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Non-isothermal crystallization kinetics of iPP/sPP blends

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ABSTRACT

Non-isothermal crystallization and subsequent melting behaviour of iPP/sPP blends of various compositions were investigated by differential scanning calorimetry (DSC). Results revealed that sPP crystallizes at a slower rate than iPP. This effect is attenuated when the cooling rate is increased up to 20 °C/min and 25 °C/min. DSC scans showed that stability of primary crystallites of sPP and perfection of iPP crystallites were both increased by decreasing cooling rate. Effective activation energy (ΔE_{X_t}) of sPP, calculated using Friedman iso-conversional method, was found to be lower in iPP/sPP blend than in neat sPP whereas ΔE_{X_t} of iPP is not modified. Results were analysed through Avrami, Ozawa and Mo models. They both showed a decrease of crystal growth dimensionality for both iPP and sPP in iPP/sPP blends compared with neat iPP and sPP. The kinetic parameters U and K_g were determined by the Hoffman–Lauritzen theory.

1. Introduction

Syndiotactic polypropylene (sPP) was first synthesized in the early 1960s with a Ziegler Natta catalyst [1,2]. Unfortunately, this new stereoregular polypropylene presenting very low syndiotacticities had poor mechanical and thermal properties that prevented sPP to have many applications. The use of new metallocene catalysts allowed Ewen et al. to synthesize a sPP with high tacticity in 1988 [3]. This new sPP exhibits interesting properties, such as important toughness and excellent elastic behaviour, and therefore has recently received greater attention and became the centre of many investigations [4–6]. The excellent elastic properties of sPP are based upon a phase transition occurring in crystalline regions during stretching. In fact, four crystalline forms have been found for sPP. In the most stable forms (form I and form II), chains are in a helical conformation whereas they are in a trans-planar conformation in the metastable forms III and IV. Previous investigations have found that stretching of sPP blends and fibers induce a transition from the stable form I or II to form III. The particularity of this transition is its reversible nature because form I or II is obtained again when the applied stress is removed [7–10]. However, besides its excellent elastic properties sPP exhibits many disadvantages such as poor mechanical properties, a very complicated polymorphism and a slow crystallization rate that hinders sPP processing steps like melt spinning [11–14].

Blending sPP with another material having better mechanical properties and a faster crystallization rate can be an alternative for improving processing of sPP and in particular melt spinning [15]. For example, many investigations have been performed on sPP blends with isotactic polypropylene (iPP). Thomman et al. [16] found that iPP/sPP blends are phase separated. They showed that crystallization of iPP and sPP occurs separately and that crystallization of iPP/sPP blend is dependant on the crystallization nature of the neat components. An iPP matrix with dispersed sPP phase or a sPP matrix with iPP dispersed phase can be obtained, depending on the blend composition. Fig. 1 shows transition electron microscopy (TEM) picture of an iPP/sPP blend of composition 75/25. It is observed that iPP constitutes the continuous phase whereas sPP forms nodules.

A co-continuous morphology was also found for nearly symmetric compositions blends [16,17]. Gorassi [15] studied mechanical properties of iPP/sPP fibers and it was shown that blending sPP with iPP improves sPP drawability significantly. Finally, Zhang et al. [11] have investigated morphology and mechanical behaviour of iPP/sPP blends and fibers. It was shown that the addition of sPP induces a decrease of the blend crystallinity and that iPP/sPP fibers exhibit good elastic properties.

Although many investigations have been done on crystallization behaviour and morphology of iPP/sPP blends [11,15–18], no work reports the crystallization kinetics of iPP/sPP blends even

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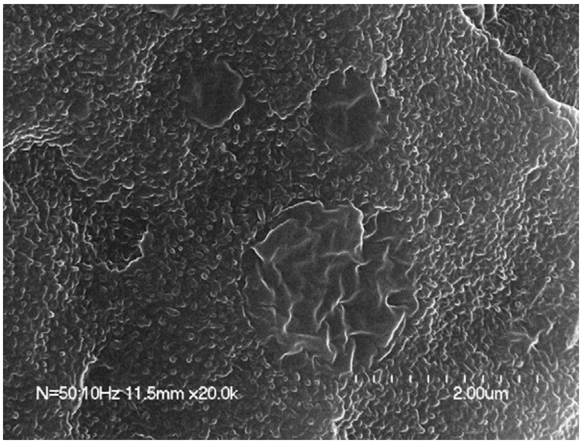

Fig. 1. TEM micrograph of an iPP/sPP blend of composition 75/25.

though crystallization kinetics is an important factor influencing processing steps of semi-crystalline materials.

The aim of this study is to analyse thermal properties and in particular crystallization kinetics of both iPP and sPP in iPP/sPP blends of various compositions. Therefore, iPP/sPP blends of different compositions are prepared and their crystallization kinetics will be investigated through non-isothermal DSC analyses. Results obtained will be analysed focusing three different kinetics models (Avrami, Ozawa and Mo analyses) in order to characterize crystallization mechanisms involved. Determination of the activation energy for both iPP and sPP crystallization in the blends will also be done. Finally, results from the three models will be discussed in the last part of the paper.

2. Experimental

2.1. Materials

Commercial grades of isotactic polypropylene and syndiotactic polypropylene were used in this study. iPP (PPH9069) and sPP (Finaplas 1751) were supplied by Total petrochemicals. PPH9069 has a melt flow index (MFI) of 25 g/min whereas MFI of Finaplas 1751 is 20 g/min.

2.2. Blends preparation

Blends of iPP/sPP (75/25, 50/50, 40/60, 30/70, w/w) were prepared in a Brabender mixer at 190 °C for 12 min with a shear rate of 50 rpm. Homopolymers of iPP and sPP were prepared identically in order to have blends and homopolymers with the same thermal history. Blends were turned into powder prior to thermal analyses using a cryogenic crushing unit.

2.3. Non-isothermal DSC measurements

Non-isothermal crystallization kinetics of iPP/sPP blends were investigated by Differential Scanning Calorimetry using a TA Instruments Q100 Calorimeter. All measurements were performed in nitrogen (nitrogen flow = 50 mL/min) to avoid degradation of the iPP/sPP blend upon heating. 8.3 ± 0.1 mg of each sample were put in a sealed aluminium pan. Samples were first heated up from 25 °C to 200 °C at a rate of 10 °C/min and held for 30 min to erase thermal history of the blend. It appeared to be the lap of time required to erase completely thermal history of a sample and there were no differences with scans performed after holding samples at 200 °C for 5 min. Then samples were cooled down at various cooling rates to 25 °C. The various cooling rates were taken as follows: 1 °C/min, 5 °C/min, 10 °C/min, 15 °C/min, 20 °C/min and 25 °C/min so that six experiments were achieved for each blend. Subsequent melting endotherms were recorded after each experiment at a rate of 10 °C/min.

Table 1
Correspondence between n_A and growth types.

n	Growth type
3–4	Spherulitic-type
2–3	Disc-like
1–2	Fibril-like

Some data could be taken from DSC analysis such as $T_{0.01}$ and $T_{0.99}$ which are temperatures at which degree of crystallinity is 1% and 99% respectively and $T_{\max}$ which is the temperature corresponding to the maximal crystallization rate. T_0 (onset temperature of crystallization) was taken as the temperature at which 0.1% of relative crystallinity is achieved. t_{100} which is the time required for both iPP and sPP to achieve 100% crystallinity can also be determined from the DSC data.

3. Theoretical background for crystallization kinetics

From DSC thermogram, the evolution of the relative crystallinity $X_t(T)$ of a component of a blend as a function of temperature can be expressed as:

$$X_t(T) = \frac{\int_{T0}^{T} (\mathrm{d}H_C/\mathrm{d}T) \times \mathrm{d}T}{\Delta H_C} \qquad (1)$$

where T_0 and T correspond to the onset temperature of crystallization and to an arbitrary temperature respectively, $\mathrm{d}H_c/\mathrm{d}T$ represents the variation of the enthalpy of crystallization as a function of temperature variation and ΔH_c is the total enthalpy of crystallization under a specific cooling rate.

If we consider that the difference of temperature between the sample and the DSC furnace is negligible, which was the case in our work, the relationship between time and temperature can be expressed as follows:

$$t = \frac{T_0 - T}{\Phi} \qquad (2)$$

where Φ corresponds to the constant cooling rate.

Using Eq. (2) it makes it possible to convert $X_t = f(T)$ curves observed from non-isothermal DSC data into $X_T = f(t)$ curves.

There are many models used to describe the crystallization kinetics of semi-crystalline polymers. In this study three models will be investigated.

First model is the Avrami model in which evolution of relative crystallinity as a function of time is formulated as follows [19–21]:

$$X_T(t) = 1 - \exp(-(K_A \times t)^{n_A}) \in [0, 1] \qquad (3)$$

K_A is the crystallization rate constant whereas n_A corresponds to the Avrami coefficient. Both of these constants are specific of nucleation and diffusion type [22]. Table 1 presents the growth type corresponding to each specific value of Avrami coefficient.

Avrami model was first designed for isothermal crystallization but it has been used for the description of nonisothermal crystallization of some semi-crystalline polymers including sPP by using the condition expressed in Eq. (2) [13,22–25].

The second model investigated will be the Ozawa model, which is an extension of the Avrami model based on derivation of Evans [26] to describe non-isothermal crystallization. This is based on the fact that non-isothermal crystallization may be equivalent to a succession of infinitesimal small isothermal crystallization steps