Polypropylene Blends with a Phenoxy

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SYNOPSIS

Polypropylene (PP) blends with a phenoxy have been prepared in various compositions using a Brabender Plasticorder. Scanning electron microscopy (SEM) micrographs showed a clean two-phase morphology. The domains were larger when PP formed the dispersed phase, probably due to the greater melt viscosity of PP. The melting peak temperature (T_m) of PP decreased marginally, whereas the glass transition temperature (T_g) of phenoxy increased by 5–10°C, in the blends. X-ray diffraction measurements indicated that PP crystallizes in a hexagonal β-form in 50/50 and 30/70 (PP/phenoxy) blends. Mechanical properties of the blends generally showed negative deviation from the additivity rule, perhaps due to the inherently immiscible nature of the blends. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Thermoplastic blends and alloys have received widespread attention during the last several decades.[1-3] Most polymers are thermodynamically immiscible. In immiscible polymer blends, morphology is affected by composition, viscosity ratio, interfacial tension, processing conditions, and so on.[4,5] Polyolefin blends are a commercially important class of materials. They include polyolefin/polyolefin,[6-8] polyolefin/nylon,[9,10] polyolefin/poly(ethylene terephthalate) (PET),[11,12] polyolefin/polycarbonate (PC),[13,14] and polyolefin/polystyrene (PS) blends.[15]

Both polypropylene (PP) and phenoxy are commercially important thermoplastics. PP is a crystalline polyolefin and has poor impact strength, especially at low temperature.[7] Phenoxy, which is a poly(hydroxy ether of bisphenol A), is a relatively tough and ductile amorphous polymer with excellent oxygen barrier property. It is reported that phenoxy is miscible with aromatic or aliphatic polyesters and with polyethers, due to the strong hydrogen bonding.[16-18]

We considered the melt blends of PP with a phenoxy. The phase behavior of PP/phenoxy blends

has not been reported in open literature. These blends should be important with regard to performance/cost improvement. Thermal, mechanical, morphological, and rheological properties of PP/phenoxy blends, prepared by melt extrusion followed by injection molding, are reported in this article. In addition, the effect of phenoxy on crystalline structure of PP was also investigated.

## EXPERIMENTAL

Materials and Compounding

Commercial grades of an isotactic PP (M_n = 54,000, M_w = 380,000, MFI = 2.3 g/10 m (2.16 kg, 230°C), Korea Petrochemicals) and a phenoxy (PKHH, Union Carbide) with M_w = 50,700 were used for blending.

Phenoxy was first dried for 3 days under vacuum at 80°C to remove moisture thoroughly. PP was dried for 5 h at the same temperature in a convection oven. The samples at the desired composition were first dry-mixed at room temperature, followed by melt-mixing at 230°C in a single screw extruder (Brabender plasticorder, L/D = 30).

Test specimens were injection molded using a BOY injection molding machine. The injection molding conditions were as follows: the barrel temperature 230°C, mold temperature 40°C, injection pressure 500 kg/cm^2, and total cycle time 45 s.
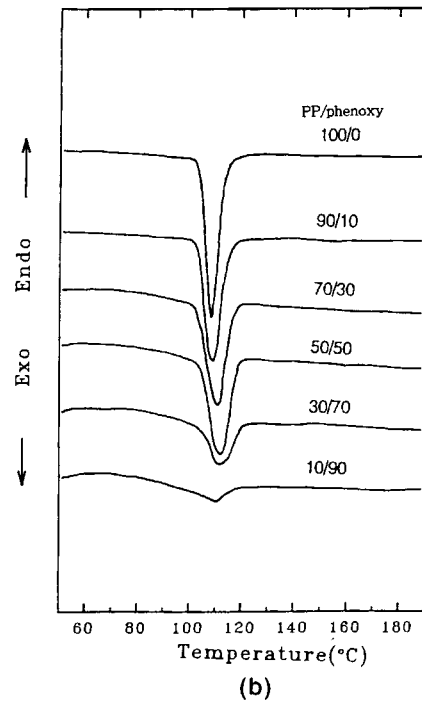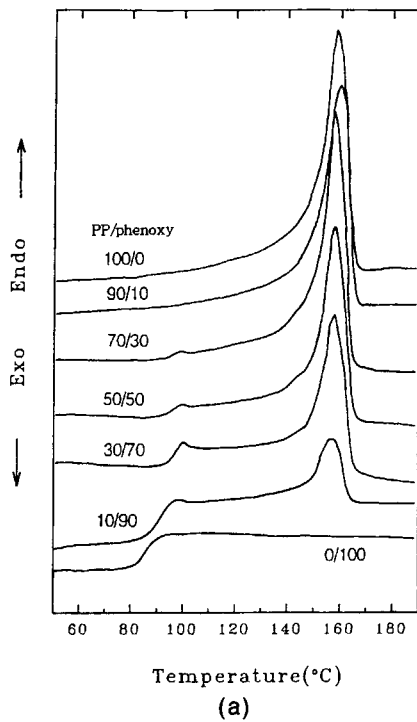
Figure 1 DSC thermograms of PP/phenoxy blends: (a) on heating; (b) on cooling.

Thermal Properties

Thermal properties of the samples were determined using a differential scanning calorimetry (Perkin-Elmer DSC-7). DSC samples were cut from the extrudates. Heating and cooling rates were both 10°C/
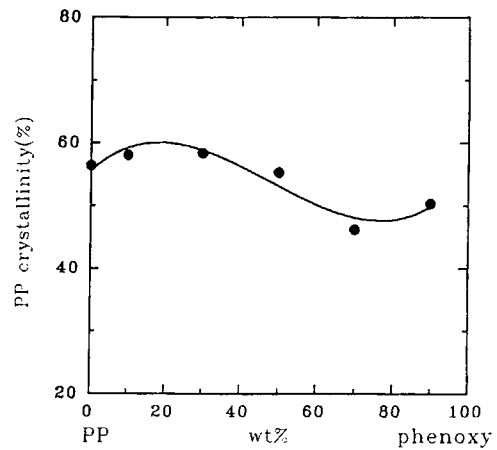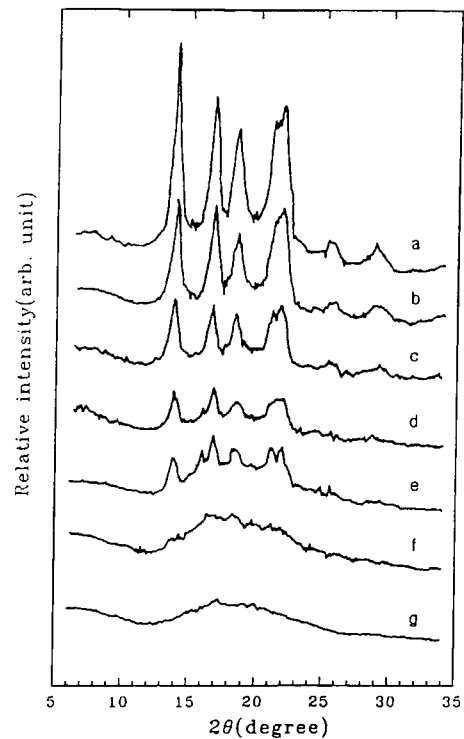

**Figure 2** Crystallinity of PP as a function of phenoxy content.

m, and measurements were made between 30°C and 160°C.

X-Ray Diffraction Profiles

Crystalline structure of the samples was determined by a wide angle X-ray diffractometer (Rigaku 2013) using CuK$_\alpha$ at 30 kV, 15 mA with a scan speed of

Figure 3 X-ray diffraction profiles of PP/phenoxy blends: (a) 100/0, (b) 90/10, (c) 70/30, (d) 50/50, (e) 30/70, (f) 10/90, and (g) 0/100.
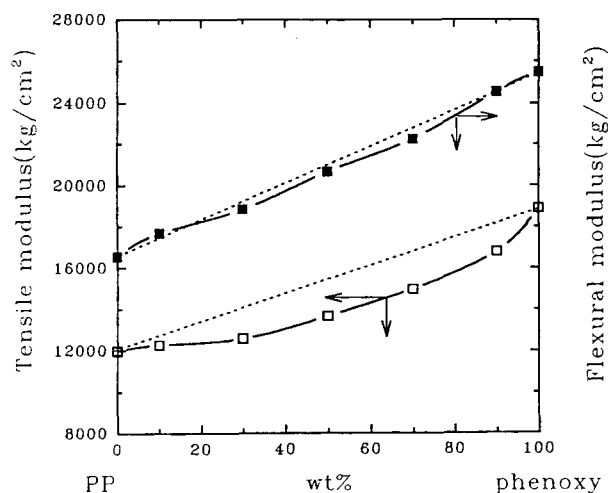
Figure 4 Tensile and flexural modulus vs. composition for PP/phenoxy blends.

2.2°/m. Injection molded specimens were mounted for through direction.

Mechanical Properties

Tensile properties were determined following the standard procedure described in ASTM D 638 with type IV specimens. A tensile tester (Tinius Olsen Series 1000) was operated at a crosshead speed of 5 mm/m. Tests were made at room temperature, and at least five runs were made to report the average. Izod impact strength was measured using an impact tester (ASTM D256). Flexural properties were also examined (ASTM D 790).

Morphology

Morphology of the blends was observed using a scanning electron microscopy (SEM, JSM820). SEM micrographs were taken from cryogenically (in liquid nitrogen) fractured surfaces of injection molded tensile specimens. The fractured surfaces were sputtered with gold before viewing. Longitudinal and transverse views, with respect to the flow direction in mold cavity, were examined near the center of cross section.

Melt Properties

Rheological properties of the blends were measured using a parallel-plate rheometer (Rheometrics Dynamics Spectrometer, RDS II). Discs measuring 12.5 mm (radius) × 1.2 mm (height) were compression molded, and measurements were carried out isothermally at 220°C, 15% strain level.
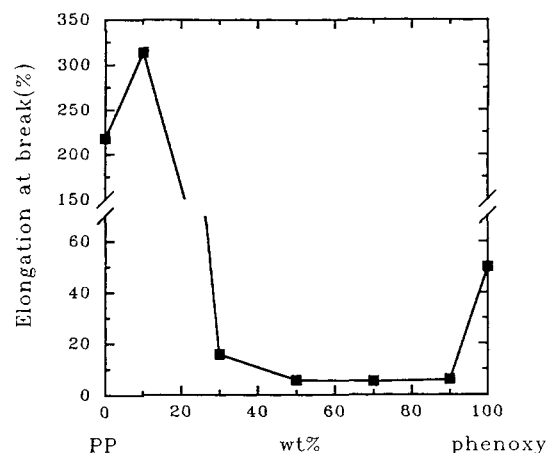

Figure 5 Elongation at break vs. composition for PP/phenoxy blends.

RESULTS AND DISCUSSION

Thermal Properties

Figure 1 shows DSC thermograms of PP/phenoxy blends obtained from the second run of heating and cooling. The melting peak temperature (T_m) of virgin PP appears at 158.2°C and the crystallization peak (T_c) at 109.8°C. T_g of virgin phenoxy appears at 86.1°C. T_m and T_c of PP in the blends are similar to those of virgin PP, and melting point depression is only about $1 \sim 2°C$. T_g of phenoxy is increased by $5 \sim 10°C$ in the blends. In crystalline/amorphous polymer blend, T_m of crystalline polymer is generally decreased owing to a dilution effect (melting point depression),[19,20] and T_g value of blends lies between the two T_g's of components. In spite of lower T_g of PP ($\sim 0°C$), T_g of phenoxy increased with PP addition. This is probably due to the migration of low
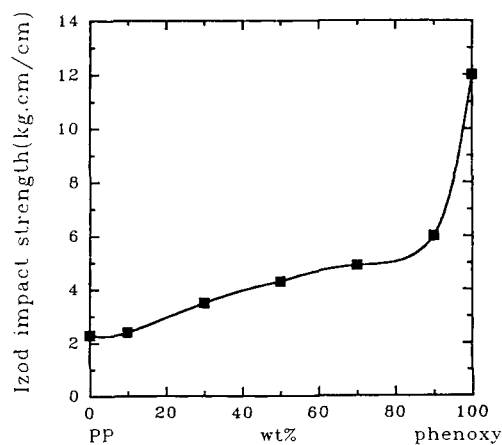
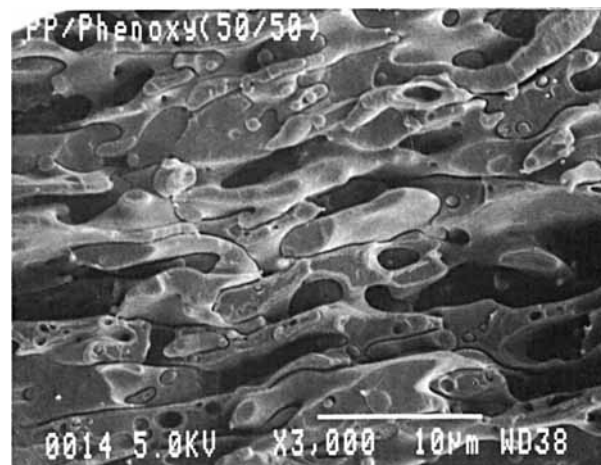

Figure 6 Izod impact strength vs. composition for PP/phenoxy blends.
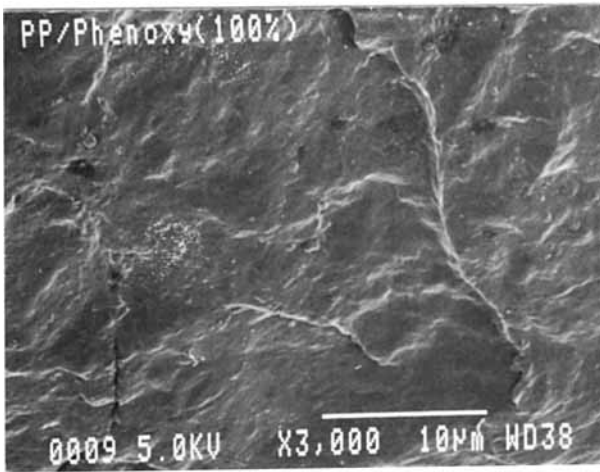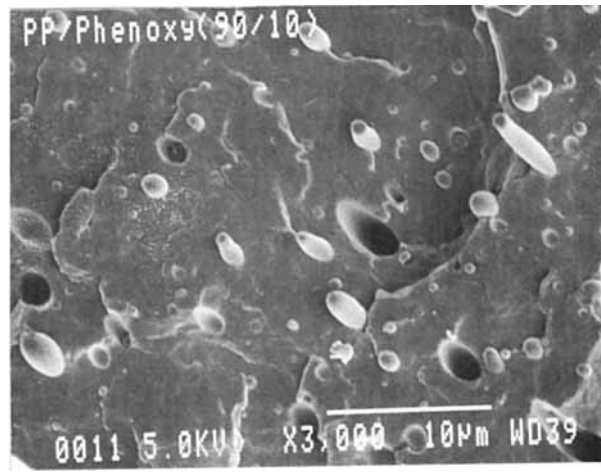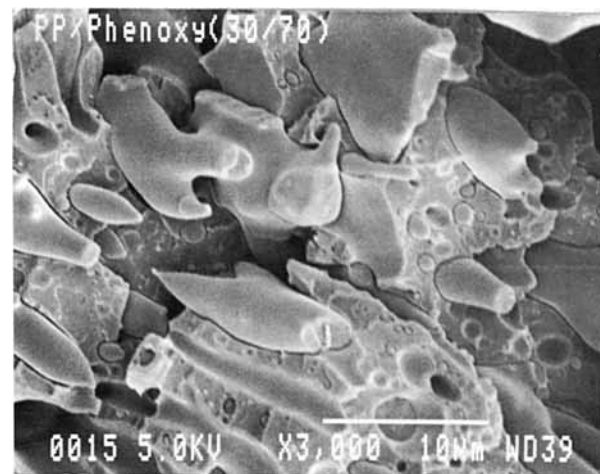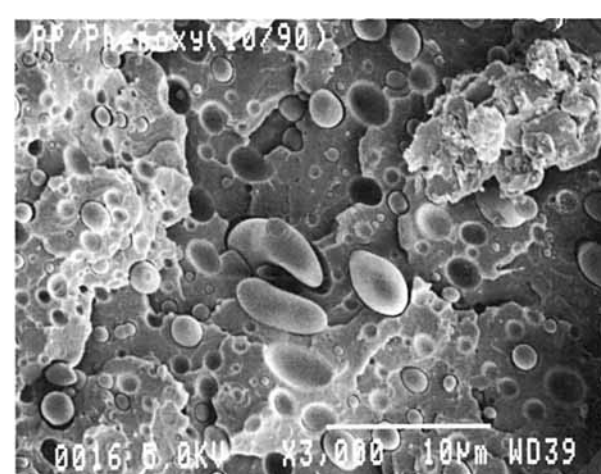
(a) 100/0

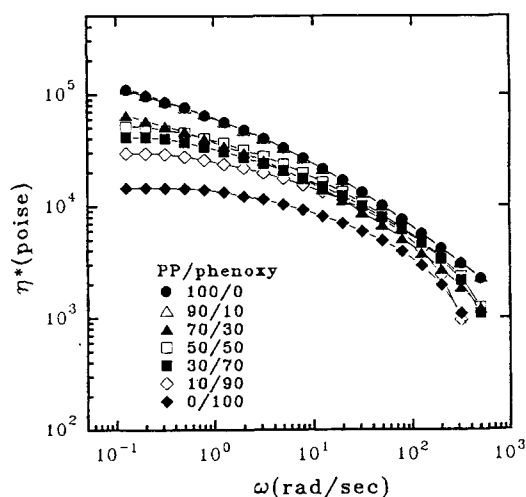(b) 90/10

(c) 70/30

(d) 50/50

(e) 30/70

(f) 10/90

Figure 7 SEM micrographs of PP/phenoxy blends fractured transversely to the flow direction: (a) 100/0, (b) 90/10, (c) 70/30, (d) 50/50, (e) 30/70, and (f) 10/90.

Figure 8   Complex viscosity as a function of blend composition at 220°C.

molar mass phenoxy molecules into the amorphous domains of PP.[21,22]

Figure 2 shows crystallinity as a function of composition. Crystallinity of PP is commonly obtained from the following equation:[8]

$$X_c = \Delta H_{blend} / (\Delta H_{pp}^0 \times \text{wt fraction of PP}) \quad (1)$$

where ΔH_{pp}^0 is taken as 132.8 J/g. The crystallinity is slightly increased in PP-rich and decreased in phenoxy-rich blends. It seems that phenoxy acts as nucleating agent for PP in PP-rich, and diluent in phenoxy-rich blends.

X-Ray Diffraction Profiles

Figure 3 shows X-ray diffraction profiles of the PP/phenoxy blends. The crystalline structure of PP is a monoclinic (α-form), with lattice constant $a = 6.65$ Å, $b = 20.96$ Å, $c = 6.50$ Å, $\beta = 99°20'$, $d = 0.936$ Å corresponding to Bragg angle 2θ

Table II 2θ Values of PP/Phenoxy Blends

Composition (PP/phenoxy)	Degree (2θ) (CuK_α)				
	(110)	(300)	(040)	(130)	(131)
100/0	14.0		16.7	18.4	21.5
90/10	14.0		16.6	18.3	21.6
70/30	14.0		16.8	18.4	21.6
50/50	14.0	15.0	16.8	18.5	21.5
30/70	14.0	14.9	16.8	18.4	21.6
10/90	13.9				

$= 14.1(110), 17.0(040), 18.5(130), 21.7°$ (doublet), respectively.[10,23] Our X-ray diffraction profile for virgin PP is consistent with the cited data. Phenoxy shows a broad diffraction profile from 14 to 25° as a typical amorphous structure. Apparently, the addition of phenoxy has no effect on the crystalline structure of PP throughout the composition.

However, a careful examination for 50/50 and 30/70 blends shows a new peak at $2\theta = 16.0°$ (300 plane), which corresponds to hexagonal (β-form). It should be mentioned that PP crystallizes in a monoclinic α-form above 132°C and in a hexagonal β-form below 132°C. With the addition of nucleating agents or other components, PP crystallizes in the β-form depending on concentration and dispersion.[24]

Mechanical Properties

Tensile and flexural moduli (Fig. 4) generally show small negative deviations from the simple additivity (dotted line in the figure), due to the poor interfacial interactions.[25,26]

Figure 5 shows elongation at break as a function of composition. The PP/phenoxy blends show both a maximum (90/10) and a minimum (phenoxy-rich). Deep and broad negative deviation especially in phenoxy-rich blends may be due to the inherent immiscibility between a nonpolar PP and a polar

Table I   Thermal Properties of the PP/Phenoxy Blends

Composition (PP/phenoxy)	T_g (°C)	T_m (°C)	T_c (°C)	ΔH_f (J/g)	ΔH_c (J/g)	Crystallinity (%)
100/0	—	158.2	109.8	77.9	86.9	56.4
90/10	—	159.5	109.8	72.2	80.7	58.1
70/30	95.7	157.6	111.7	56.4	62.1	58.3
50/50	95.4	157.9	111.9	38.2	45.7	55.3
30/70	95.7	158.2	110.6	19.2	19.9	46.2
10/90	90.9	158.1	109.9	7.0	4.2	50.4
0/100	86.1	—	—	—	—	—
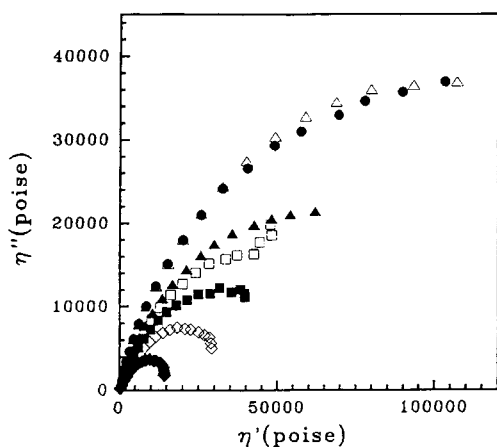
Figure 9 Cole–Cole plot for PP/phenoxy blends. See Figure 8 legends.

phenoxy. Synergism obtained with the 90/10 blend would be closely related to the morphology as follows: When small amounts of brittle particles are dispersed in a ductile matrix, a synergism in elongation could be obtained as in PC/PMMA[27] and PC/SAN blends.[28]

Figure 6 shows Izod impact strength as a function of composition. In semicrystalline polymer/amorphous polymer blends, it is known that a considerable decrease in impact strength is obtained when the component polymers have limited miscibility.[29] It is seen that the impact strength of phenoxy dramatically decreased with 10% PP, beyond which it decreased smoothly. At ambient PP and phenoxy fracture in the ductile mode via shear yielding. But the fracture mechanism seems to be changed in the blends. That is, the energy needed for crack propagation (notched sample) would be lower than that of shear yielding owing to the phase-separated structure.

Morphology

Figure 7 shows SEM micrographs of the transversely fractured surface of the blends. Phenoxy forms the dispersed domain in PP-rich and PP forms the dispersed phase in phenoxy-rich blends. In the 50/50 composition, the blend is cocontinuous and shows highly complicated morphology. Comparing symmetric compositions, i.e., 90/10 vs. 10/90 and 70/30 vs. 30/70, the dispersed domain is larger in size when PP is dispersed. For 90/10, domain size of phenoxy is in the order of submicron, and droplets are well dispersed in PP matrix. Elongation toughening observed in Figure 5 should come from this dispersion effect. Negative deviation of strength and

modulus from the mixing rule is also related to the morphology. A number of debonded holes on fractured surfaces indicate weak interfacial interactions between matrix and dispersed phase.

Melt Properties

Figure 8 shows the complex viscosity as a function of oscillation frequency for PP/phenoxy blends. PP shows a typical shear thinning behavior and phenoxy less shear dependent viscosity at low frequency. During extrusion and injection molding, dispersed PP droplets are hard to break, whereas phenoxy droplets can easily deform due to its lower viscosity.[4] This viscosity effect is clearly seen in the SEM micrographs.

Figure 9 shows a Cole–Cole plot for PP/phenoxy. It is noted that the 50/50 blend shows a drift from semicircularity. Since the Cole–Cole plot gives information about relaxation time distribution,[3,30] one can see that 50/50 blend has two relaxation time regions. The drift represents increase in η'' (the elasticity of the melts) at low frequency region, indicating the presence of longer relaxation time. This probably is due to the instability of the structure at subsequently higher stresses. The morphological complication of 50/50 blend is presumably the cause of the drift from semicircularity. This behavior is commonly observed in rubber-toughened thermoplastics[31] and particulate-filled or fiber-filled composite materials.[3]

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