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Non-isothermal crystallization kinetics of isotactic polypropylene nucleated with 1,3:2,4-bis(3,4-dimethylbenzylidene) sorbitol

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Abstract Non-isothermal crystallization kinetics of isotactic polypropylene (iPP) nucleated with 1,3:2,4-bis(3,4-dimethylbenzylidene) sorbitol (DMDBS) was studied by using differential scanning calorimetry (DSC). The modified Avrami theory of Jeziorny and the Mo method were used to analyze the DSC data. The results suggested that the two methods were both suitable for crystallization kinetics of iPP nucleated with DMDBS. Half time of the crystallisation ($t_{1/2}$) of virgin iPP was larger than that of nucleated iPP under the same cooling rate. Meanwhile, the required cooling rate of virgin iPP was higher than that of iPP nucleated with DMDBS in order to reach the same relative crystallinity, both of which showed that the addition of nucleating agent DMDBS could increase the crystallization rate of iPP. In addition, incorporation of DMDBS changed the manner of nucleation and development.

Keywords Isotactic polypropylene · Non-isothermal crystallization · Nucleating agent · 1,3:2,4-bis(3,4-dimethylbenzylidene) sorbitol (DMDBS)

Introduction

Isotactic polypropylene (iPP) is a widely used thermoplastic. However, transparency and mechanical properties of iPP are not very good. Addition of nucleating agents into iPP is an effective method to improve mechanical and optical properties which are related to crystallization and morphology [1–9]. Sorbitol derivatives are a type of highly efficient nucleating agents for α-iPP and addition of only small amounts (i.e., 0.2 wt%) of this type of nucleating agents may also greatly enhance the transparency and reduce the haze value of iPP. In contrast to most classical nucleating agents for iPP, such as organic carboxylic acid salts discussed in the literature [10], sorbitol derivatives can partially dissolve in the molten iPP during processing so that dispersion of nucleating agents in iPP melt could be improved, which is similar with some other artificial nucleating agents soluble in iPP melt [11]. Therefore, sorbitol derivatives have been widely used during the past decade as nucleating agents for improving transparency of iPP. The most representative example of sorbitol derivatives is 1,3:2,4-dibenzylidene sorbitol (DBS), which is called as a first generation of sorbitol derivatives. The second generation of sorbitol-based nucleating agents comprises its alkyl and halo-derivatives, such as 1,3:2,4-bis(p-methylbenzylidene) sorbitol (MDBS). More recently, 1,3:2,4-bis (3,4-dimethylbenzylidene) sorbitol (DMDBS) was developed as a representative product of the third generation sorbitol derivatives by Milliken Chemical Co. and it is the most recent example of sorbitol-based nucleating agents for iPP.

Many researchers have studied the mechanical properties and crystallization behaviors of iPP nucleated with sorbitol derivatives [12–17]. Kristiansen et al. [14, 15], for instance, studied the influences of the third generation sorbitol derivative DMDBS on mechanical and optical properties of iPP. Marco et al. [16, 17] studied the nucleation activity of the third generation sorbitol-based nucleating agents for iPP and the isothermal crystallization of iPP nucleated with these sorbitol derivatives. Shepard et al. [13] studied the nucleation efficacy of a second generation sorbitol derivative 1,3:2,4-di-p-methylbenzylidene sorbitol in iPP. However, there are few systematic researches concerning

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crystallization kinetics of iPP nucleated with the third generation sorbitol derivative DMDBS [17] and the crystallization kinetics of iPP nucleated with DMDBS in these researches was mostly studied under the isothermal conditions. In addition, from a technological point of view, non-isothermal crystallization conditions approach more closely the industrial conditions of polymers processing, so that the study of crystallization of polymers under non-isothermal conditions is of great practical importance. At the same time, the isothermal crystallization analysis is often limited in narrow temperature range because of low accuracy of crystallization rates of the samples at too high or too low crystallization temperatures [18]. At present there are many papers reported methods for studying the non-isothermal crystallization kinetics of polymer, such as modified Avrami theory of Jeziorny [19], Ozawa method [20], Mo method [21, 22]. However, the Ozawa method can not adequately describe the non-isothermal crystallization of polymers because of secondary crystallization in polymers during non-isothermal crystallization [21]. In this paper, the modified Avrami theory of Jeziorny and the Mo method were used to study the non-isothermal crystallization kinetics of iPP nucleated with DMDBS.

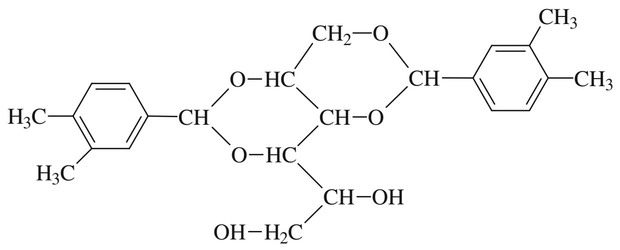
Experimental

Materials

iPP T30S with a MFR of 2.5 g 10 min^{-1}, supplied by SINOPEC Jiujiang Co. (China), were used in this work. Nucleating agent DMDBS (provided by Milliken Chemical Co., USA), whose structure is shown in Scheme 1, was used.

Sample preparation and DSC analysis

The iPP powders and nucleating agents DMDBS (0.2 wt%) were mixed in a high-speed mixer for 5 min. Then the mixture was extruded by a twin-screw extruder through a strand die and was cut into pellets which were used for subsequent DSC analysis.



Scheme 1 Molecular structure of nucleating agent DMDBS

The non-isothermal crystallization kinetics was investigated by using a Perkin Elmer Pyris 1 DSC (Perkin Elmer Company, USA). All DSC operations were carried out under a nitrogen environment. Samples weights were 2–3 mg and all samples were heated to 200 °C and hold in the molten state for 5 min to erase their thermal history. Then the samples were cooled from 200 to 50 °C by using constant cooling rates ϕ (selected from 2.5 to 40 °C min^{-1}) and the exothermal curves of heat flow as a function of temperature were recorded.

Results and discussion

The non-isothermal crystallization kinetics analyzed by the modified Avrami theories of Jeziorny

The non-isothermal crystallization of virgin iPP and iPP nucleated with DMDBS were carried out by DSC with cooling rates from 2.5 to 40 °C min^{-1}. The thermograms of virgin iPP and iPP nucleated with DMDBS are reported in Fig. 1. With increase of the cooling rate, crystallization peak temperature (T_{cp}) of iPP shifts to lower temperature. With the addition of nucleating agent DMDBS, T_{cp} of iPP is increased greatly. When the cooling rate is 10 °C min^{-1}, T_{cp} of iPP nucleated with DMDBS is increased from 118.7 °C of virgin iPP to 130.1 °C.

It can be seen in Fig. 1 that with increase of the cooling rate, the crystallization peak of iPP becomes wider, the temperature interval and peak temperature of the crystallization (T_{cp}) move to lower temperature, which shows that the extent of super-cooling increases with increase of the cooling rate. The activity of molecular chain becomes worse and the difference of crystallization extent is larger under lower temperature so that the crystallization peak becomes wider. Comparing Fig. 1a and b it can be seen that the crystallization temperature of nucleated iPP is higher than that of virgin iPP because nucleating agent acts as the heterogeneous nuclei of crystallization, which makes easy occurrence of crystallization.

The Avrami equation is expressed as follows:

$$1 - X_t = \exp(-Z_t t^n) \qquad (1)$$

where n is the Avrami exponent, Z_t is the Avrami rate constant and X_t is the relative crystallinity at temperature T, which is defined by

$$X_t = \frac{X_t(t)}{X_t(\infty)} = \frac{\int_0^t (\mathrm{d}H(t)/\mathrm{d}t)\mathrm{d}t}{\int_0^\infty (\mathrm{d}H(t)/\mathrm{d}t)\mathrm{d}t} \qquad (2)$$

where $(\mathrm{d}H(t)/\mathrm{d}t)$represents the heat flow, $X_t(t)$ and $X_t(\infty)$ denote the absolute crystallinity at time t and at the termination of the crystallization process, respectively.

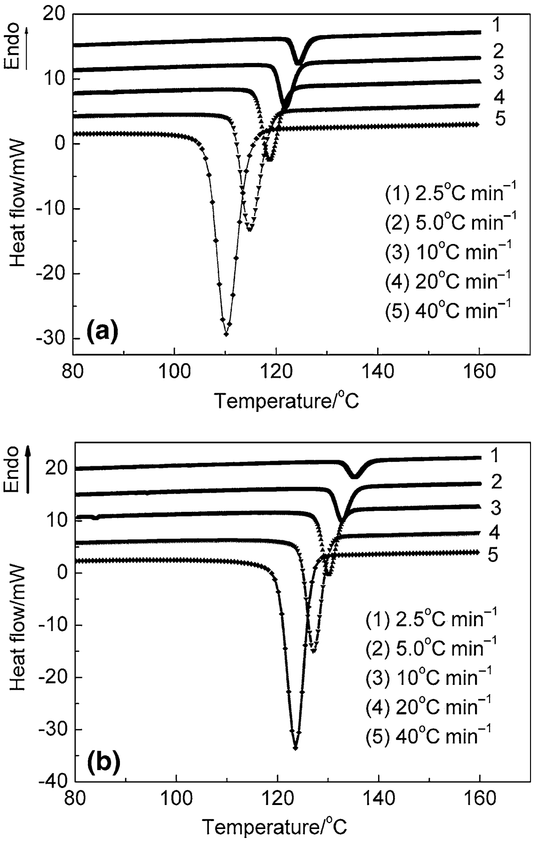


Fig. 1 DSC cooling curves of virgin iPP (**a**) and iPP nucleated with DMDBS (**b**) during non-isothermal crystallization

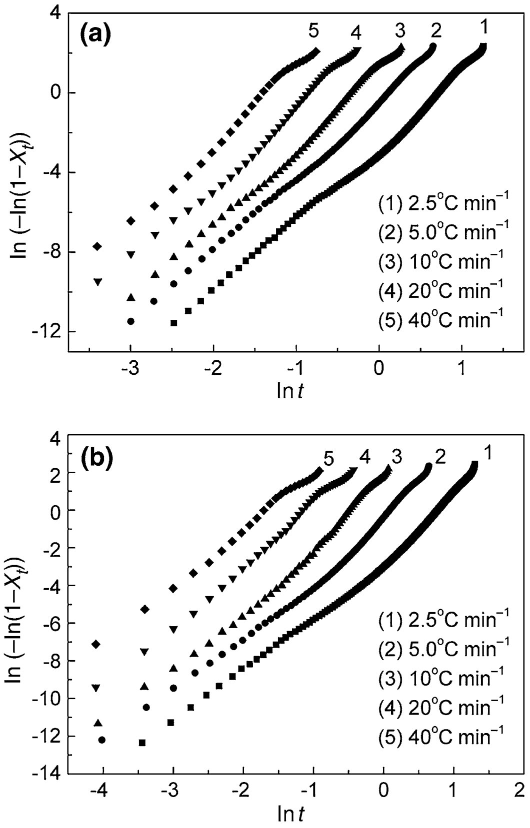


Fig. 2 Plots of $\ln[-\ln(1-X_t)]$ versus $\ln t$ for virgin iPP (**a**) and iPP nucleated with DMDBS (**b**)

Taking a double logarithm of Eq. 1 gives:

$$\ln[-\ln(1-X_t)] = \ln Z_t + n\ln t \tag{3}$$

but the Avrami equation expresses the relation of X_t and time (t), the conversion of temperature to time should be done, and it can be done with equation $t=(T_0-T)/\phi$ (where T is the temperature at time t, T_0 is the initial temperature when crystallization begins, ϕ is the cooling rate).

So the Avrami exponent n and the crystallization rate parameter Z_t could be estimated from the slope and intercept respectively in the plot of $\ln[-\ln(1-X_t)]$ versus $\ln t$ for the crystallization process of iPP (Fig. 2). It can be observed in Fig. 2 that there are good linear relations between $\ln[-\ln(1-X_t)]$ and $\ln t$, which shows that this method is suitable for the non-isothermal crystallization kinetics of iPP nucleated with DMDBS.

Considering the non-isothermal characters of the crystallization process investigated, Jeziorny [18] pointed out that the parameter for value of rate constant Z_t should be adequately corrected. The factor that should be considered was the cooling rate ϕ applied in crystallization of the polymer. Assuming a constant or approximately constant cooling rate ϕ, the final form of the parameter characterizing the kinetics of non-isothermal crystallization was given as the equation $\ln Z_c = \ln Z_t/\phi$, so the parameters of crystallization process can be calculated and the results are listed in Table 1.

It can be seen in Table 1 that $t_{1/2}$ decreases with the increase of cooling rate, that is to say, the higher the cooling rate is, the shorter is the time of crystallization completion, and accordingly the smaller is the value of $t_{1/2}$. $t_{1/2}$ of virgin iPP is larger than that of iPP nucleated with DMDBS at the same cooling rate. $t_{1/2}$ of virgin and nucleated iPP is 0.67 and 0.56 min, respectively, when the cooling rate is 10 °C min^{-1}, which indicates that the addition of DMDBS can greatly increase the crystallization rate of iPP. In non-isothermal crystallization, $t_{1/2}$ decreases with increase of the cooling rate because of quickly freezing of chain mobility at high cooling rate. Meanwhile, it can be observed in Table 1 that the value of n of virgin iPP is larger than that of nucleated iPP, which indicates that nucleating agent acted as heterogeneous nuclei and lead to the change of nucleation and development. Here, for virgin iPP, the average value of Avrami exponent n is 3.91 closing to 4.0, which corresponds to the thermal nucleation and three-dimensional spherical growth. While for iPP nucleated with DMDBS, the average value of Avrami exponent n is 3.28

Table 1 Non-isothermal crystallization parameters of virgin iPP and iPP nucleated with DMDBS when analyzed by the Jeziorny method

Sample	ϕ/°C min^{-1}	n	Z_t	Z_c	$t_{1/2}$/min^{a}	T_{cp}/°C	$\bar{n}$
Virgin iPP	2.5	3.79	0.0621	0.3290	1.89	124.4	3.91
	5	3.83	0.6189	0.9085	1.03	121.9	
	10	4.00	3.4397	1.1349	0.67	118.7	
	20	3.95	28.5835	1.1825	0.39	115.0	
	40	3.99	244.0795	1.1473	0.23	110.2	
iPP/DMDBS	2.5	3.27	0.1091	0.4122	1.76	135.2	3.28
	5	3.33	1.0217	1.0043	0.89	132.6	
	10	3.50	5.1161	1.1773	0.56	130.1	
	20	3.28	38.1452	1.1996	0.29	127.1	
	40	3.00	260.6761	1.1492	0.14	123.4	

[a] $t_{1/2} = (\ln 2/Z_t)^{1/n}$

closing to 3.0, which corresponds to the athermal nucleation and three-dimensional spherical growth.

The non-isothermal crystallization kinetics analyzed by the Mo method

As the relative crystallinity is related to the cooling rate ϕ and the crystallization time t (or temperature T), Mo et al. [21, 22] pointed out that the relation between ϕ and t could be build up at a given relative crystallinity. Consequently, a new kinetic equation of non-isothermal crystallization can be derived by combining the Avarmi and Ozawa equations as follows:

$$\ln Z_t + n \ln t = \ln K(T) - m \ln \phi \qquad (4)$$

and the Eq. 4 can be further rewritten as

$$\ln \phi = \ln F(T) - a \ln t \qquad (5)$$

where the parameter $F(T) = [K(T)/Z_t]^{1/m}$ refers to the value of cooling rate, which has to be chosen at unit crystallization time when the measured system amounts to a certain relative crystallinity. It can be seen that $F(T)$ has a definite physical and practical meaning. According to Eq. 5, at a given relative crystallinity, the plot of ln ϕ versus ln t will give a straight line with the intercept of ln $F(T)$ (Fig. 3). It can be seen in Fig. 3 that there are good linear correlations between these two factors, which indicates that the Mo method is suitable for the non-isothermal crystallization kinetics of iPP nucleated with DMDBS.

The values of $F(T)$ can be estimated from the intercept of the straight lines and the results are listed in Table 2.

At a certain relative crystallinity, a high value of $F(T)$ means a high cooling rate needed to reach this relative crystallinity in unit crystallization time, which reflects the difficulty extent of the crystallization process. The value of $F(T)$ systematically increases with increase of the relative crystallinity (Table 2), which indicates that the cooling rate should be increased in order to reach a given relative crystrallinity in unit crystallization time. When the relative crystallinity increases from 20% to 80%, the needed cooling rate of virgin iPP and nucleated iPP increases from 2.85 and 1.21 to 4.29 and 1.64, respectively. Meanwhile, it can be seen that the required cooling rate of virgin iPP is larger than that of nucleated iPP for reaching the same relative crystallinity. When the relative crystallinity is 20%, the required cooling rate of virgin and nucleated iPP

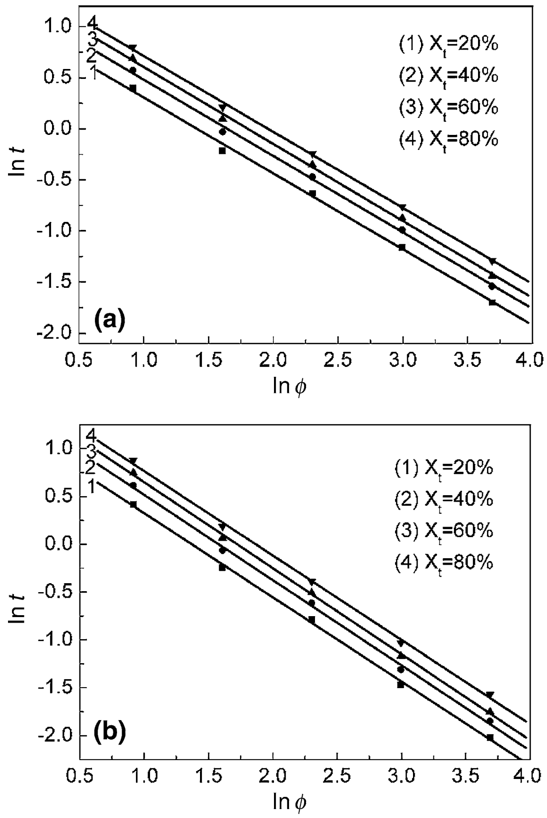


Fig. 3 Plots of ln ϕ versus ln $t$for virgin iPP (**a**) and nucleated iPP (**b**)

Table 2 Non-isothermal crystallization parameters of virgin iPP and iPP nucleated with DMDBS when analyzed by the Mo method

Sample	X_t/%	$F(T)$
Virgin iPP	20	2.85
	40	3.41
	60	3.89
	80	4.29
iPP/DMDBS	20	1.21
	40	1.41
	60	1.55
	80	1.64

is 2.85 and 1.21, respectively, namely, the cooling rate of iPP nucleated with DMDBS needed for reaching the same relative crystallinity is lower than that of virgin iPP, which indicates that the addition of nucleating agent DBDBS can improve the crystallization rate of iPP efficiently. The results are consistent with those obtained in the above Jeziorny method.

Conclusions

The study on non-isothermal crystallization kinetics of virgin iPP and iPP nucleated with DMDBS showed that the modified Avrami theory of Jeziorny and Mo method are both suitable for the crystallization kinetics of iPP nucleated with DMDBS. $t_{1/2}$ of virgin iPP is larger than that of iPP nucleated with DMDBS under the same cooling rate. Meanwhile, the required cooling rate needed by virgin iPP is higher than that needed by iPP nucleated with DMDBS in order to reach the same relative crystallinity, both of which indicates that the addition of nucleating agent DMDBS can improve the crystallization rate of iPP. In addition, addition of nucleating agent DMDBS changed crystal growth patterns of iPP. The crystal growth patterns of virgin iPP and iPP nucleated with DMDBS were thermal nucleation and three-dimensional spherical growth and athermal nucleation and three-dimensional spherical growth, respectively.

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