig. 4. All copolyesters demonstrate shear

Table 5. The Decomposition Temperature of PET and Phosphorus-Containing Copolyesters Under Nitrogen/Oxygen Atmosphere.

Sample	$T_d^a$ ( $^\circ\text{C}$ ) Under $\text{N}_2$	$T_d^b$ ( $^\circ\text{C}$ ) Under $\text{O}_2$
PET	442	382
P07	431	386
P20	419	394
P30	413	397

<sup>a</sup>Onset decomposition temperature under nitrogen.

<sup>b</sup>Onset decomposition temperature under oxygen.

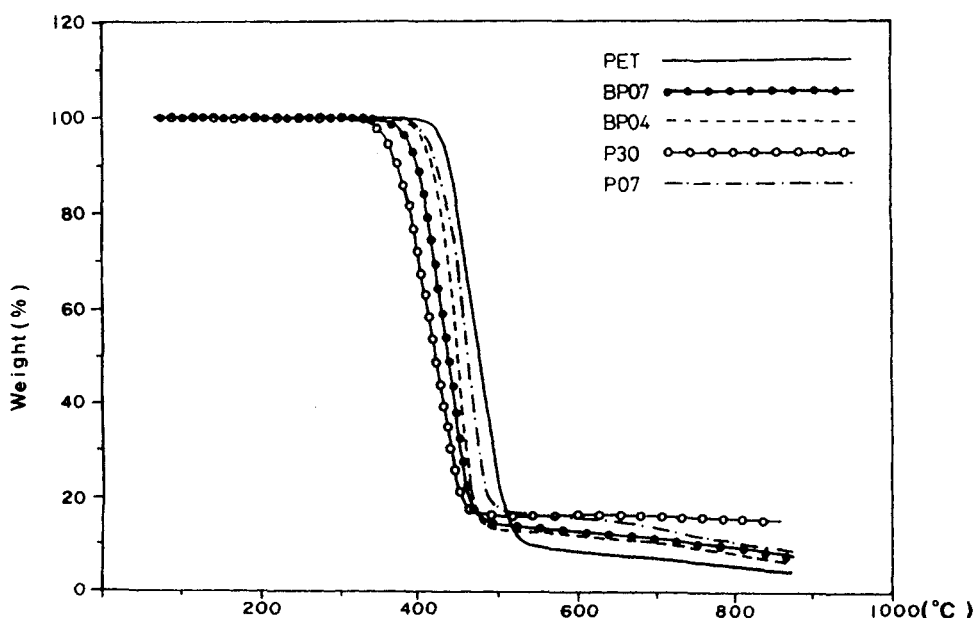


Fig. 3. TGA thermograms of various phosphorus-containing polyesters under nitrogen atmosphere.

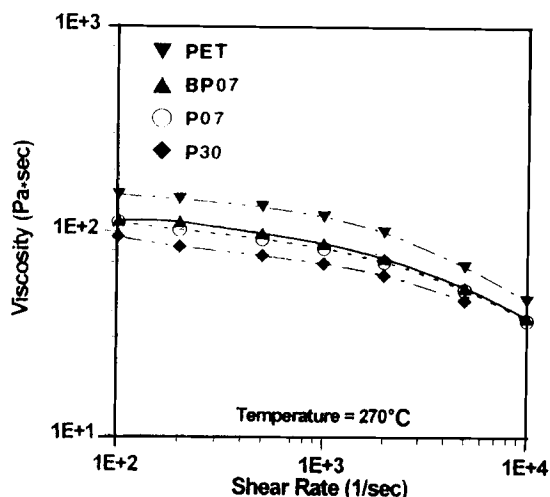


Fig. 4. Melt viscosity as function of shear rate for various phosphorus-containing polyesters.

thinning behaviors similar to PET. The melt viscosity decreases slightly with the increase of the phosphorus content because of the lower melting temperature of phosphorus-containing copolyesters.

#### Characterizations of Phosphorus-Containing Copolyester/PET Blends

The phosphorus content, P30/PET blending ratio,  $T_m$ ,  $T_g$ ,  $T_{hc}$ ,  $T_{cc}$ , and intrinsic viscosity of BP04 and BP07 are listed in Table 6. As can be seen in Fig. 1, both BP04 and BP07 blended polyesters exhibit single  $T_g$  and single  $T_m$ . Furthermore,  $T_g$  of these P30/PET blended polyesters is located between the  $T_g$  of P30 and PET. Therefore, these polyester blends can be considered to be miscible.  $T_m$  of the blended polyester decreases with an increase of phosphorus content. The P07 copolyester has substantially lower  $T_m$  than that of the BP07 blend (236°C vs. 251°C), although both have equal phosphorus content.  $T_g$  also shows a similar trend (77.2°C vs. 78.8°C).  $T_m$  and  $T_g$  of the P07 copolyester are the lowest among all since P07 is a random phosphorus-containing copolyester (15). Relative to PET, the P07 copolyester has higher  $T_{hc}$  (165°C) and lower  $T_{cc}$  (176°C) while the blended polyesters BP04 and BP07 have lower  $T_{hc}$  (138°C and 143°C) and higher  $T_{cc}$  (198°C and 196°C). These results imply that the P30 in these blends is able to act as a nucleation agent in accelerating the rate of PET crystallization. Presence of a foreign surface will reduce the free energy barrier for nuclei formation (16). Thus, nucleation will occur more easily for those blended polyesters through heterogeneous nucleation. Since the

P07 copolyester is a random copolyester, it will nucleate and grow crystals through a homogeneous matrix at a slower rate than would be expected. In addition, the P07 copolyester possesses bulky phosphorus side groups that tend to retard crystallization relative to the virgin PET. The P30 copolyester does not crystallize during the heating scanning because it contains too many bulky phosphorus side groups. Thus,  $T_{hc}$  of P07 copolyester is higher than that of PET while its  $T_{cc}$  is lower than that of PET.

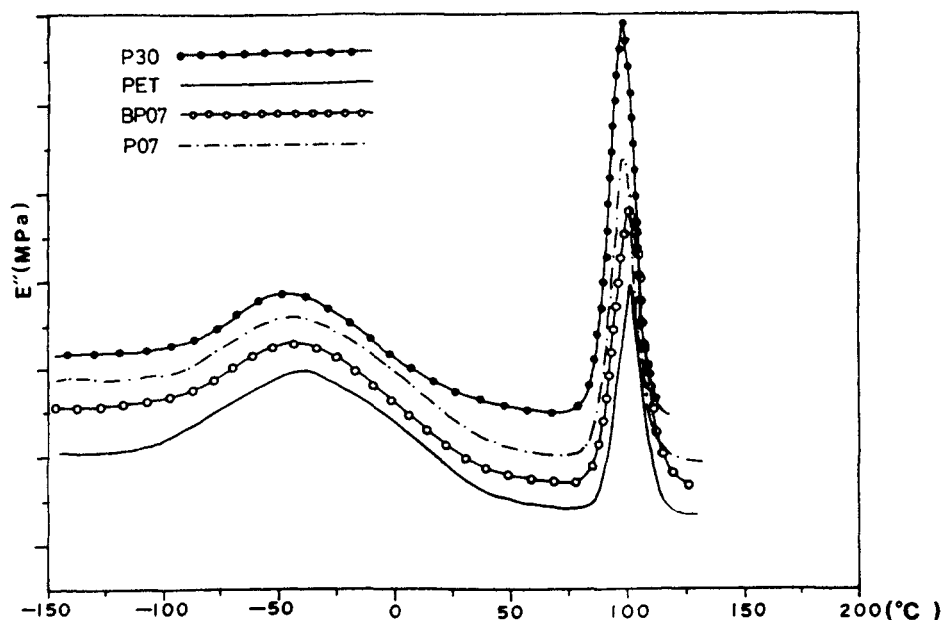
As illustrated in Fig. 3, all polymers investigated are degraded in a one-step process. A one-step degraded process implies that the blended polyester is well mixed. By comparison, the P07 copolyester has a higher thermal decomposition temperature ( $T_d = 431^\circ\text{C}$ ) than those of the blended polyesters of BP04 ( $T_d = 410^\circ\text{C}$ ) and BP07 ( $T_d = 407^\circ\text{C}$ ) under nitrogen atmosphere. This can be interpreted as the blended polyesters containing less thermally stable P30 copolyester that is able to exert a flame retarding effect. When the phosphorus content is increased,  $T_d$  shifts to lower temperatures. However, the P07 copolyester is a random copolyester containing relatively weaker phosphorus linkages as pendant groups. When the thermal degradation occurs through the P-O bond cleavage, the copolyester backbone can still be maintained and degrades at a higher temperature. Therefore, the P07 copolyester has a higher  $T_d$ .

Curves of loss modulus ( $E''$ ) versus temperature from the dynamic mechanical analyses (DMA) of PET, P07, BP07, and P30 are illustrated in Fig. 5. All the samples give two transition temperatures. The lower temperature (around  $-50^\circ\text{C}$ ) corresponds to the secondary transition (17, 18) owing to the rotation of ester ( $-\text{COO}-$ ) and methylene ( $-\text{CH}_2-$ ), while the higher temperature (around  $100^\circ\text{C}$ ) corresponds to a glass transition result in the main chain motion of the amorphous region. P07, P30 copolyesters and the BP07 blended polyester demonstrate a similar dynamic mechanical behavior to that of the virgin PET (19) with slightly lower  $T_g$  transition temperature, at around  $97-102^\circ\text{C}$  ( $E''$  is usually higher than  $\tan\delta$ ). In terms of micro-scale, PET is a homopolymer with homogenous sequence. On the contrary, these phosphorus-containing copolyesters are random copolyesters with heterogeneous sequential lengths ( $\overline{L}_{np} = 1.313$  for P30 copolyester and  $\overline{L}_{np} = 1.025$  for P07 copolyester) (15). The width of transition peak has the trend of P30 > P07 > PET owing to longer  $\overline{L}_{np}$  of the P30. The amorphous region of the copolyester increases with the increase of the  $\overline{L}_{np}$ . The shape of transition peak of the BP07 blended polyester is similar to that of the P07 copolyester. Peaks of BP07 and P07 shift slightly to

Table 6. Phosphorus Content, Thermal Properties, and Intrinsic Viscosity of P30/PET Blends.

Sample	P (wt%)	P30/PET (wt% / wt%)	$T_{cc}$ ( $^\circ\text{C}$ )	$T_{hc}$ ( $^\circ\text{C}$ )	$T_m$ ( $^\circ\text{C}$ )	$T_g$ (DSC) ( $^\circ\text{C}$ )	IV (dl/g)
BP04	0.4	13.3 / 86.7	198	138	255	79.2	0.634
BP07	0.7	22.6	196	143	251	78.8	0.632

Fig. 5. The loss modulus ( $E''$ ) vs. temperature from DMA spectra of P07, BP07, P30, and PET.



lower temperatures than that of PET. The order of transition temperature is: PET > BP07 blend > P07 copolyester > P30 copolyester. This observed DMA result again emphasizes that the P30 copolyester is compatible or miscible with PET.

As seen in Fig. 4, the melt viscosity of the BP07 blend is close to the P07 copolyester but is slightly lower than the PET within the shear rate range of  $10^2$ – $10^4$  1/sec. Therefore, the BP07 blended polyester, phosphorus-containing copolyester P07, and PET have similar rheological characteristics.

The limiting oxygen index (LOI) value can be used as an indicator to evaluate polymer flame-retardancy (11–13). Table 7 lists the LOI values and phosphorus contents of various P30/PET blends. Figure 6 depicts the relationship between LOI and total phosphorus contents of P30/PET blends and various copolyesters (P07, P20, and P30). These P30/PET blends were prepared by using P30 copolyester as a flame retardant. Figure 6 demonstrates that a higher LOI value is obtained by increasing phosphorus content in both copolyesters and blends. However, it reaches a plateau when the phosphorus content approaches 0.7 wt%. From an economic viewpoint, in the blended polyester

with as little as 0.4 wt% of phosphorus, the LOI can reach 28 to meet the flame retardant criterion. A material with LOI of 28 or higher is rated as a flame retardant material.

Stannett *et al.* (20, 21) reported that a reactive type flame retardant is more effective than that of an additive type because a reactive flame retardant can react and be attached to the polymer backbone to yield a more homogeneous system. As illustrated in Fig. 6, the LOI of P07 copolyester is almost equal to the LOI of the BP07 blended polyester. This result indicates that the same flame retardancy can be achieved either through copolymerization or blending provided that the blend is compatible or miscible.

Figure 7 shows the SEM/EDX micrograph of the fractured surface of the BP07 blended polyester. No

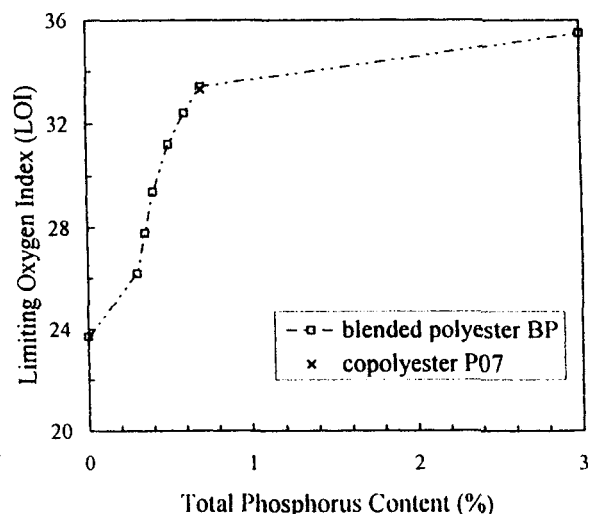


Fig. 6. Limiting oxygen index (LOI) vs. total phosphorus content in P30/PET blends.

Table 7. Limiting Oxygen Index (LOI) Values and Various Phosphorus Contents of P30/PET Blends.

Sample	P (wt%)	P30 / PET (wt% / wt%)	LOI
BP03	0.3	10 / 90	26.2
BP035	0.35	12 / 88	27.8
BP04	0.4	13.3 / 86.7	29.4
BP05	0.5	16.6 / 83.4	31.2
BP06	0.6	20 / 80	32.4
BP07	0.7	23 / 77	33.4
BP12	0.7	23 / 77	34.0



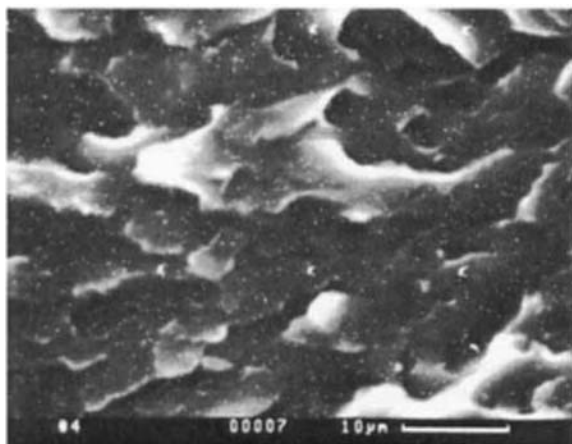


Fig. 7. SEM/EDX micrograph of the fracture surface of the injection molded BP07.

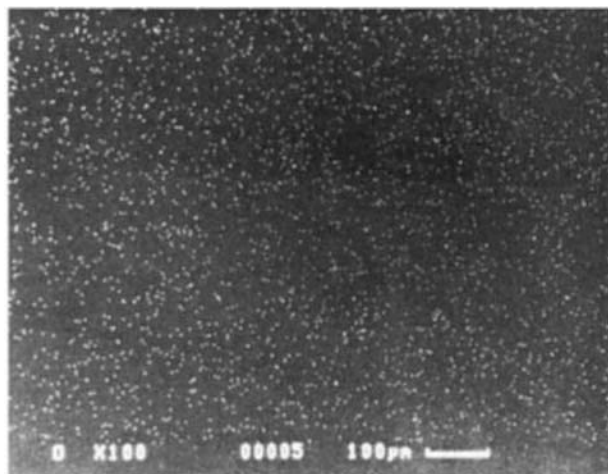


Fig. 8. EDX elemental mapping image of the injection molded BP07 blend based on element phosphorus.

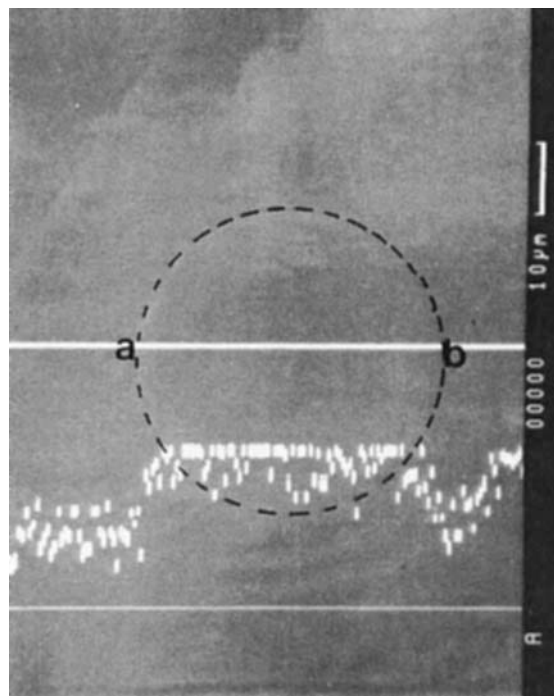


Fig. 9. The SEM/EDX phosphorus elemental line scanning image of the BP07 fiber cross section.

obvious phase separation can be observed at this specified magnification. This result indicates that the phosphorus-containing copolyester P30 and PET are fairly compatible, if not totally miscible. The EDX phosphorus mapping image of the BP07 blend at a higher magnification of the cross section from an injection molding specimen is shown in Fig. 8. Again, these phosphorus moieties (white points) disperse quite uniformly throughout the cross section of the BP07 tensile specimen. Figure 9 shows the SEM/EDX phosphorus elemental line scanning image throughout the cross section of a BP07 fiber (the circle drawn dashed line represents the cross section of the BP07 fiber). The phosphorus intensities within the diameter (a-b) of the fiber are quite uniform and higher than outside of the diameter (which is the base line). That means the phosphorus moiety of the BP07 fiber is also uniformly distributed. This result indicates that regardless of the material being processed or fabricated, the phosphorus component can be dispersed quite uni-

formly throughout the cross section of the products. This result also suggests that the phosphorus-containing copolyester P30 is compatible or miscible with PET. If the P30/PET blend is incompatible, the lower melt viscosity component (P30 copolyester) should concentrate more on the outer layer. The extent of the transesterification reaction between two polyesters depends on the blending time, temperature, composition, residual polyester catalysts, and the added catalyst (22). In this study, the lapse of blending time is too short (about 2 minutes) for detectable transesterification, which was confirmed by proton NMR. The BP07 was separated by a continuous extraction hot chloroform for 36 hours in a Soxhlet extraction apparatus. Proton NMR spectra of the Soxhlet extraction solid part (PET) and liquid part (P30) did not show any product from transesterification.

The tenacity and elongation at break are shown in Figs. 10 and 11, respectively. The tenacities of the as-spun fibers of PET, P07 copolyester, and P30/PET blends are approximately at 0.4 g/d. At a drawing ratio of 3, the tenacities of the P30/PET blended fibers (BP04 and BP07) are around 1.5 to 1.7 g/d, higher than that of the P07 copolyester (1.25 g/d). The tenacity increases with the increase of PET content because the PET has higher tenacity. A similar trend was also observed for the measured elongation-to-break (Fig. 11). The tenacity of P07 copolyester fiber tows was measured as a function of different drawing ratios; the results are shown in Fig. 12. The tenacity increases gradually from 0.4 g/d for the as-spun fibers to about 2.8 g/d for fibers with a drawing ratio of 5. A higher

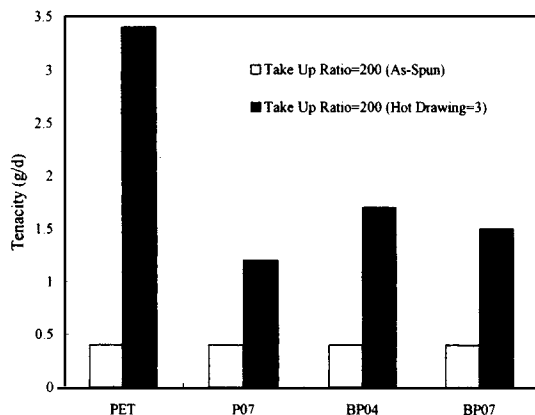


Fig. 10. The tenacity of fibers of various phosphorus-containing polyesters.

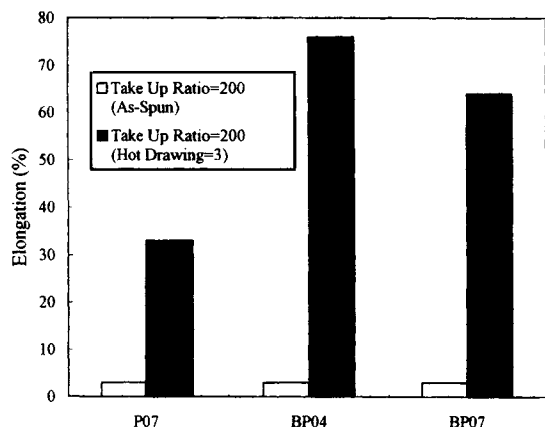


Fig. 11. The elongation of fibers of various phosphorus-containing polyesters.

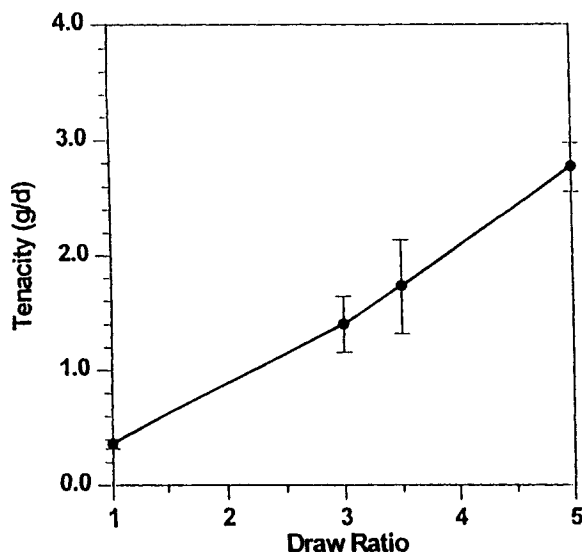


Fig. 12. Tenacity vs. drawing ratio of fiber P07.

Table 8. The Tensile Strength and Izod Impact of PET, BP04, BP07, P07 and P30.

Sample	P (wt%)	P30 / PET (wt% / wt%)	Tensile Strength (MPa)	Impact Strength (J/M)
PET	0	0 / 100	60	20.9
BP04	0.4	13.3 / 86.7	52	22.7
BP07	0.7	23 / 77	44	23.6
P07	0.7	—	41	24.3
P30	3.0	100 / 0	30	27.6

tenacity with a higher drawing ratio is due to higher orientation of fibers.

Table 8 delineates the tensile strength and Izod impact of the injection molded specimens for the blended polyesters (BP04, BP07), copolyesters (P07, P30) and PET. The general trend shows lower tensile strength with higher phosphorus content. However, the Izod impact increases with the increase of the phosphorus content. The presence of phosphorus-containing copolyester P30 in PET matrix tends to reduce PET crystallinity and results in lower tensile strength but higher impact toughness.

## CONCLUSIONS

For a phosphorus-containing copolyester, the incorporation of phosphorus moieties into its molecular chain has a significant effect on its crystallization and flame retardancy behavior. Higher phosphorus content results in lower crystallinity and higher char formation after thermal degradation. The rheological behavior remains similar to that of PET. The P30/PET blend possesses a higher crystallization rate than the corresponding copolyester with equal phosphorus content. Thermal and rheological behaviors of P30/PET blends are similar to PET or the phosphorus-containing copolyesters. The P30/PET blends are miscible, as a single  $T_g$  was observed by DSC or DMA. The SEM/EDX phosphorus mapping image of the P30/PET blend shows uniform distribution of the phosphorus moieties within the P30/PET matrix, another indication of a compatible or miscible blend between the phosphorus-containing copolyester P30 and PET. The flame retardancy of the P30/PET blend is identical to that of the phosphorus-containing copolyester if the total phosphorus contents are equal. Blending of high phosphorus content copolyester with virgin PET provides an easy and feasible way to obtain a flame resistant PET with LOI greater than 28.

## ACKNOWLEDGMENT

The authors would like to express our gratitude to Professor P. D. Hong of Department of Textiles and Polymer Engineering, National Taiwan Institute of Technology for conducting experiments on X-ray diffraction analyses.

REFERENCES

1. SRI International, *Flame Retardants*, in Specialty Chemicals—A Multiclient Report (1993).
2. S. R. Sandler and W. Karo, *Polymer Synthesis Academic*, Vol. 1, p.367, New York (1974).
3. C. F. Cullis and M. M. Hirscher, *The Combustion of Organic Polymers*, 241, Clarendon Press, Oxford, England (1981).
4. W. C. Kuryla and A. J. Pappa, *Flame Retardancy of Polymer Materials*, Vol. 1, Marcel Dekker, New York (1975).
5. I. S. Toyama, M. S. Uoza, and A. K. Toyama, U.S. Patent 5,026,757.
6. I. S. Toyama, M. S. Uoza, and A. K. Toyama, U.S. Patent 5,041,490.
7. L. S. Cohen and R. W. Stackman, Be 769,229.
8. K. Helmut, H. Walter, and C. Haraid, DE 2,148,348.
9. S. Endo, K. Kashihara, A. Osako, T. Shizuki, and T. Ikegami, U.S. Patent 4,127,590.
10. S. J. Chang, Y. C. Sheen, R. S. Chang, and F. C. Chang, *Polym. Degrad. Stab.*, **54**, 365 (1996).
11. M. Sato, H. Kondo, and M. Yokoyama, *J. Appl. Polym. Sci.*, **29**, 299 (1984).
12. C. P. Yang and S. S. Wang, *J. Polym. Sci.*, **A27**, 3351 (1989).
13. C. J. Hilado, *Flame Retardants*, p. 1, Technomic, Westport, Conn., (1973).
14. M. Bank, J. R. Ebdon, and M. Johnson, *Polymer*, **34**, 4547 (1994).
15. S. J. Chang and F. C. Chang, *Polymer*, to appear.
16. R. J. Young and P. A. Lovell, *Introduction to Polymers*, 2nd Ed., p. 204, Chapman & Hall, London (1991).
17. I. M. Ward, *Trans. Faraday Soc.*, **56**, 648 (1960).
18. K. H. Iller and H. J. Breuer, *Colloid Sci.*, **18**, 1 (1963).
19. H. F. Mark, N. M. Bikales, C. G. Overberger, G. Menges, and J. I. Kroschwitz, *Encyclopedia of Polymer Science and Engineering*, 2nd Ed., Vol. 12., p.24, John Wiley & Sons, Inc., New York (1988).
20. R. Liepins, J. R. Surles, N. Morosoff, and V. T. Stannett, *J. Appl. Polym. Sci.*, **21**, 2529 (1977).
21. R. Liepins, J. R. Surles, N. Morosoff, V. T. Stannett, J. J. Duffy, and F. H. Day, *J. Appl. Polym. Sci.*, **22**, 2403 (1978).
22. S. C. Lee, K. H. Yoon, L. H. Park, H. C. Kim, and T. W. Son, *Polymer*, **38**, 4831 (1997).

Received July 12, 1997  
 Revised November 1997