

Fractionated Crystallization of High-Density Polyethylene as an Evidence of Dispersed Phase Morphology in PET/HDPE Blends

S. Mbarek^{1,2}, C. Carrot¹, Y. Chalamet¹, M. Jaziri², B. Elleuch²

¹Laboratoire de Rhéologie des Matières Plastiques, UMR CNRS 5223, Ingénierie des Matériaux Polymères Université Jean Monnet, Faculté des Sciences et Techniques, 23, Rue du Docteur Paul Michelon, 42023 SAINT-ETIENNE Cedex 2, France

URL: www.univ-st-etienne.fr/lrmp

e-mail: carrot@univ-st-etienne.fr

²Laboratoire Eau-Energie-Environnement

Ecole Nationale d'Ingénieurs de Sfax, Université de Sfax, 3038 Sfax, Tunisia

URL: www.enis.rnu.tn

ABSTRACT: The fractionated crystallization of HDPE as a dispersed phase in immiscible polymer blends with PET at composition of 15 wt-% was investigated. The dramatic influence of the molecular weight of the HDPE on its melt viscosity and therefore on the dispersion is reflected on the relative intensities of the twin peaks that are observed during the crystallization of the PE phase. The minimum volume of a nucleated domain was found to be in agreement with the typical size of PE spherulites. The effect of the addition of a compatibilizer of the E-GMA type was also studied.

Key words: Compatibilization, Fractionated Crystallization, Polymer Blends

1 INTRODUCTION

Polymer blending in the melt provides a cheap and reliable route to combine specific properties from different polymers in one material. If the components to be mixed are semi-crystalline, a complex behaviour can arise because of the interplay between the crystallization and morphology.

Especially, when the crystallisable bulk polymer is dispersed into droplets in an immiscible matrix, a fractionated crystallization phenomenon is observed if the number of droplets is higher than the number of heterogeneities that act as nuclei [1,2,3].

This phenomenon leads to multiple crystallization peaks at supercoolings that are higher than that of the bulk crystallization. If the droplets do not contain any heterogeneity, they might crystallize through homogeneous nucleation at the largest attainable degree of supercooling.

In this paper, we would like to focus on the influence of the viscosity of the dispersed phase and on the effect of a compatibilizer acting as emulsifier that both have a deep impact on the state of dispersion of the minor component.

The purpose of this work is to check the reliability of the fractionated crystallization process to trace the

dispersion of a crystalline polyethylene in a continuous matrix of polyethylene terephthalate.

2 MATERIALS AND EXPERIMENTS

2.1 Materials

The materials investigated are poly(ethylene terephthalate), PET, as the matrix (85 wt-%) and high density polyethylene, HDPE, as the dispersed phase. HDPE with various molecular weights were investigated as indicated in Table 1.

Table 1. Molecular weight data of the polyethylenes.

HDPE	Mw [g/mol]	Polydispersity
PE53K	53000	5.5
PE90K	90000	4.6
PE150K	150000	12

For some blends, a random copolymer of ethylene and glycidyl methacrylate (E-GMA), Lotader AX8840 from Arkema, was used as a compatibilizer. The copolymer has a glycidyl methacrylate content of 8 wt-%. The selected composition for this study was 85/12.5/2.5 (PET/PE/E-GMA).

2.2 Processing of PET-HDPE blends

PET and HDPE with and without compatibilizer were melt blended in a co-rotating intermeshing twin-screw extruder. The extrusion conditions were selected to ensure the best compromise between the residence time, mixing intensity and to minimize the degradation of the components. All polymers were dried under vacuum before their use and have been equally processed.

2.3 Thermal Analysis

Differential scanning calorimetry (DSC) measurements were carried out in TA Q10 device on samples after extrusion. Typical thermal cycle applied to the samples was: first heating at a scanning rate of 10°C/min from 25°C to 275°C (Run#1) to erase the thermal history of the samples, cooling at 10°C/min from 275 to 25°C (Run#2) to evaluate the crystallization, second heating at 10°C/min from 25°C to 275°C (Run#3) to determine the bulk crystallinity of PET and HDPE.

2.4 Scanning Electron Microscopy (SEM)

Morphology of the blends was investigated using a scanning electron microscope after breaking at liquid nitrogen temperature. The pictures were processed using the ImageJ software to obtain the size distribution of particles and the average size of the dispersed PE domains.

2.5 Rheology of the Neat Polymers

The rheology of the neat polymers was measured by dynamic oscillatory measurements in the melt on a Rheometrics ARES device. Master curves were built in order to calculate the melt viscosity at 260°C, which is the temperature of blending.

3 RESULTS AND DISCUSSION

3.1 Thermal Properties of Neat HDPE

Figure 1 shows the DSC traces that were obtained during the cooling stage for HDPE alone (Run#2) showing normal expected behaviour.

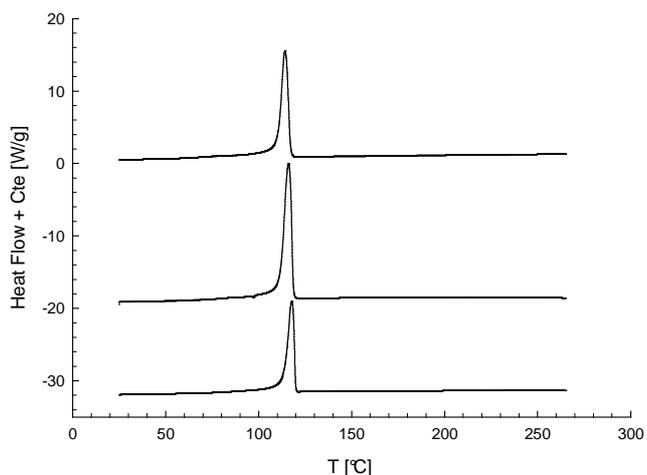


Fig. 1. DSC trace (Run#2) of PE53K, PE90K, and PE150K (from top to bottom).

3.2 Crystallization of PET/HDPE (85/15) Blends

DSC traces during the first cooling scan (run#2) of PET/HDPE blends containing 15wt-% of PE are shown in Figure 2. The crystallization peaks associated to each polymer are readily observable. Due to the presence of HDPE droplets in the PET matrix, the hot crystallization temperature of PET decreases in PET/HDPE blends in comparison with that of neat PET.

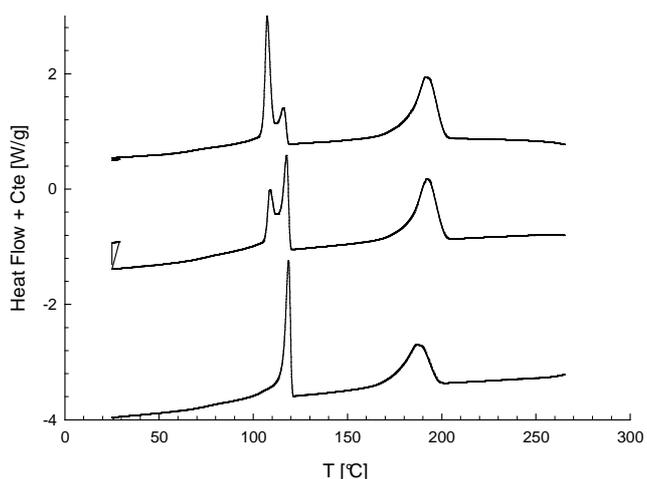


Fig. 2. DSC trace (Run #2) of PET/HDPE blends (from top to bottom with PE53K, PE90K, and PE150K).

But the most remarkable feature is the twin crystallization peaks that are developed for blends with PE53K and PE90K. In both cases, the first peak is close to that of neat PE while the second peak occurs at significantly lower temperature. Such a phenomenon is not observed with PE150K. The

intensity of the first peak with the highest crystallization temperature is all the more pronounced as the molecular weight of PE is high while the intensity of the second peak follows the reverse tendency until the peak is no more observed for PE150K. It has been checked that the melting of the PE phase is not altered.

3.3 Morphology of PET/HDPE (85/15) blends

The SEM pictures of the surface fractures of the various blends at the same magnification are shown in Figure 3. Photographs show morphologies that are typical of immiscible blends. In the same condition of blending, the final blend morphology is clearly connected with the HDPE molecular weight. The size of the domains is given in Table 2. Distributions of sizes are also plotted on Figure 3.

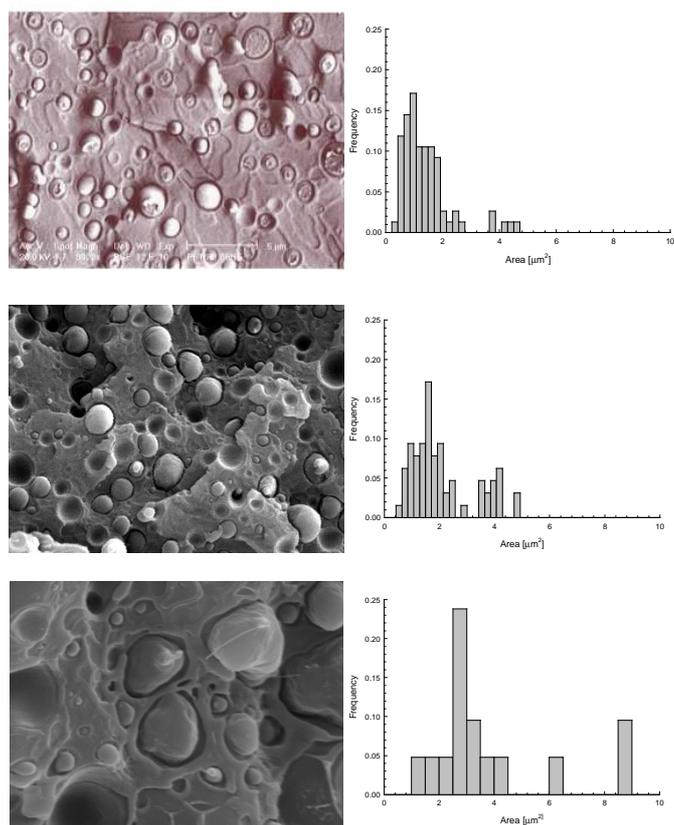


Fig. 3. SEM micrographs of the fractured surface and related distributions of sizes for blends with PE53K, PET/PE90K and PE150K from top to bottom.

Table 2. Average area of the PE domain in non-compatible blends (calculated on 2D surface).

Blend	Number average area (μm^2)
PET/PE53K (85/15)	1.41
PET/PE90K (85/15)	2.24
PET/PE150K (85/15)	8.21

This dependency of the size of the dispersed

domains on the molecular weight is a consequence of the effect of the latter on the melt viscosity. This is the primary reason for the finest dispersion of PE53K in PET and of the coarser domains of PE150K. Indeed, at the processing temperature of 260°C, the matrix to droplet viscosity ratio is close to 30 for PE53K, while it is 4 for PE90K and 0.7 for the most viscous PE150K.

3.4 Fractionated Crystallization of PE in Blends.

The variation of the blend morphology in connection with the melt viscosity of the PE phase, which is itself related to the molecular weight of the polymer, is at the origin of the twin crystallization peaks. Because of the matrix-droplet morphology, a fractionated crystallization process occurs. Indeed, for small droplets, the number of nuclei in HDPE is lower than the number of dispersed particles and the crystallization of HDPE in un-nucleated particles proceeds in a homogeneous way while that of nucleated droplets remains heterogeneous and similar to that of neat PE.

The fractionated crystallization process of HDPE minor phase was observed for PET/PE53K and PET/PE90K. Finer morphology induces a higher number of particles and a larger amount of un-nucleated PE. In this case the relative intensity of the low temperature peak increases.

On the opposite, for PE150K, the high molecular weight of the HDPE minor phase in the PET/PE blend and therefore the high viscosity induces a coarse morphology and prevents the fractionated crystallization process.

Assuming that a droplet will crystallize when its volume is large enough to contain at least one nucleus, using the relative areas of the peaks and the distribution of sizes, enables the calculation on the minimum area of a nucleated domains. The minimum volume is $1.5\mu\text{m}^3$ and its inverse gives approximately the number of nuclei per unit volume, $7.2 \cdot 10^{17}$ nuclei/ m^3 . The radius of spherulites in polyethylene can be calculated assuming a complete filling of the volume and the dimension ($1.7 \mu\text{m}$) is in agreement with the observed radius of spherulites in polyethylene.

3.5 Effect of a Compatibilizer of the E-GMA Type.

The effect of the addition of a compatibilizer on the HDPE crystallization was examined for blends containing 2.5 wt-% E-GMA random copolymer.

The thermograms of PET/PE90K and PET/PE150K blends with or without compatibilizer are shown on Figure 4 during the cooling cycle as typical results.

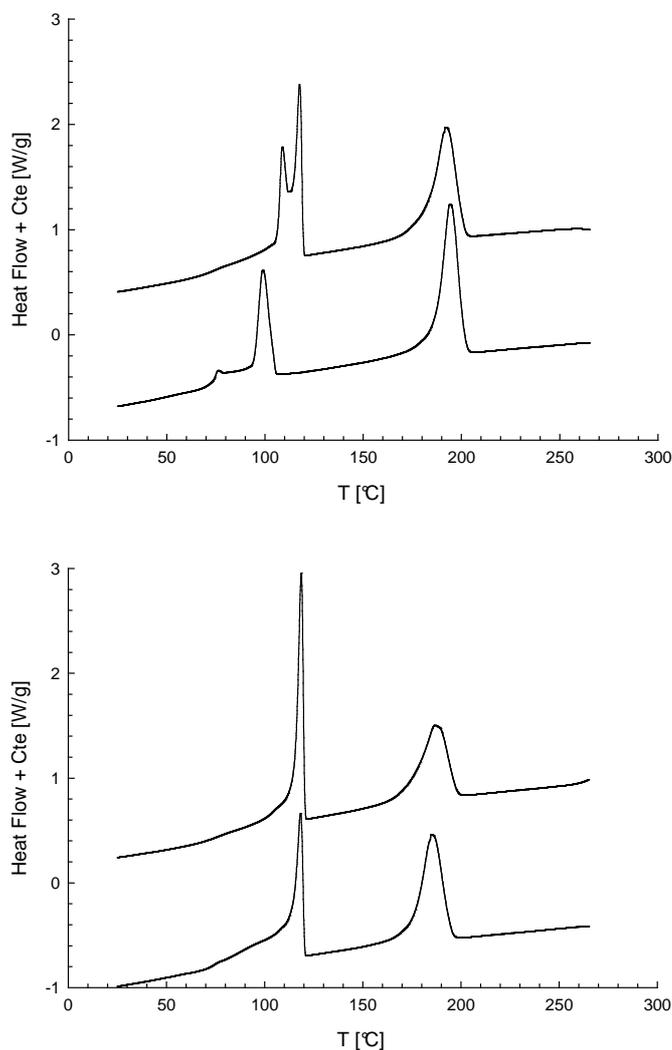


Fig. 4. DSC trace (Run#2) of blends PET/PE90K and PET/PE90K/E-GMA (top) and PET/PE150K and PET/PE150K/E-GMA (bottom).

For blends containing the high molecular weight PE, the compatibilizer does not induce any change in the thermograms. For blends containing PE53K and PE90K, four major effects are noticeable: at first, the twin crystallization peaks are no more observed and only the low temperature crystallization is observed. Secondly, a small shoulder is nevertheless visible at nearly 75 °C. Third, the crystallization temperature of the HDPE is lowered in compatibilized blends in comparison with pure HDPE. At last, the difference of molecular weight is not visible.

The first effect is related to fractionated crystallization. In compatibilized blends, with PE53K and PE90K, the disappearance of the crystallization peak at high temperature is related to

the change of morphology that is caused by the addition of E-GMA. During extrusion, the compatibilizer will locate at the interface. The olefinic segments are expected to be partially miscible with HDPE (inducing a lowering of the crystallization of HDPE) while the active groups (GMA) react with the hydroxyl ends of the PET matrix. The in-situ formation of PET-HDPE copolymers reduces the interfacial tension and suppresses coalescence. Compatibilized blends with only 2.5 wt-% of compatibilizer show well-dispersed HDPE particles inside the PET matrix, with small size (less than 0.3 μm^2). Therefore, the homogeneous crystallization process gives rise to a single peak at low temperature and the effect of molecular weight is no more visible.

4 CONCLUSIONS

The influence of the molecular weight on the melt viscosity and therefore on the dispersion is reflected on the fractionated crystallization process that is observed in immiscible polymer blends containing a semi-crystalline polymer. The minimum volume of a nucleated domain is 1.5 μm^3 in agreement with the typical size of PE spherulites. The minimum size can be equally achieved by the addition of a compatibilizer of the E-GMA type, which acts as an emulsifier.

ACKNOWLEDGEMENTS

This work was supported by a MIRA project (Rhône-Alpes Region, France) and by a Franco-Tunisian CMCU cooperation project.

REFERENCES

1. G. Pompe, P. Potschke and J. Pionteck, Reactive Melt Blending of Modified Polyamide and Polypropylene: Assessment of Compatibilization by Fractionated Crystallization and Blend Morphology. *J. Appl. Polym. Sci.* 86 (2002) 3445-3453.
2. R.T. Tol, V.B.F. Mathot and G. Groeninckx, Confined Crystallization Phenomena in Immiscible Polymer Blends with Dispersed Micro and Nanometer Sized PA6 Droplets, Part1: Uncompatibilized PS/PA6, (PPE/PS) / PA6 and PPE PA6 Blends. *Polymer* 46 (2005) 369-382.
3. V. Balsamo and L.M. Gouveia, Interplay of Fractionated Crystallization and Morphology in Polypropylene / Poly(ϵ -caprolactone) Blends. *J. Polym. Sci.: Part B: Polym. Phys.* 45 (2007) 1365-1379.