

## **Homogeneous nucleation of the dispersed crystallisable component of immiscible polymer blends**

**O. O. Santana and A. J. Müller\***

Grupo de Polímeros USB, Departamento de Ciencia de los Materiales, Universidad Simón Bolívar, Apartado 89000, Caracas 1080-A, Venezuela

### **Summary**

Immiscible melt mixed blends of a crystallisable polyolefin (isotactic polypropylene, PP) and atactic polystyrene (PS) were prepared in a wide composition range. It was found that when PP is the major component in the blend its crystallisation behaviour is not affected by blending it with PS. However if PP is the minor component, it will be dispersed in the immiscible PS matrix, hence the nucleation mechanism changes from predominantly heterogeneous to predominantly homogeneous as long as the size of the dispersed PP droplets is below a critical value (of the order of 1-2  $\mu\text{m}$ ).

### **Introduction**

When immiscible blends are prepared by melt mixing the resultant morphology is a complex function of the rheological characteristics of the homopolymers to be mixed, the composition of the blend and the processing variables (1,2).

It is well known that the usual morphology developed, when there is an excess of one component in an immiscible blend, is a dispersion of the minor component in a matrix of the major component. If the blend is thermodynamically immiscible, there will be no interactions between the components, a fact that usually leads to mechanical incompatibility in the resultant blend. However, some immiscible blends can exhibit mechanical compatibility, synergistic effects or peculiar deviations from linear mixing rules.

The main purpose of this study is to determine whether the morphology could induce a change in the vitrification or the crystallisation of the individual components of an immiscible blend. Such changes could lead to unexpected thermal or mechanical behaviour in the blends.

### **Experimental**

*Materials.* The materials used in this study were an isotactic polypropylene (PP) manufactured by Polipropileno del Caribe S.A. (Propilco, Colombia) and an atactic polystyrene (PS) manufactured in Venezuela by Estizulia. Their characteristics are presented in Table 1. A styrene-butadiene-styrene triblock (SBS) was used as a compatibilising agent in selected blends.

*Melt Mixing Conditions.* The blending temperature was selected by choosing similar melt viscosities at high shear rates from capillary rheometry experiments on the homopolymers. The criteria of using the same melt viscosities to produce the best possible dispersion have been proposed by many authors (1) and have been used by us with excellent results in polyolefin blends (3-6). The polymers were melt

\*Corresponding author

**Table 1.** Density and Melt Flow Index of the materials used in this study.

Materials	MFI <sup>(a)</sup> (g/10 min)	Density (g/cm <sup>3</sup> )
PP D01H41	1,4 * <sup>1</sup>	0,903 <sup>(b)</sup>
PS 1500	2,4 * <sup>2</sup>	1,050 <sup>(c)</sup>
SBS Stereon 840A	12,0 * <sup>2</sup>	0,960 <sup>(c)</sup>

(a) ASTM D1238: \*1: 230°C/2,16 kg ; \*2: 200°C/5,00 kg.

(b) ASTM D1505

(c) ASTM D792.

mixed at 220 °C and 100 rpm by twin screw extrusion (Werner and Pfleiderer ZSK-30). The following blends were prepared by melt mixing:

100/0, 90/10, 80/20, 70/30, 50/50, 30/70, 20/80, 10/90, 0/100

PP/PS weight/weight. Blends with SBS were also prepared, where the SBS was used as a compatibiliser in a proportion always equivalent to 10% by weight with respect to the dispersed component.

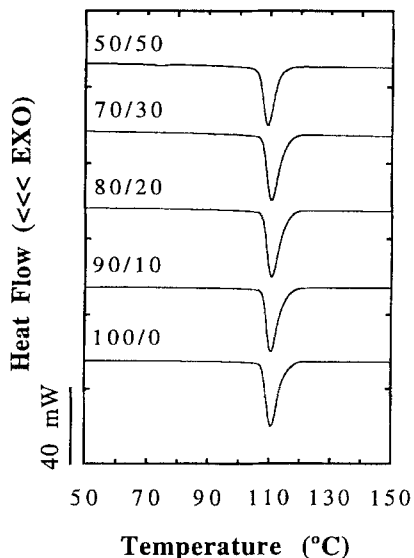
*Differential Scanning Calorimetry.* The extruded materials were compression moulded at 220 °C into 0.5 mm sheets. From these sheets small flat cylindrical samples (cylinders with diameters much bigger than their heights) were cut so that their weight was approximately 12 mg. In this way the shape, size and weight of all the DSC samples were standardised. The samples were encapsulated in Aluminium pans and high purity dry nitrogen was used as an inert atmosphere. A Perkin Elmer Calorimeter DSC-7 was utilised. All the DSC cooling curves presented here were recorded at 10 °C/min after the samples were held in the melt at 230 °C for 3 minutes.

*Scanning Electron Microscopy.* Samples from the same compression moulded sheets used for DSC were cryogenically fractured and gold coated before observing the blend morphology by a Phillips 505 Scanning Electron Microscope.

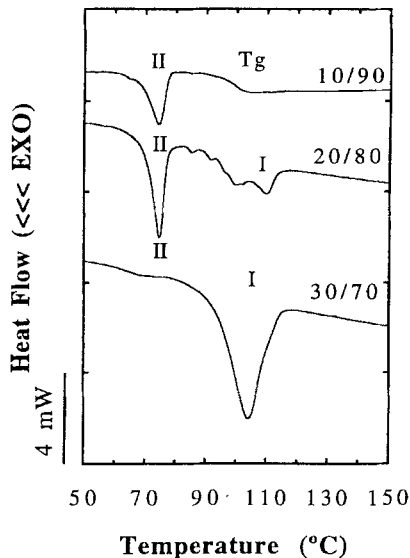
## Results and Discussion

Figure 1 shows the DSC cooling thermograms of the PP homopolymer and its blends with PS up to 50% by weight. It can be seen that the crystallisation of the PP component is not qualitatively affected by blending as long as the excess component in the blend is PP.

The crystallisation behaviour of the PP changes radically, when it is present in the blend as a minor component. This is shown in Figure 2, where the dynamic crystallisation of the PP component in the blend can be appreciated. Several features emerge from a detailed look at this Figure. First, it should be noted that the scale bar in this graph only represents a heat flow equivalent to 4 mW, this indicates that the evolved heat of crystallisation in these PP poor blends is small as compared to the PP rich blends (Figure 1). This fact remains true even if a normalisation is performed by the weight of the crystallisable component in the blend (Figure 3). Second, the main crystallisation exotherm of the PP homopolymer that appears in the material used here around 110 °C (Figure 1), labelled I in Fig. 2, is shifted to lower temperatures in the 30/70 and in the 20/80 PP/PS blends. Furthermore, exotherm I is very small in the 20/80 blend and disappears



**Figure 1.** DSC cooling curves (10  $^{\circ}C/min.$ ) for PP/PS blends at the indicated compositions.

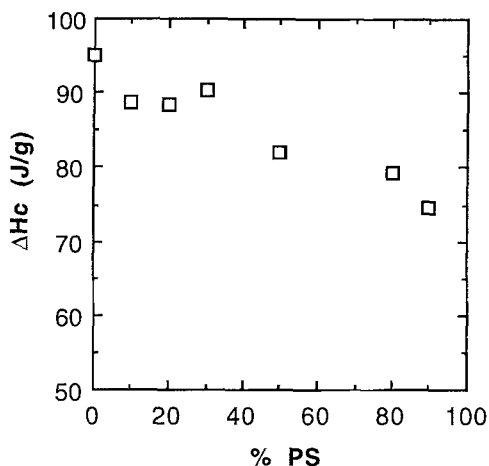


**Figure 2.** DSC cooling curves (10  $^{\circ}C/min.$ ) for PP/PS blends at the indicated compositions.

completely in the 10/90 blend. It can also be seen that the vitrification of the PS component appears as an exothermic step at around 100  $^{\circ}C$  in all the blends, this secondary transition overlaps with the final stages of the first crystallisation process (exotherm I). Finally and most surprising, a second crystallisation exotherm (labelled II in Fig. 2) appears at around 75  $^{\circ}C$  (at a temperature below the glass transition temperature of the PS component) in the 20/80 and in the 10/90 blend. There is a hint of exotherm II in the 30/70 blend.

The peculiar thermal behaviour of the PS rich blends was rationalised after their morphology was observed under the electron microscope. Figure 4 shows the morphology of the 20/80 PP/PS blend that corresponds to the DSC thermogram of the same blend in Fig. 2. It can be seen that the PP component is very finely dispersed in a PS matrix. The average size of the PP component in the blend is approximately equal to 1-2  $\mu m$ . Since the average spherulite size of pure PP is usually much larger than this size, it was proposed that the fine dispersion of the PP in the glassy matrix was inducing homogeneous nucleation.

The results can be well understood if it is considered that the first crystallisation process (exotherm I) is produced by heterogeneous nucleation and the second (exotherm II) by homogeneous nucleation. Such explanation is consistent with the fact that as long as the PP component constitutes the matrix in the blend, the nucleation is preferentially heterogeneous. The first hint of homogeneous crystallisation appears when the PS component constitutes 70% by weight in the PP/PS blend. The relative areas of exotherms I and II should be proportional to the relative proportion of crystals that were grown from heterogeneous and from homogeneous nuclei: for the 10/90 blend all the nucleation process was probably homogeneous (exotherm I is completely absent

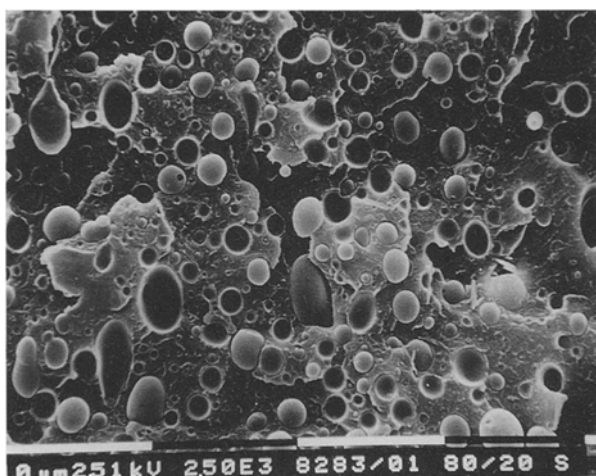


**Figure 3.** Enthalpy of crystallization ( $\Delta H_c$ ) of the Polypropylene component in the PP/PS blends.

for this blend in Fig. 2); for the 20/80 blend approximately 35% of the crystals were homogeneously nucleated, whereas for the 30/70 blend only 2% of the crystals grew from homogeneous nuclei. SEM micrographs indicated that the average size of the PP domains in the 30/70 PP/PS blend was around 7-9  $\mu\text{m}$ . If the PS component in the blend is increased to 80%, a fine dispersion is produced (Fig. 4), with particle sizes of around 1-2  $\mu\text{m}$ . Clearly there should be a critical size of the dispersed phase when the number of PP dispersed particles is much greater than the number of heterogeneities present in the system, whereby homogeneous nucleation is promoted.

The interpretation of the results presented here can be derived directly from the work of Burns and Turnbull (7). These authors produced a fine dispersion of PP droplets in an inert liquid medium and then followed the crystallisation process in a polarising optical microscope. They found that most droplets crystallised in a temperature range of 77-79  $^{\circ}\text{C}$  while only a few crystallised at 105  $^{\circ}\text{C}$  (the usual  $T_c$  of their bulk PP samples). Furthermore, they observed that the droplets that crystallised at higher supercoolings had diameters of less than 6  $\mu\text{m}$  and those that crystallised at low supercoolings had greater sizes, in the range of 6-20  $\mu\text{m}$ . They concluded that those droplets that contain heterogeneities crystallised in the normal temperature range whereas those without them had to wait until a homogeneous nucleation process developed at higher supercoolings. A similar conclusion was reached by the same group of researchers in a previous paper when they developed the droplet crystallisation technique using linear polyethylene (8); a classic work where the predominance of the heterogeneous nucleation process in bulk polyethylene was established.

Another important reference to the work reported here is the paper by Baitoul et al. (9). They studied the crystallisation of the low density polyethylene (LDPE) component in LDPE/PS blends. They found similar results to those presented above, except for the fact that the amount of material that was homogeneously nucleated was small compared to that heterogeneously nucleated.

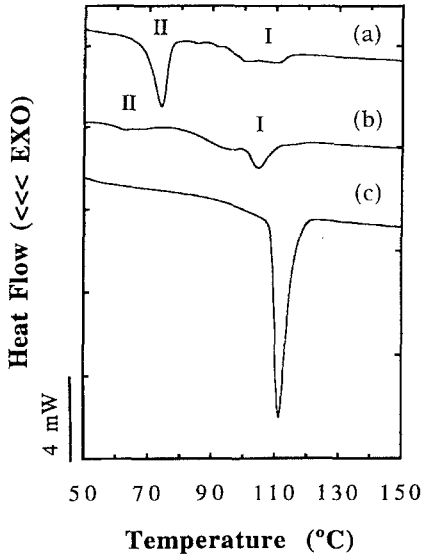


**Figure 4.** SEM micrograph of a cryogenically fractured section from a 20/80 PP/PS compression moulded specimen. Scale bar: 10  $\mu\text{m}$ .

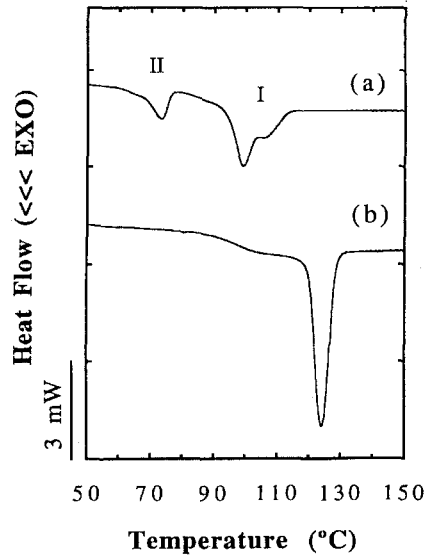
It could be that the method and conditions of blending that they used, did not produce an optimum dispersion, where most of the LDPE droplets were not below the critical size required for homogeneous nucleation to develop.

It should be stressed that the DSC thermograms presented above were qualitatively reproducible for different samples of sheets prepared using the same conditions of pressure and temperature during compression moulding. Figure 5 (a) shows a DSC cooling curve of a sample cut from a different sheet of the same material 20/80 blend. It serves to illustrate the level of reproducibility obtained. Figure 5 (c) presents another evidence for the effect reported in Figs. 2 and 5 (a) to be due to the fine dispersion of the PP component in the PS matrix. Using the same weight proportions of PP and PS as in a 20/80 blend, the samples of both homopolymers were placed in a DSC pan but separated by Aluminium foil (such a sample was termed "unmixed blend"). Figure 5 (c) clearly shows that the PP is crystallising from heterogeneous nuclei and the vitrification of the PS can be observed in the left hand side of the exotherm at around 100  $^{\circ}\text{C}$ .

The effect of adding a triblock copolymer, SBS, as a compatibiliser was also studied. Here we only present the result obtained for the 18/80/2 PP/PS/SBS blend. It should be stated that SEM did not show (at least in samples taken from the same compression moulded sheets used for DSC) any qualitative difference between the morphology of this blend and the one without SBS, i.e., the size of the dispersed PP spheres was approximately the same. This result could indicate that the SBS did not act as an emulsifying agent for this particular blend, a fact that was consistent with the lack of improvement in the tensile and impact properties of the blends after addition of SBS (10). We therefore did not expect a substantial change in the crystallisation behaviour of the 18/80/2 PP/PS/SBS sample as compared to the 20/80/0 PP/PS/SBS. However, Fig. 5 (b) shows that exotherm II is much smaller than in Fig. 5 (a) and it is displaced to lower temperatures. Even though the explanation for this behaviour remains unclear for the time being, we believe that the SBS may be transferring heterogeneities to the PP component and in this way



**Figure 5.** DSC cooling curves (10  $^{\circ}C/min.$ ) for PP/PS/SBS blends: (a) 20/80/0, (b) 18/80/2 and (c) 20/80/0 "unmixed blend".



**Figure 6.** DSC cooling curves (10  $^{\circ}C/min.$ ) for 20/80 PP/PS "hand mixed" blends: (a) without and (b) with phthalocyanine blue.

reducing the homogeneous nucleation process. The transfer of nucleating particles between polymers, promoted by shear during melt mixing, in similar systems is well documented in the literature (11). We are still studying the complex role of the SBS and the results for all the blend composition range will be reported separately (10).

In order to test even further our explanation of the peculiar crystallisation behaviour of these blends, we performed the following experiment. A small amount of the 20/80 PP/PS melt mixed pellets obtained by twin screw extrusion were melted on a hot plate at 220  $^{\circ}C$  and manually mixed with a glass rod with a 1% by weight phthalocyanine blue (a powerful nucleating agent for PP; it shifted the dynamic crystallisation peak of pure PP from 110  $^{\circ}C$  to 125  $^{\circ}C$ ). The same procedure was applied to a reference sample without the nucleating agent since the strain rates applied by this "hand mixing" process are obviously not the same as those applied during extrusion. It is common for the disperse component of thermodynamically immiscible systems such as PP/PS to undergo coalescence if the post processing involves lower shear rates than the original melt mixing conditions (a fact that also remains true for our compression moulded sheets, it was found by SEM that the original melt extruded pellets had even smaller sizes of the dispersed PP phase in the PP poor blends than the compression moulded sheets (10)).

The crystallisation behaviour of the reference "hand mixed" 20/80 PP/PS blend is shown in Fig. 6 (a). The blend still displays homogeneous nucleation (as judged by the area of exotherm II) even if some coalescence did occur. Upon addition of the nucleating agent, Fig. 6 (b), only heterogeneous nucleation took place as it is indicated by the disappearance of exotherm II. Hence, there is no doubt that the peculiar exotherms labelled II throughout this work are representative

of a homogeneously nucleated crystallisation process. The glass transition of the PS component can now clearly be appreciated (Fig. 6 (b)) because of the shift to higher temperatures of the crystallisation of the PP component in the blend, caused by the addition of phthalocyanine blue.

We have performed similar experiments to those reported here in other immiscible blends: Low density polyethylene/atactic polystyrene; linear low density polyethylene/atactic polystyrene and isotactic polypropylene/linear low density polyethylene. These results will be communicated shortly (10), they appear to indicate that the reported change in nucleation mechanism is general for crystallisable dispersed components in immiscible blends.

### Conclusions

The nucleation mechanism of the crystallisable component in immiscible PP/PS blends can be strongly influenced by the morphology of the blend. If the crystallisable PP component is finely dispersed in the matrix of the amorphous PS component, the nucleation mechanism changes from preferentially heterogeneous to preferentially homogeneous as the size of the dispersed component decreases below a critical value.

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