

Isothermal Melt Crystallization Kinetics of PP/organoclay Blends

Kunyan WANG^{a*} and Bin LI^b

Department of Materials Chemistry, Huzhou University, Huzhou, 313000, China

^awkyan01@163.com¹, ^blb3015@hutc.zj.cn.com

Abstract. Polystyrene (PP)/organoclay (OMMT) blends were prepared by co-rotating twin-screw extruder. The effects of OMMT on isothermal crystallization behaviors of blends was studied by differential scanning calorimetry (DSC). Using Avrami equation analysis the crystallization kinetics of materials. The analysis result shows that the OMMT act as effective nucleating agents, accelerating the crystallization of PP, then lead the rate of crystallization increased. Avrami exponent n is between 2.04~3.57, which indicating that PP/OMMT blends crystallization process might correspond to a two-dimensional or three-dimensional growth process. The activation energies for isothermal crystallization were determined by the Arrhenius equation.

1. Introduction

Polypropylene is one of widely used polyolefins as an engineering plastic. It has some excellent properties, such as easy processibility, high melting temperature, and excellent chemical resistance[1]. A number of studies on PP matrix have been carried out [2-5]. The crystallization of PP matrix blends have also been reported, such as PP/PA6 [6], PP/PC/nanosilica [7] and PP/graphene[8]. E. Parparita et. al. [9] reported the effects of lignocellulosic on the crystallization of PP. Lignocellulosic act as a nucleating agent for PP, and the crystallinity increased. Z.T. Tao et. al.[10] studied the shell waste incorporated to reinforce polypropylene and investigated the crystallization by DSC. The introduction of modified powder could promote the heterogeneous nucleation of PP matrix.

Polymer crystallization process has an important influence on its morphological, mechanical, and thermal properties. And it is necessary to study the isothermal crystallization kinetics of composites incorporating crystallizable polymers because the practical production processes usually proceed under isothermal crystallization conditions.

The isothermal crystallization researches can offer significant information for optimizing processing parameters. In this work, organoclay was used to prepare the PP/OMMT composites and studied the isothermal crystallization kinetics of the blends by differential scanning calorimetry (DSC). The Avrami equation was applied to analyze its isothermal

* Corresponding author:wkyan01@163.com

crystallization process. The activation energies for isothermal crystallization were determined by the Arrhenius equation.

2 Experimental Section

2.1 Materials

Polypropylene was purchased from Shanghai Petrochemical Co. Ltd. (China). Organo-modifier is methyl tallow bis (2-hydroxyethyl) ammonium and DK2 has the cation exchange capacity of 120 meq/100g.

2.2 Specimens Preparation

Before melt mixing, PP and the organoclay were completely dried in a vacuum oven at 80 °C for 12h.

The PP/OMMT blends were 100/1, 100/3, 100/5 by weight, named by OMMT1, OMMT2 and OMMT3, respectively. Blending was mixing by using twin-screw extruder with a screw speed of 60rpm. The temperature profiles of the barrel were 170-190-220-220-220-210 °C from the hopper to the die. Extrudated rods were cooled in a water bath and pelletized.

2.3 Characterizations

Differential scanning calorimetry was used to measure the melting and crystallization temperature of samples. The isothermal crystallization of the samples were performed as follows: the samples were heated from 25 °C to 200 °C at a heating rate of 80 °C /min and held there for 3 min to eliminate any previous thermal history; then they were cooled at -100 °C/min to the predetermined crystallization temperature, in the range 116-124 °C and maintained for 15min. The isothermal melt crystallization exotherms were recorded.

3 Results and Discussion

3.1 Isothermal Melt Crystallization Kinetics

The Avrami equations can be used to describe the isothermal crystallization behavior. The Avrami equation is given as follows:

$$\ln[-\ln(1- X(t))] = \ln K + n \ln t$$

Where K is the growth rate constant, and n is the Avrami exponent. X(t) is the relative degree of crystallinity at time, t, obtained from the area of the DSC exothermic peak at time t divided by the total area under the exothermic peak as shown in Eq. (1).

$$X(t) = \frac{\int_{t_0}^t \left(\frac{dH}{dt}\right) dt}{\int_{t_0}^{t_\infty} \left(\frac{dH}{dt}\right) dt} \quad (1)$$

The relative crystallinity (X (t)) is calculated at different crystallization time, and the plots of X (t) versus time of PP/OMMT blend with different OMMT are shown in Fig. 1. The figure demonstrates that the curves at different crystallization temperature are very similar. The crystallization time shifted toward higher temperatures with increasing crystallization

temperature. One can see from Fig.1 that the crystallization rate of the blends are faster than that of pure PP at the same crystallization temperature, which indicating that OMMT has acted as a heterogeneous nucleation agent for PP and increase the crystallization rate.

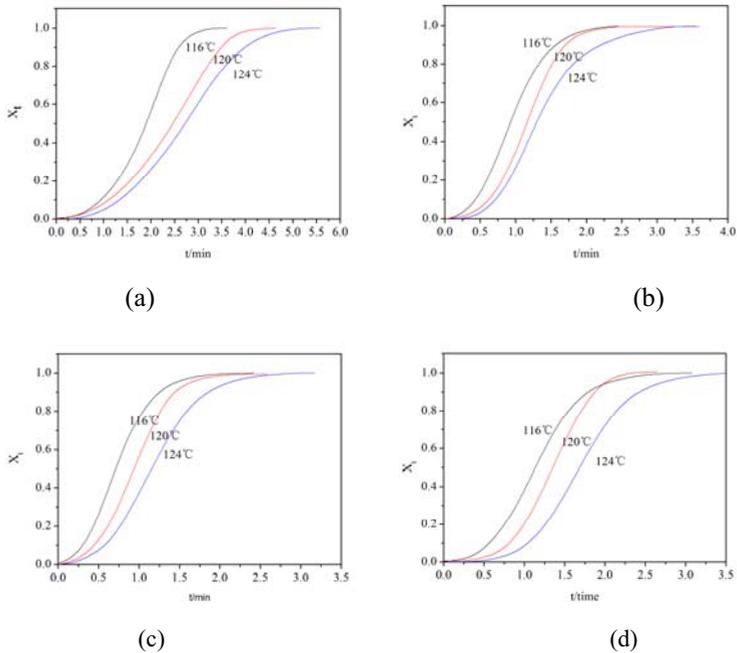


Fig. 1 Relative crystallinity $X(t)$ versus different crystallization time t in the process of isothermal crystallization for samples: (a) PP, (b) OMMT1, (c) OMMT2 and (d) OMMT3
 The plot of $\ln[-\ln(1-X(t))]$ versus $\ln t$ at different cooling rates are shown in Fig. 2. Each plot has a linear portion in the early stage of crystallization and then subsequently tends to level off, which probably attributing to the secondary crystallization caused by the spherulite impingement and perfection of internal spherulite crystallization in the later stage of the crystallization process [11].

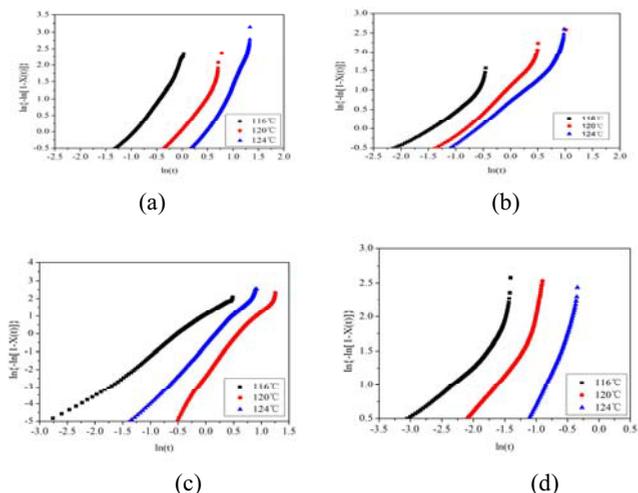


Fig.2 Plot of $\ln[-\ln(1-X(t))]$ as a function of $\ln t$ for (a) PP, (b) OMMT1, (c) OMMT3 and (d) OMMT5.

The values of Avrami exponent and K are listed in Table 1. The values of Avrami exponent are between 2.04 and 3.57 for pure PP and blends, which indicating the crystallization process might correspond to a two-dimensional growth or three-dimensional growth. The K values decrease with increasing of the crystallization temperature.

sample	T _c /°C	n	K	t _{1/2} /min	ΔE /KJ·mol
PP	116	2.04	1.980	1.907	18.648
	120	2.40	0.921	2.460	
	124	2.66	0.214	2.724	
OMMT1	116	2.04	1.559	0.925	22.278
	120	2.29	1.136	1.165	
	124	2.23	0.785	1.298	
OMMT2	116	3.57	2.283	0.702	21.895
	120	2.10	1.013	0.940	
	124	3.21	0.588	1.153	
OMMT3	116	2.11	1.624	0.932	24.440
	120	2.37	1.132	1.232	
	124	2.20	0.796	1.382	

3.2 Crystallization Activation Energy

The crystallization rate constant K can be approximately described by an Arrhenius equation:

$$K^n = k_0 \exp\left(\frac{-\Delta E}{RT_c}\right) \quad (2)$$

where k_0 is a temperature-independent pre-exponential factor, R is the universal gas constant and T is the absolute temperature. ΔE is the total activation energy. The plot of $(1/n) \ln K$ versus $1/T_c$ are showed in Fig.3. The values of the crystallization activation energy of samples are listed in Table 1. The values of ΔE for PP/OMMT blends are higher than that of pure PP.

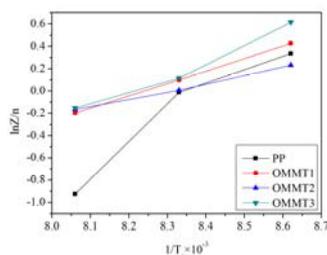


Fig.3. Polts of $(1/n) \ln K$ versus $1/T_c$

4 Conclusions

The effect of OMMT on the isothermal crystallization kinetics of PP with various amounts of the OMMT were studied by DSC. Avrami was used to describe the isothermal crystallization process. The crystallization rate of PP/OMMT blends is faster than that of pure PP. Avrami exponent n is between 2.04~3.57, which indicating that PP/OMMT blends crystallization process might correspond to a two-dimensional or three-dimensional growth process. The activation energies for isothermal crystallization were determined by the Arrhenius equation. The values of ΔE for PP/OMMT blends are higher than that of pure PP.

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