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Non-isothermal crystallization kinetics of polypropylene and hyperbranched polyester blends ☆

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ABSTRACT

Polypropylene (PP) with different contents of the second generation hyperbranched polyester (HBP) is prepared by melt blending method. The non-isothermal crystallization kinetics of PP and PP/HBP blends is investigated under differential scanning calorimetry (DSC). The Mo equation is used to analyze the DSC data. The results show that the Mo theory is suitable for crystallization kinetics of the blends. Fast cooling rate is not good for crystallizing and nucleating. The values of half crystallization time ($t_{1/2}$), crystallization enthalpy (ΔH_c) and temperature range (ΔT) of PP/HBP blends decrease when HBP is added. The required cooling rate of PP is higher than that of PP/HBP blends in order to reach the same relative crystallinity. Crystallization rate increases with the addition of HBP. The crystallization rate reaches a maximum when the content of HBP is 5%. In addition, the activation energies of PP and PP/HBP blends are calculated by Kissinger equation, revealing that the content of HBP has a little effect on the crystallization activation energy.

1. Introduction

Polypropylene (PP) is one of the most widely used polyolefin in plastic industry due to its excellent performance, easy processing and low price. However, mechanical properties of PP are not very good, which limits its applications. Addition of nucleating agents into PP is an effective method to improve mechanical properties which are related to crystallization [1–3].

The hyperbranched polyester (HBP) has been applied in many fields due to their unique three-dimensional structure, a large number of reactive end-groups and easy preparation. HBP can be processed as additives [4], rheology modifiers [5], compatibilizers [6], and toughenners [7], *etc.* Jannerfeldt *et al.* [8] studied the compatibilizing effect of PP grafted with hyperbranched polymers in PP/polyamide-6 blends.

In this paper, PP was blended with the second generation HBP. In order to determine the effects of the complex thermal conditions during processing, it was important to study the crystallization kinetics of blends under non-isothermal conditions and its relationship to the final properties. Practically, most industrial processing techniques are generally proceeded under dynamic non-isothermal conditions [9–16]. At present there are many papers reporting methods for studying the non-isothermal crystallization kinetics of polymer, such as the modified Avrami theory of Jeziorny [17], the Ozawa theory [18], and the Mo theory [19,20]. Tao *et al.* [21] studied the non-isothermal crystallization kinetics of PP by virtue of Jeziorny and Ozawa methods. Under certain conditions, the two methods can be used to deal with the non-isothermal crystallization kinetics of PP. Yang *et al.* [22] studied the crystallization kinetics of polymers. Mo methods can be used to describe the whole non-isothermal crystallization process. Compared to the Jeziorny and Ozawa equations, the Mo equation is a simple, convenient and effective dynamic method.

Thus, the Mo theory is chosen in this paper to deal with the non-isothermal crystallization kinetics of PP and PP/HBP blends. The crystallization activation energies based on Kissinger's equation and nucleating activity are also calculated.

2. Experimental

2.1. Materials

Polypropylene (power, industrial, T-30) was provided by China Petroleum & Chemical Corp Wuhan Branch, having a number-average molecular weight of 1.0×10^5 g·mol^{-1}. And the melting temperature was between 165 and 170 °C. The second generation hyperbranched polyester was self-prepared [23]. The reactive monomer was 3-[bis-(2-hydroxy-ethyl)-amino]-propionic acid methyl ester and the reactive

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catalyst was 4-toluene sulfonic acid. The number-average molecular weight was 1.3×10^4 g·mol^{-1}.

2.2. Preparation of PP/HBP blends

The HBP was blended with PP in an internal mixer (type SU-70C, Changzhou Suyan Science and Technology Co., LTD. China). The temperature of the barrel was set at 200 °C. The mass ratios of HBP to PP in the blends were 1%, 2%, 5% and 10%. Then, the mixture samples were cooled and granulated. The granules of PP/HBP blends were extruded under an injection molding machine (type TY200, Dongguan Dayu Machinery Co., Ltd). Injection-molded samples were labeled PP/(1%)HBP, PP/(2%)HBP, PP/(5%)HBP and PP/(10%)HBP.

2.3. Differential scanning calorimeter measurements

The non-isothermal crystallization kinetics was investigated by using a Perkin Elmer Diamond differential scanning calorimeter (DSC). All operations were carried out under a nitrogen environment. The weights of samples were 6–8 mg. Samples were heated from room temperature to 200 °C at a rate of 10 °C·min^{-1}. In order to erase the thermal history, the temperature was held at 200 °C for 5 min, and then the samples were cooled to the predetermined crystallization temperature (T_c) with cooling rates of 10, 15, 20, and 25 °C·min^{-1}, respectively.

3. Results and Discussion

3.1. Non-isothermal crystallization behavior of PP/(5%)HBP blend

The non-isothermal crystallization of PP and PP/HBP blends was carried out by DSC at different cooling rates. One of the figures was considered as the representative cure because all the samples showed similar types. The crystallization rate reached a maximum when the content of HBP was 5%. Thus, the figure of PP/(5%)HBP was as the representative cure. The thermograms of PP and PP/(5%)HBP blend are shown in Fig. 1. The parameters of non-isothermal crystallization are listed in Table 1.

It can be seen in Table 1 that the peak temperature of the crystallization (T_p) moves to lower temperature with increasing cooling rate. This reveals that the fast cooling rate is not good for crystallizing and nucleating. When the cooling rate is too fast, the movement of the molecular chains cannot keep up the changes of the temperature. Under the same cooling rate, the crystallization onset temperatures of PP/HBP blends are higher than that of PP, suggesting that the blends can be crystallized at a higher temperature. Thus, the degree

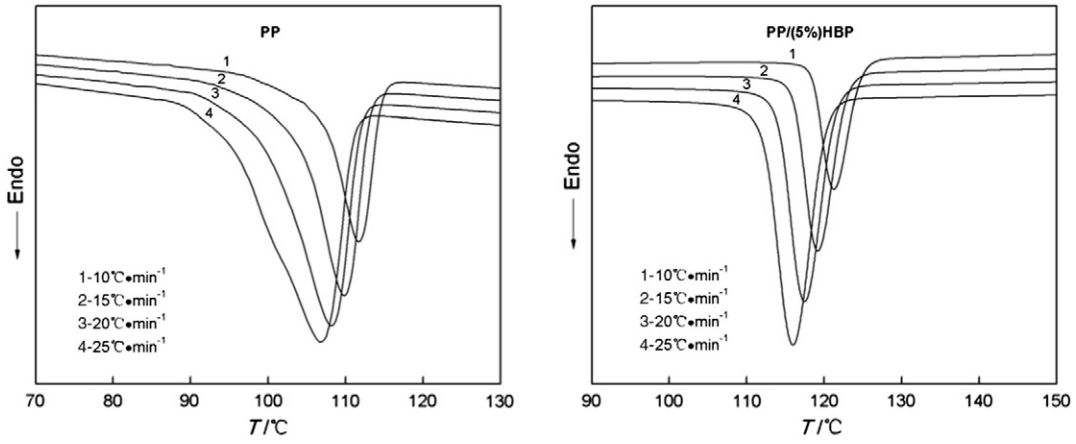

Fig. 1. DSC thermograms of PP and PP/(5%)HBP blend at different cooling rates.

Table 1
Parameters of non-isothermal crystallization for PP and PP/HBP blends

Sample HBP/%	ϕ/°C·min^{-1}	T_{onset}/°C	T_p/°C	ΔT①/°C	$t_{1/2}$/min	ΔH_c/kJ·g^{-1}	ΔE/kJ·mol^{-1}
0	10	119.6	111.7	7.9	1.09	101.4	−224.81
	15	117.2	109.6	7.6	0.74	100.5	
	20	115.6	108.0	7.5	0.57	98.0	
	25	114.1	106.6	7.5	0.47	97.0	
1	10	126.9	120.1	6.9	0.79	97.7	−216.29
	15	124.7	117.91	6.8	0.60	98.9	
	20	122.7	115.8	6.8	0.44	97.1	
	25	121.2	114.6	6.6	0.37	95.5	
2	10	127.3	120.5	6.8	0.75	91.7	−228.79
	15	125.0	118.4	6.6	0.55	92.7	
	20	123.2	116.8	6.5	0.41	90.8	
	25	121.7	115.3	6.4	0.36	88.6	
5	10	127.6	121.1	6.5	0.66	86.3	−230.55
	15	125.6	119.3	6.3	0.51	86.0	
	20	123.7	117.4	6.2	0.40	84.6	
	25	122.3	116.1	6.2	0.31	83.8	
10	10	128.9	122.2	6.7	0.72	86.8	−225.98
	15	126.7	120.2	6.6	0.55	86.2	
	20	124.9	118.3	6.5	0.42	84.6	
	25	123.3	115.5	6.4	0.34	83.9	

① $\Delta T = T_{onset} - T_p$.