Thermal Behavior and Rheology of Polypropylene and Its Blends with Poly(ε-caprolactone)

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Introdiction

Nucleated crystallization kinetics from rheological measurement has been investigated by Khanna (1). From the isothermal crystallization study by RMS, Khanna has shown that the rheological measurement is more sensitive than the conventional measurement like differential scanning calorimetry (DSC). In addition, Khanna has proposed a relation between the crystallization fraction (X_t) and the shear storage modulus under isothermal crystallization process. Recently, the X_t during isothermal crystallization was calculated from the dynamic moduli of semi-crystalline polymer using Takayanagi model (2) and percolation theory by Boutahar et. al. (3).

In this study, we examine the crystallization behavior of the homo PP and PP in the PP-poly(ε-caprolactone) (PCL) blends by DSC and Advanced Rheometric Expansion System (ARES). The crystallization of polymer is considered as a heterogeneous mixture which consists of spherulites (solid phase) and polymer melts (liquid phase). By using the rheological properties, X_t was calculated and compared with the results of thermal analysis.

Experimental

The isothermal crystallization of the homo PP and PP in the PP-PCL blends were analyzed by using a Perkin-Elmer DSC-7. For the isothermal crystallization of the homo PP and PP in the PP-PCL blends, samples were melted at 210 °C for 5 min, and then rapidly cooled to the isothermal crystallization temperature. During isothermal crystallization of the homo PP and PP in the PP-PCL blends, the heat flow was recorded until no change of heat flow with time was detected.

Rheological measurements were carried out on Advanced Rheometirc Expansion System in oscillatory shear at 0.3-0.6 % strain in the parallel-plate arrangement with 25 mm plate. The sample used in this study was fabricated in a disk with 2 mm in thickness. For the isothermal crystallization of the homo PP and PP in the PP-PCL blends, samples were melted at 210 °C for 5 min, and then rapidly cooled to the isothermal crystallization temperature. In order to keep the constant shearing effect, the torque was maintained at about 50 gcm.

Results and Discussion

Crystallization of homo PP and PP in the PP-PCL Blends

Isothermal crystallization of the homo PP was studied using differential scanning calorimetry (DSC). From isothermal crystallization thermograms of homo PP from 130 to 133 °C. the crystallization fraction at time t is determined by Martuscelli et al.(4). A numerator is the heat generated after time t and a denominator is the heat generated after time goes infinite. The crystallization kinetics of the homo PP under isothermal crystallization was analyzed by Avrami equation (5). From the Avrami plots of the homo PP, the n was calculated and found to range from 2.8 to 3.0 with isothermal crystallization temperature. The Avrami exponent is related to the dimension of crystals, and the value of 3.0 indicates that the homo PP crystal forms three-dimensional spherulites from instantaneous nuclei under the isothermal crystallization condition.

Isothermal crystallization of the PP and PP in the PP-PCL blends was studied using DSC at 133 °C. The crystallization fraction (X_t) of the homo PP and PP in the PP-PCL blends was determined and the X_t is shown in Figure 1. From Figure 1. it is observed that as the weight fraction of PCL increases. the crystallization curve shifts to longer times. indicating slower bulk crystallization rates.

Also. crystallization kinetics of the homo PP and PP in the PP-PCL blends under isothermal crystallization was analyzed by Avrami equation and the result is shown in Figure 2. From the Avrami plots of the PP in the PP-PCL blends, the n was found to similar with the results of the homo PP during isothermal crystallization.

Rheology of PP and PP-PCL Blends

In order to calculate the volume fraction of crystallized material from rheological measurements. eq (1) can be used from the measured storage modulus. Nielsen (6) has introduced a generalized Einstein coefficient and a function which considers the maximum volumetric packing fraction (ϕ_p) of the filler phase as follow:

$$\frac{G}{G_m} = \frac{1 + AB\phi_i}{1 - B\varphi\phi_i} \tag{1}$$

where G and G_m are the modulus of filler filled polymer and matrix. respectively. ϕ_i is the volume fraction of filler. A is a constant which takes into account such factors as geometry of the filler and Poisson's ratio (v) of the matrix. B is the relative moduli of the filler and matrix phases. φ is a constant which depends on the maximum packing fraction (ϕ_p) of filler.

From eq (1). the volume fraction (X_t) of crystallized material of homo PP is calculated with time. From the comparison of X_t with the DSC and rheological

measurements results, Boutahar et al. (7) reported that the estimation of X_t from rheological measurements is very limited. This limitation is due to the occurrence of yield effect in highly filled polymer system.

The X_t of the homo PP was found to be higher in the rheological measurements than in the DSC. The observed acceleration in crystallization from the rheological measurements may be due to the increase in nucleation rate and orientation of chains in melt crystalline aggregate. From the comparison of X_t with the DSC and rheological measurements results, it is observed that the X_t from the various models appears similar results. From the above results, it is suggested that the eq (1) can be used to estimate the X_t of the homo PP from the rheological measurements.

Figure 3 shows the crystallization kinetics of the homo PP and PP in the PP-PCL blends under isothermal crystallization, which are obtained from the storage modulus (G') with time for the homo PP and PP in the PP-PCL blends crystallized at 133 °C (Figure 4). By comparing the X_t of PP in the PP-PCL blends from the DSC data (Figure 2) and ARES data (Figure 3), it is observed that the X_t of PP in the PP-PCL blends obtained from the thermal analysis and rheological measurements is not consistent. From the results of Figure 2 and 3, it is thought that this discrepancy of X_t may be due to the morphological changes resulted from the different crystallization kinetics of PP in the PP-PCL blends.

Acknowledgment

References

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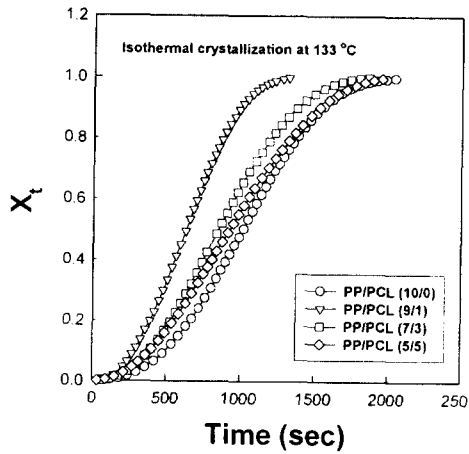7. Boutahar, K., Carrot, C., and J. Guillet, *J. Appl. Polym. Sci*. **60**, 103 (1996).

Fig.1. Isothermal crystallization kinetics data for PP in the PP-PCL blends with various compositions: plots of X_t vs. time.
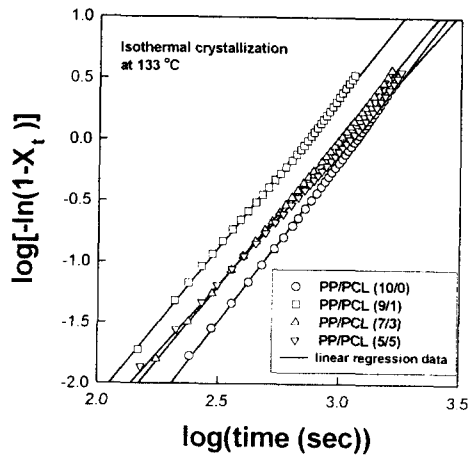

Fig. 2. Isothermal crystallization kinetics data for PP in the PP-PCL blends with various compositions: Avrami plots from DSC data.
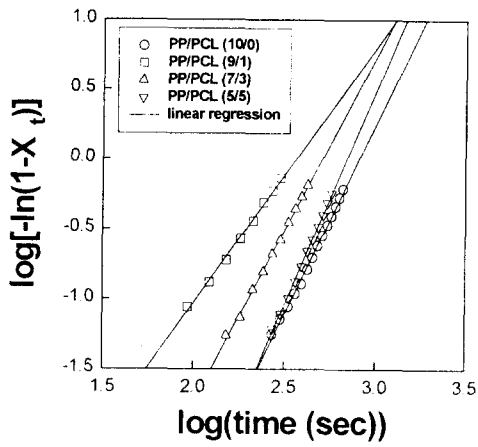

Fig. 3. Isothermal crystallization kinetics data for PP in the PP-PCL blends with various compositions: Avrami plots from plots from ARES data.
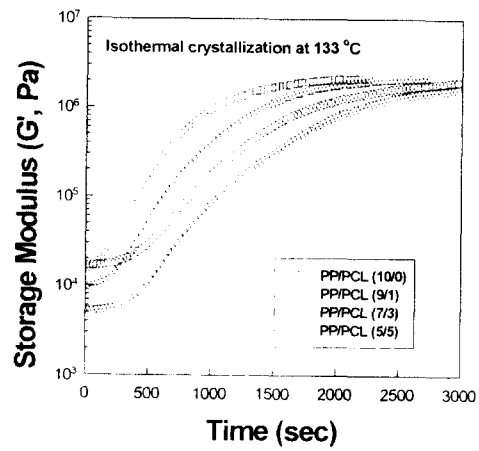

Fig. 4. Effect of time on the storage modulus (G') of PP-PCL blends with various compositions during isothermal crystallization.