Macromol. Symp. **2005**, *220,* 75-83

Raman and Wide-Angle X-Ray Diffraction Studies on Molecular Structure, Crystallinity, and Morphology of Uncompatibilized and Compatibilized Blends of High Molecular Weight Polyethylene/Nylon 12

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Summary: Molecular structure, crystallinity and morphology of uncompatibilized and compatibilized blends of high molecular weight polyethylene (HMWPE) and Nylon 12 were investigated by using Fourier-transform (FT) Raman spectroscopy, wide-angle x-ray diffraction (WAXD), and scanning electron microscopy (SEM). One of the important purposes of the present study is to compare the present results for HMWPE/Nylon 12 with the previously obtained results for high-density polyethylene (HDPE/Nylon 12). Uncompatibilized and compatibilized blends of HMWPE/Nylon 12 with a Nylon 12 content ranging from 10 to 90 wt% at increments of 10 wt% were prepared. The compatibilized polymer blends were prepared by adding a small amount of maleic anhydride (MAH), and SEM images show that the addition of the small amount of MAH (0.5 wt%) yields a marked improvement of dispersion of HMWPE and Nylon 12. To evaluate the crystallinity of HMWPE from Raman spectra, the relative intensities of bands at 1418 and 1129 cm^{-1} to the intensity of a band at 1000 cm^{-1} (I_{1418}/I_{1000} and I_{1129}/I_{1000}) were estimated for all the uncompatibilized and compatibilized blends of HMWPE/Nylon 12. From the comparison of the relative intensities (I_{1418}/I_{1000} and I_{1129}/I_{1000}) between the uncompatibilized and compatibilized blends of HMWPE/Nylon 12 it was found that when the Nylon 12 content reaches 40 wt% the crystallinity of HMWPE in the compatibilized blends becomes higher than that of HMWPE in the uncompatibilized blends. The uncompatibilized and compatibilized blends of HMWPE/Nylon 12 (50/50) show quite different x-ray diffraction patterns; the compatibilized blend shows a significantly larger orientational effect in the x-ray pattern of HMWPE. It seems that the increase of interaction of MAH-HMWPE with the Nylon 12 matrix leads to the additional crystallinity.

DOI: 10.1002/masy.200550206

Keywords: compatibilized polymer blend; crystallinity; morphology; Raman spectroscopy; scanning electron microscopy; uncompatibilized polymer blend; x-ray diffraction

Introduction

Polymer blends of Nylon and polyethylene (PE), polypropylene (PP) or polystyrene (PS) have been investigated extensively because they show high notched Izod impact strenghts.[1-4] It is very difficult to obtain a good dispersion in Nylon/PE, Nylon/PP, or Nylon/PS blends, if they are only mechanically blended.[1-5] However, it is known that blending with a maleic anhydride (MAH)-grafted copolymer as a compatibilizer yields clear dispersion of the polymer blends of PE and Nylon.[2,3,5] This appears to be caused by the formation of a certain graft polymer between MAH in PE and terminal amino groups of Nylon 12. Several research groups reported that the addition of small amounts of third ingredients to binary blends stabilizes the phase morphology.[1,7-9] It is very interesting to compare the structure and physical properties between the uncompatibilized and compatibilized blends of PE/Nylon 12.

We have been investigating the molecular structure, crystallinity and morphology of the uncompatibilized and compatibilized blends of high-density polyethylene (HDPE)/Nylon 12 by using Fourier transform (FT)-Raman spectroscopy, wide-angle x-ray diffraction (WAXD), differential scanning calorimetry (DSC), and scanning electron microscopy (SEM).[10,11] Combination of these techniques has allowed us to explore morphology, structure, and physical properties of the blends comprehensively. In our previous study we particularly investigated comparison of crystallinity between the uncompatibilized and compatibilized blends as a function of the blend compositions. We found that the crystallinity of HDPE in the compatibilized blends becomes higher than that of HDPE in the uncompatibilized blends when the Nylon 12 content increases beyond 70 wt%. The difference suggests that the effect of the high viscosity of the Nylon 12-rich phase on the crystallinity is more significant than the effect of the impurity (MAH-grafted PE). It seems that the extension of the Nylon 12-rich phase during the extrusion process leads to orientational effects because of the increase in the interaction between MAH and HDPE.

The purpose of the present study is to investigate differences in molecular structure, crystallinity, and physical properties between the uncompatibilized and compatibilized blends of high molecular weight polyethylene (HMWPE)/Nylon 12 and compare the present results for

HMWPE/Nylon 12 with the previous results for HDPE/Nylon 12. The molecular weight of the HMWPE used in this study is 210000 while that of the HDPE in the previous study was 70000-100000.

Experimental Section

Preparation of the Compatibilized and Uncompatibilized Blends. The polymers used in this study were HMWPE, SUNTEC-HD J240 Polyethylene (Asahi Chemical Industry Co., Ltd.) and Nylon 12 (UBE INDUSTRIES LTD). The uncompatibilized and compatibilized blends of HMWPE/Nylon 12 were prepared by compounding Nylon 12 with HMWPE and MAH-HMWPE at 220 °C in a twin-screw extruder, respectively. MAH-HMWPE was prepared by use of the same extruder by supplying maleic anhydride to HMWPE at 220 °C. The concentration of MAH was adjusted to yield MAH-HMWPE with 0.5 wt% MAH. Blending ratios of HMWPE/Nylon 12 were 10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/20, and 90/10, respectively.

Scanning Electron Microscopy (SEM). A scanning electron microscope, SEM (JEOL JSM-5800LVC), was employed to obtain SEM images of the uncompatibilized and compatibilized blends of HMWPE/Nylon 12.

Wide-Angle X-ray Diffraction (WAXD). The wide-angle x-ray diffraction data for HMWPE/Nylon 12 were measured at room temperature by use of a RIGAKU R-AXIS IV imaging plate diffractometer. Cu Kα radiation (wavelength, 1.5418 nm) from a RIGAKU Ultra-X18 rotating anode x-ray generator was used as an incident x-ray source (40kV, 100mA).

Fourier Transform-Raman Spectroscopy (FT-Raman). The FT-Raman spectra of the uncompatibilized and compatibilized polymer blends of HMWPE/Nylon 12 were measured with a JEOL JRS-FT6500N FT-Raman spectrometer equipped with a cooled InGaAs detector. An excitation wavelength at 1064 nm was provided by a cw Nd:YAG laser (Spectron SL301), and the laser power at the sample position was typically 200 mW. Raman scattered light was collected in a 180° back scattering geometry. The Raman data were collected at a spectral resolution of 4 cm^{-1} and 500-1000 scans were accumulated to achieve a satisfactory signal-to-noise ratio.

Results and Discussion

Morphology of the Polymer Blends. SEM images of the uncompatibilized and compatibilized blends of HMWPE/Nylon 12 with a Nylon 12 content of 20, 50, and 80 wt%, respectively, are shown in Fig.1. It is noted that the SEM images of the compatibilized blends are quite different from those of the uncompatibilized blends. The SEM images of the uncompatibilized polymer blends show a typical "sea-island" structure while in the compatibilized blends the presence of the small amount of MAH (0.5 wt%) yields a marked improvement of dispersion of HMWPE and Nylon 12. The SEM images of the uncompatibilized and compatibilized blends of HMWPE/Nylon 12 are very similar to previously reported SEM images of uncompatibilized and compatibilized blends of HDPE/Nylon 12, respectively.[10]

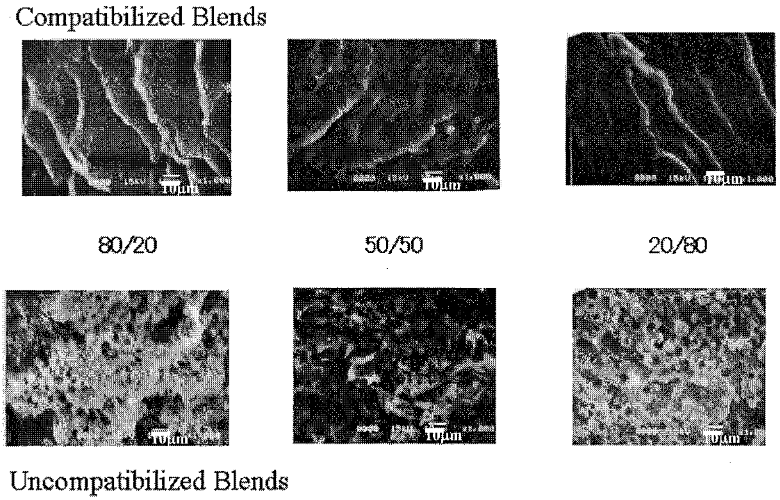

Figure 1. SEM images of HMWPE/Nylon12 compatibilized (top) and uncompatibilized (bottom) blends. Nylon 12 content is 20 (left), 50 (center), and 80 (right) wt%.

Raman Spectroscopy. Figure 2 (a), (b), (c), and (d) shows Raman spectra of MAH-grafted HMWPE, HMWPE, MAH-grafted HDPE, and HDPE, respectively. Raman spectra of HDPE, LDPE (low density polyethylene), and LLDPE (linear low density polyethylene) have been investigated extensively.[12-16] Detailed band assignments have been proposed for these PEs, and characteristic bands corresponding to the crystalline and amorphous structures and *all-trans* conformations have been investigated thoroughly.[12-16] Bands at 1440, 1418, 1296, and 1063 cm^{-1} are assigned to CH_2 bending, CH_2 twisting, symmetric C-C stretching, and asymmetric C-C stretching, respectively. The 1418 cm^{-1} band has been used as a marker band for the crystalline state of PEs.[15] The relative intensity of the band at 1418 cm^{-1} to that of the band at 1461 cm^{-1} is stronger in the Raman spectrum of HDPE (Figure 2 (d)) than in that of HMWPE (Figure 2 (b)), indicating that the crystallinity of HDPE is higher than that of HMWPE. This conclusion is in good agreement with the general idea of the crystallinity of HMWPE and HDPE. The relative intensity of the band at 1418 cm^{-1} is very similar between MAH-grafted HDPE (Figure 2 (c)) and MAH-grafted HMWPE (Figure 2 (a)). This shows that MAH-grafted HDPE and MAH-grafted HMWPE have similar crystallinity.

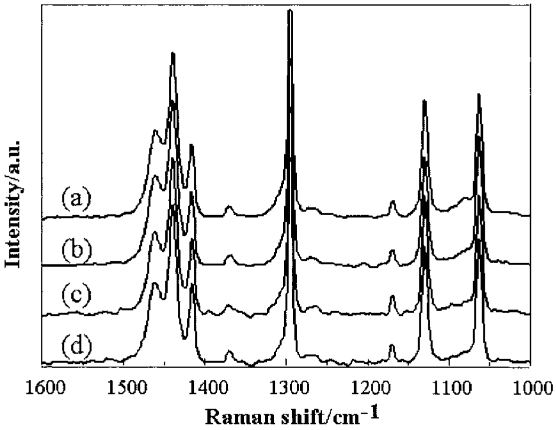

Figure 2. FT-Raman spectra of (a) MAH-grafted HMWPE, (b) HMWPE, (c) MAH-grafted HDPE, and (d) HDPE.

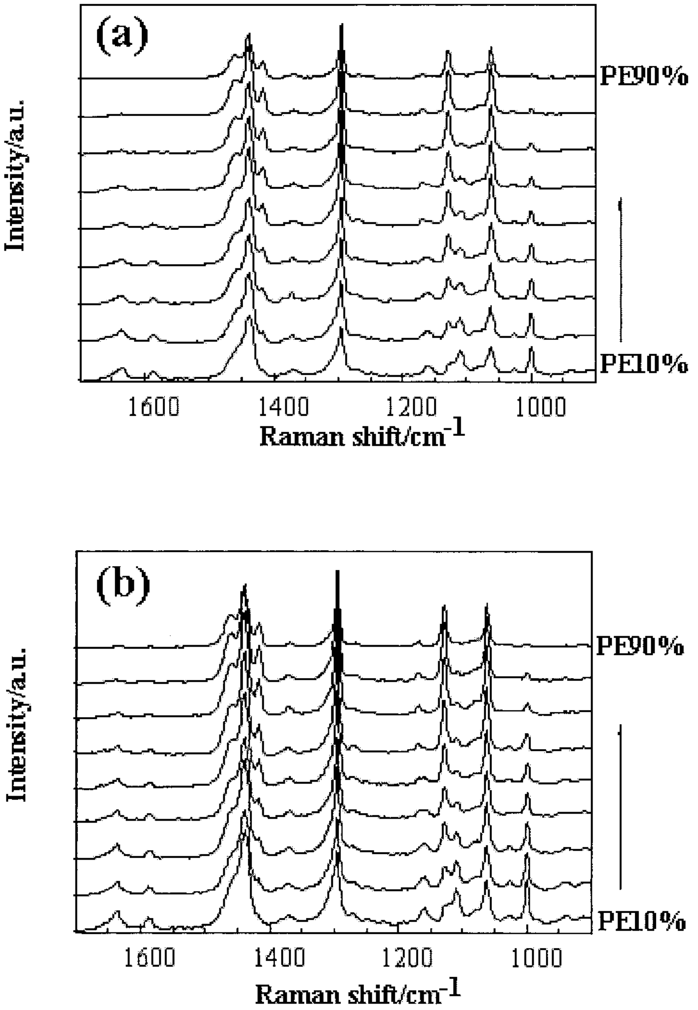

Figure 3. FT-Raman spectra of HMWPE/Nylon12 blends ;(a) uncompatibilized blends (b) compatibilized blends.

Figure 3 (a) and (b) depicts Raman spectra of the uncompatibilized and compatibilized blends of HMWPE/Nylon 12, respectively. In Figure 3 (a) and (b), Raman bands at 1636, 1110, and

1000 cm^{-1} are solely due to Nylon 12. A Raman spectrum of Nylon 12 does not show bands at 1418 and 1129 cm^{-1},[17-19] and thus we use these bands as characteristic bands for HMWPE. These two bands can be employed to evaluate the crystallinity of HMWPE. We estimated the relative intensities of the two bands at 1418 and 1129 cm^{-1} for all the spectra shown in Figure 3 (a) and (b). For this purpose, we used the intensity of the band at 1000 cm^{-1} due to Nylon 12 as an internal intensity standard (I_{1417}/I_{1000} and I_{1126}/I_{1000}). Then, we calculated the ratios of the relative intensities between the uncompatibilized and compatibilized blends (R_{uncom}/R_{com}). Figure 4 illustrates R_{uncom}/R_{com} versus the HMWPE content. It is noted that the ratio is reversed at a HMWPE content of 60 wt%. This observation suggests that when the Nylon 12 content reaches 40 wt%, the crystallinity of HMWPE in the compatibilized blends becomes higher than that of HMWPE in the uncompatibilized blends. In other words, phase inversion happens when the Nylon 12 content reaches 40 wt%. In the HDPE/Nylon 12 blends, it occurs when the Nylon 12 content increased beyond 70 wt%.[10] Therefore, the phase inversion occurs at the higher Nylon 12 content in the HDPE/Nylon 12 blends.

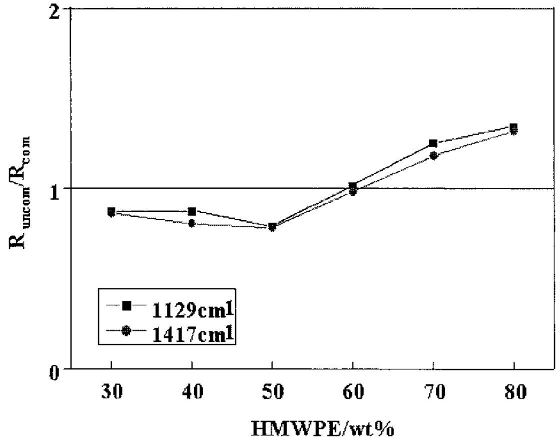

Figure 4. R_{uncom}/R_{com} versus the HMWPE content.

Wide-Angle X-ray Diffraction. Figure 5 (a) and (b) shows the WAXD patterns of uncompatibilized and compatibilized blends of HMWPE/Nylon 12 (50/50), respectively, at room temperature. The patterns of both blends show the (110) and (200) reflections of HMWPE and the (220) reflection of Nylon 12. The angle of 2θ ranges from direct beam to 40 degrees. It can be seen from Figure 5 that the uncompatibilized and compatibilized blends yield quite different x-ray diffraction patterns. It is noted that the compatibilized blend of HMWPE/Nylon 12 (50/50) shows a significantly larger orientational effect in the x-ray diffraction pattern than the uncompatibilized blend. We observed similar result for the HDPE/Nylon 12 blends.[10] It was found that the compatibilized blends of HDPE/Nylon 12 with a Nylon content > 70 wt% show larger orientational effects in the x-ray pattern. We attributed this effect to the increase of interaction of MAH-HDPE with the Nylon 12 matrix. Probably, we can consider a similar effect for the HMWPE/Nylon 12 blend; the increase in the interaction of the MAH-HMWPE with the Nylon 12 matrix, which leads to the additional crystallization.

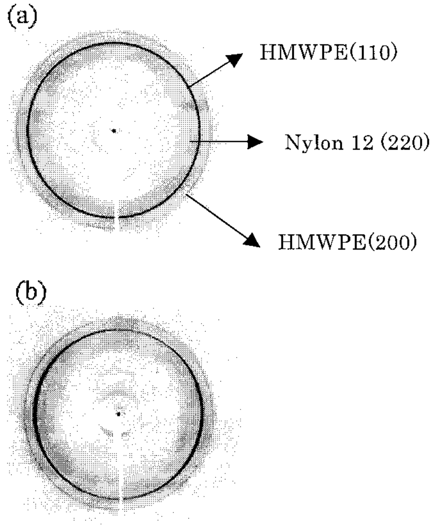

Figure 5. Wide-angle x-ray diffraction patterns of (a) uncompatibilized and (b) compatibilized blends of HMWPE/Nylon 12 (50/50).

Conclusions

The following conclusions can be reached from the present study.

(i) The SEM images have shown a significantly different morphology of the components for the uncompatibilized and compatibilized polymer blends. In the presence of maleic anhydride-grafted HMWPE, a good dispersion of HMWPE and Nylon 12 is obtained in the compatibilized blends.

(ii) The Raman spectra of the uncompatibilized and compatibilized polymer blends have suggested that the crystallinity of HMWPE in the compatibilized blends is higher than in the uncompatibilized polymer blends when the Nylon 12 content exceeds about 40 wt %.

(iii) The compatibilized blend of HMWPE/Nylon 12 with a Nylon content of 50 wt% shows a larger orientation effect than the uncompatibilized blend. This effect may be due to the increase in the interaction of the MAH-HMWPE with the Nylon 12 matrix.

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