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SHORT COMMUNICATION

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On the crystallization of syndiotactic polypropylene (sPP)/high density polyethylene (HDPE) blends

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Abstract The crystallization kinetics of syndiotactic polypropylene (sPP)/high-density polyethylene (HDPE) blends were investigated by thermal and microscopical methods. Isothermal crystallization obtained by differential scanning calorimetry (DSC) was used to study the nucleation ability of HDPE on sPP crystallization. Morphological studies with polarized light microscopy (PLM) of solution cast films resulted in a transcrystalline-like overgrowth of the sPP on HDPE spherulites. The arrangement of the HDPE lamellar crystals in the blend were observed in transmission electron microscopy (TEM). But from these results, no straightforward conclusion about the transcrystalline nature of the sPP crystals can be given.

Key words Crystallization – syndiotactic polypropylene – polyethylene – blends – nucleation

Introduction

Although, interesting properties of sPP (i.e. high optical transparency and mechanical ductility) are known since a few years [1], not many commercial applications came to our knowledge till now [2, 3]. Besides many other factors, the slow crystallization rate [4, 5] is a large obstacle for the processing behavior of the material. Certainly, nucleation agents will be developed in the future and used in the different processing methods, but none of it appeared in scientific or patent literature till now. Additionally, blending sPP with other thermoplastic materials may further improve its properties for specific applications. Blending sPP with iPP already improves some properties of sPP [3, 6, 7]. It is the purpose of this paper, to report some even more drastic changes in the properties of sPP, concerning its crystallization and morphology, when blended with HDPE.

Experimental

Materials and sample preparation

The HDPE used in the experiments was Lupolene 6021D from BASF AG Ludwigshafen, Germany, and the sPP was kindly supplied by the Fina Oil and Chemical Company. The mixtures were prepared by solution blending in xylene as a common solvent and acetone as a precipitant. The precipitated powder was dried in vacuum for 12 h. Blend compositions are indicated as (HDPE [wt%]/sPP [wt%]): 1/99, 5/95, 10/90, 30/70, 50/50 and 70/30.

Calorimetry (DSC)

The device used was a DSC 2920-system from TA-Instruments coupled with a TA-200 control system.

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Measurements were carried out isothermally or with heating/cooling rates of 10 K/min. The weight of all samples was 10 mg.

Optical microscopy

For the optical investigations a Leitz DMRB light microscope was used. All samples were melted between two cover glasses and isothermally crystallized from the melt at different temperatures in an oven. The photographs were made using the polarization contrast.

Transmission electron microscopy (TEM)

Thin films of the blended polymers were solution cast from a 0.1 wt% solution in xylene on the surface of glycerin at 100 °C and slowly cooled to room temperature. Unfortunately, due to experimental difficulties it was not possible to keep the same thermal treatment as used with the samples in the calorimetric investigations. The films were mounted on copper grids and used directly for transmission electron microscopy (TEM) observations in the defocus imaging mode. The contrast was obtained without any staining. A Philips CM200 electron microscope operated at 200 kV.

Results and discussion

Differential scanning calorimetry

Figure 1 is an overlay diagram of DSC cooling curves for sPP, HDPE and its blends with different sPP-concentrations. With a cooling rate of 10 K/min, pure sPP exhibits its maximum for the crystallization rate at 79.7 °C and for HDPE at 114.4 °C. In the blends an enormous temperature shift of the sPP crystallization towards higher temperatures was observed, while for the HDPE component the crystallization behavior is unchanged in the blends. Blending only one wt% HDPE, increases the crystallization maximum of sPP to 84.1 °C and for a 70 wt% sPP/HDPE blend a crystallization maximum of 97.2 °C was detected.

In order to investigate the influence of HDPE on the crystallization kinetics, specific DSC traces were performed to measure the degree of crystallinity depending on the crystallization time for an isothermal crystallization at 113 °C. The isothermal studies were carried out by melting the samples in the DSC at 160 °C for 10 min. Subsequently, the samples were isothermal crystallized at 113 °C for different crystallization times. After the isothermal crystallization, the samples were cooled to room temperature by switching off the heating facility of the DSC. The occurring crystallization exotherm during the cooling is a measure for the enthalpy of the remaining crystallization. Figure 2 shows the described crystallization curves for pure sPP, isothermal crystallized at 113 °C for $t_c = 0$, 30, 50 and 90 min. The crystallization enthalpy of sPP measured from the continuous cooling curve ($t_c = 0$ min) of sPP is set as ΔH_c^0. The material, which is still molten after the isothermal crystallization at 113 °C at $t_c \neq 0$ and which is crystallizing in the subsequent cooling event, exhibits a crystallization exotherm, which obviously is smaller than that of $t_c = 0$. The crystallization enthalpy during the subsequent cooling to room temperature is set equal to ΔH_c^t. The relative crystallinity (X_c) increase obtained by the cooling from 113 °C to room temperature, is calculated by

$$X_c = \frac{\Delta H_c^0 - \Delta H_c^t}{\Delta H_c^0} \times 100\% \tag{1}$$

and is a rough measure, how much of the total crystallinity, obtained after cooling to room temperature, has been created during the isothermal crystallization.

The same measurements were carried out on blends with HDPE concentrations of 1, 5 and 10 wt%, respectively, and with various crystallization times (t_c). In Fig. 3

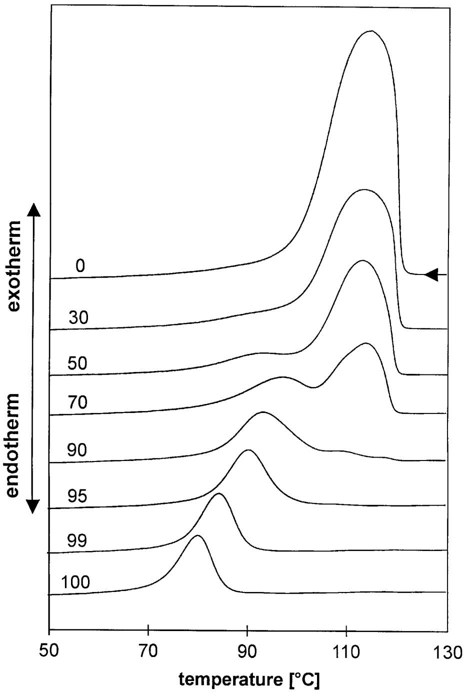


Fig. 1 DSC cooling curves for HDPE, sPP and blends with different sPP concentrations (cooling rate: 10 K/min)

Fig. 2 DSC plots of cooling curves after isothermal crystallization at 113 °C for different times

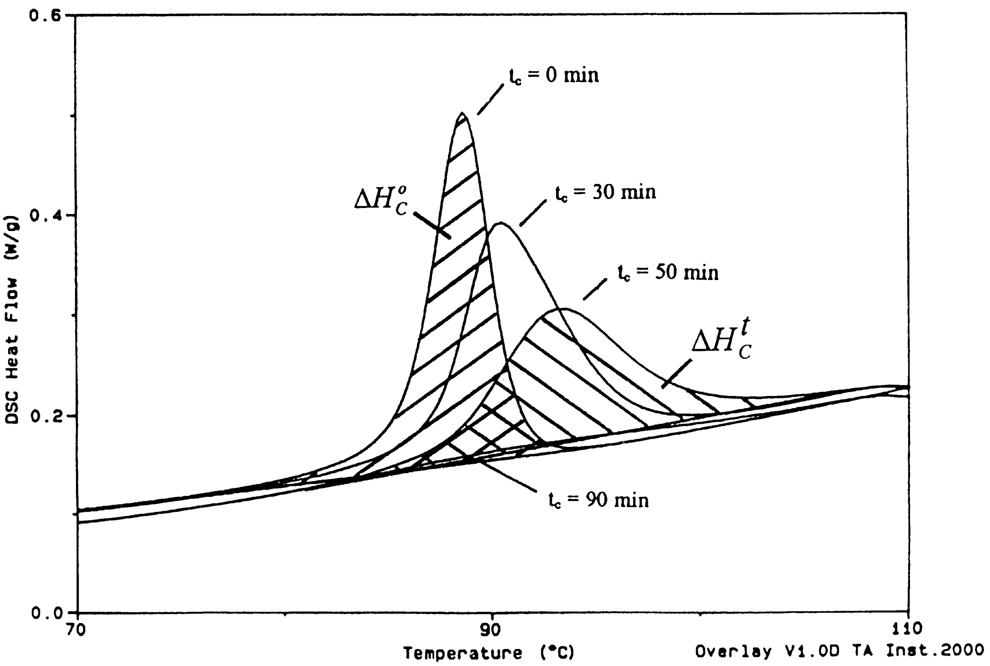
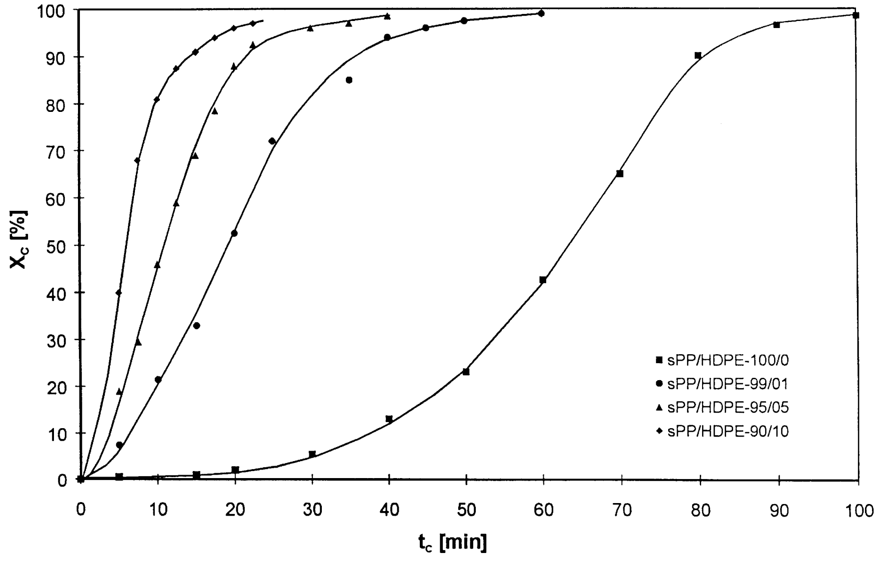


Fig. 3 Plot of the degree of relative crystallinity (X_c) against time (t_c) for pure sPP and blends with different HDPE-concentrations after isothermal crystallization at 113 °C



these relative crystallinities X_c are plotted versus the crystallization times for isothermal crystallization at 113 °C for pure sPP and its blends with different HDPE-concentrations. Each point in the graphs corresponds to an isothermal crystallization measurement at 113 °C and subsequent cooling. From these curves it can be recognized, that the crystallization of the sPP in the blends is drastically increased.

Transmission light microscopy

To follow the nucleation effect of HDPE to the crystallization of sPP, transmission light microscope investigations of isothermal crystallized blends were made.

Figures 4 and 5 show a sPP/HDPE-20/80 and a sPP/HDPE-50/50 blend, isothermal crystallized for 3 days at 100 °C. Especially in the 50/50 blend (Fig. 5),

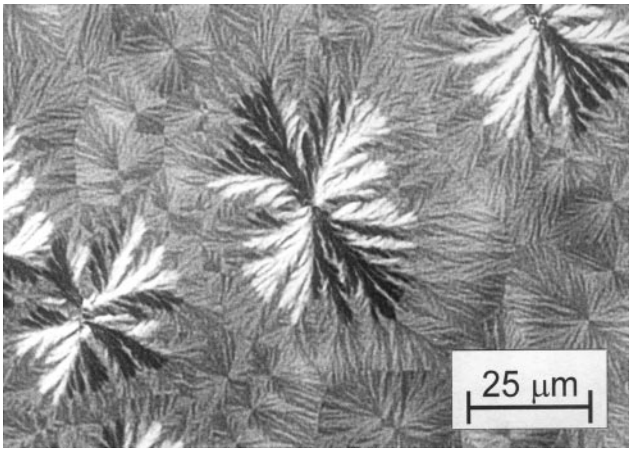


Fig. 4 Transmission light micrograph for a sPP/HDPE-80/20-blend isothermal crystallized at 100 °C for 3 days

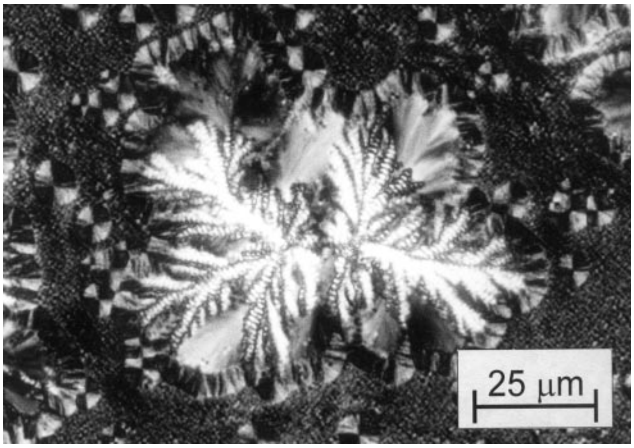


Fig. 5 Transmission light micrograph for a sPP/HDPE-50/50-blend isothermal crystallized at 100 °C for 3 days

a transcrystallization of the sPP around the PE spherulites (bright contrast) is clearly seen (contrast of darker ribbon surrounding the PE spherulites). But also in the 20/80 blend (Fig. 4), a nucleation effect of the PE spherulites (dark/bright contrast) onto the surrounding sPP spherulites can be deduced from the orientational alignment of the sPP spherulites.

Transmission electron microscopy (TEM)

In order to identify the nuclei for the transcrystallization, TEM investigations on some blends were performed. Figure 6A presents the morphology of a cast film from a 20/80-PE/sPP blend. From this micrograph, no distinct contrast belonging to the sPP can be detected. The dark dots are agglomerates of PE lamellae. In the larger magnification (Fig. 6B), the lamellae in the PE agglomerates are resolved more clearly but again, the contrast of the sPP crystals is too poor to give any hint on their nucleation sites. But it can be recognized from these micrographs, that the dispersion of the HDPE in the sPP matrix is on the order of micometers. It is supposed, that epitaxy may play a major role in the nucleation event of the blends. It is known [8], that sPP crystallizes epitaxially onto uniaxially oriented PE films with a very sharp texture. Also, from the epitaxy of PE on iPP it is known, that secondary nucleation of the PE on $(h, k, 0)$ iPP crystal surfaces causes epitaxial nucleation [9–11]. Accordingly, it is speculated that in the sPP/PE blends similar mechanisms are acting for the nucleation of the sPP on the PE lamellae. But from the TEM micrographs, presented in this paper, no proof can be given for this hypothesis. It will be a topic of a forthcoming paper, to investigate epitaxy and nucleation in sPP/PE blend systems.

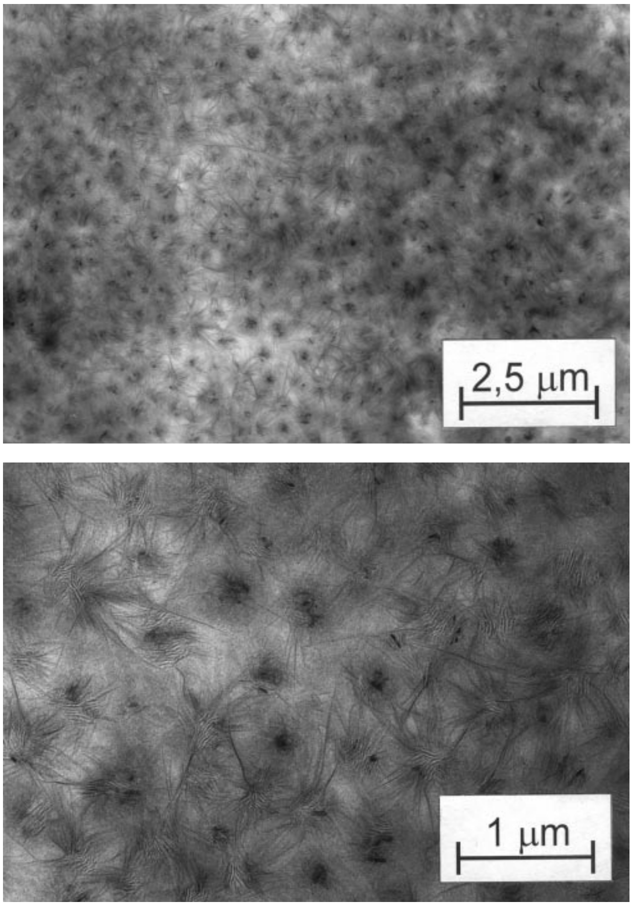


Fig. 6 (A) Transmission electron brightfield micrograph for a sPP/HDPE-80/20-blend. (B) Enlargement of Fig. 6(A)

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