SUPPLEMENTARY MATERIAL TO
The influence of glass fibers on the morphology of β-nucleated isotactic polypropylene evaluated by differential scanning calorimetry

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THEORETICAL BACKGROUND

From the DSC scans (isothermal crystallization at given $T_c$ and then melting of the crystallized sample), the equilibrium melting temperature $(T_m^0)$ was determined by the Hoffman–Weeks method:1

$$ T_m^0 = T_m (\gamma - 1) \frac{T_c}{\gamma} $$ (1)

where $\gamma$ is a constant that represents the ratio between the final thickness of the crystalline lamellae and the initial critical thickness, and $T_m$ is the observed melting temperature of the sample isothermally crystallized at $T_c$. According to the kinetic theory of polymer crystallization,2 assuming that the growth of lamellae is controlled by a process of secondary nucleation, the temperature dependence of the overall kinetic constant, $k$, is given by the Eq. (2):

$$ \log(k/n) = A_0 - \frac{\Delta F^*}{2.3RT_c} - \frac{\Delta \Phi^*}{2.3KT_c} $$ (2)

where $A_0$ is a constant (assuming that the primary nucleation density at each $T_c$ examined does not vary with time), $\Delta F^*$ is the activation energy for the transport of crystallizing units across the liquid–solid interface, $K$ is the Boltzmann constant, $n$ is the Avrami exponent, and $\Delta \Phi^*$ is the energy of formation of a nucleus with critical dimensions, expressed by Eq. (3):2

$$ \Delta \Phi^* = \frac{4h_0\sigma_e\sigma_e T_m}{\Delta\text{mel}H\Delta T} $$ (3)

where $h_0$ is the molecular thickness, and $\sigma$ and $\sigma_e$ are the crystal growth lateral surface energy and the crystal fold surface energy, respectively. $\Delta\text{mel}H$ is the enthalpy of fusion and

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ΔT = T_0 - T_c is the supercooling. ΔF* is usually expressed as the activation energy of viscous flow given by the Williams–Landel–Ferry relation, Eq. (4):

\[ \Delta F^* = \frac{C_1 T_c}{T_g + T_c - T_g} \]  

where \( C_1 \) and \( C_2 \) are constants \( (C_1 = 17.2 \text{ kJ mol}^{-1}; C_2 = 51.5 \text{ K}) \) and \( T_g \) is the glass transition temperature. In further calculations, the literature value of \( T_g = 260 \text{ K} \) was used for iPP.\(^4\) The plot of: \[ \log k/n + \Delta F^*/2.3RT_c \] vs. \( T_m/T_c \) yields a straight line with a negative slope equal to:

\[ 4b_0\sigma_b = \frac{2.3K\Delta_{\text{fus}}H}{\Delta T_y} \]  

from which \( \Delta F^* \) and \( \sigma_b \) are obtained assuming that \( b_0 = 0.525 \text{ nm}^5 \) and \( \Delta_{\text{fus}}H \) of 193 and 209 J g\(^{-1}\), and \( \sigma = 0.1b_0\Delta_{\text{fus}}H \).

To calculate the nucleation activity (\( \theta \)) of foreign additives and substrates during the crystallization of a polymer melt, a method was proposed by Dobreva \textit{et al.}\(^6\) for analyzing DSC data. \( \theta \) is defined as:

\[ \theta = \frac{A_{k3}^0}{A_{k3}} \]  

where

\[ A_{k3}^0 = \frac{16\pi\sigma V_m^2}{3\Delta_{\text{melt}}S^22\Delta_T^2} \]  

is the work of homogeneous nucleation, in which \( V_m \) is molar volume of the crystallizing substance, \( \Delta_{\text{melt}}S \) is entropy of melting and \( \Delta T = T_m - T_{\text{cmax}} \) (where \( T_{\text{cmax}} \) corresponds to the crystallization peak temperature in the nonisothermal regime), and \( A_{k3} \) is the work of heterogeneous nucleation. Clearly, \( \theta \) is unity for absolutely inert substrates and is practically zero for very active substrates. Following the formalism presented by Dobreva \textit{et al.}\(^6\) the Avrami equation\(^7\) (8):

\[ \alpha = 1 - \exp(-kt^n) \]  

for nonisothermal conditions can be transformed into:

\[ \log(V_c) = \text{const} - \frac{B^0}{2.3\Delta T^2} \]  

where

\[ B^0 = \frac{16\pi\sigma V_m^2}{3T_m^2\Delta_{\text{melt}}S^2} \]  

and where \( V_c \) is the cooling rate. The activity of a substrate, \( \theta \), is then given by the ratio of the two slopes \( B^* \) and \( B_0 \).

REFERENCES


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