RAMAN MAPPING STUDY OF POLYETHYLENE / POLYPROPYLENE BLENDS

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Abstract: The present study is aimed at investigating molecular structure, crystallinity, and morphology of polyethylene (PE) and polypropylene (PP) blends. For this purpose, Raman mapping is used. Because it enables simultaneous exploration of the morphology and molecular structure of polymer blends. In this study, the following three methods are also used to investigate the PE/PP blends; scanning electron microscope (SEM), wide angle x-ray diffraction (WAXD), and differential scanning calorimetry (DSC).

Experiment: The following three kinds of PE was used; high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE), and metallocene polyethylene (MEPE). MEPE is one of the LLDPEs but its density is very low. Each blends of PE/PP with a PP content ranging from 20 to 80 wt% with an increment of 20 wt% were prepared. All blends were prepared by compounding PE with PP at 220°C in a twin-screw extruder, respectively. Melt blending was carried out using a co-rotating intermeshing twin-screw extruder with an *l/d* of 42 (30mm screw diameter) at barrel temperatures ranging from 160°C at the feed zone to 220°C at the metering and die zones.

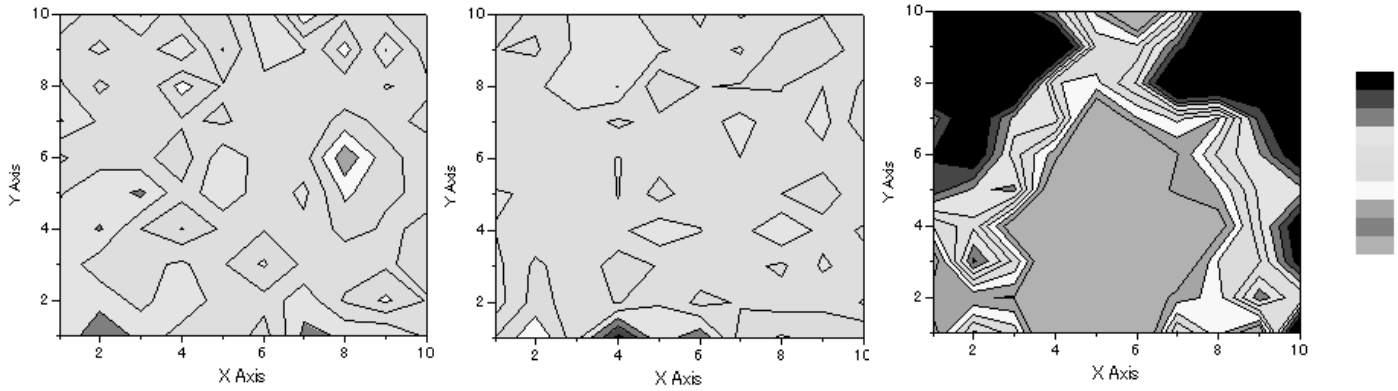
Raman spectra are measured with spectrometer equipped with a CCD detector. An excitation wavelength at 532 nm was provided by a frequency doubled Nd/YAG laser. Raman mapping images were generated by measuring Raman spectra for each with areas of 10 μm^2 in step sizes of 1 •m (for 10×10 probe spots). The spatial resolution was better than several micrometers (the size of the laser beam was 1 μm).

Results and Discussion: Figure 1A, 1B, and 1C show Raman mapping images of the area of 10•m^2 of HDPE/PP, LLDPE/PP and MEPE/PP with the PE content of 80 wt%, respectively. To develop the maps, the intensity ratio of two bands at 1128 and 974 cm^{-1} (I_{1128}/I_{974}) due to the C-C stretching mode of PE and the CH_3 rocking mode of PP, respectively, was employed. As can be seen in Figure 1, the Raman mapping images of MEPE/PP are markedly different from those of HDPE/PP and LLDPE/PP. High concentrations of PE appear black in each mapping image. Only the Raman mapping images of the MEPE/PP blends show a clear "sea–island"structure. The results of the Raman mapping images reveal that the MEPE/ PP blends have an inhomogenous structure. Although MEPE is a kind of LLDPE, the results of Raman mapping of MEPE/PP blends are quite different from those of LLDPE/PP blends. It is very likely that the dispersibility of PE and PP depends on the kinds of PE, and that the properties of branch influence the dispersibility of PE and PP.

The Raman spectra in Figure 2A, 2B and 2C were collected from the two positions in Figure 1A, 1B, and 1C. Each two points in figure 1A, 1B and 1C have quite different color in the maps. As can be seen in Figure 2A and 2B, these two spectra are very similar to each other in terms of the relative intensities of the bands at 1128 and 974 cm^{-1}. In contrast, the two spectra in Figure 2C yield significantly different relative intensities of the bands, revealing that MEPE/PP blend has a heterogeneous structure.

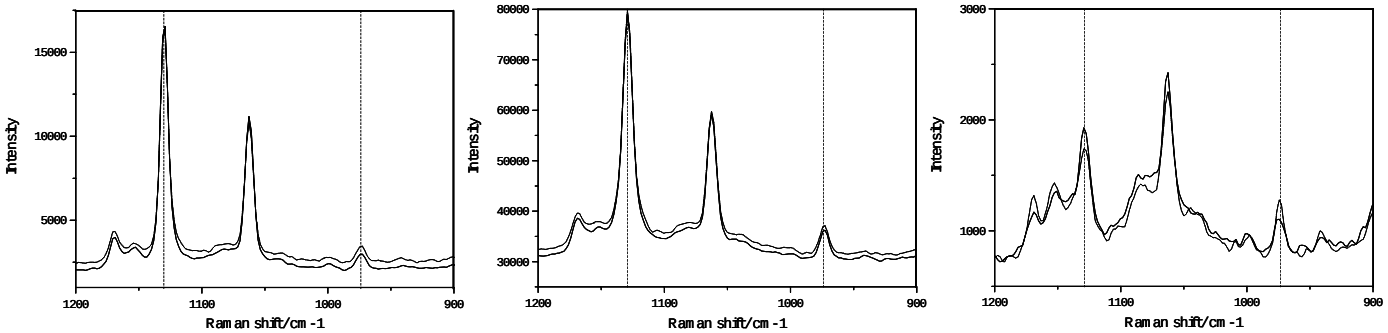
For comparison, SEM images are observed. Note that the SEM images of the MEPE/PP blends are clearly different from those of the HDPE/PP and LLDPE/PP blends. The HDPE/PP and LLDPE/PP blends show good dispersibility in the both blending ratio. On the other hand, the SEM images of

the MEPE/PP blends show a typical "sea-island" structure. The SEM results are in good agreement with those of the Raman mapping images.



(A) HDPE/PP=80/20 (B) LLDPE/PP=80/20 (C) MEPE/PP=80/20

Fig1. Raman mapping of the area of 10 μm^2 of the (A) HDPE/PP, (B) LLDPE/PP, (C) MEPE/PP with PE content of 80 wt%



(A) HDPE/PP=80/20 (B) LLDPE/PP=80/20 (C) MEPE/PP=80/20

Fig2. Raman spectra of the quite different color in Fig1A, 1B, and 1C

Conclusion: The Raman mapping images and the SEM images have shown that the MEPE/ PP blends have a different dispersibility behavior from the HDPE/PP and LLDPE/PP blends. The MEPE/PP blends have a typical "sea•island" structure while the rest have homogeneous structures.

WAXD and DSC results indicate that the crystallinity of PP is affected by the blending ratio in the MEPE blends, and that peak areas show all a linear change with the change in the blending ratio, respectively.

References:

1. L. Markwort, and B. Kip, *J Appl. Polym. Sci*. **61**, 231 (1996).
2. R. Appel, T. W. Zerda, and W. H. Waddell, *Appl. Spectrosc.* **54**, 1559 (2000).
3. H. Sato, S. Sasao, K. Matsukawa, Y. Kita, T. Ikeda, H. Tashiro, and Y. Ozaki, *Appl. Spectrosc.*, **56**, 1038 (2002).
4. A. Gupper, P. Wilhelm, M. Schmied, S. G. Kazarian, K. L. Chan, and J. Reubner, *Appl. Spectrosc.* **56**, 1515 (2002).