

The evaluation of the state of dispersion in immiscible blends where the minor phase exhibits fractionated crystallization

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Summary

Differential Scanning Calorimetry (DSC) can provide a qualitative measure of the state of dispersion of an immiscible blend if the minor phase exhibits fractionated crystallization when dispersed into fine particles. The technique is only sensitive to the volume of the dispersed particle and not to its shape and can only be used when the exotherms of interest do not overlap with other thermal transitions present in the multicomponent system. Self-nucleation is a valuable tool to ascertain the presence of fractionated crystallization. The morphology induced by fractionated crystallization in immiscible blends could lead to enhanced plastic deformation during yielding of the matrix.

Introduction

Recently, we reported the effect of producing a fine dispersion of a crystallizable polymer (isotactic polypropylene, iPP) in an immiscible amorphous matrix (atactic polystyrene, PS) on its nucleation mechanism (1). It was found that if the number of dispersed iPP particles is greater than the number of heterogeneities originally present in the bulk sample, a new crystallization process develops at much lower temperatures than those typically encountered in heterogeneously nucleated iPP. Similar processes have been reported in the literature for crystallizable components that constitute the dispersed phase of several polymer blends and the term of fractionated crystallization has been introduced to describe these phenomena (2). Ghijssels et al. (3) found fractionated crystallization phenomena, when studying the crystallization behavior of the iPP dispersed phase in thermoplastic rubber/iPP blends, they suggested that DSC could be applied to study the state of dispersion in such blends. In this paper, we use Differential Scanning Calorimetry (DSC) in conjunction to Scanning Electron Microscopy (SEM) in order to assess the state of dispersion in immiscible blends of PS/Linear Low Density Polyethylene (LLDPE), where the LLDPE dispersed phase exhibits the phenomenon of fractionated crystallization. Additionally, we investigate the influence of the addition of atactic Polypropylene (aPP) to LLDPE/iPP blends. Finally, preliminary results on the relationship between the morphology and the mechanical properties of blends whose dispersed phase crystallizes in a fractionated fashion are presented.

Experimental

The materials used in this study were: two 1-butene LLDPE's (Dupont Sclair 11D1 and 11U4, 0.6 and 1.4 g/10 min MFI at 190 °C respectively), one iPP (Propilven F300, 1.4 g/10 min

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MFI at 230 °C), one aPP (Hoescht HN with a viscosity range of 8000-30000 mPa.s) and one PS (Estizulia PS1500, 2.4 g/10 min MFI at 200 °C). All blends were prepared in a Werner & Pfleiderer ZSK-30 twin screw extruder. The PS/LLDPE-11D1 blends were extruded at 100 rpm and 190 °C and two different screw configurations were used, see below (4). The LLDPE-11U4/iPP/aPP blends were mixed at 210 °C and 100 rpm using screw configuration type 2. A Perkin-Elmer DSC-7 was used to record cooling scans at 10 °C/min after melting for 3 minutes at 200 °C. SEM observations of Pt/Pd coated cryogenically fractured specimens were performed in a Phillips P-SEM 505 electron microscope. From the micrographs obtained the average number and volume radii (r_n and r_v) of the particle cross-sections were measured from counting at least 100 particles. The dispersity (D) of the sizes obtained and the average number of particles/cm³ were also calculated.

Results and Discussion.

Effect of twin-screw mixing elements. The main difference between screw configuration 1 and configuration 2 is the presence of three left oriented (L) kneading blocks in screw type 1 while there is none in screw type 2 (both screws contain right oriented, R, kneading blocks). A detailed drawing of both screw configurations can be found in a previous work (4). It should be expected that the presence of L as well as R kneading blocks in screw type 1 will increase the pressure gradient developed within the extruder as compared to screw type 2, this in turn will increase the levels of applied mean shear stresses which according to Plochocki et al. (5) produces a reduction in particle size, a fact corroborated here. SEM observations of 70/30 PS/LLDPE blends revealed that screw type 1 produces a better dispersion with smaller LLDPE particles (~0.9 μm mean diameter) than screw type 2 (~1.3 μm). Extensive analysis by SEM along parallel and perpendicular flow directions showed that the dispersed phase has the shape of elongated ellipsoids (minor axis < 1 μm) for the 70/30 PS/LLDPE blends prepared with screw type 1 and short cylinders for those prepared using screw type 2 (<1 μm cross-section, up to approximately 4 μm in length, see Fig. 1).

The DSC cooling runs for these blends showed the crystallization of the LLDPE component and the vitrification of the PS component, as expected. The crystallization of the LLDPE component is not qualitatively affected by blending as long as the excess component in the blend is LLDPE. However, when the LLDPE is present as a minor dispersed component the crystallization behavior changes and two exotherms can clearly be seen upon cooling, as shown in Figure 2. We have shown in previous works (1,4,6-7) that the high temperature exotherm (labeled I) corresponds to the usual crystallization of heterogeneously nucleated LLDPE, while the lower temperature exotherm (appearing at around 75 °C, and labeled II) corresponds to either homogeneously nucleated crystal formation or to the crystallization after the activation of an unknown second type of heterogeneity as suggested by Frensch et al. (2) for the general phenomenon of fractionated crystallization.

Homogeneous nucleation and/or fractionated crystallization is due to the confinement of LLDPE in particles of such a small size that the number of particles is higher than the number of active heterogeneities that normally nucleate commercial polyolefins. Therefore in this case, the proportion of material crystallizing in exotherm II can be considered as a criterion of evaluating the dispersion of the blend. The dispersion in the blends with 30% LLDPE is better for samples prepared with screw type 1 than those prepared with screw type 2 as indicated by the higher proportion of crystals grown at lower temperatures (i.e., higher values of area II, in relative terms, exotherm II has an area 50% bigger for the screw type 1 blend than the corresponding exotherm II for screw type 2 blend, see Fig. 2). The rest of the results reported in this paper are for blends prepared with screw configuration type 2.

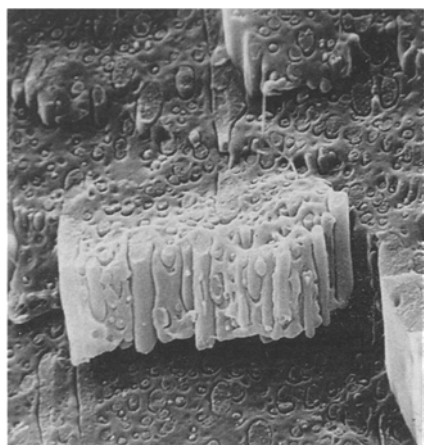
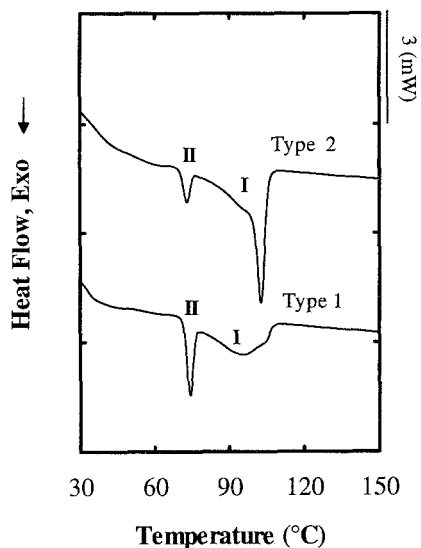
4 μm 

Figure 1. SEM micrograph from a 70/30 PS/LLDPE compression moulded specimen.

Figure 2. DSC cooling curves ($10^{\circ}\text{C}/\text{min}$) for 70/30 PS/LLDPE blends.

Evaluation of blend dispersion. PS/LLDPE blends. Table 1 contains a summary of SEM observations on the PS/LLDPE blends. As expected, the mean particle cross-section increases in size upon increasing the content of the dispersed phase from 10 to 40% by weight; the dispersity in particle cross-section exhibits the same trend. The blend compositions that are rich in LLDPE do not display fractionated crystallization behavior, therefore the DSC technique can not be used at all as an indirect evidence of the state of dispersion in PS/LLDPE blends that contain more than 40% LLDPE (beyond that composition phase inversion occurs and LLDPE ceases to be the dispersed phase of the blend).

Table 1. Summary of data from DSC and SEM analysis.

Samples	$T_{c\text{ I}}$ ($^{\circ}\text{C}$)	$T_{c\text{ II}}$ ($^{\circ}\text{C}$)	Relative Area (%)		r_n ($\times 10^4\text{cm}$)	r_v ($\times 10^4\text{cm}$)	D	N_p ($\times 10^{-11}/\text{cm}^3$)
			I	II				
LLDPE 11D1	103.9							
LLDPE 11U4	101.4							
aPP	86.4							
iPP	108.0							
PS/LLDPE:								
90/10	105.3	72.8	1	99	0.22	0.66	3.1	0.94
80/20	104.8	73.8	57	43	0.24	0.79	3.2	0.88
70/30	101.6	71.4	89	11	0.35	1.04	3.0	0.70
60/40	103.5	73.5	97	3	0.45	2.14	4.4	0.11
PE/iPP/aPP:								
80/7/13	103.0	72.6	91	9				
80/13/7	103.0	75.7	87	13	0.38	0.61	1.62	2.1
80/20/0	102.1	86.0	75	25	0.26	0.39	1.53	8.1
80/20/0-SN	135.4	109.2						
80/13/7-SN	134.0	108.7						

The DSC cooling scans for PS rich blends and for the neat polymers are shown in Figure 3 (a). It can be appreciated that as the amount of LLDPE in the blend increases, the size of the exotherm associated with heterogeneously nucleated high temperature crystals (exotherm I) increases at the expense of a decrease in size of the low temperature exotherm. This result can be explained if the particle size of the dispersed phase is considered (Table 1).

Table 1 shows how the particle size increases as the amount of LLDPE increases, causing a decrease in the mean number of particles per unit volume. It should be pointed out that the calculations presented in Table 1 were done using the sizes of the cross-sectional areas of the dispersed particles (measured from SEM photographs) and assuming that they are spheres, even though in most cases the dispersed phase had the shape of ellipsoids or very short cylinders. The usual number of heterogeneities per unit volume (N_i) that can nucleate polyethylene at low undercoolings in the bulk polymer is in the range of $N_i \geq 10^9 \text{ cm}^{-3}$ (8), it is clear from Table 1 that when the number of particles per unit volume (N_p) is much greater than this number, then the crystallization of the LLDPE at its usual temperature is nearly completely suppressed (i.e., for the 90/10 PS/LLDPE blend). When the value of N_p is closer to N_i , then the high temperature exotherm is not completely suppressed. Table 1 shows how the relative contribution of the two exotherms can be used as a qualitative indication of the state of dispersion, since the higher the proportion of exotherm II the finer the dispersion of LLDPE particles in the PS matrix; a plot of r_n vs. %relative area II could be used as a calibration curve. One limitation of the quantification of the areas of the exotherms is that the vitrification of the PS component overlaps with the final stages of the high temperature crystallization of the LLDPE component (i.e., exotherm I). This will introduce an error in the enthalpies that should be considered when integrating the exotherms in the cooling scans.

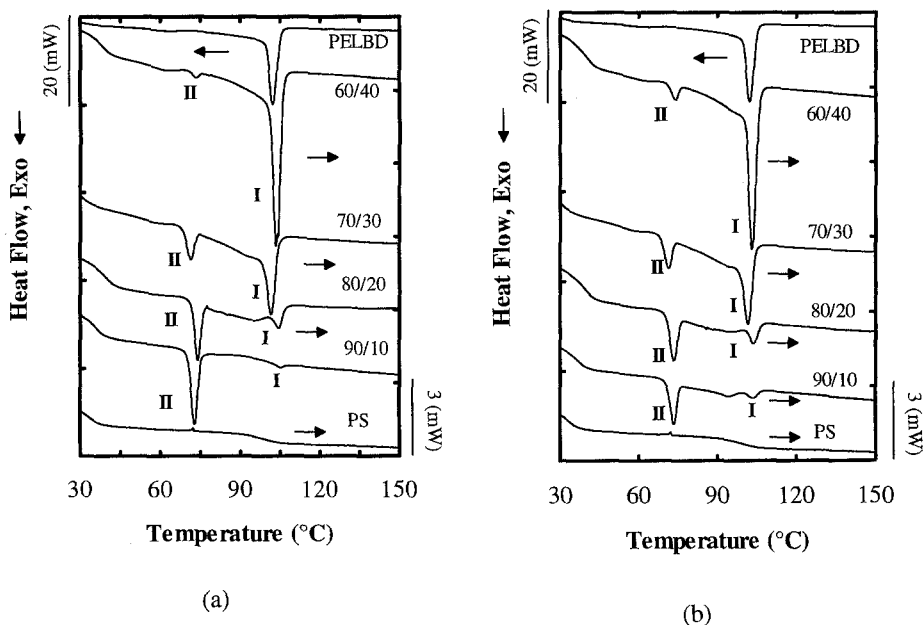


Figure 3. DSC cooling curves ($10^\circ\text{C}/\text{min}$) for PS/LLDPE blends at the indicated compositions : (a) compression moulded sheets and (b) same samples after melting in a torsional rheometer for 30 min (see text).

From the compression molded sheets used to obtain the data in Table 1, flat cylindrical specimens were cut in order to measure dynamic rheological properties in a torsional rheometer. Even though the rheological properties are not the subject of the present paper, it is interesting to report the morphological and thermal changes that occurred after such treatment. The morphology obtained by melt mixing in a twin screw extruder using high shear stresses can not be maintained in an immiscible blend if it is processed subsequently in the melt using high temperatures and lower shear forces (9). Coalescence can occur depending on the diffusion rates of the particles in the melt matrix.

Figure 3 (b) shows DSC cooling scans of the same blends as in Fig. 3 (a) after they were heated from 160 °C to 210 °C for approximately 30 min in the torsion rheometer while doing frequency scans. A simultaneous Thermal Analyser (STA by Polymer Labs.) was used to check that no significant degradation of the samples took place. From just the DSC evidence, one would tend to infer that no morphological changes occurred since the DSC behavior is almost the same as in Fig. 3 (a). However, when the samples were observed in the SEM, an increase in the cross-section of the dispersed phase was detected and this time the dispersed phase consisted of nearly perfectly rounded spheres. These results can only be rationalized if coalescence did not occur and the heat treatment only altered the shape of the particles (i.e., the cylinders were transformed into spheres in the absence of high strains) but not their volume. Therefore, the distribution of heterogeneities in the blends could have remain intact if no coalescence occurred even if there was a change in the shape of the dispersed phase. In this case, the DSC technique can not be used to monitor such morphological changes, since it is only sensitive to nucleation changes that in turn depend on the distribution of heterogeneities in the crystallizing phase.

LLDPE/iPP/aPP blends. We will first examine the behavior of a 80/20 LLDPE/iPP blend where the iPP is finely dispersed in a LLDPE matrix. Since both polymers are capable of crystallization upon cooling from the melt, an "unmixed blend" sample was used in order to have a reference cooling scan. Such a sample was prepared using the same weight proportions of LLDPE and iPP as in a 20/80 melt mixed blend, but placing both polymers in a DSC pan separated by Aluminum foil (i.e., with no contact whatsoever between the two polymers, see ref. 10). Figure 4 (a) clearly shows the crystallization exotherm of the iPP at 108 °C followed by the crystallization of the LLDPE at 101 °C (Table 1), these peak temperatures (T_c) correspond to the crystallization of each component after heterogeneous nucleation in the bulk state. Cooling scans for the neat polymers agree with the T_c values of the unmixed blend (Table 1).

Figures 4 (a) and (b) compare the dynamic crystallization behavior of the "unmixed sample" with the melt mixed 80/20/0 blend. When the iPP is well dispersed in the LLDPE matrix, the high temperature exotherm that correspond to the formation of heterogeneously nucleated crystals of iPP (i.e. at 108 °C, see Table 1) disappears completely. In fact, it can be seen in Fig. 4 (b) that a phenomenon of fractionated crystallization of the iPP component follows in such a way that the iPP crystals can only form at the same temperature as those of the LLDPE matrix (i.e., in the exotherm exhibited by the blend at 102 °C, this would represent coincident crystallization as has been reported for other systems in ref. 2) and/or at lower temperatures, since a small second exotherm is observed at 86 °C which we have demonstrated that is associated with the lower temperature crystallization (i.e., fractionated crystallization) of the dispersed iPP phase (see below).

The addition of aPP to a LLDPE/iPP blend could be interesting because of the change in mechanical properties that might be induced in the system. The aPP used here is not

completely atactic as revealed by the fact that it is capable of crystallizing a modest amount (ΔH_c , at $10^\circ\text{C}/\text{min}$, is only 11 J/g as compared to 87 J/g for the iPP used here). Nevertheless, due to the low value of its crystallization enthalpy, if it is mixed with only LLDPE (Fig. 4(e)), its crystallization exotherm falls within the tail of the wide range crystallization exotherm that characterizes the cooling scans of LLDPE (10).

Figure 4 also shows the dynamic crystallization behavior of the ternary blends LLDPE/iPP/aPP (Figs. 4(c) and (d)), where the matrix is always 80% by weight of LLDPE and the 20% dispersed phase is a mixture of iPP and aPP of two different weight by weight ratios. The iPP component in these blends always exhibits a fractionated crystallization behavior regardless of the aPP content. However, the exotherm that corresponds to the low temperature crystallization of the iPP phase seems to be dependent on the aPP content, a fact that could be related to changes in the dispersion (i.e., in the mean particle size, shape or particle size distribution). We have measured the average particle size and size distribution by SEM for two of these blends and the results are shown in Table 1. When the dispersed phase is pure iPP the relative area of the low temperature exotherm amounts to approx. 25% of the total area and the average particle diameter is only $\sim 0.6\ \mu\text{m}$. If the dispersed phase has a proportion of 13/7 iPP/aPP the average particle diameter increases and correspondingly, the size of the low temperature exotherm decreases. It is also possible that the presence of the aPP is bringing new heterogeneities in the system that are active at higher temperatures than those at which the small low temperature exotherm appears.

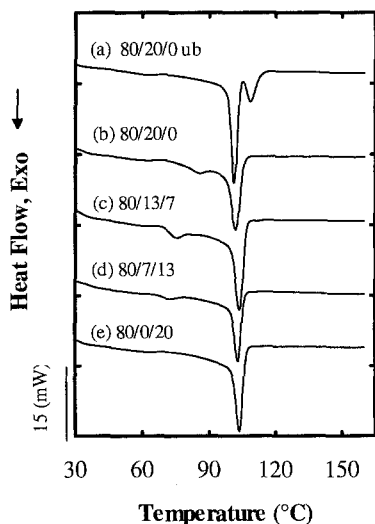


Figure 4. Crystallization exotherms of LLDPE/iPP/aPP blends. ub: "unmixed blend".

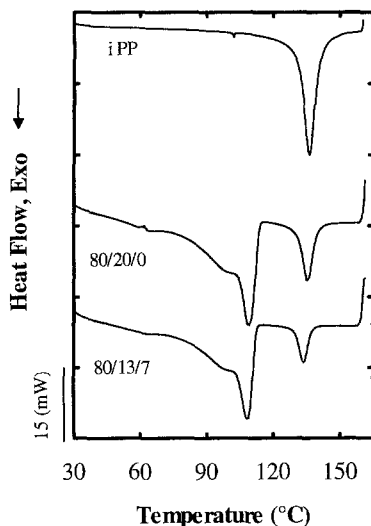


Figure 5. Crystallization exotherms of iPP and LLDPE/iPP/aPP blends after partial melting at $T_s = 162^\circ\text{C}$.

The fact that the low temperature exotherms that are displayed in Fig. 4 by all the blends with iPP forming at least part of the dispersed phase are due to the change in nucleation mechanism brought about by the confinement of iPP into very small particles was demonstrated by the self nucleation experiments that follow (11). It is well known that

polymers can be self seeded and a recent reference describes how such treatments can be efficiently performed using DSC (12). We have followed the method that Fillon et al. (12) have applied to pure iPP, in order to investigate the nucleation behavior of the iPP component in immiscible blends. The samples were first melted at high temperature (200 °C) for 3 minutes with the purpose of erasing any previous thermal history, then they were cooled at 10 °C/min to room temperature to create a "standard" crystalline state (12). Then the samples were heated at 10 °C/min up to the self nucleation temperature ($T_s=162$ °C, a temperature just above the peak of the melting endotherm, i.e., within "domain II" of the melting region, as defined by Fillon et al.), where partial melting took place for 5 minutes. The DSC traces shown in Fig. 5 were recorded immediately upon cooling from T_s . It can be seen how the T_c of the pure iPP shifts from 108 °C (Table 1) to 135 °C when it is self nucleated. The self-nucleated blends now exhibit a very clear separation between the crystallization of the self-nucleated iPP component at approximately $T_c=135$ °C and that of the LLDPE component that has been itself nucleated by the iPP and therefore its T_c has been shifted from 102 °C to 108-109 °C (Table 1, where SN stands for self-nucleation). We have previously shown that because of the fact that LLDPE is nucleated by iPP, iPP-rich blends where LLDPE is dispersed into a matrix of iPP do not exhibit fractionated crystallization of the LLDPE phase (6,7). It should be noted that the low temperature exotherm, that was present in the cooling scans of the blends (Fig. 4) at around 75-85 °C is now absent in the self-nucleated blends. The induction of a dispersed phase to crystallize at much lower temperatures than when it is in the bulk is due to the lack of enough heterogeneities that are active at low undercoolings. Table 1 shows that the average number of iPP particles in these blends is in the order of 10^{11} particles/cm³, such number is much greater than the usual number of heterogeneities present in commercial iPP (known to be active at low undercoolings, as judged by the number density of spherulites produced from such nuclei) approx. 10^6 heterogeneities/cm³ (12). In fact, Fillon et al. report that self-nucleation can increase the nuclei concentration to ca. 10^{12} - 10^{13} nuclei/cm³, this would be in line with our results, where after self-nucleation all the dispersed iPP seems to be crystallizing at high temperatures. A similar effect to that caused by self-nucleation, i.e., an enormous increase in the number of available nuclei, can be induced by the addition of a suitable nucleating agent with qualitatively similar results (1).

The effect of fractionated crystallization of the dispersed phase on the mechanical properties of the blends. It should be expected that any structural change in the dispersed phase of a two-phase material influences its mechanical properties. In the case of the LLDPE/iPP blends, upon quenching, iPP will start its crystallization process at lower temperatures in view of the results of the previous section. This could mean that these dispersed iPP particles will probably crystallize less than if it had all the necessary nuclei to start crystallizing at higher temperatures. Such behavior was experimentally verified for PS/iPP blends (1) and for PS/LLDPE blends (6). In fact, we have shown that in 80/20 LLDPE/iPP blends the yield strain was much larger than in blends of the same composition but with added nucleating agent, so that no fractionated crystallization was present (7). Table 2 shows a similar effect for the LLDPE/iPP/aPP ternary blends. In particular, it should be noted that pure LLDPE exhibited its typical double yielding behavior (13-14) while the blends and the pure iPP exhibited only one yield point. If the strain for the first yielding process of any of the blends is compared to the equivalent values for the neat polymers, it can be seen that the blend possesses a remarkably high strain at yield that must be the result of a highly effective plastic deformation mechanism. Such high deformability could be linked with currently unknown morphological details present in the dispersed particle, an area that clearly needs further work. The rest of the

mechanical properties exhibit a trend that approximately conforms to the additivity rule with respect to the composition.

Table 2. Tensile Properties of LLDPE/iPP/aPP blends.

Samples	% iPP	Tensile Modulus (MPa)	Yield Stress (MPa)	Yield Strain (%)	Break Stress (MPa)	Break Strain (%)
LLDPE 11U4	0	150 ± 10	8 ± 1 9 ± 1*	13 ± 2 33 ± 3*	25 ± 2	580 ± 40
iPP	100	780 ± 60	30 ± 1	9 ± 1	43 ± 2	470 ± 20
PE/iPP/aPP:						
80/0/20	0	120 ± 10	7 ± 0,5	32 ± 3	18 ± 1	580 ± 40
80/7/13	33,3	110 ± 10	8 ± 0,5	27 ± 3	17 ± 2	500 ± 50
80/13/7	66,6	180 ± 20	10 ± 0,5	27 ± 3	17 ± 2	430 ± 30
80/20/0	100	240 ± 20	12 ± 0,5	24 ± 2	21 ± 2	390 ± 30

*Second yielding of LLDPE 11U4 (13-14).

Conclusions

The degree of dispersion of immiscible polymer blends can be characterized not only by SEM observations but also by DSC measurements if the dispersed phase exhibits fractionated crystallization when dispersed into fine particles. If only DSC is used, a qualitative measure of the state of dispersion can be found but no information on the exact particle shape (i.e., droplets, ellipsoids or cylinders) will be gathered. Self-nucleation experiments are useful to ascertain the presence of fractionated crystallization. The plastic deformation capability of immiscible blends such as those prepared here can be increased by the morphological change induced by fractionated crystallization.

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