Evaluation of the Fractionated Crystallization of Isotactic Polypropylene and High Density Polyethylenes in Their Blends with Cycloolefin Copolymers

Sylvie Pimbert

Laboratoire Polymères & Procédés, Université de Bretagne Sud, 56100 Lorient, France
E-mail: sylvie.pimbert@univ-ubs.fr

Summary: Crystallization of semi-crystalline polyolefins (i-polypropylenes and HD-polyethylenes) in their blends with amorphous cycloolefin copolymers (COC) were studied. The thermal behaviour of the blends was characterized by Differential Scanning Calorimetry (DSC) whereas blend morphologies were investigated by Scanning Electronic Microscopy (SEM). In iPP/COC blends, a phenomenon of fractionated crystallization is evidenced when i-PP is finely dispersed in the COC matrix. Such a behavior is generally observed when the number of droplets is much larger than the number of heterogeneities originally present in the bulk polymer. In HDPE/COC blends, complex morphologies are observed which do not fit good correlation with DSC results. The nucleation and crystallization modes seem to be largely influenced by the characteristics of the micro-dispersed phase, largely dependent on the PE molecular weights and polydispersity indices.

Keywords: cycloolefin copolymer; fractionated crystallization; morphology; polymer blends; polyolefins

Introduction

In binary blends of non miscible polymers, when the crystallizable minor phase is dispersed in a matrix, a particular crystallization process is sometimes observed. Such behavior has been attributed to a fractionated crystallization phenomenon and is the subject of several recent thermal and rheological studies. Most of these works have been rewiewed by Frensch *et al.*[1] and Arnal *et al.*[2] Recently Muller research group[3,4] investigated nucleation and rheological aspects of fractionated crystallization in polyolefin blends, more particularly in blends of polypropylene with ethylene/α-olefin copolymers. In this work, we have studied the crystallization of polyolefins (iPP and HDPE) in their blends with an ethylene-norbornene

DOI: 10.1002/masy.200351330

copolymer (cycloolefin copolymer COC) which is an amorphous polyolefin resulting from recent progress in metallocene catalysis. Fractionated crystallization was evidenced and correlated to the dispersion state of the semi-crystalline polyolefin in the COC matrix through morphological investigations.

Experimental

Isotactic polypropylene (iPP) Escorene 3684 F3 supplied by Exxon Chemicals, high density polyethylenes (HDPE), respectively Rigidex 5802 (HDPE 1) and Rigidex 6070 (HDPE 2) supplied by BP Chemicals were used for this study. The cycloolefin (COC) used is an ethylene/norbornene statistical copolymer with 35% (mol/mol) norbornene units (Topas® 8007 from Ticona).

Blends were prepared in a laboratory batch mixer (Lab Station from Brabender) by melt-mixing of the components at respectively 180 °C for HDPE blends and 230 °C for iPP blends with a mixing time of 15 min and a rotor speed of 10 rpm. A wide composition range was studied with iPP and HDPE contents varying from 2 to 100 weight percent.

Morphological investigations were realized on compression molded films (5 mm thick), quenched in ice water.

A Perkin Elmer DSC Pyris 1 was used to record cooling runs at 10 $K.min^{-1}$ after complete melting for 2 minutes at 180°C (HDPE blends) or 230°C (PP blends). High purity dry nitrogen was used as an inert atmosphere.

Blend morphologies were examined with a JEOL JSM 6301F Scanning Electronic Microscope (SEM) working at an acceleration voltage of 9 kV on Au-Pd coated cryogenically fractured samples.

Results and Discussion

iPP/COC Blends

The DSC thermograms recorded during crystallization of pure i-PP and i-PP in its blends with COC are shown in Fig 1. For pure PP and blends containing more than 40 % iPP, an unique crystallization exotherm at 110 °C, attributed to the heterogeneous nucleation of polypropylene. For lower iPP contents, a new crystallization exotherm appears at largest supercooling values.

When iPP becomes the minor phase (less than 20% w/w), the crystallization peak at 110 °C disappears and the whole i-PP shows a delayed crystallization at 73 °C. In this case, the heterogeneous nucleation of the PP component seems to be nearly suppressed.

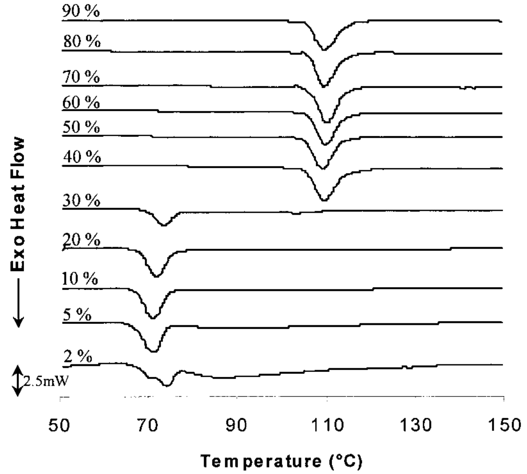
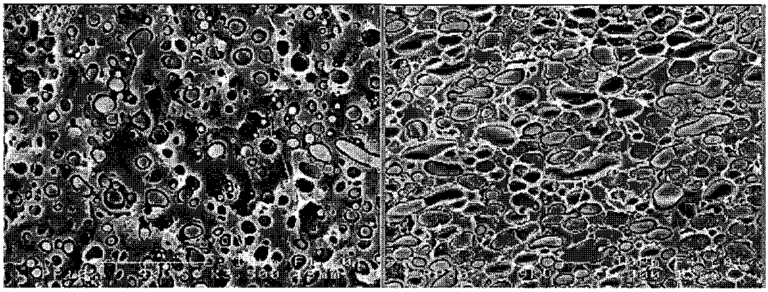


Fig. 1. iPP-COC blends : DSC cooling curves at 10 K.min^{-1}.

Morphologies of these blends were examined using SEM. We can observe for i-PP content lower than 20% a two-phase morphology typical of immiscible blends with a fine dispersion of PP droplets in the COC matrix (Fig. 2a). When the PP content increases, the blends exhibit mixed morphologies including spheres, elongated droplets and cylinders with some coalescence (Fig. 2b). These morphologies are in good accordance with the hypothesis of a fractionated crystallization in two steps (two crystallization temperatures), each step corresponding to the crystallization of a different population of droplets. In low iPP blends, we can suppose that the inclusions are too small to contain enough heterogeneities able to induce heterogeneous crystallization; leaving homogeneous nucleation to occur at a lower temperatures. An estimation of the number of droplets per volume unit gives values near 10^{11} particles per cm^3, that is much greater than the number of heterogeneities present in this polypropylene and estimated by Polarized Microscopy to be about 10^7 heterogeneities per cm^3. In blends showing mixed morphologies, the two crystallization exotherms observed by DSC can be justified by the presence of both small spherical inclusions and large nodules.



a- i-PP/COC 10/90 b- i-PP/COC 30/70

Fig. 2. SEM micrographs of iPP/COC blends.

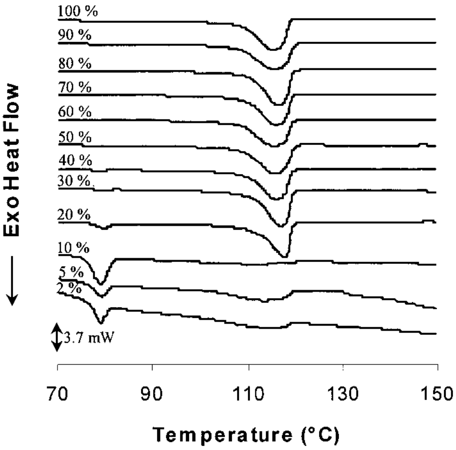
HDPE/COC Blends

The DSC thermograms recorded during crystallization on cooling of pure polyethylenes or their blends with COC are shown in Fig. 3. For both polyethylenes, the usual crystallization peak near 115-116 °C is observed on the whole composition range, corresponding obviously to HDPE heterogeneous nucleation. An unusual crystallization exotherm is also noticed near 78-80 °C which should be attributed to a fractionated crystallization of HDPE, as observed in i-PP blends. However, HDPE 1 and HDPE 2 behaviors are different: In HDPE 1/COC blends, this phenomenon is observed for quite high PE content (between 2 and 50%) whereas in HDPE 2/COC blends, the delayed crystallization is only present for low PE content (lower than 20%), i.e when polyethylene is the minor phase.

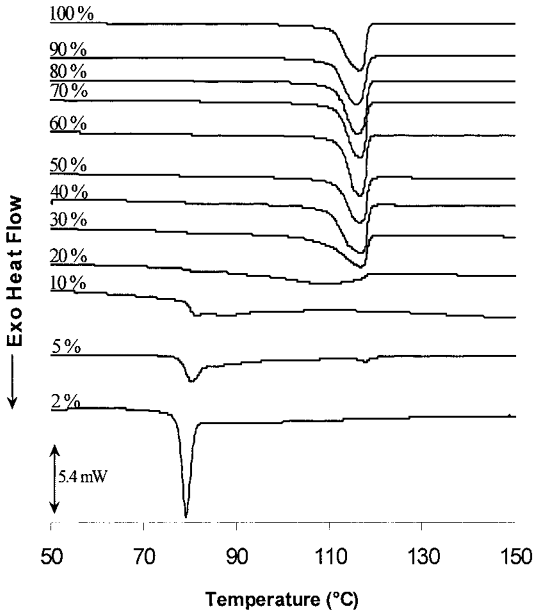
A probable explanation lies in the rheology of these blends, resulting from a great difference between HDPE molecular weights (M_w) and particularly polydispersity indices (I_p), respectively 179,000 g.mol^{-1} and 26.2 for HDPE 1 and 69,000 g.mol^{-1} and 4.2 for HDPE 2.

Morphology investigations show differences in the dispersion state of HDPE in the COC matrix according to the HDPE used (Fig. 4). Obviously, the minor component dispersion in the matrix would be better for the low molecular weight sample.

For HDPE 1/COC blends, co-continuity is observed with only about 30 % polyethylene and the 50/50 blend presents a characteristic morphology of layers without any droplets. In this case, the presence of a delayed crystallization peak could not be justified by the hypothesis of homogeneous nucleation in the droplets that do not contain heterogeneities: there is no more observable droplets.

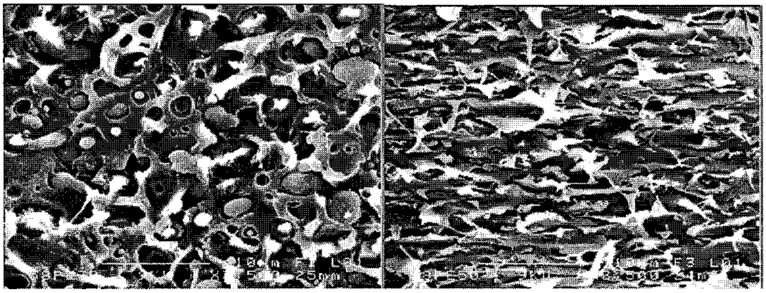


a- HDPE 1 /COC blends

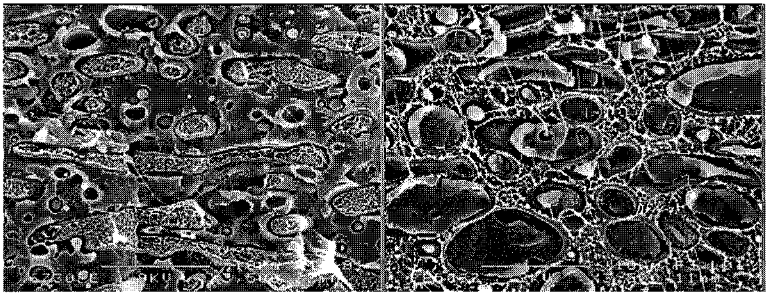


b- HDPE 2 /COC blends

Fig. 3. DSC cooling curves at 10 K.min^{-1}.



a) HDPE 1 /COC 30/70 b) HDPE 1 /COC 50/50



c) HDPE 2 /COC 30/70 d) HDPE 2 /COC 50/50

Fig. 4. SEM micrographs of HDPE/COC blends.

SEM observations of HDPE 2/ COC do not give evidence of co-continuous phases. In the 30/70 blend, large PE domains containing nodules and elongated droplets are observed. Some coalescence is also noticed. For a 50/50 blend composition, after the phase inversion, large COC nodules are dispersed in a HDPE matrix that appears very soft and shows some pulling out.

Conclusion

The thermal properties and morphologies of iPP/COC blends fit well with presious models of immiscible blends, including homogeneous nucleation in droplets to explain the delayed iPP crystallization. By contrast, unusual behaviors and morphologies were observed in HDPE/COC blends, showing the influence of low molecular weight PE fraction.

Acknowledgments

We wish to thank Ticona for Topas® samples and J.Le Lannic from CMEBA (University of Rennes) for SEM observations.

[1] H.Frensch, P.Harnischfeger and B.J.Jungnickel in "*Multiphase Polymers : Blends and Ionomers*", L.A.Utracki, R.A Weiss Eds, ACS Symp.Series 395:101 (1989)
[2] M.L.Arnal, M.E.Matos, R.A.Morales, O.O.Santana and A.J.Muller, *Macromol.Chem.Phys.*, **1998**, 199, 2275
[3] A.C.Manaure, R.A.Morales, J.J.Sanchez and A.J.Muller, *J.Appl.Polym.Sc.*, **1997**, 66, 2481-2493
[4] A.C.Manaure and A.J.Muller, *Macromol.Chem.Phys*, **2000,** 201, 958-972