Preparation and Properties of Polar Polypropylene Blends Containing Phenolic Resin

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ABSTRACT: It is often pointed out that low water absorption and moisture permeability are drawbacks of polypropylene (PP). In this study, blending with an amorphous polymer was used to modify PP. For improving the properties of PP without any property depression, PP was blended with phenolic resin-Novolak type (PRN). PP/PRN blends were investigated by a contact angle test for surface properties to determine whether PP had hygroscopic characteristics due to the existence of PRN in the blends. In addition, for the sake of efficient investigation in this blend, chemical structure, mechanical measurement, thermal analysis, and morphological observations were also studied. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1029–1038, 1999

Key words: polypropylene; phenolic resin; blends

INTRODUCTION

Polypropylene (PP), a verstatile thermoplastic polymer, is extensively used in technical applications due to its low water absorption and moisture permeability, poor impact strength below −9.4°C, imperviousness to fungi or bacteria, and wide availability and low cost. PP has a nonpolar property; its poor wettability makes it difficult to dye and paint. To overcome these problems, some techniques have been developed.[1–3] Without any property depression, many studies on blending, chemical modification, additives, and physical treatment of PP have been conducted.[4–8] In particular, studies of development of new material and chemical modification of pre-existing polymer are ongoing.[9–11] For examples of blending PP to improve its properties, PP/polystyrene blends were carried out by J. Shimizu,[12] PP/polyethylene blends were investigated by J. I. Ito,[13] PP/polyamide blends were studied by Z. Liang,[14] and

PP/ethylene-vinylacetate (EVA) blends were investigated by A. K. Gupta.[15] Moreover, a series of experiments related to this study has been investigated, such as PP/phenoxy blends[16] and PP/poly(vinyl alcohol-coethylene) blends[17] for improved hydrophilicity of PP.

On the basis of these techniques, blending with other amorphous oligomers could be one of techniques to raise the surface free energy of PP. PP could be used in a blend with phenolic resin-Novolak type (PRN) to improve its ability to be dyed and painted. Phenolic resins have several types of synthetic thermosetting resin obtained by the condensation of phenol or substituted phenols with aldehydes such as formaldehyde, acetaldehyde, and furfural. Phenol-formaldehyde resins are typical and constitute the chief class of phenolics. Novolak, a thermoplastic phenol-formaldehyde-type resin, can be obtained primarily from acid catalysts and excess phenol. Generally, it is alcohol soluble and requires reaction with hexamethylenetetramine, p-formaldehyde, and so on for conversion to cured, cross-linked structures by heating at 93–204°C.

In this study, an attempt has been made to study the change in the surface properties of PP when

Table I   Summary of Contact Angles and Surface Free Energies of PP and PP/PRN Blends

| Sample | Contact Angle (degrees) | | I_{sw}^n | γ_s^d | γ_s^p | γ_{sv} |
	c-Hexane	i-Octane				
				(erg/cm^2)		
PP	159.5	152	3.81	51.98	0.07	52.05
PP/PRN 1%	157	150	4.48	51.95	0.10	52.05
PP/PRN 3%	156	149	4.99	53.29	0.13	53.42
PP/PRN 5%	153	146	6.21	56.25	0.19	56.48
PP/PRN 7%	152	145	6.64	57.30	0.22	57.52
PP/PRN 10%	150	143	7.53	60.15	0.28	60.43
PP/PRN 20%	147	139	9.16	68.85	0.42	69.27
PP/PRN 30%	136	136	14.38	70.61	1.04	71.65

blended with phenolic resin-Novolak type (PRN) in various proportions, performed by the contact angle test. The general properties of this blend—chemical structure, mechanical properties, thermal properties, and morphology—are also analyzed.

EXPERIMENTAL

Materials

Isotatic PP was supplied by Yu-Kong Co. Ltd., Ulsan, Korea, with a melt flow and rate (MFI) of 25. Phenolic resin-Novolak type (PRN) under an H_2SO_4 catalyst, KNR-1200 (softening temperature 98°C), supplied by KOLON Oil-Chemical Co. Ltd., Kimchun, Korea, was used. It was used before it was cured for this experiment.

Melt Blending and Specimen Preparation

Melt blending was done by a twin-screw PLE 331 (Brabender, Germany), with a speed of 50 rpm and a temperature of 180°C for 5 min at the various of requisite ratios of PRN: 1, 3, 5, 7, 10, 20, and 30 wt %. The standard specimens were prepared by a capillary rheometer (Rosand Precision Co. Ltd.), with an L/d ratio of 16 and a temperature of 180°C. The rate of the take-up winder was 200 rpm, and the diameter of the bobbin was 11.5 cm. Film-shape specimens were prepared by Tester Industry Co. Ltd., Japan, with a temperature of 180°C.

Contact Angle Test for Polarity

The contact angle was determined using a contact angle meter (ERMA G40, Japan). The two-liquid method[18,19] was used to measure the contact angle in this blend, by dropping 2 μl of water using a microsy-

ringe after putting a specimen in the glass cell filled with saturated hydrocarbon liquid. Both the right and the left side contact angles of the specimens were measured and averaged in summary.

Density Measurement

Density was measured using liquid CCl_4 and n-heptane combined under room temperature.

Analysis of Chemical Structure

A Fourier transform infrared (FTIR) spectrophotometer (Shimadzu DR-8011, Japan) was used on specimens prepared by a Tester Industry presser to analyze their chemical structures in this blend

Figure 1   Density of PP and PP/PRN blends.

Figure 2 FTIR spectra of PP and PP/PRN blends.

by radiated IR spectrum with a resolution of 4 cm^{-1} and 200 scan numbers.

Thermal Behavior and Viscosimetric Measurement

A differential scanning calorimeter (DSC; TA-9900, DuPont, U.S.) was used to determine the heat capacities of specimens, to investigate the available shift of melting temperature (T_m), crystallization temperature (T_c), and softening temperature for an amorphous oligomer. Heating and a cooling rates were at 10°C/min conducted from 30–200°C and

vice versa. Rheological measurement was done by a piston-pattern capillary rheometer described in preparation. Both the long and short die were 1.0 mm in diameter. The shear stress and shear viscosity were evaluated by the shear rate.

Mechanical Measurement

In this measurement, specimens of the blends were prepared by a capillary rheometer, to get a fiber-like shape taken by a winder limited to a test speed of 200 rpm and with a bobbin 11.5 cm

(a) Heating

(b) Cooling

Figure 3   Thermograms of heating (a) and cooling (b) curves of PP and PP/PRN blends.

Figure 4 Apparent shear viscosity of PP and PP/PRN blends at 180°C.

in diameter. Mechanical properties were determined using a Testerometric Micro 350 with a 2 kgf load-sell, a gauge length of 40 mm, and a test speed of 100 mm/min.

Morphological Observation

Fractured sections of specimens were observed using a S-4100 scanning electron microscope (SEM; Hitachi Co. Ltd., Japan). Specimens were fractured under liquid N_2 gas. To gain a better view of the sections, magnification of 1,000 was applied during SEM scanning.

RESULTS AND DISCUSSION

Determining Contact Angle and Calculating Surface Free Energy of Blends

The contact angle and surface free energy can characterize the polarity of a polymer. An inter-

facial tension γ_{sl} exists between a solid and a liquid. If the liquid resides as a drop on the surface of the film, then additional surface tensions liquid vapor (γ_{lv}) and solid vapor (γ_{sv}) exist. The vector diagram of these three interfacial tensions indicates that liquids do not spread totally on solid, smooth surfaces but rather form a somewhat flattened droplet with a contact angle θ between the surface of the solid and the edge of the droplet according to the Young equation (1),[20,21] as follows:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta \qquad (1)$$

The γ_{lv} is the interfacial tension between liquid and gas, γ_{sv} is the surface free energy of solid, γ_{sl} is the interfacial tension between solid and liquid, and θ is the contact angle of solid. Interfacial tension involves two parts, the one (γ^d) produced by chromatic dispersion and the other (γ^p) pro-

Figure 5   Shear stress of PP and PP/PRN blends at 180°C.

duced by couple pole. Equations (2) and (3) can be derived from these facts:

$$\gamma_{lv} = \gamma_l^d + \gamma_l^p \tag{2}$$

and

$$\gamma_{sv} = \gamma_s^d + \gamma_s^p \tag{3}$$

Experimentally, many methods for measurement of surface free energy of solids have been carried out so far, by, for example, Zisman,[22] Fowkees,[23–25] Owens and Wendt,[26] Dann,[27] Kaelble,[28,29] Panzer,[30] and others. Tamai's method[18,19] using two liquids—cyclo-hexane and iso-octane, which do not mingle together—was selected for this study. Tamai suggested the following equation to decribe nondispersive interaction energy (I_{sw}^n):

$$I_{sw}^n = \gamma_w - \gamma_H + \gamma_{H \cdot w} \cos \theta$$
$$+ 2(\gamma_s^d)^{1/2}[(\gamma_H)^{1/2} - (\gamma_w^d)^{1/2}] \tag{4}$$

The liquid parameters have been determined in the literature; $\gamma_w = 72.7$, $\gamma_w^d = 23.0$, $\gamma_w^p = 49.7$ erg/cm^2 for water, $\gamma_H = 25.0$ and $\gamma_{H \cdot w} = 50.0$ erg/cm^2 for cyclo-hexane, $\gamma_O = 18.9$ and $\gamma_{O \cdot w} = 50.0$ erg/cm^2 for iso-octane. So the I_{sw}^n and γ_s^d can be calculated, and a polar component (γ_s^p) of surface free energy of solids can be calculated from the I_{sw}^n value, using the following equation:

$$\gamma_s^p = \frac{(I_{sw}^n)^2}{4\gamma_w^p} \tag{5}$$

Contact angles and surface free energies of the various films in the blends are summarized in Table 1. Water contact angles in systems of *cyclo*-hexane and *iso*-octane were gradually decreased from roughly 159.5° of the original isotatic PP to 135° of 30 wt % of PRN contents. This means that the blends had an increasing tendency toward hydrophilicity. Nondispersive interaction energy between the solid film and the water was also considered as a measurement of film hydrophilic-

Figure 6   Apparent shear viscosity of PP and PP/PRN blends at shear stress at 180°C.

ity. A tendency toward increasing interaction energy with increasing PRN content was found. Moreover, surface free energies were also increased, as shown in Table 1. The dispersion component of surface free energy of PP was increased by blending it with PRN, and, the polar component was also increased, possibly because phenolic rings from PRN contributed to the matrix of PP with hygrosopical characteristics in the blends.

When the PRN content increased, the polarity of the blends also increased. The increasing tendency of surface free energy was estimated. The contact angle verified this fact, shown in Table 1.

Density and Chemical Structure of PP/PRN Blends

The densities of specimens are shown in Figure 1. This density simply describes the blend, proving fine dispersion of PRN into PP under our assumption. FTIR spectra of PP/PRN blends are shown in Figure 2, in the order of PRN weight percent. Original isotatic PP got a C—H bond at 3300 cm^{-1} as shown by a little sharp absorption peak

(doublet band), and also it was found that 1450– 1375 cm^{-1}, a wide-scope wave number, proved C—H, C—H$_2$, and C—H$_3$ of alkane in polypropylene.

In the blends, a phenolic ring of absorption peak was found at 1600 cm^{-1} as a sign of PRN. However, there was no extrodinary peak from the blends. It was assumed that PRN dispersed well in the matrix of PP as a result of the physical modification of PP achieved by the melt mixing.

Analysis of Thermal Behavior in PP/PRN Blends

Thermal behaviors of the blends at heating and at cooling are shown in Figure 3. The melting temperature (T_m) of PP was found to be 170.4°C. As PRN content increases, T_m curves of the blends shift slightly lower, approximately 167.7°C, as shown in Figure 3(a). In crystalline and amorphous polymer blends, T_m of crystalline polymer is normally decreased, due to a dilution effect (melting point depression).[31,32] Addition of PRN led to a reduction in the perfection of the crystalline region of PP. Crystallization temperatures

(T_c), was found to be 108.58°C for PP, and T_c curves of the blends were shifting to high temperatures while PRN contents were increasing. This may be because PRN, as an amorphous polymer, caused the amorphous region of PP to be active, possibly due to an increased physical interaction between the dispersed PRN and the matrix of PP, promoting faster crystallization during the cooling process.[33]

Melt-Flow Property

Melt flows of the blends under high shear rates are shown in Figures 4–6. PRN content scope within 10 wt % followed as structural behaviors independent of shear rate as a whole. Newtonian flow behaviors were found over 20 wt %, PRN content scope at the shear rate between 10^2 and 10^3 S^{-1}. This may be because the small scope—1–10 wt % of PRN content—did not give a rise to a changing temporal relationship between the forces and deformations of PP.

Mechanical Measurement

Initial modulus in PRN content to 5 wt % was increased, but then declined over 5 wt %, as shown in Figure 7(a). Tenacity of the blends increased in PRN content to 10 wt % and decreased over 10 wt %, as plotted in the same figure. Strain of the blends, plotted in Figure 7(b), thoroughly declined with increasing PRN content. It could be supposed that a small amount of PRN in the matrix of PP strongly interacted with PP to give unseparated dispersions.

Morphological Observation

This study is relevant to the rheological investigation and surface properties in the blends. SEM photographs of fractured parts of the blends are shown in Figure 8. A fractured part of original isotatic PP was shown to be quite rough, and fractured parts of the blends to 10 wt % of PRN content also were shown to be as rough as that of PP.

It was found that droplets of PRN became gradually bigger with increasing PRN content, and phase separations were roughly observed from over 7 wt % of PRN content. Moreover, the fine dispersion of PRN into the matrix of PP was easily observed, proving that it caused an increase in the surface free energies of the blends with increasing PRN content.

(a)

(b)

Figure 7   Initial modulus, tenacity (a), and strain (b) of PP and PP/PRN blends.

Consequently, it might be surmised that PRN gave no different properties to PP within 7 wt % of PRN content, although the blends had high surface free energies.

Figure 8 SEM photographs of PP and PP/PRN blends.

CONCLUSIONS

Based on the foregoing discussions, the following conclusions can be reached. First, the important factor—the polarity of the blend—was verified by investigation of both contact angle and surface free energy and also supported by other experiments that played an important role in determin-

ing whether or not the blend had property depression.

From a chemical viewpoint, density had a tendency to increase with increasing PRN content. FTIR spectra showed no extrodinary peak from the blends. It was assumed that PRN dispersed well in the matrix of PP as a manifestation of the physical modification of PP achieved by the melt mixing.

In thermal analysis, T_m curves shifted to low temperatures and T_c curves to high temperatures by PRN content. Initial modulus had a tendency to increase with PRN content to 5 wt %, and tenacity was increased by PRN content to 10 wt % in mechanical measurement. Rheological study showed that PRN content to 10 wt % did not change the temporal relationship between forces and deformations of PP. PRN content within 7 wt % gave no different properties to PP in morphological observation.

In terms of polarity of the blends, although polar components were found to not quite change, an increase in surface free energy resulted in a tendency toward hydrophility.

Consequently, low PRN content (within 10 wt %) does not give PP any marked property depression in mechanical, morphological, thermal properties, and melt flow, whereas the blends had better hygroscopical properties than original isotatic PP.

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