

# Graft Copolymers of Nylon 6 and Polyphenylene Oxide: Syntheses and Their Role in Compatibilizing Nylon 6/Polyphenylene Oxide Blends

YU-CHIN LAI\*

Engineered Materials Research Center, Allied-Signal Inc., Morristown, New Jersey 07960

## SYNOPSIS

Poly(2,6-dimethyl-*p*-phenylene) oxides (PPO) grafted with nylon 6 were prepared by first quantitatively brominating the PPO, followed by reacting the brominated products with nylon 6 of different molecular weights. The molecular weights of PPOs were kept intact during bromination. These graft copolymers with well-defined structures were used as compatibilizers for nylon 6/PPO blends. Some compatibilization phenomena were observed, as indicated by the mechanical properties of the blends. The best compatibilization was achieved when the graft copolymer is most block-copolymer-like. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

The physical blending of two or more existing polymers to obtain new products is of great technical and commercial importance, particularly when the development of new polymers becomes cost ineffective and environmentally unfavorable. Although a few polymer blends with miscible components have been reported, polymers are seldom compatible. However, polymer blends can be made in useful forms through many means, including the use of a third component as compatibilizer or interfacial agent.<sup>1</sup> Here the compatibilizer is designed to (1) reduce the interfacial energy between the phases, (2) permit a finer dispersion during mixing, (3) provide a measure of stability against segregation, and (4) improve the interfacial adhesion.

As an engineering plastics,<sup>2</sup> poly(caprolactam), or nylon 6, exhibits a number of advantages and a few deficiencies when compared to other plastic materials of comparable cost. The advantages include excellent solvent resistance and good processability. The deficiencies include low heat deflection tem-

perature, poor dimensional stability, and low impact strength.<sup>3</sup>

Poly(2, 6-dimethyl-*p*-phenylene) oxide (PPO)<sup>4</sup> has maintained a key position within engineering plastics since its inception in the late 1960s. It exhibits high dimensional stability and good thermal properties. However, deficiencies such as poor solvent resistance and processibility prohibit it from a broad usage. In general, PPO is used to form a blend with high-impact polystyrene.

The key properties of nylon 6 and PPO are compiled in Table I for comparison.

The inherent properties of nylon 6 and PPO suggest that a combination of nylon 6 and PPO would give a useful blend with improved thermal stability, dimensional stability, and solvent resistance and good processability. Nylon 6 and PPO are not compatible, and thus it is reasonable to expect that some form of compatibilization would be required to prepare a useful blend. Nylon 6/PPO blends with some ambiguous form of compatibilizer were studied before. For example, pellets derived from a blend of maleic anhydride-styrene (1 : 9) copolymer (50 parts) and nylon 6 (50 parts) were combined with PPO in a 40 : 60 ratio to give a blend with good impact strength and elongation.<sup>5</sup> Maleic anhydride modified PPO was also used as a compatibilizer for nylon 6/PPO blend.<sup>6</sup> In this work, the synthesis of

\* Present address: Bausch & Lomb Inc., Rochester, New York 14692.

**Table I** Physical Properties of Nylon 6 and PPO

	Nylon 6	PPO
Thermal		
$T_m$ (°C)	215	257
HDT (°C) at 264 psi	65	174
Dimensional stability	Poor	Good
Water absorption (%)		
24 h	1.6	0.03
50% relative humidity	2.7	0.03
Saturation	10.5	0.10
Solvent resistance	Good	Poor

PPO-nylon 6 graft copolymers with well-defined structure and the use of these graft copolymers as compatibilizers for making nylon 6/PPO blends were evaluated. The effect of graft-copolymer structure on compatibilization was assessed.

## EXPERIMENTAL

### Materials

Nylon 6 samples with number average molecular weights ( $M_n$ ) of 20,200, 10,100, 6,700 (Allied Fibers), and 20,800 (Nylon Corporation of America) were obtained. Their molecular weights were determined by the acid numbers and amine numbers of each sample, which in turn were determined by standard acid-base titration.

The PPO, with  $M_n = 21,900$ , was obtained from Aldrich Chemical Co. All solvents (from Aldrich) used in this study were used as received.

### Preparation of Brominated PPO: General Procedure

A 2-L round-bottom flask equipped with a reflux condenser was charged with 60 g of PPO and 400 mL of solvent, the system was brought to reflux, and then bromine in the same solvent (10 wt %) with varying amount depending on the degree of bromination desired was added into the solution over a period of 5–10 min. The system was kept refluxed for an additional hour and then the product was recovered by precipitating into 3.5 L of methanol. The product was filtered and further purified by dissolution/precipitation. The final product was then dried *in vacuo* at 100°C for 24 h. Quantitative yield was obtained normally. The degrees of bromination on methyl groups and aromatic ring were determined by a Varian 400-MHz nuclear magnetic resonance (NMR) spectrophotometer.

### Preparation of PPO-g-nylon 6: -General Procedure

Into a 2-L round-bottom flask equipped with reflux condenser and mechanical stirrer was charged nylon 6 (45 g) and *N*-methyl pyrrolidone (NMP, 400 mL). The contents were heated to 190°C with stirring until homogeneous solution was obtained. Hot (110°C) solution of brominated PPO was added slowly into the nylon solution over a period of 2 h. The solution was kept on heating and stirring for an additional hour and then poured into a 4-L beaker containing 3 L of water and 1 g of sodium hydroxide to recover the product. It was then filtered and washed with water and dried.

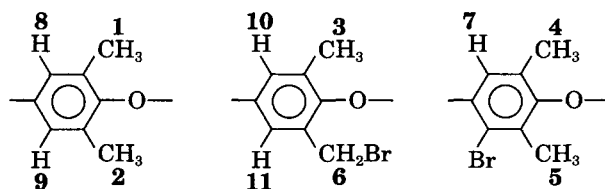
The graft copolymer was obtained by successive extraction of the crude product with, first, chloroform, and then, trifluoroethanol to remove PPO and nylon 6, respectively. These three fractions were identified by infrared (IR) spectra taken on a Beckman instrument.

### Mixing and Injection Molding of Blends of Nylon 6 and PPO

The components which made up the blends (nylon 6 of  $M_n = 20,200$ , PPO, and graft copolymer) were first ground into powders, mixed in a plastic bag, and then thoroughly dried in a vacuum oven. They were then extruded through a Leistritz twin screw extruder (model 5854) and pelletized. These pellets were dried further in a vacuum oven and then injection molded into specimens suitable for testing by using an Arburg injection molding machine. All samples containing different graft-copolymer samples were processed under the same conditions. Nylon 6 and PPO control samples were also processed

**Table II.** Assignments of NMR Peaks of Brominated PPO

H	Peak (ppm)
1, 2, 3	2.1
4	2.0
5	2.3
6	4.35
7	6.0–6.3
8, 9, 10, 11	6.3–6.8



**Table III Bromination of PPO in Chlorinated Solvent**

Solvent	Reaction Temperature (°C)	Brominated PPO	
		% —CH <sub>2</sub> Br	% Br
CHCl <sub>3</sub>	65	None	100
ClCH <sub>2</sub> CH <sub>2</sub> Cl	85	Immeasurable	100
Cl <sub>2</sub> CHCH <sub>2</sub> Cl	110	29	71
C <sub>6</sub> H <sub>5</sub> Cl	135	89	11
Cl <sub>2</sub> CHCHCl <sub>2</sub>	148	93	7

to make specimen for testing. For comparison purpose, samples that did not undergo twin screw extruder mixing were also injection molded into specimen in the same fashion for mechanical testing.

### Measurements of Physical Properties

The tensile, flex, impact, and heat deflection temperatures were measured according to the American Society for Testing and Materials (ASTM) standards D-638, D-790, D-256, and D-648, respectively. Ten samples were used for tensile and flex strength testing, two samples for heat deflection temperature (HDT) testing, and eight samples for notch Izod impact strength testing. All results were reported in psi, ft-lb/in., and °C.

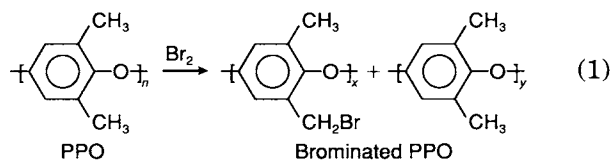
Water absorption was determined by subjecting thoroughly dried plastic bars to a water bath for 24 h. The percent gain in weight was reported.

## RESULTS AND DISCUSSION

It is generally understood that for block or graft copolymers to be effective as compatibilizer they must locate preferentially at the blend interface.<sup>1</sup> In order to study the effect of graft-copolymer structure on compatibilization of nylon 6/PPO blends, graft copolymers with one, two, or four grafting joints were targeted for the synthesis. To make graft copolymers of PPO with nylon 6, either PPO or nylon 6 must be functionalized in a manner that offers easy grafting reaction. In the following, a convenient method is described that involved the bromination of methyl groups of PPO followed by reaction with nylon 6.

### Synthesis of Brominated PPO

Bromination of PPO has been studied before.<sup>7</sup> In this study, PPO was brominated with molecular bromine as follows:



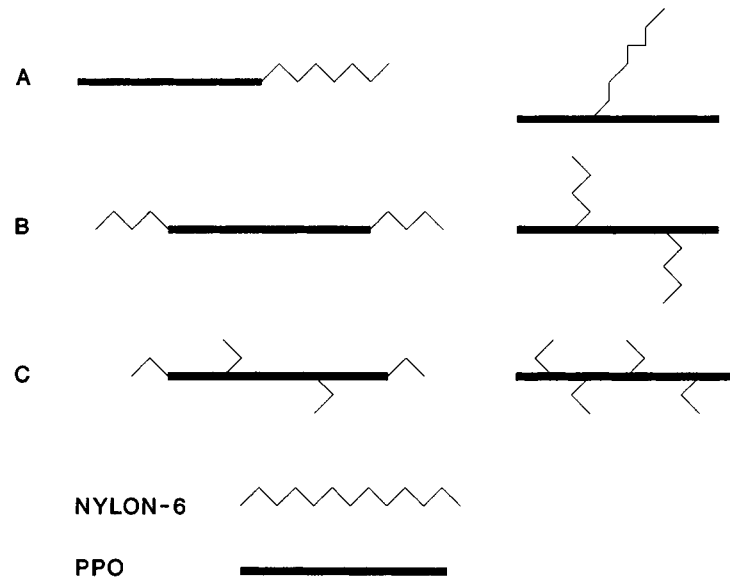
This bromination reaction was carried out under different temperatures by using chlorinated solvents with different boiling temperatures. The structures of brominated products were analyzed by high-resolution NMR spectroscopy. The assignments of NMR peaks are presented in Table II. Table III summarizes the structures of the brominated products as analyzed by NMR spectroscopy. These results suggested that to get over 90% methyl bromination (vs. ring bromination), the bromination must be carried out at temperatures no less than 135°C in either chlorobenzene or 1,1,2,2-tetrachloroethane. Thus, brominations were then carried out at high temperature to different degrees (from 0.5 to 100% per PPO unit). Although hydrochloride gas was generated, there was no indication that severe chain scission of PPO occurred as the viscosities of the brominated PPO remained constant (see Table IV).

### Preparation of PPO-g-Nylon 6

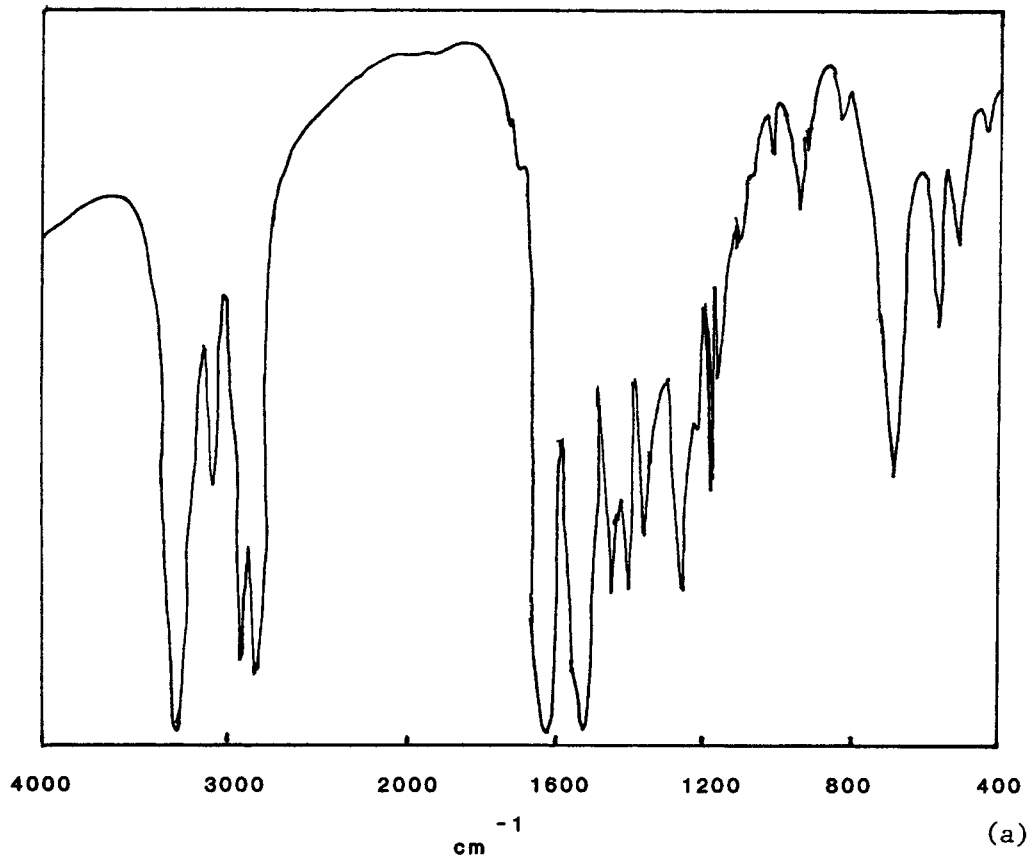
Equation (2) shows the grafting reaction of brominated PPO with nylon 6:

**Table IV Viscosity of Brominated PPO by (Molar) Ratio**

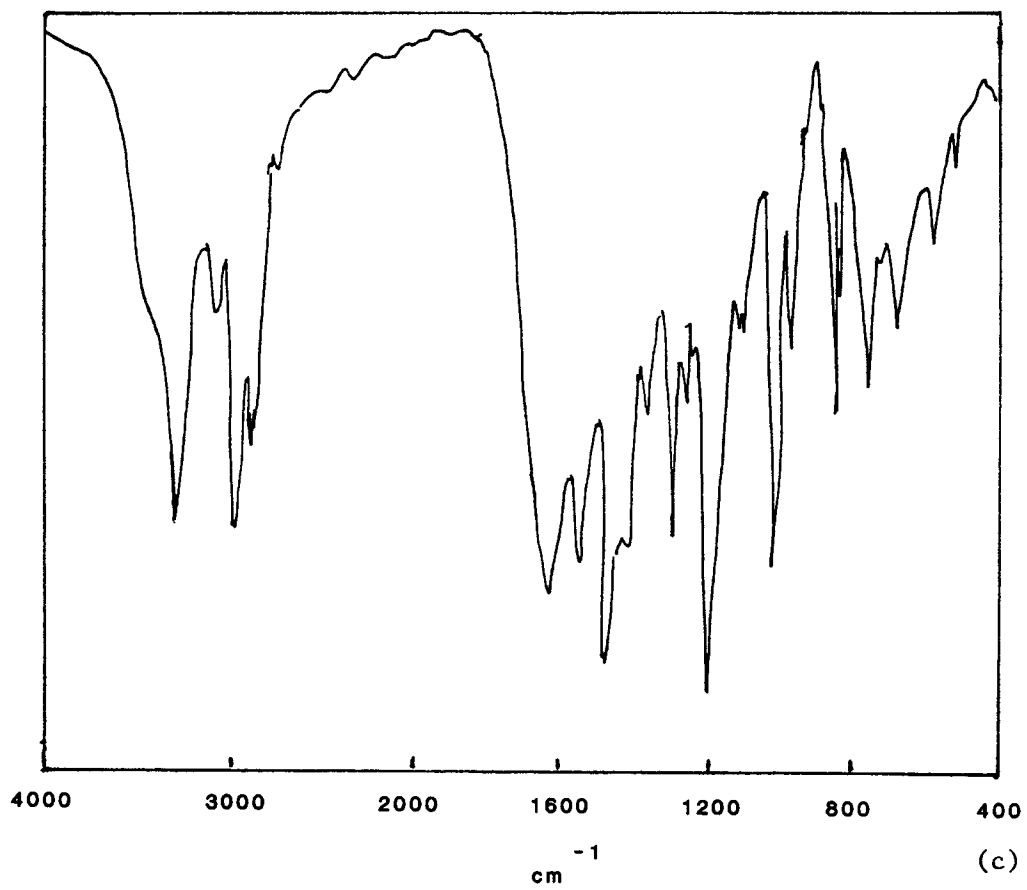
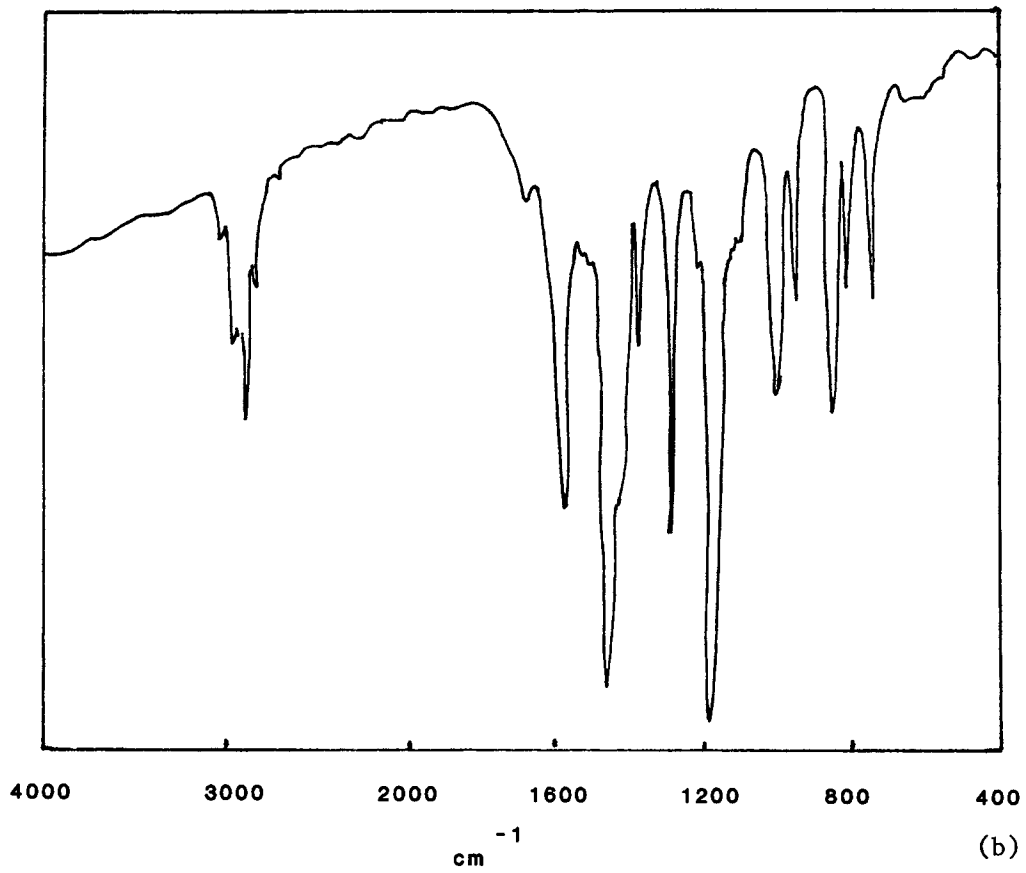
Br/PPO Feed	0	1 : 200	1 : 20	1 : 4	1 : 1
$n_{sp}/c$ at 0.5% CHCl <sub>3</sub>	0.57	0.67	0.52	0.60	0.57



**Figure 1** Structures of graft copolymers of nylon 6 and PPO.



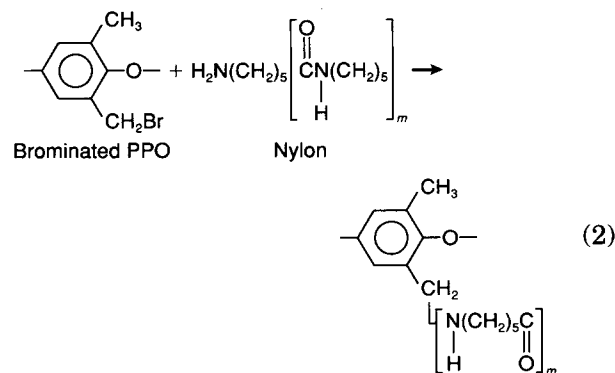
**Figure 2** (a) Infrared spectrum of (a) Nylon 6, (b) PPO, and (c) graft copolymer (A in Table V).



**Figure 2** (Continued from the previous page)

**Table V Graft Copolymers of PPO and Nylon 6**

Code	Derived from		Structure PPO/Nylon 6
	PPO with % CH <sub>2</sub> Br	Nylon 6 of M <sub>n</sub>	
A	0.5	20,800	1 : 1
B	1.0	10,100	2 : 1
C	2.0	6,700	4 : 1



To minimize crosslinking and separation problems, a large excess of nylon 6 was used and the amount of grafted copolymer was determined by successive extraction with chloroform, a good solvent for PPO, and trifluoroethanol, a solvent for nylon 6. Those insoluble in either solvent and non-crosslinked were grafted copolymers. The grafting reaction was carried out in NMP at high temperature and normally no crosslinking was observed.

As stated earlier, to study the effect of PPO-nylon 6 graft-copolymer structure on the compatibilization of nylon 6/PPO blend, graft copolymers with one, two, or four nylon 6 molecule per PPO molecule on average, but of equal weight of PPO and nylon 6, were prepared by using PPO with different degree of bromination as described before and nylon 6 of different molecular weight. These graft copolymers have the ideal structures shown in Figure 1. However, experimental evidence to demonstrate the structures shown in Figure 1 was difficult due to lack of appropriate analytical methods, although the copolymer nature of these products could be identified easily by comparing the IR spectrum of the product (copolymer A) with those of nylon 6 and PPO. Figures 2(a)–(c) show the spectra of nylon 6, PPO, and the graft copolymer, respectively. The graft copolymer has absorption peaks at 3300 (NH stretching), 3060, 1640 (amide I band), and 1540 (amide II band) cm<sup>-1</sup>, which are all characteristic

of a nylon 6 sample, and has absorption at 3020 (hindered), 1605 (aromatic C=C), 1305, 1020, and 750 cm<sup>-1</sup>, which are all characteristic of a PPO sample.

Table V lists the graft copolymers prepared and were used in compatibilization study after blending with PPO and nylon 6.

### PPO/Nylon 6 Graft Copolymers as Compatibilizer in Nylon 6/PPO Blends

As a model for studying the effect of the structure of graft copolymers of PPO and nylon 6 on nylon 6/PPO blends, nylon 6/PPO blends with 80/20 weight ratio that contained 10 wt % graft copolymers were prepared and injection molded into specimens suitable for analysis. To get more reliable and consistent results, a twin screw extruder was used in mixing to make pellets, which were then processed into specimens for testing. For comparison purpose, samples that did not undergo twin screw extruder mixing were also injection molded, employing the same processing conditions, into specimen suitable for mechanical testing. The key mechanical properties of these blends and those of nylon 6 and PPO control samples are summarized in Tables VI and VII for comparison.

These data indicated that, without twin screw mixing, all nylon 6/PPO blends gave the same tensile strength, tensile modulus, flex modulus, and impact strength and very poor elongation data. However, with efficient mixing through a twin screw ex-

**Table VI Tensile Properties of PPO/Nylon 6 (20/80) Blends with or without 10% Graft Copolymer<sup>a</sup>**

Composition <sup>b</sup>	Strength <sup>c</sup>	Modulus <sup>c</sup>	Percent Elongation
Nylon 6	9.20	393	70
Nylon 6/PPO	10.7	372	2.5
	(8.6)	(385)	(2.3)
Nylon 6/PPO/A	11.0	380	16
	(9.4)	(391)	(5.5)
Nylon 6/PPO/B	10.5	375	11
	(9.1)	(376)	(3.6)
Nylon 6/PPO/C	10.8	380	7.9
	(8.9)	(390)	(3.5)
PPO	10.7	295	30

<sup>a</sup> Data in parentheses from specimen fabricated from samples without prior twin screw extruder mixing.

<sup>b</sup> A, B, and C represent graft copolymers shown in Table V.

<sup>c</sup> Units for tensile strength and modulus are in 10<sup>3</sup> psi.

**Table VII Mechanical Properties of PPO/Nylon 6 (20/80) Blends with or without 10% Graft Copolymer<sup>a</sup>**

Composition <sup>b</sup>	Flexural Modulus, <sup>c</sup> psi	Notched Izod Impact Strength, ft-lb/in.
Nylon 6	340	1.4
Nylon 6/PPO	353 (355)	0.9 (0.9)
Nylon 6/PPO/A	356 (345)	1.1 (1.0)
Nylon 6/PPO/B	355 (345)	0.9 (0.9)
Nylon 6/PPO/C	360 (350)	0.9 (0.9)
PPO	305	1.2

<sup>a</sup> Data in parentheses from specimen fabricated from samples without prior twin screw extruder mixing.

<sup>b</sup> A, B, and C represent graft copolymers shown in Table V.

<sup>c</sup> Units for tensile strength and modulus are in 10<sup>3</sup> psi.

truder, all nylon 6/PPO blend samples gave the same tensile strengths regardless of which graft copolymer was used, and these tensile strengths were much better than those without twin screw mixing (1100 vs. 900 psi). But efficient mixing did not make a difference in the modulus and impact strength.

These mechanical testing data also suggested that, even though twin screw mixing gave no difference in modulus among all nylon 6/PPO blends with different graft copolymers or without the presence of a copolymer, there existed different elongations at break, depending on the structure of the graft copolymer added as compatibilizer. For example, the blend without a graft copolymer was very brittle, with an elongation of only 2.5%, which was very poor when compared to blends with a graft copolymer (which were 8–16%). When comparing the blends with graft copolymers of different structures, the most block-copolymer-like graft copolymer (i.e., graft copolymer A, which was prepared by using 1 : 1 ratio of PPO to nylon 6) gave the best elongation. This blend also gave the same level of notched Izod impact strength as did PPO. Both tensile modulus and impact strength data suggested that a reasonable compatibilization of nylon 6/PPO blend has been reached with the use of this block-copolymer-like graft copolymer A.

It should be noted here that nylon 6 and PPO have about the same low level of notched Izod impact strength. Whether the use graft copolymer has or has not improved the impact strength for their

blends is hard to judge. This is different from those blends of a polymer of high  $T_g$  and low impact strength, and a polymer of low  $T_g$  and high impact strength, such as polystyrene and low-density polyethylene. In those cases, the inclusion of block and graft copolymer showed improvement in impact strength as long as the blends contain a sufficient fraction of high-impact polymer.<sup>8</sup>

It should also be noted here that the tensile modulus and flex modulus are a function of blend composition only, suggesting no third-phase formation, which usually causes a decrease in the modulus.<sup>8</sup>

Although further processing studies were desirable, the model studies here demonstrated that graft copolymer did serve as compatibilizer and the block-copolymer-like structure served the best in a polymer blend, which is generally considered true<sup>9</sup> and is demonstrated in the case of nylon 6/PPO blends.

The HDTs of these nylon 6/PPO (80/20) blends are given in Table VIII, and they were all the same, indicating that HDT is a function of composition only.

As mentioned earlier, nylon 6 gives poor dimensional stability, as exemplified by water absorption. Table VIII also lists the water absorption of nylon 6/PPO blends as well as those of nylon 6 and PPO under the same test condition. The lower water absorption of nylon 6/PPO blends than that of nylon 6 indicated they are more dimensionally stable. Thus the dimensional stability problem associated with nylon 6 was partially alleviated by blending with PPO.

Heat deflection temperature determines the usage temperature for plastic. The HTD–nylon 6/PPO composition relationship is depicted in Figure 3.

## Conclusion

Grafted copolymers of PPO and nylon 6 with well-defined structure were prepared. Nylon 6/PPO

**Table VIII Heat Deflection Temperature and Water Absorption of PPO/Nylon 6 Blends (20/80)**

Composition	HDT at 264 psi (°C)	Water Absorption, 24 h
Nylon 6	58	1.8%
Nylon 6/PPO	68	1.3%
Nylon 6/PPO/A	69	1.3%
Nylon 6/PPO/B	72	1.3%
Nylon 6/PPO/C	68	0.9%
PPO	175	0.0%

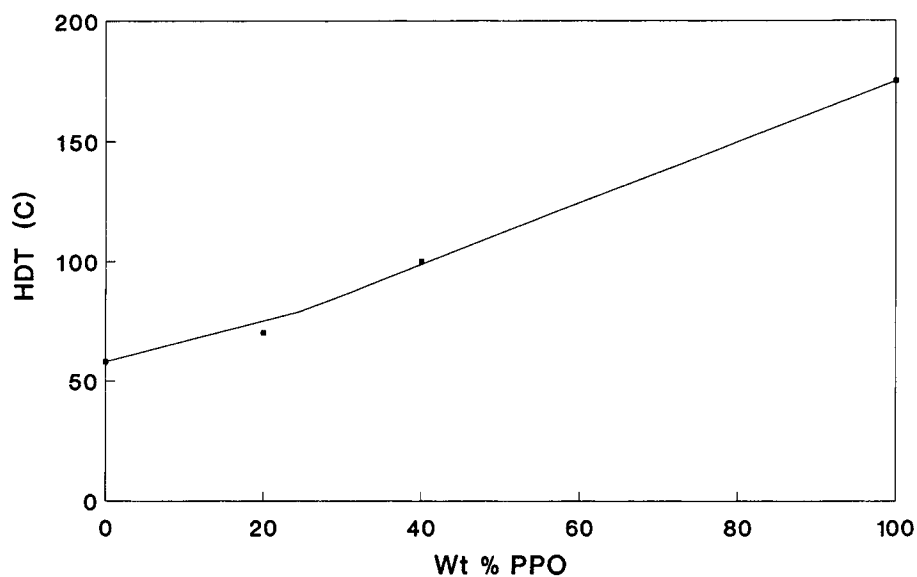


Figure 3 HDT vs. weight percent of PPO in nylon 6/PPO blends.

blends with 10% graft copolymers show satisfactory mechanical properties, except elongation. As expected, block-copolymer-like graft copolymer is the most compatible to nylon 6/PPO blend. More work on processing needs to be done to give the best desirable properties.

The author expresses his sincere thanks to M. Martin for some graft copolymer preparations, R. Lofquist for providing low- $M_n$  nylon 6, R. Morgan for processing, and N. Buik for mechanical property measurements.

## REFERENCES

1. D. R. Paul, in *Polymer Blend*, Vol. 2, D. R. Paul, Ed. 1978, p. 35.
2. D. C. Clagett, in *Ency. Polym. Sci. Tech.*, 2nd ed., Wiley, New York, 1986, Vol. 6, p. 94.
3. R. J. Welgos, in *Ency. Chem. Tech.*, 2nd ed., Wiley, New York, 1982, Vol. 18, pp. 406-425.
4. D. M. White and G. D. Cooper, in *Ency. Chem. Tech.*, 2nd ed., Wiley, New York, 1982, Vol. 18, pp. 594-615.
5. H. Kasabara, K. Fukuda, and H. Suzuki, EP 46,048 (1980).
6. Unitika, Ltd., JP 84 59,724 (1984).
7. A. S. Hay, U.S. Pat. 3,378,505 (1968).
8. D. Heikens, N. Hoen, W. Barentsen, P. Piet, and H. Ladan, *J. Polym. Sci., Polym. Symp.*, **62**, 309 (1978).
9. G. Riess and Y. Jolivet, in *Copolymers, Polyblends and Composites*, N. A. Platzer Ed., Adv. in Chem. Ser., **142**, 243 (1975).

Received March 10, 1993

Accepted March 4, 1994