Journal of Thermal Analysis and Calorimetry, Vol. 73 (2003) 735–743

CRYSTALLIZATION, MELTING AND STRUCTURE OF POLYPROPYLENE/POLY(VINYLIDENE-FLUORIDE) BLENDS

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(Received December 15, 2002; in revised form February 2, 2003)

Abstract

Blends were prepared from isotactic polypropylene (iPP) along with its β-nucleated form and poly(vinylidene-fluoride) (PVDF). Melting, and crystallization characteristics as well as structure of the blends were studied by polarized light microscopy (PLM) and differential scanning calorimetry. According to PLM studies, the phase structure of these blends is heterogeneous in the molten state. The temperature range of crystallization of PVDF during cooling is higher than that of iPP. PVDF has a strong α-nucleating effect on iPP. The crystallization of iPP starts on the surface of dispersed PVDF droplets and an α-transcrystalline layer forms on the surface of the crystalline PVDF phase. The iPP matrix crystallizes predominantly in α-form in spite of the presence of a highly active β-nucleating agent.

Keywords: calorimetry, crystallization, α-iPP, β-iPP, isotactic polypropylene, melting, α-nucleating agent, β-nucleating agent, polarized light microscopy, polymer blends, poly(vinylidene-fluoride), transcrystallinity

Introduction

The primary goal of preparing polymer blends is to achieve the properties, which are more advantageous than that of their components. The improvement of the impact strength of isotactic polypropylene (iPP) by the introduction of elastomers is one of the most important examples for blending in industrial practice. iPP-based blends are widely studied and discussed in the literature. The review paper of Utracki and Duomulin [1] summarizes the most important experimental observations related to iPP based blends. iPP is a polymorphic material, which has three different crystalline modifications: i.e. α, β, γ [2]. Since the β-modification of iPP (β-iPP) has several advantageous characteristics in comparison with the traditional α-form i.e. better impact resistance, higher tensile and pendulum impact strength as well as tear strength [3], it was promising to explore the possibility of producing blends with β-iPP matrix. The conditions for the study of this problem are provided in our laboratory, because

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1388–6150/2003/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

we can produce highly active and selective β-nucleating agents. In the presence of latter, iPP crystallizes exclusively in the β-form, if the crystallization thermal conditions are appropriate [2–4]. Previously we studied the melting and crystallization characteristics of several β-nucleated iPP blends. We found, that β-iPP/elastomer [5, 6], β-iPP/LDPE [6, 7], and β-iPP/sPP [8] blends can be prepared in a wide concentration range. Our observation on β-nucleated iPP/elastomer blends was confirmed later by Shi [9] and Grein *et al.* [10]. However, iPP crystallizes in mixed polymorphic composition in β-nucleated iPP/HDPE blends, which indicates the α-nucleating effect of semicrystalline HDPE [6, 7].

In the present study we investigated the crystallization and melting characteristics of β-nucleated iPP-PVDF blends as well as their phase morphology. Similarly to HDPE, PVDF is semicrystalline and its melting point is close to that of iPP [11].

Experimental

Materials

An iPP homopolymer Tipplen H-781 (MFI=0.7 g/10 min at 230°C/2.16 kg) produced by TVK, Hungary and its β-nucleated form were used as matrix polymer thoughout the study. The Solef 6010 grade supplied by Solvay was chosen as the PVDF component (MFI=2 g/10 min at 230°C/2.16 kg), which was added to iPP in 1, 3, 5, 10, 20, 30 mass%. The Ca-salt of the suberic acid [4] was used as highly active β-nucleating agent and it was introduced into the blends in 0.1 mass%.

Techniques

The blends were prepared in a Brabender PLE 610 twin screw extruder. The temperature of the three heating zones were set to 195, 200, 205°C, while that of the die was 205°C. Extrusion was carried out at a rate of 50 rpm. Blends with sufficient dispersity can be prepared only at low PVDF content (i.e. up to 10 mass%). Thus our detailed study focuses on this concentration range.

The crystallization and melting characteristics of the blends were studied by polarized light microscopy (PLM) and differential scanning calorimetry. The melting, as well as the isothermal and non-isothermal crystallization curves were recorded, by a Perkin Elmer DSC 7 apparatus. The mass of the samples was between 3 and 5 mg. Both heating (V_h) and cooling (V_c) rates were kept of 10°C min^{-1}. In order to erase the effect of the thermal history, the samples were heated up to 220 °C and held there for 5 min. It is known [2, 6] that β-iPP samples, which are cooled below 100°C before remelting, recrystallize into the α-modification during heating. We proved earlier [2, 6] that the α to β recrystallization susceptibility can be eliminated by using a restricted recooling temperature. As a consequence, we set the final temperature of non-isothermal crystallization to 100°C. This limited recooling technique permits the exact determination of the polymorphic composition of the blends from the melting endotherms. To ensure identical thermal histories, both non-nucleated and β-nucleated blends were cooled up to 100°C.

The morphological studies of the blends were carried out on a Leitz Dialux 20 microscope equipped with a Mettler FP82 hot stage in polarized light applying a first-order red filter (λ-plate). After erasing the thermal history, the samples were crystallized under isothermal or non-isothermal conditions, and then melted again. Heating and cooling rate was 5°C $\min^{-1}$. The PLM micrographs were recorded by a digital camera (DMC Model 1) and they were evaluated by Image-Pro Plus photo editor software.

Results and discussion

The phase morphology of the blends in molten state was studied by PLM. Figure 1 shows the PLM micrograph of the blends containing 5 mass% PVDF captured at 190°C. At this temperature, both components are molten. PVDF is dispersed in the form of droplets in a continuous iPP matrix. Such heterogeneous phase structure in the melt forms in the case of immiscibility of components. The size of the droplets changes in a relatively wide range. The features of crystallization are illustrated by a series of micrographs of a blend containing 10 mass% of PVDF in Fig. 2. During sample preparation, the dispersed droplets can accidentally coalesce and form relatively large PVDF units, which is advantageous for the PLM study (Fig. 2a). PVDF with a higher melting point crystallizes first around 155°C and forms negative radial spherulites. iPP is in the molten state at this temperature (Fig. 2b). When the temperature reached 135°C, crystallization was continued under isothermal conditions (Fig. 2b–d). This moment is reported as the starting point of the isothermal crystallization process. The crystallization of iPP is induced on the surface of the dispersed PVDF droplets where an α-transcrystalline layer developed (Fig. 2c and d). In spite of the presence of the highly active β-nucleating agent, the iPP matrix crystallizes predominantly in α-form. As a consequence, the iPP matrix consists mostly of the α-modification and β-spherulites with negative birefringence can be observed sporadically in the sample. The PLM micrographs clearly proved that PVDF has a strong α-nucleating effect in iPP and it suppresses the formation of β-iPP in the blends.

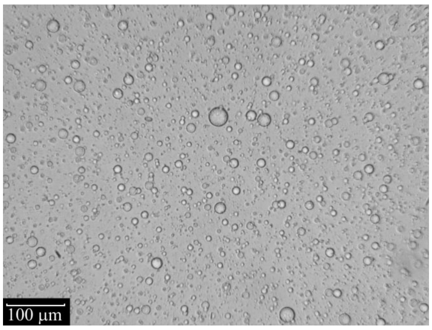

Fig. 1 PLM micrograph on iPP/PVDF blend containing 5 mass% PVDF (T=190°C)

Crystallization and melting characteristics of the blends were also investigated by differential scanning calorimetry. The crystallization curves of the non-nucleated blends are shown in Fig. 3. The crystallization peak of iPP is located in the vicinity of

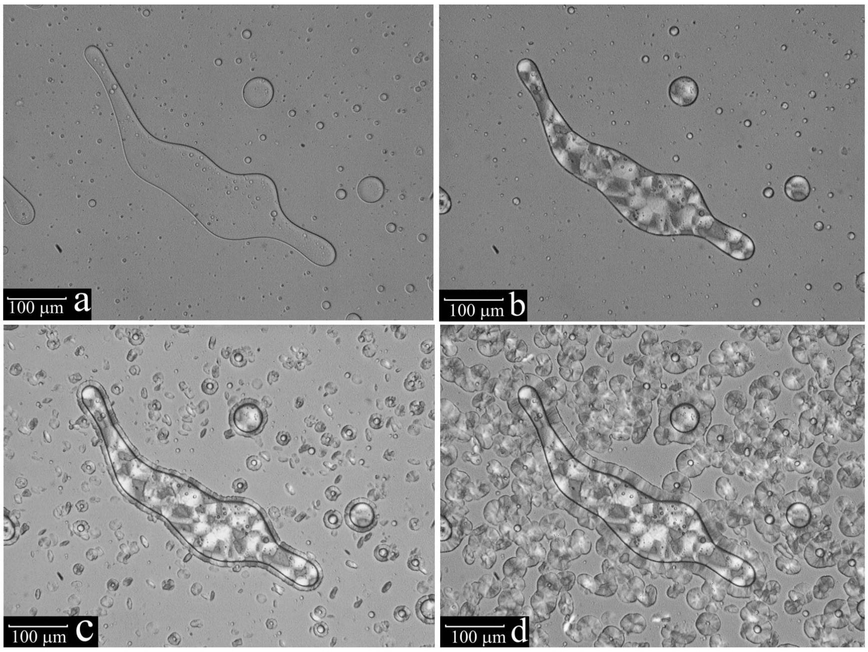

Fig. 2 PLM micrographs of β-nucleated iPP/PVDF blend containing 10 mass% PVDF recorded during cooling of the sample: a – phase structure of melt at 200°C; b – structure of the blend at T_c=135°C, t_c=0 min; c – at T_c=135°C, t_c=10 min; d – at T_c=135°C, t_c=15 min

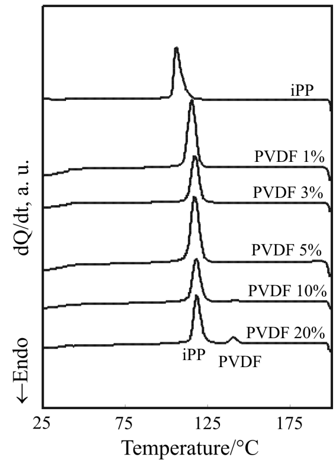

Fig. 3 Crystallization curves of iPP/PVDF blends of different composition (cooling rate V_c=10°C min^{-1})

110°C and shifts to 120°C in blends containing different amounts of PVDF. Similarly to PLM observations, this shift indicated the α-nucleating effect of PVDF. The crystallization peak of PVDF is situated at a higher temperature, at about 140°C, but it can be detected only at higher PVDF contents. The melting curves of non-nucleated blends can be seen in Fig. 4. The sharp melting peak observed around 165°C corresponds to the melting of α-iPP. The melting peak of PVDF is located at about 172°C and can be detected only in the blends containing 5 mass% or more of PVDF. This peak becomes more pronounced with increasing PVDF content.

The crystallization curves of β-nucleated iPP/PVDF blends are shown in Fig. 5. The temperature range of crystallization of the iPP component is situated near 120°C independently of the PVDF content, as a consequence of the co-operative effect of the β-nu-

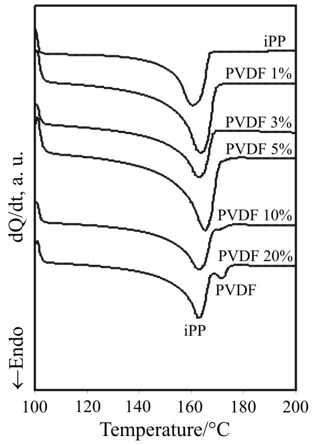

Fig. 4 Calorimetric melting curves of iPP/PVDF blends of different composition crystallized at a cooling rate of V_c=10°C min^{-1}; heating rate V_h=10°C min^{-1}

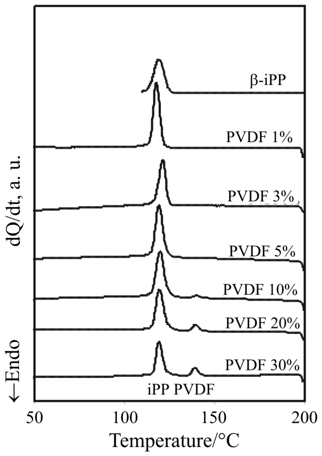

Fig. 5 Crystallization curves of β-nucleated iPP/PVDF blends of different composition (cooling rate V_c=10°C min^{-1})

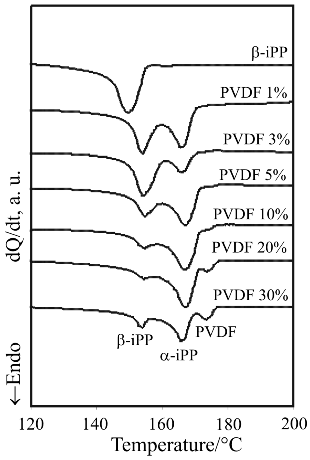

Fig. 6 Calorimetric melting curves of β-nucleated iPP/PVDF blends of different composition crystallized at cooling rate V_c=10°C min^{-1} (end temperature of cooling T_R =100°C, heating rate V_h=10°C min^{-1})

cleating agent and the dispersed polymer phase. The crystallization peak of PVDF could be detected only at higher (≈5 mass%) concentration in this case, too. A mixed polymorphic composition of iPP is formed in the β-nucleated blends; the peaks appearing near to 150°C on their melting curves refer to the melting of β-iPP (Fig. 6). The higher peaks at about 160°C correspond to the α-iPP. The melting peak of the PVDF at about 170°C becomes sufficiently intensive at 5 mass% and higher PVDF content. The intensity of the α-peaks increases monotonously with increasing PVDF content at the expense of the β-peak. It should be emphasized that the α- and β-forms of iPP crystallize simultaneous and only a single crystallization peak appears in spite of the formation of two separate polymorphic forms (Figs 5, 6). The DSC measurements confirm completely the PLM observations concerning the strong α-nucleating effect of PVDF.

To show the α-nucleating ability of PVDF, isothermal DSC measurements were carried out on non-nucleated PP/PVDF blends. Crystallization isotherms were recorded at 135°C. Figure 7 shows the isotherm crystallization curves. The rate of crystallization was characterized by the time of the highest crystallization rate (t_{max}). Figure 8 shows the

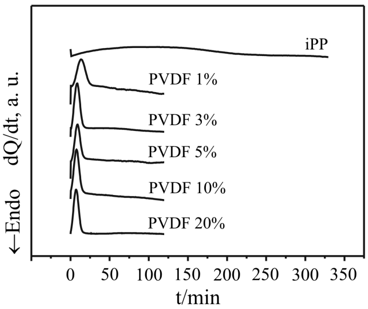

Fig. 7 The isotherm crystallization curves of iPP/PVDF blends at T_c=135°C

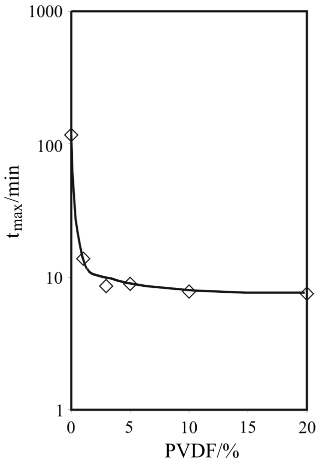

Fig. 8 The effect of PVDF – content on the crystallization peak time (t_{max}) at T_c=135°C

t_{max} values as a function of PVDF content. The t_{max} values decrease dramatically if PVDF is present, but the increasing of the amount of PVDF does not matter much. Like the above-mentioned DSC and PLM measurements, this experiment also verified that PVDF has a strong α-nucleating effect.

On the basis of the results of PLM and DSC experiments, we can conclude, that PVDF suppresses the formation of the β-phase in β-nucleated iPP/PVDF blends and iPP crystallizes predominantly in the α-form. The essential reason for this phenomenon is, that PVDF crystallizes in a higher temperature range than iPP (Fig. 5) and it exerts its α-nucleating effect (Fig. 2).

We compare in Table 1 the characteristics of the iPP/PVDF blends to other β-nucleated blends studied earlier. According to the table, β-nucleated iPP blends can be produced without any difficulty in the presence of amorphous polymers [5, 6, 9, 10]. The crucial condition for the preparation of β-nucleated iPP blends with semicrystalline polymers is that the second polymer must not have an α-nucleating effect. In the case of polymer with an α-nucleating effect, the temperature range of their crystallization should be lower than that of β-iPP, as in the case of iPP/LDPE [6, 7] and iPP/sPP [8] blends. The iPP/PVDF blend is an extreme example in that regards that β-iPP does not form in them in spite of the presence of a highly active β-nucleating agent. The experimental results presented here complete the series of studies on β-nucleated iPP blends and show the limits of the preparation of β-iPP based blends.

It was shown, that several semicrystalline synthetic [2, 12] and natural polymers [e. g. 13, 14] and liquid crystalline polymers [e. g. 15] also initiate the nucleation of the α-form of iPP. Moreover, recent studies of Wang and Hwang [16, 17] proved that another fluor containing polymer – PTFE – is an active α-nucleating agent for iPP. The qualitative comparison of PVDF with other polymers indicates that PVDF has practically the strongest α-nucleating activity among them shown also by the fact that it induces transcrystallization of iPP in a higher temperature range than other known polymers.

Table 1 Some specific features of β-nucleated polypropylene blends

System	Characterization of the second component				Polymorphic composition	Ref.
	Type	Phase state	Crystallization interval	α-nucleation ability		
iPP/EPM	EPM	amorphous	–	no	exclusively β-iPP matrix	[5–8]
iPP/EVA	EVA	low crystalline	lower	no	exclusively β-iPP matrix	[6]
iPP/LDPE	LDPE	semicrystalline	lower	week	β-iPP matrix (up to 60%)	[6, 8]
iPP/LLDPE	LLDPE	semicrystalline	overlapping	week	mixed	[8]
iPP/HDPE	HDPE	semicrystalline	similar	week	mixed	[6, 8]
iPP/sPP	sPP	semicrystalline	lower	week	β-iPP matrix (up to 80%)	[7]
iPP/PVDF	PVDF	semicrystalline	higher	strong	predominantly α-iPP matrix	this study

The authors would like to acknowledge the Hungarian Scientific Research Foundation (OTKA) for supporting this research (T 034230).

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