Kasetsart J. (Nat. Sci.) 43 : 347 - 352 (2009)

Isothermal Crystallization Kinetics of Polypropylene/$CaCO_3$ Blends

Supreya Trivijitkasem[1]* and Kriengkri Timsorn[2]

ABSTRACT

Crystallization of polypropylene (PP) and PP blended with 10, 15, and 20 wt% $CaCO_3$ was investigated using Differential Scanning Calorimetry (DSC) under isothermal conditions at four different crystallization temperatures of 110, 115, 120 and 125°C. The kinetic parameters were analyzed using the Avrami equation. The results show that the Avrami exponent, n, decreased with increasing crystallization temperature, except for a crystallization temperature T_C of 125°C where the opposite effect was observed. At the same crystallization temperature, the values of n for PP/$CaCO_3$ blends were slightly lower than for PP, which suggests that the addition of $CaCO_3$ to PP caused a slight decrease in heterogeneous nucleation. Both PP and PP/$CaCO_3$ blends followed three-dimensional crystallization growth. The value of the crystallization rate constant, k, strongly depended on the crystallization temperature, which decreasing with increasing crystallization temperature and $CaCO_3$ content. The rate of the three-dimensional crystallization growth was reduced by increasing the crystallization temperature and $CaCO_3$ content.

Key words: PP, PP/$CaCO_3$, isothermal, crystallization kinetics

INTRODUCTION

The most widely used polymeric materials are high-density polyethylene (HDPE) and polypropylene (PP), which have moderate mechanical and thermal properties. Some common additives are added to the polymer to improve the mechanical and thermal properties, the most commonly used additive being $CaCO_3$ in amounts of 5-40 wt%.

PP is a semicrystalline polymer. The physical properties of PP and its blends depend on the extent of crystallinity and the crystalline morphology. Examinations concerned with the extent of the crystallization features in PP and its blends with additives have been published by several authors, (Xu *et al*., 2003; Arbelaiz *et al*., 2006; Tao *et al*., 2008). Analysis using Differential Scanning Calorimetry (DSC) is a common, effective technique to investigate polymeric crystallization, (Privalko *et al*., 2005; Wang *et al*., 2006). The crystallization kinetics can be analyzed using several crystallization kinetic equations, (Krumme *et al*., 2004; Arbelaiz *et al*., 2006). In the present study, the crystallization process of PP and PP/$CaCO_3$ blends was carried out under isothermal conditions.

1 Department of Physics, Faculty of Science, Kasetsart University, Bangkok 10900, Thailand.

2 Faculty of Science and Agricultural Technology, Rajamangala University of Technology Lanna, Chiang Mai 50200, Thailand.

* Corresponding author, e-mail: fscisum@ku.ac.th

MATERIALS AND METHODS

PP and PP blended with 10, 15 and 20 wt% $CaCO_3$ were purchased from the Thantawan Industry, Nakorn Pratum. Crystallization of PP and PP/$CaCO_3$ blends was performed in a differential scanning calorimeter (DSC 7, Perkin-Elmer) using samples of about 3.5±0.3 mg. All measurements were carried out in a nitrogen atmosphere with a 20 ml/min flow rate. The samples were heated at a rate of 50°C/min to 220°C and maintained at this temperature for 5 min in order to erase all previous thermal history of the melts. The melts were rapidly cooled at a rate of 50°C/min to four different crystallization temperatures: 110, 115, 120 and 125°C and kept at that temperature for a while, in order to crystallize the melts under isothermal conditions. The heat flow was recorded as a function of time. The crystallinity kinetics were then evaluated from the enthalpy evolved during crystallization, and the results were analyzed using the Avrami equation.

RESULTS AND DISCUSSION

Isothermal thermograms obtained by cooling the molten PP and PP/$CaCO_3$ blends to the crystallization temperature T_C are presented in Figure 1. Crystallization of PP and its blends was similarly affected by the crystallization temperature T_C. The exothermic peaks became flatter and shifted to longer times at higher T_C.

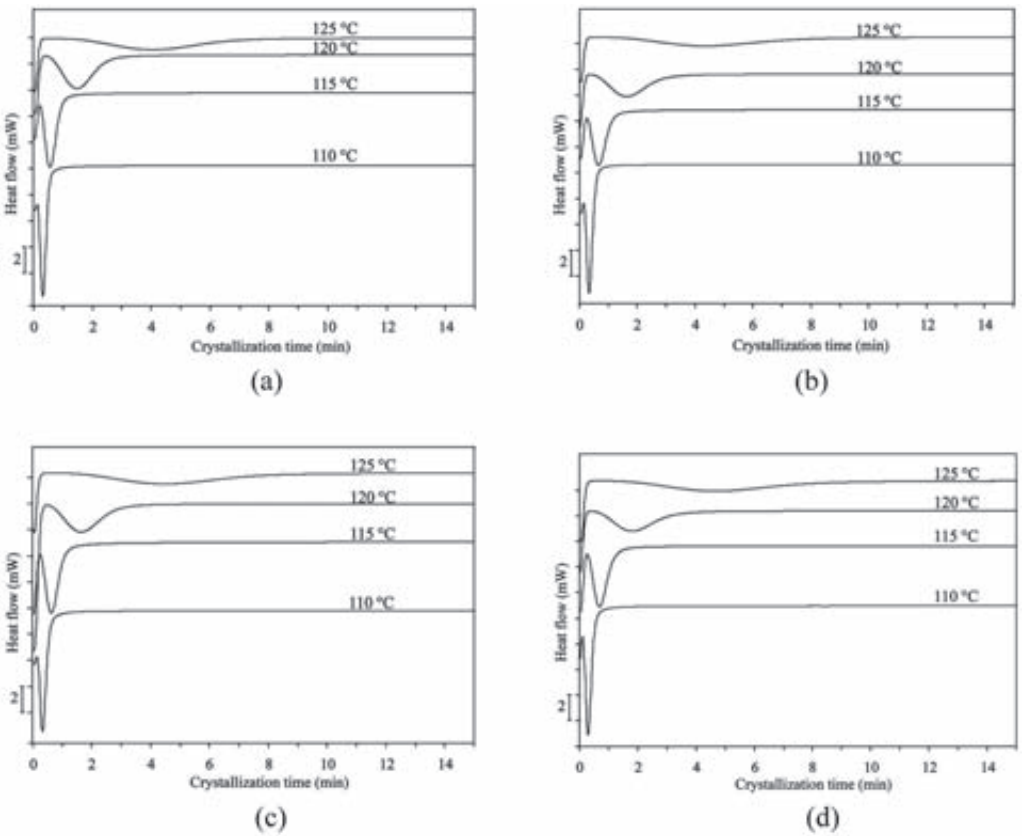

Figure 1 DSC thermograms as a function of isothermal crystallization time at different crystallization temperatures for PP blended with $CaCO_3$ at: (a) 0 wt%; (b) 10 wt%; (c) 15 wt% and (d) 20 wt%.

The time to complete the crystallization increased at higher T_C. Hence, the crystallization rate decreased with increasing T_C.

Assuming that the evolution of crystallinity is linearly proportional to the heat evolution released during crystallization, the relative degree of crystallinity at time t , $\chi(t)$, can be obtained from Equation (1) (He *et al*., 2007):

$$\chi(t) = \frac{\int_0^t \frac{dH}{dt} dt}{\int_0^\infty \frac{dH}{dt} dt} = \frac{\Delta H_t}{\Delta H_\infty} \quad (1)$$

where, dH/dt is the rate of heat evolution , ΔH_t is the heat evolution at time t , and ΔH_∞ is the total heat evolution up to the end of the crystallization process.

Figure 2 shows the relative crystallinity, $\chi(t)$, as a function of time for different crystallization temperatures of the isothermal crystallization process, where the sigmoidal isothermal curves shifted to the right with increasing isothermal crystallization temperature, and a slower crystallization rate.

The crystallization kinetics under isothermal crystallization conditions can be analyzed using the Avrami equation (Papageorgiou *et al*., 2005) as shown in Equation (2):

$$\chi(t) = 1\text{-}\exp[-kt^n] \quad (2)$$

where, n is the Avrami exponent depending on the type of nucleation and growth of the crystals, k is the crystallization rate constant involving both nucleation and growth rate parameters.

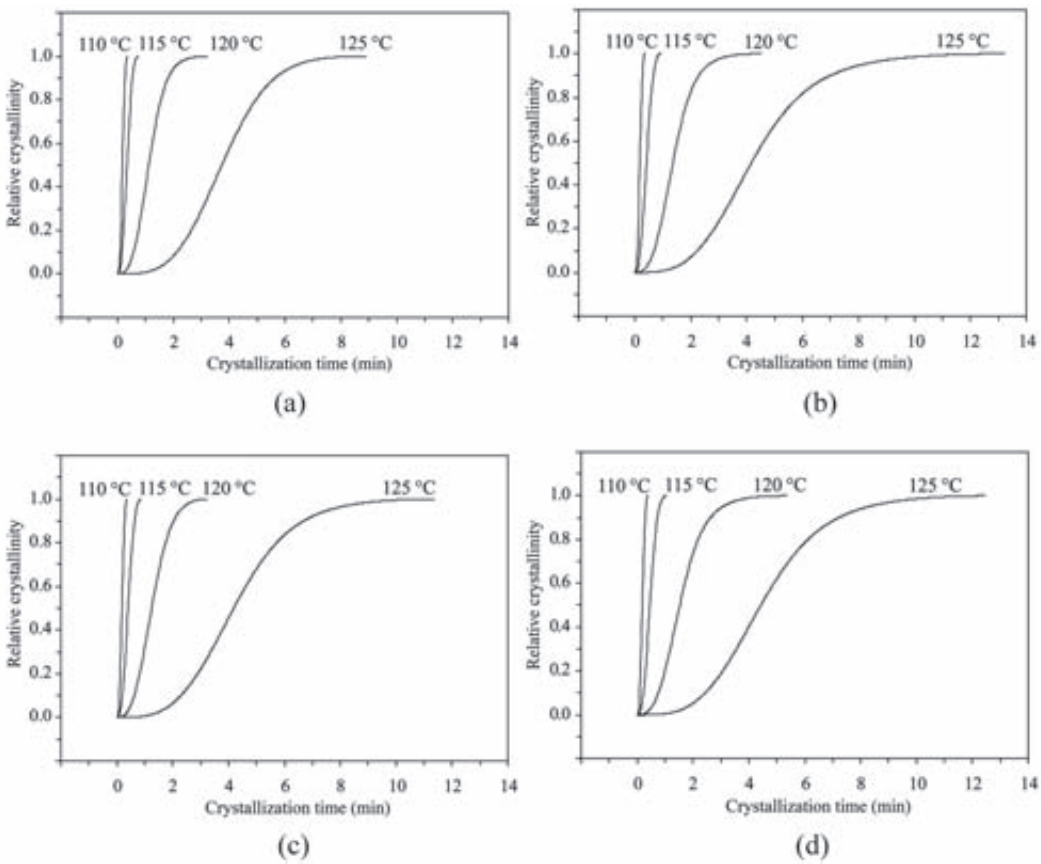

Figure 2 Relative crystallinity $\chi(t)$ as a function of isothermal crystallization time, t, for PP blended with CaCO at: (a) 0 wt%; (b) 10 wt%; (c) 15 wt% and (d)20 wt%.

Using the double logarithmic form in Equation (2), Equation (3) is obtained:

$$\log[-\ln(1-\chi(t))] = \log k + n \log t \quad (3)$$

Fitting the experimental data of relative crystallinity $\chi(t)$ at time t into Equation (3) and plotting $\log[-\ln(1-\chi(t))]$ versus log t, a series of straight lines was obtained, where the kinetic parameters, n and k, can be derived from the slope and the intercept, respectively. Figure 3 shows plots of $\log[-\ln(1-\chi(t))]$ versus log t for various crystallization temperatures for PP and PP/$CaCO_3$ blends, which show almost straight lines at the beginning, and subsequently taper off. Thus, the Avrami equation can be applied to describe the beginning of isothermal crystallization for PP and PP/$CaCO_3$ blends, while the deviation is probably due to secondary crystallization (Chen *et al.*, 2007).

The Avrami parameters, n and k, are listed in Table 1. The exponent, n, informs the nature of nucleation and the growth process. The value of n should be an integer from 1 to 4 depending on the crystallization mechanisms.

The observed value of n decreased with increasing crystallization temperature, except for a crystallization temperature of 125°C, where n increased, indicating that at T_C=125°C, more nucleation occurred. At the same crystallization temperature, the value of n for the PP/$CaCO_3$ blends was slightly lower than that for PP, which

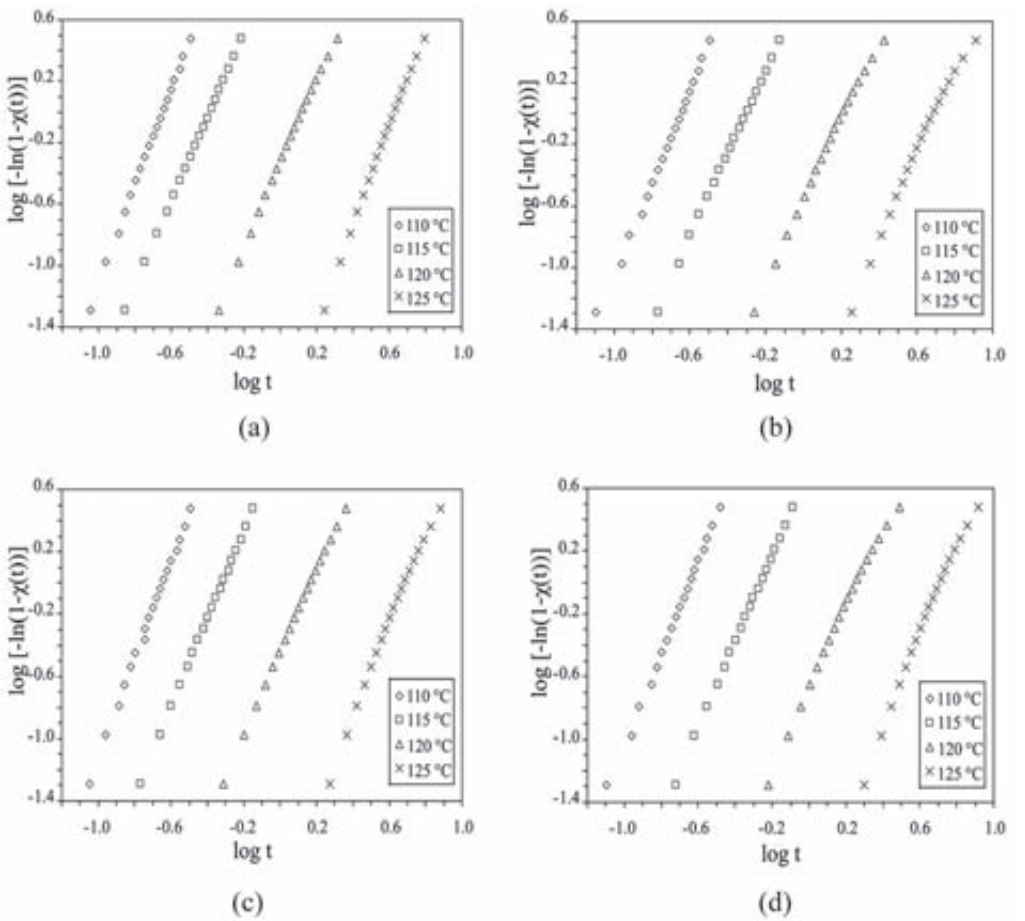

Figure 3 Plots of $\log[-\ln(1-\chi(t))]$ versus log t for four isothermal crystallization temperatures for PP blended with $CaCO_3$ at: (a) 0 wt%; (b) 10 wt%;(c) 15 wt% and (d) 20 wt%.

suggests that both PP and PP/$CaCO_3$ blends followed a similar crystallization mechanism of initiated heterogeneous nucleation and three-dimensional crystallization growth (Zhang *et al.*, 2006). The value of n ranged from 2.7 to 3.2 for PP and from 2.5 to 3.0 for the PP/$CaCO_3$ blends. Hence, the addition of $CaCO_3$ to PP caused a slight decrease in nucleation.

The crystallization rate constant, k, strongly depended on the crystallization temperature. The observed value of k decreased with increasing crystallization temperature and $CaCO_3$ content, indicating that the rate of the three-dimensional crystallization growth was reduced by increasing the crystallization temperature and $CaCO_3$ content.

The crystallization half time, $t_{1/2}$, is defined as the time at which relative crystallinity $\chi(t)$ is 50%. The half time can be obtained directly from Figure 2. Generally, the reciprocal of the half time ($1/t_{1/2}$) is related to the crystallization rate constant, k. That is, half time, $t_{1/2}$ can be calculated from k, which can be derived from Equation (2) as Equation (4) (Zhang *et al.*, 2005):

$$t_{1/2} = \left(\frac{\ln 2}{k}\right)^{1/n} \quad (4)$$

The value of $t_{1/2}$ is reported in Table 1, which increased with increasing T_C and $CaCO_3$ content. The value of $t_{1/2}$ is used to characterize the rate of crystallization; the higher the value of $t_{1/2}$, the lower the rate of crystallization. Hence, the rate of crystallization for PP/$CaCO_3$ was slower than that of PP. This suggests that $CaCO_3$ can act as a retardative nucleation agent that decelerates the crystallization of PP in the composite; the addition of $CaCO_3$ to PP caused a slight increase in the crystallization time and reduced the rate of isothermal crystallization.

CONCLUSION

Polypropylene (PP) and PP blended with $CaCO_3$ at 10, 15 and 20 wt% were used to

Table 1 Avrami kinetic parameters for different crystallization temperatures, T_C, for PP and PP/$CaCO_3$ blends.

Content of $CaCO_3$	T_C (°C)	n	k (min^{-1})	$t_{1/2}$ (min)
0 wt%	110	3.15	30.753	0.30
	115	2.74	3.083	0.58
	120	2.68	0.230	1.51
	125	3.11	0.008	4.19
10 wt%	110	3.00	21.153	0.32
	115	2.69	1.956	0.68
	120	2.62	0.155	1.77
	125	2.75	0.009	4.75
15 wt%	110	3.05	20.387	0.33
	115	2.82	2.336	0.65
	120	2.63	0.164	1.73
	125	2.93	0.007	4.74
20 wt%	110	2.94	15.180	0.35
	115	2.74	1.772	0.71
	120	2.53	0.126	1.96
	125	2.88	0.007	4.98

investigate isothermal crystallization behavior. Differential scanning calorimetry (DSC) was employed with a crystallization temperature of 110, 115, 120 and 125°C. The Avrami method was applied for crystallization kinetic analysis. The value of the Avrami exponent, n, ranged from 2.7 to 3.2 for PP and 2.5 to 3.0 for the PP/$CaCO_3$ blends. The slightly different values of n suggested a similar crystallization mechanism for the heterogeneous nucleation and the three-dimensional crystallization growth. The values of the crystallization rate constant, k, and half time, $t_{1/2}$, indicated the rate of crystallization. The crystallization rate constant of PP was higher than that of the PP/$CaCO_3$ composites and decreased with increasing crystallization temperature. The addition of $CaCO_3$ to PP caused a slight increase in the crystallization time and reduced the rate of isothermal crystallization.

ACKNOWLEDGEMENT

This research was financially supported by the Kasetsart University Research and Development Institute (KURDI).

LITERATURE CITED

Arbelaiz, A., B. Feranadez, J.A. Ramos and I. Mondragon. 2006. Thermal and crystallization studies of short flax fibre reinforced polypropylene matrix composites: Effect of treatments. **Thermochim. Acta.** 440: 111-121.

Chen, X., C. Li and W. Shao. 2007. Isothermal crystallization kinetics and melting behaviour of PET/ATO nanocomposites prepared by in situ polymerization. **Eur. Polym. J.** 43: 3177-3186.

He, Y., Z. Fan, Y. Hu, T. Wu, J. Wei and S. Li. 2007. DSC analysis of isothermal melt crystallization, glass transition and melting behavior of poly (L-lactide) with different molecular weights. **Eur. Polym. J.** 43: 4431-4439.

Krumme, A., A. Lehtinen and A. Viikna. 2004. Crystallization behavior of high density polyethylene blends with bimodal molar mass distribution, Basic characteristics and isothermal crystallization. **Eur. Polym. J.** 40: 359-369.

Papageorgiou, G.Z., D.S. Achilias, D.N. Bikiaris and G.P. Karayannidis. 2005. Crystallization kinetics and nucleation activity of filler in polypropylene/surface-treated SiO_2 nanocomposites. **Thermochim. Acta.** 427: 117-128.

Privalko, V.P., R.V. Dinzhos and E.G. Privalko. 2005. Enthalpy relaxation in the cooling/heating cycles of polypropylene/organosilica nanocomposites: I Non-isothermal crystallization. **Thermochim. Acta.** 432: 76-82.

Tao, Y., Y. Pan, Z. Zhang and K. Mai. 2008. Non-isothermal crystallization, melting behavior and polymorphism of polypropylene in β – nucleated polypropylene/recycled poly (ethylene terephthalate) blends. **Eur. Polym. J.** 44: 1165-1174.

Wang, H.L., T. J. Shi, S.Z. Yang and G. P. Hang. 2006. Crystallization behavior of PA6/SiO_2 organic-inorganic hybrid material. **Mater. Res. Bul.** 41: 298-306.

Xu, W., G. Liang, W. Wang, S. Tang, P. He and W.P. Pan. 2003. Poly(propylene) – Poly(propylene) - Grafted Maleic Anhydride – Organic Montmorillonite (PP-PP-g-MAH-Org-MMT) Nanocomposites. **J. Appl. Polym. Sci.** 88: 3093-3099.

Zhang, Y., X. Jiang, Y. Guan and A. Zheng. 2005. Crystallization kinetics of ATPU grafted polypropylene. **Mater. Lett.** 59: 3626-3634.

Zhang, C., H. F. Wu, C. A. Ma and M. Sumita. 2006. Effect of vapor grown carbon fiber on non-isothermal crystallization kinetics of HDPE/PMMA blend. **Mater. lett.** 60: 1054-1058.