

Thermal behavior and rheology of polypropylene and its blends with poly(ϵ -caprolactone)

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Abstract

The crystallization behavior of homo polypropylene (PP) and PP in the PP-poly(ϵ -caprolactone) (PCL) blends during isothermal crystallization has been investigated using differential scanning calorimeter (DSC) and advanced rheometric expansion system (ARES). From the storage modulus data of the homo PP and PP-PCL blends during isothermal crystallization, the volume fraction of crystallized material (X_t) of the homo PP and PP in the PP-PCL blends was calculated using the various rheological models. The results of X_t of the homo PP and PP in the PP-PCL blends from ARES measurement were compared with the results from DSC. The X_t of the homo PP was found to be higher in the ARES measurement than in the DSC. The crystallization rate of the homo PP was found to be faster in the rheological measurements than in the thermal analysis. The X_t of PP in the PP-PCL blends with various compositions was obtained from the thermal analysis and rheological measurements. The X_t of PP in the PP-PCL blends obtained from the thermal analysis and rheological measurements are not consistent. 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.

Keywords : crystallization behavior, rheological measurement, thermal analysis, crystallization kinetics

1. Introduction

The effect of shear and elongational deformation on the crystallization of various semi-crystalline polymers has been studied by many investigators (Yeh and Hong, 1979; Chang and Kushner, 1979; Khanna, 1993; Boutahar *et al.*, 1998). Chang and Kushner (1979) have studied the crystallization of polymer under oscillatory shear using the Rheometrics Mechanical Spectrometer (RMS). From the measured rheological properties during isothermal crystallization, they have reported that crystallization of polypropylene (PP) is accelerated significantly without affecting the final degree of crystallinity by increasing frequency of oscillatory shear. This result has been explained by the increase in nucleation rate and orientation of chains in crystalline aggregate.

Nucleated crystallization kinetics from rheological measurement has been investigated by Khanna (1993). From the isothermal crystallization study by RMS, Khanna (1993) has shown that the rheological measurement is more sensitive than the conventional measurement like differential scanning calorimetry (DSC). In addition, Khanna (1993) 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 (1961) and percolation theory (Sahimi, M., 1994) by Boutahar *et al.* (1998).

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.

2. Experimental

The sample used in this study was obtained from commercial source. The characteristics of the isotactic polypropylene (i-PP) and the PCL are shown in Table 1. The PP was supplied by Honam Oil Refinery Co. and PCL (Tone P-787) was supplied by Union Carbide Co., respectively. The blends of PP and PCL were prepared using a 20 mm diameter laboratory scale screw extruder, with a 24 : 1 length to diameter screw. The extruder was set at 140°C in the barrel zones and die was kept at 160°C. Pellet of the two poly-

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Table 1. Characteristics of polypropylene and poly(ϵ -caprolactone) used in this study

	T_m ($^{\circ}\text{C}$) ^a	T_c ($^{\circ}\text{C}$) ^a	T_g ($^{\circ}\text{C}$) ^a	ρ (g/cm^3) ^b	MI ^c
PP ^d	157.0	106.0	-10.0	0.903	1.68
PCL ^e	57.1	19.7	-64.0	1.12	-

^aMeasured in our laboratory by DSC.

^bMeasured in our laboratory by specific gravity chain balance.

^cMelt index, Measured in our laboratory at 230 $^{\circ}\text{C}$.

^dSupplied by Honam Oil Refinery Co.

^eSupplied by Union Carbide Co.

mers were mixed to the desired composition and dried for 24 hr before use to ensure removal of any moisture absorbed.

The isothermal crystallization of the homo PP and PP in the PP-PCL blends were analyzed by using a Perkin-Elmer DSC-7. Temperature calibration was performed using indium ($T_m=156.6^{\circ}\text{C}$, $\Delta H_f=28.5$ J/g). For the isothermal crystallization of the homo PP and PP in the PP-PCL blends, samples were melted at 210 $^{\circ}\text{C}$ 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 Rheometric 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 $^{\circ}\text{C}$ 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.

3. Results and Discussion

3.1. 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 $^{\circ}\text{C}$, the crystallization fraction at time t is determined as follow (Martuscelli *et al.*, 1984):

$$X_t = \frac{\int_0^t (dH/dt)dt}{\int_0^{\infty} (dH/dt)dt} \quad (1)$$

where X_t is the volume fraction of crystallized material after time t . 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 the following

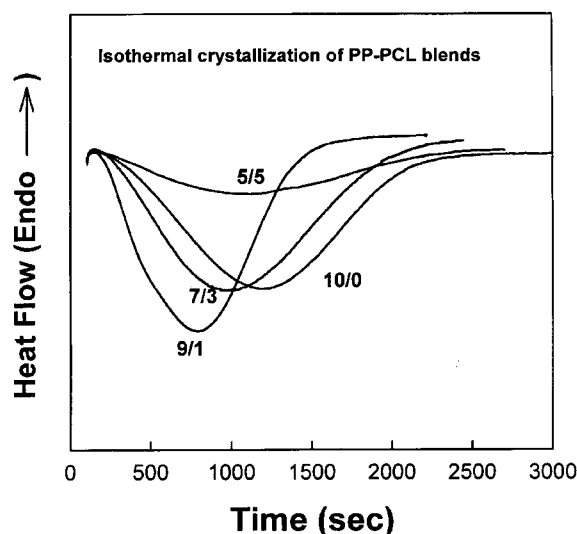


Fig. 1. DSC isothermal crystallization thermograms of PP in the PP-PCL blends with various compositions.

Avrami equation (1940).

$$\log[-\ln(1-X_t)] = \log K + n \log t \quad (2)$$

where n is the Avrami exponent and K is the overall crystallization rate constant, respectively. 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 in the PP-PCL blends

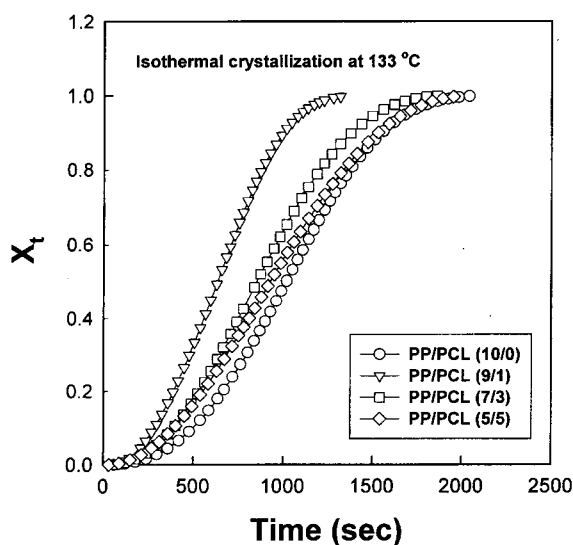


Fig. 2. Isothermal crystallization kinetics data for PP in the PP-PCL blends with various compositions: plots of X_t vs. time.

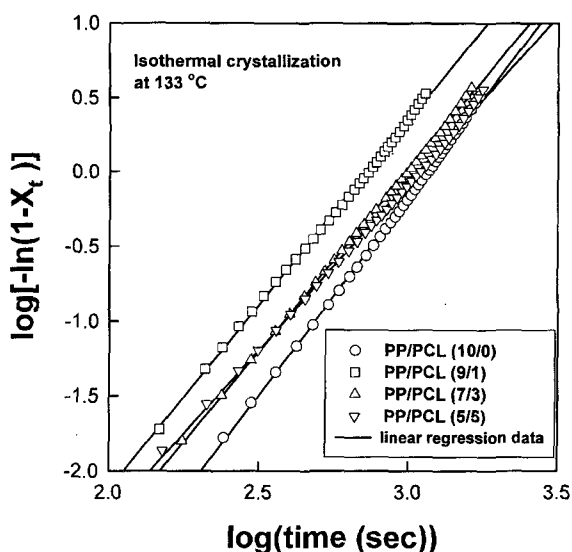


Fig. 3. Isothermal crystallization kinetics data for PP in the PP-PCL blends with various compositions: Avrami plots from DSC data.

was studied using DSC. The isothermal crystallization thermograms of the homo PP and PP in the PP-PCL blends at 133°C are shown in Fig. 1. From Fig. 1 and eq (1), 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 Fig. 2. From Fig. 2, 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 eq (2) and the result is shown in Fig. 3. 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.

3.2. Rheology of PP and PP-PCL Blends

Many investigators have proposed the viscoelastic models for multiphase of polymer system (Nielsen, 1970; Kerner, 1956; Paliarne, 1990). In order to calculate the volume fraction of crystallized material from rheological measurements, eq (3) can be used from the measured storage modulus. Among the various rheological models, Nielsen (1970) has proposed the generalized equation for the elastic moduli of composite materials. He has introduced a generalized Einstein coefficient and a function which considers the maximum volumetric packing fraction (ϕ_p) of the filler phase as follow:

$$\frac{G}{G_m} = \frac{1 + AB\phi_i}{1 - B\phi_i} \quad (3)$$

where G and G_m are the modulus of filler filled polymer and matrix, respectively. ϕ_i is the volume fraction of filler.

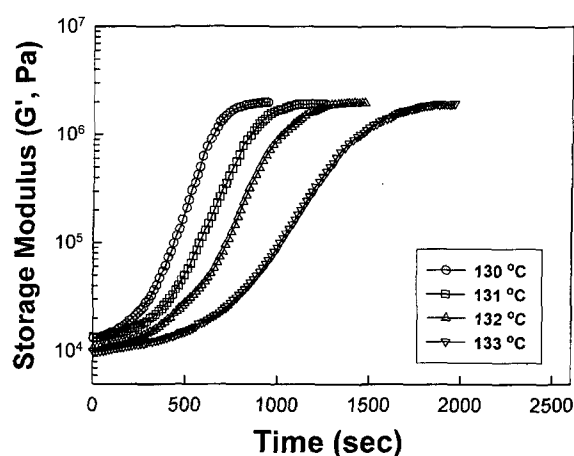


Fig. 4. Effect of time on the storage modulus (G') of homo PP during isothermal crystallization.

A is a constant which takes into account such factors as geometry of the filler and Poissons ratio (ν) 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.

For the filler-filled system, ϕ_p is 0.5236 and for the polymer spherulites with impingement, ϕ_p can be as low as 0.37 (Nielsen and Landel, 1994). Therefore, it can be assumed that ϕ_p is $0.5236 - 0.15 \phi_i^2$ when ϕ_i is greater than 0.5236.

Fig. 4 shows the variation of shear storage modulus (G) with time for the homo PP crystallized at various temperatures under the frequency of 1 rad/sec. The sigmoidal curves are similar to those observed for X_t from DSC. They consist mainly of three regions, such as the onset of crystallization, the accelerated growth, and the pseudo-equilibrated growth. In Fig. 4, the G at time zero is considered as the modulus of matrix (G_m) and the G at pseudo-equilibrated region is considered as the modulus of filler (G_i).

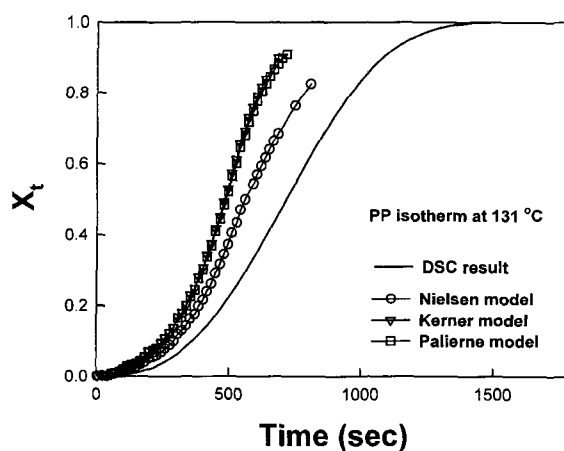


Fig. 5. Comparison between the X_t of homo PP obtained from the various rheological models.

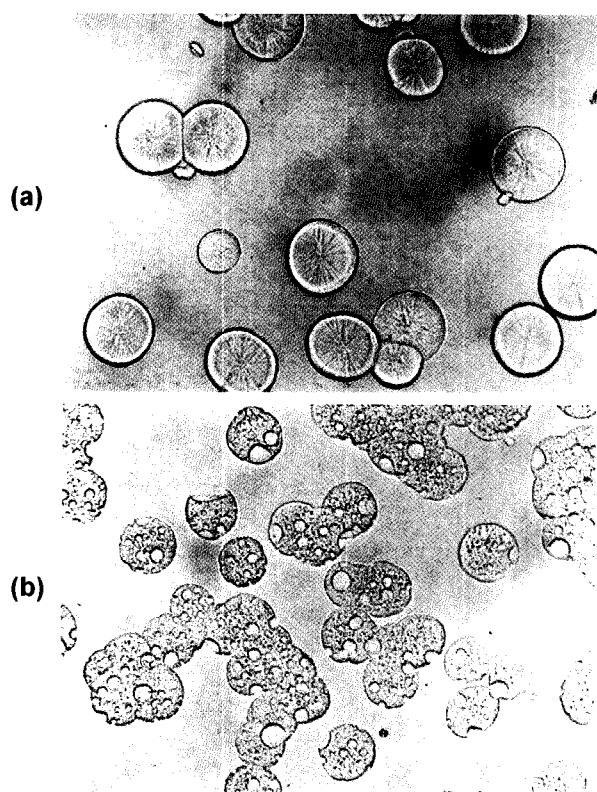


Fig. 6. Optical micrographs of the PP and PP-PCL blend at 133°C.

From eq (3), the volume fraction (X_t) of crystallized material of homo PP is calculated with time and shown in Fig. 5. From the comparison of X_t with the DSC and rheological measurements results, Boutahar *et al.* (1996) reported that the estimation of X_t from rheological measurements are very limited. This limitation is due to the occurrence of yield effect in highly filled polymer system.

In Fig. 5, the X_t obtained from the thermal analysis and rheological measurements is shown. The X_t was calculated from the rheological data (Fig. 4) using the various rheological models (Kerner, 1956; Paliarne, 1990; Nielsen; 1970).

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 Figure 5, it is observed that the X_t from the various models appears similar results. From the above results, it is suggested that the eq (3) can be used to estimate the X_t of the homo PP from the rheological measurements.

Fig. 6 and 7 shows optical micrographs and the storage modulus (G') with time for the homo PP and PP in the PP-PCL blends crystallized at 133°C, respectively. From Fig. 6, it is observed that morphology of pure PP is different from PP-PCL blends. In PP-PCL blends, the PP spherulites are not homogeneous while they are homogeneous in pure PP. Fig. 8 shows the crystallization kinetics of the homo PP

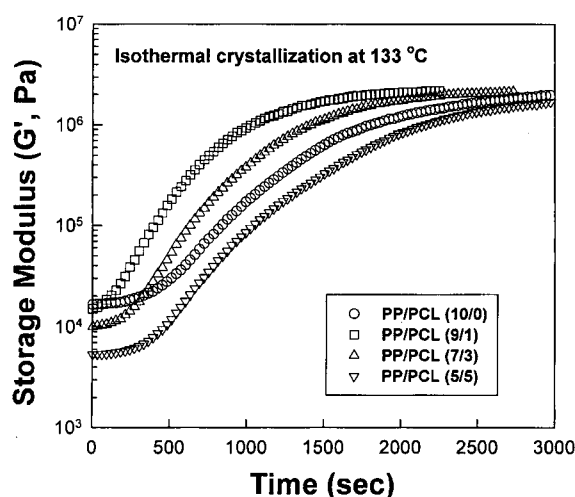


Fig. 7. Effect of time on the “storage modulus (G')” of PP-PCL blends with various compositions during isothermal crystallization.

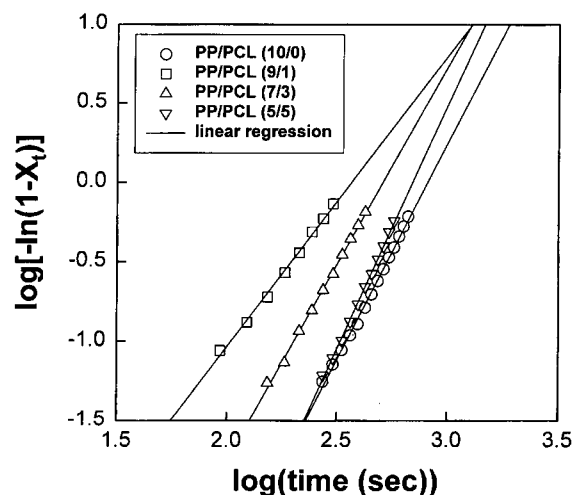


Fig. 8. Isothermal crystallization kinetics data for PP in the PP-PCL blends with various compositions: Avrami plots from ARES data.

and PP in the PP-PCL blends under isothermal crystallization, which are obtained from Fig. 7. By comparing the X_t of PP in the PP-PCL blends from the DSC data (Fig. 3) and ARES data (Fig. 8), 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 Fig. 3, 6, and 8, 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.

4. Conclusions

The crystallization fraction (X_t) of the homo PP and PP

in the PP-PCL blends with time was calculated from the thermal analysis using DSC and the rheological measurements using ARES. 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 results obtained by ARES and DSC measurements, it is suggested that the rheological measurements can be used to obtain the crystallization behavior of the homo PP in the dynamic oscillation.

The X_t of PP in the PP-PCL blends with various compositions was obtained from the thermal analysis and rheological measurements. The X_t of PP in the PP-PCL blends obtained from the thermal analysis and rheological measurements are not consistent. 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

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