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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]

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

where γ 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):

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

where A_0 is a constant (assuming that the primary nucleation density at each T_c examined does not vary with time), ΔF^* 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]

$$\Delta \Phi^* = \frac{4b_0 \sigma \sigma_e T_m}{\Delta_{melt} H \Delta T} \quad (3)$$

where b_0 is the molecular thickness, and σ and σ_e are the crystal growth lateral surface energy and the crystal fold surface energy, respectively. $\Delta_{fus}H$ is the enthalpy of fusion and

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$\Delta T = T_m^0 - T_c$ is the supercooling. ΔF^* is usually expressed as the activation energy of viscous flow given by the Williams–Landel–Ferry relation, Eq. (4):[3]

$$\Delta F^* = \frac{C_1 T_c}{(C_2 + T_c - T_g)} \tag{4}$$

where C_1 and C_2 are constants (C_1 = 17.2 kJ mol^{-1}; C_2 = 51.5 K) and T_g is the glass transition temperature. In further calculations, the literature value of T_g = 260 K was used for iPP.[4] The plot of: [log $k/n + \Delta F^*/2.3RT_c$] *vs.* $T_m'/T_c\Delta T$ yields a straight line with a negative slope equal to:

$$\frac{4b_0\sigma\sigma_e}{2.3K\Delta_{fus}H} \tag{5}$$

from which ΔF^* and σ_e are obtained assuming that b_0 = 0.525 nm[5] and $\Delta_{fus}H$ of 193 and 209 J g^{-1}, and $\sigma = 0.1b_0\Delta_{fus}H$.

To calculate the nucleation activity (θ) of foreign additives and substrates during the crystallization of a polymer melt, a method was proposed by Dobreva *et al.*[6] for analyzing DSC data. θ is defined as:

$$\theta = \frac{A_{k3}^*}{A_{k3}^0} \tag{6}$$

where

$$A_{k3}^0 = \frac{16\pi\sigma V_m^2}{3\Delta_{melt}S^2\Delta T_p^2} \tag{7}$$

is the work of homogeneous nucleation, in which V_m is molar volume of the crystallizing substance, $\Delta_{melt}S$ is entropy of melting and $\Delta T_p = T_m^0 - T_{cmax}$ (where T_{cmax} corresponds to the crystallization peak temperature in the nonisothermal regime), and A_{k3}^* is the work of heterogeneous nucleation, Clearly, θ is unity for absolutely inert substrates and is practically zero for very active substrates. Following the formalism presented by Dobreva *et al.*,[6] the Avrami equation[7] (8):

$$\alpha = 1 - \exp(-kt^n) \tag{8}$$

for nonisothermal conditions can be transformed into:

$$\log(V_c) = \text{const} - \frac{B^0}{2.3\Delta T_p^2} \tag{9}$$

where

$$B^0 = \frac{16\pi\sigma V_m^2}{3T_m^0\Delta_{melt}S^2} \tag{10}$$

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

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