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NON-ISOTHERMAL CRYSTALLIZATION KINETICS OF FILLED BLENDS OF POLYPROPYLENE AND LOW DENSITY POLYETHYLENE

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Non-isothermal crystallization kinetics of filled polymer blends was investigated by DTA. Crystallization in hybrid matrices containing small amounts of low density polyethylene was shown to proceed more rapidly than that in pure polypropylene. This effect was more pronounced in the presence of a mineral filler. The Kolmogorov-Avrami kinetic model can be used to describe the crystallization process under non-isothermal conditions.

Processing of thermoplastics involves cooling through the crystallization region. Under non-isothermal conditions, the length of the processing cycle depends to a certain extent on the kinetic behaviour of the systems undergoing phase transformations. It is possible to accelerate the crystallization process with suitable additives.

The joint effects of polymer and mineral additives on crystallization and melting temperatures have been studied on polypropylene (PP) [1]. The rate of nucleation in PP, as judged by the value of the initial slope of the crystallization exotherm for the blends is greater than that for the pure PP sample and shows a maximum at a low density polyethylene (LDPE) content of 15%. This is in good agreement with the result obtained for blends of PP and high density polyethylene [2]. Thermoanalytical techniques can be used to measure the time evolution of phase transformations under non-isothermal conditions [3, 4]. The case of non-isothermal crystallization more closely simulates the fabrication process. DTA has not been employed to investigate non-isothermal kinetics of crystallization in ternary systems PP/LDPE/mineral filler. Only a few papers are concerned with the applica-

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tion of DTA or DSC to study the non-isothermal crystallization kinetics of particulate filled polymers [5, 6]. The Avrami parameter value for high density polyethylene filled with calcium carbonate or unfilled is 2 (1.7-2.3) and is not influenced by the cooling rate or filler content. A reduction in the Avrami parameter with increasing cooling rate and filler concentration was observed for nylon-6 crystallization [6]. The present work deals with the effect of the particulate filler on the rate of non-isothermal crystallization in hybrid polymer matrices.

Experimental

The various PP (melt flow index MFI = 0.7) and LDPE (MFI = 2.1) combinations containing 30 vol.% of chalk were mixed in a roller mixer at 453 ± 5 K, and sheets 1 mm thick were then prepared by compression molding at 463 ± 5 K. DTA measurements were performed with a MOM derivatograph [7]. In each case, 200 mg powdered samples were taken. The samples were heated up to 475 K at a heating rate of 5 deg/min, and then cooled down at a cooling rate of 5 deg/min to 320-330 K. The degree of crystallinity was determined from the area of the melting peak. The degree of conversion α(t) attained at a fixed time was determined from point-by-point area measurement of the crystallization peak, assuming that the fractional crystallinity at a given time is proportional to the ratio of the crystallization peak area up to that time to the total area A of the peak, according to the following equation:

$$\alpha(t) = \frac{1}{A}\int_{o}^{t} \Delta T \mathrm{d}t \qquad (1)$$

where ΔT is the difference between the temperatures of the sample and reference material.

Results and discussion

Figure 1 shows the fraction of crystallized material α (t) as a function of time (log t). The non-isothermal crystallization in PP containing 5-10% LDPE proceeds more rapidly than that in the pure PP. The addition of 30% of chalk decreases the PP crystallization rate. However, in the hybrid matrices PP95/LDPE5 and PP70/LDPE30 filled with chalk, the rate of crystallization is appreciably larger than that the filled PP matrix. The variations in the crystallization half-times $\tau 1/2$ are given in Table 1.

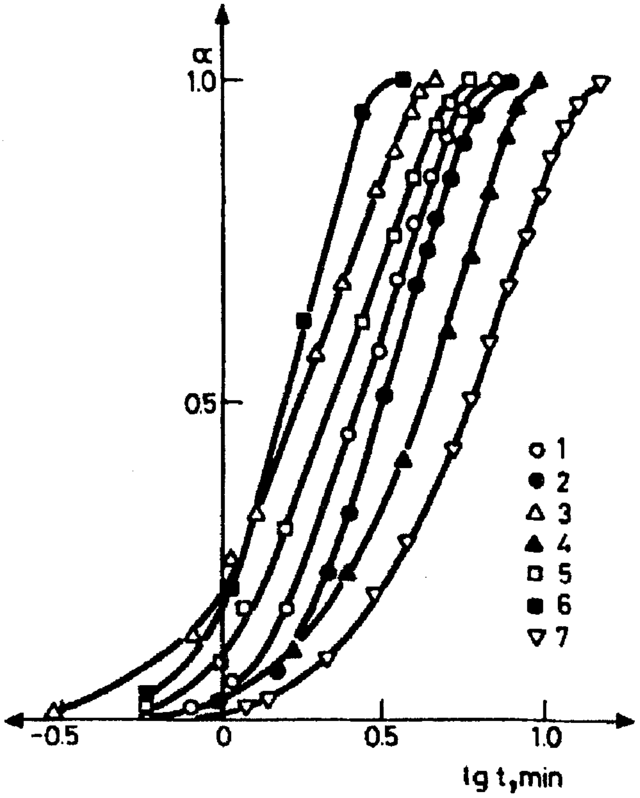

Fig. 1 Fraction of crystallized material as a function of logarithm of time for crystallization under non-isothermal conditions: o - PP; • - PP + chalk 30 vol.%; □- PP95/LDPE5; ■- PP95/LDPE5 + chalk 30 vol.%; Δ- PP90/LDPE10; ▲ - PP70/LDPE30; ∇ - PP70/LDPE30 + chalk 30 vol. %

The more rapid crystallization in the hybrid matrices may be attributed to the presence of a vast area of interphase. Low molecular weight species and impurities are rejected during processing toward interphases due to rheological peculiarities of flow [87]. The remaining material becomes more homogeneous the rejected molecular species and impurities are able to diffuse into non-crystallizable regions in the interphases. It is known that an increase in concentration of impurities in the melt results in an appreciable reduction in rate of growth [9]. In consequence of the removal of the impurities and low molecular weight species, the remaining material crystallizes with greater rate.

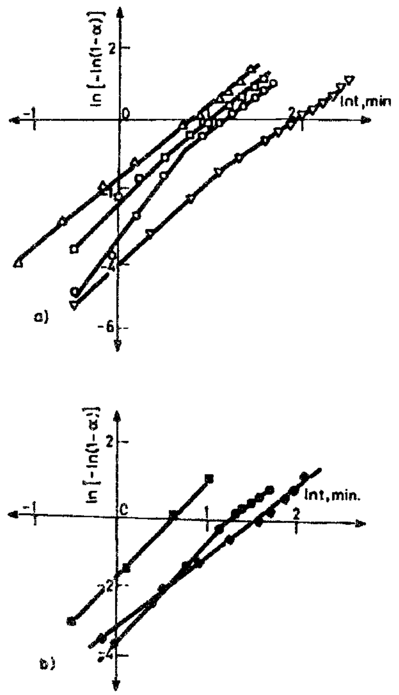

Fig. 2 Dependence of ln [$-\ln(1-\alpha)$] vs. ln t for unfilled (a) and filled with 30 vol.% of chalk (b) PP and blends PP/LDPE. The symbols are the same as at Fig. 1

A plot of ln [-ln(1-α)] vs. ln t under non-isothermal conditions yields a straight line with a slope of n for hybrid matrices filled with 30 vol.% of chalk (Fig. 2). The experimental data for PP, PP95/LDPE5, PP90/LDPE10 and PP70/LDPE30 are consistent with a two-stage process of crystallization, as shown by two sets of straight lines with differing slopes (Fig. 2). Table 1 lists the values of n for primary and secondary crystallization processes. The linear dependence of ln [-ln(1-α)] against ln t is the reason why the Kolmogorov-Avrami equation is fulfilled in the case of the non-isothermal crystallization of filled PP/LDPE blends.

Table 1 Crystallization parameters for PP matrices in composites*

Material	Crystallization half-time, ^ τ 1/2, min	Avrami parameter nI	nII	Degree of H, %
		PP/LDPE Blends		
PP	2.7	3.5	2.2	72
PP95/LDPE5	2.2	2.8	2.0	68
PP90/LDPE10	1.7	2.2	2.0	65
PP85/LDPE15	2.6	2.2	2.2	62
PP80/LDPE20	1.9	2.0	1.8	60
PP70/LDPE30	5.9	2.3	1.9	53
		Filled with 30 vol.% of chalk		
PP	3.2	3.0	2.2	60
PP95/LDPE5	1.6	2.8	-	58
PP70/LDPE30	4.3	2.0	-	50

*Cooling rate 5 deg/min

Kolmogorov [10] solved in general form the problem of the theoretical description of phase transformations involving nucleation and growth. The crystallization kinetics equation may be written in the following general form:

$$\alpha(t) = 1 - \exp[-\int_{o}^{t} \dot{N}(\tau) . V(t, \tau) d\tau] \qquad (2)$$

where $\dot{N}(\tau)$ is the nucleation rate at time t; $V(t, \tau)$ is the volume of a particle of the product phase at time t which started growth at time τ.

Equation (2) holds for both non-isothermal and isothermal crystallization conditions. In special cases, the integral on the right side of Eq. (2) may be solved. For instance, under isothermal conditions it can be assumed that the growth rate and the nucleation rate will be constant. Equation (2) then reduces to the Avrami equation [11]:

$$\alpha(t) = 1 - \exp[-k t^{n}] \qquad (3)$$

where k is the crystallization rate constant containing the nucleation and growth rates, and n is a constant called the Avrami parameter.

Furthermore, it has been found [12] that in the case of non-isothermal crystallization Eq. (3) can be approximated by the following expression:

$$\alpha(t) = 1 - \exp[K^{*}(at)^{n}] \tag{4}$$

where K^* is constant with respect to time at constant cooling rate and *at* is the reduced time.

Thus, a plot of ln [-ln(1-α)] against ln t should be a straight line with a slope of n, whether the process is isothermal or non-isothermal.

The Avrami parameter obtained from the non-isothermal crystallization kinetics in the first stage for PP is equal to 3.5 (Table 1). The same value has been obtained for PP crytallization under isothermal conditions [13, 14]. The reduction in the Avrami parameter in filled and hybrid matrices may be attributed to the change in geometry of the growth of crystalline structures in consequence of the heterogeneity of the materials. Evidence in favour of such an explanation has been given by morhological studies [15]. The second stage probably involves lamellar crystal growth within spherulites [14, 16, 17]. In consequence of the two-dimensional growth of the crystals, the value of n should be equal to 2. The Avrami parameter value does not change with composition because the lamellar crystal growth proceeds within the spherulites.

Conclusions

The addition of small amounts of LDPE to PP, and especially to PP loaded with chalk, results in an appreciable increase in the rate of non-isothermal crystallization. The two sets of straight lines with differing slopes obtained for the plot of ln[-ln(1-α)] against ln t in the non-isothermal process are in agreement with a kinetic scheme involving two consecutive crystallization processes. Only the first stage of the process is influenced by the additives.

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Zusammenfassung - Mittels DTA wurde die nichtisotherme Kristallisationskinetik von gestreckten Polymergemischen untersucht. Es konnte gezeigt werden, daß die Kristallisierung in einer Hybridmatrix mit einem Gehalt an Polyethylen geringer Dichte schneller vor sich geht, als in reinem polypropylen. Dieser Effekt wird im Falle eines Minerals als Streckmittel noch ausgeprägter. Zur Beschreibung des Kristallisationsprozesses unter nichtisothermen Bedingungen kann das kinetische Modell von Kolmogorov-Avrami benutzt werden.