

THE INFLUENCE OF MORPHOLOGY AND COMPATIBILITY ON THE THERMAL AND MECHANICAL PROPERTIES OF POLYMER BLENDS

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Abstract

The influence of several structural parameters on the miscibility, morphology, thermal and mechanical behaviour of polyolefin blends was studied. Here, we only present data on two types of blends based on Polypropylene (PP) and on High Density Polyethylene (HDPE). The blends of Linear or Ultra Low Density Polyethylene (LLDPE or ULDPE) with Linear Polyethylene (HDPE) illustrate the effect of chain branching on the miscibility and the mechanical properties of the system. The blends of LLDPE or ULDPE with isotactic Polypropylene (PP) present examples of thermodynamically immiscible blends that are mechanically compatible and display interesting crystallization behaviour such that, depending on composition the blends can exhibit either nucleation of the PE by the PP or fractionated crystallization of the PP.

I. INTRODUCTION

We have studied the effect of structural variables such as molecular weight, branch type and their distribution on the morphology, thermal, rheological and the mechanical properties of polyolefin based blends. The systems examined include: HDPE and Ultra High Molecular Weight Polyethylene (1), Linear Low Density Polyethylene (LLDPE) and Low Density Polyethylene (LDPE) (2-6), TREF fractions of LDPE and LLDPE (7), PP (isotactic and atactic) and LLDPE (8-11), Polystyrene (PS) and LLDPE, and PS/PP (12-13). In this paper we present the relationship between calorimetric properties of selected polyolefin blends (that include HDPE and PP) and their mechanical behaviour.

II. EXPERIMENTAL

The materials used in this study were a LLDPE 1-butene copolymer (DuPont Sclair 11U4, $\rho = 0.922$ g/cc, 1.5 g/10 min MFI at 190 °C), an ULDPE terpolymer (Enichem, $\rho = 0.885$ g/cc, 1.5 g/10 min MFI at 190 °C), isotactic PP (Propilven J400, $\rho = 0.910$ g/cc, 3.0 g/10 min MFI at 230 °C), High Impact PP (a propylene-ethylene block copolymer, Propilven J440, $\rho = 0.910$ g/cc, 5.0 g/10 min MFI at 230 °C) and a HDPE (Altaven 7000F, $\rho = 0.956$ g/cc, 0.05 g/10 min MFI at 190 °C). The blends were prepared in a Haake Rheocord EU10 twin screw extruder at 40 rpm and 210 °C and later compression molded. A DSC7 Perkin-Elmer was used to record cooling runs (after complete melting

for 5 min, at temperatures of at least 20 °C above the apparent melting temperature, and subsequent heating runs). Tensile tests were performed in a T5003 JJ Lloyds equipment at 50 mm/min and instrumented impact tests in a MKII CEAST fractograph. A Rheometrics Dynamic Analyzer RDA II was used to perform dynamic rheological measurements using a 25 mm plate-plate geometry and applying a constant deformation of 10%.

III. RESULTS AND DISCUSSION

The crystallization behaviour of LLDPE, HDPE and their blends is presented in Figure 1a. These DSC scans should be compared with those of Figure 1b, where "unmixed blends" (prepared using the same weight proportions of HDPE and LLDPE as in the corresponding blend, but placing both polymers in a DSC pan separated by Aluminum foil, see ref. 6) scans are also presented. In Fig 1b it can be clearly observed the two main crystallization exotherms of both polymers in the blends, the high temperature peak corresponding to the crystallization of HDPE and the low temperature peak corresponding to the crystallization of LLDPE. If the 80/20 and the 20/80 blends are now considered, and the unmixed blends are compared to the melt mixed blends, it should be apparent that the blends are partially miscible and that a linear HDPE rich phase is co-crystallizing at high temperatures while those fractions of higher branch content are crystallizing at progressively lower temperatures in a very broad exotherm down

to 30 °C.

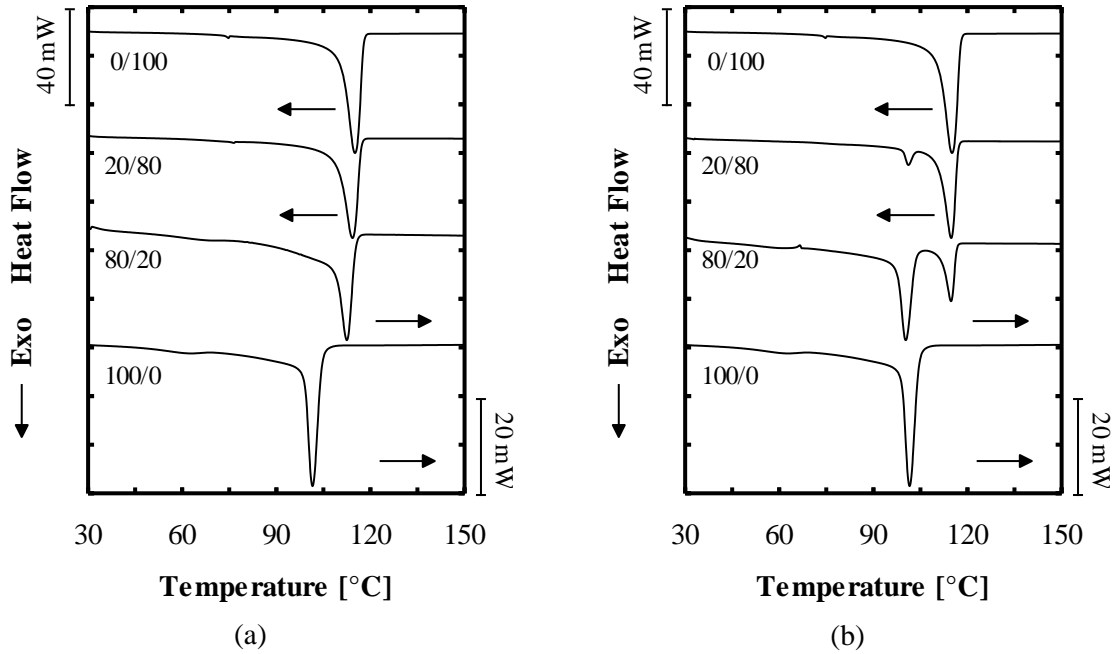


Figure 1. DSC scans of compression moulded sheets of LLDPE/HDPE blends cooled at 10 °C/min, from 170 °C: (a) Melt mixed blends and (b) Unmixed blends

The subsequent melting scans, presented in Figures 2a and 2b, confirm the above explanation in view of the absence of two melting peaks in the blends and

the observation of a melting point depression for the linear rich phase as compared to pure HDPE.

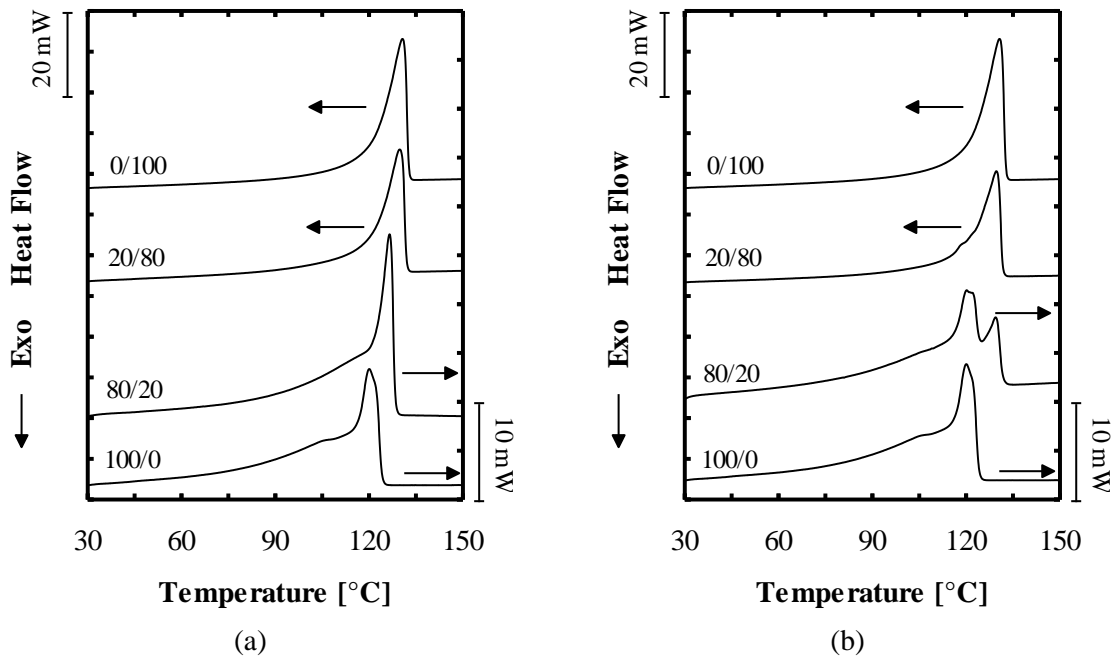


Figure 2. DSC scans of compression moulded sheets of LLDPE/HDPE blends heated at 10 °C/min, after the controlled

cooling shown Fig 1: (a) Melt mixed blends and (b) Unmixed blends

The 80/20 blend is a particularly good example since the unmixed blend shows that the detection of the individual components' peaks for that composition ratio is very clear (Fig 2b) and the melt mixed blend (Fig 2a) exhibits a very different melting endotherm where only one sharp peak is present at high temperatures and a broad shoulder at low temperatures in good correspondence to its crystallization behaviour (Fig 1a).

The crystallization behaviour for the ULDPE/HDPE blends is presented in Figure 3a and that of the corresponding unmixed samples in Figure 3b. The

results parallel those of the LLDPE/HDPE blends. In Fig 3b the two main crystallization exotherms of both polymers in the blends are evident, although in view of the vastly different ΔH_c , the 20/80 ULDPE/HDPE blend only exhibits a very small peak at approximately 76 °C for the crystallization of the most linear fraction of the ULDPE which is barely perceptible at the scale used in the graph. If the 80/20 blend is considered in Fig 3a, it should again be apparent that the blends are partially miscible and that a linear rich phase is co-crystallizing at around 112 °C while those fractions of higher branch content are crystallizing at progressively lower temperatures in an extremely broad exotherm down to 30 °C.

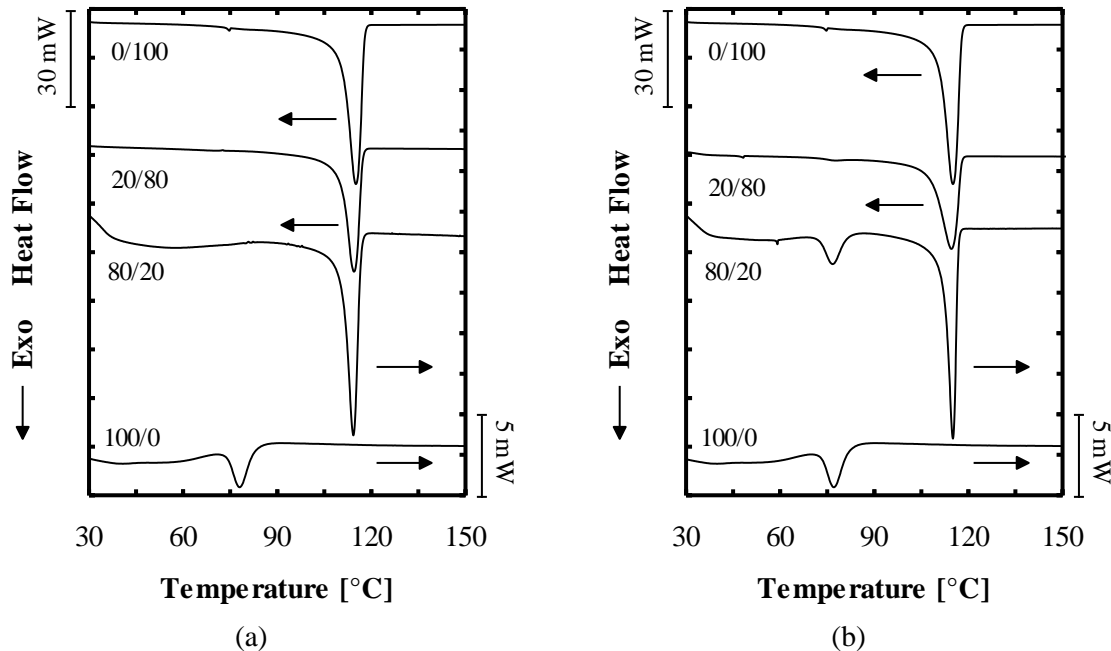


Figure 3. DSC scans of compression moulded sheets of ULDPE/HDPE blends cooled at 10 °C/min, from 170°C: (a) Melt mixed blends and (b) Unmixed blends

The subsequent melting scans confirmed the above explanation using identical arguments as above, i.e., absence of two peaks and a small melting point depression for the HDPE rich phase (Figures 4a and 4b). It is worth noticing that in this case the phase segregation during crystallization of the branched rich phase is more noticeable than with the LLDPE/HDPE blends in view of the higher branch content of the ULDPE. The results presented above for the linear and branched polyethylene systems are consistent with our previous studies on blending

TREF fractions of LDPE and LLDPE where we were able to detect a dependence of the miscibility on the branch content (7).

The second type of blends chosen to be presented here are the Polypropylene based LLDPE/PP and ULDPE/PP blends (see Figures 5 to 8). Figure 5a shows the crystallization behaviour at 10°C/min of the LLDPE/PP blends as compared to the unmixed blends (Fig 5b). Even though these blends exhibit only one main exotherm (Fig 5a) they are immiscible

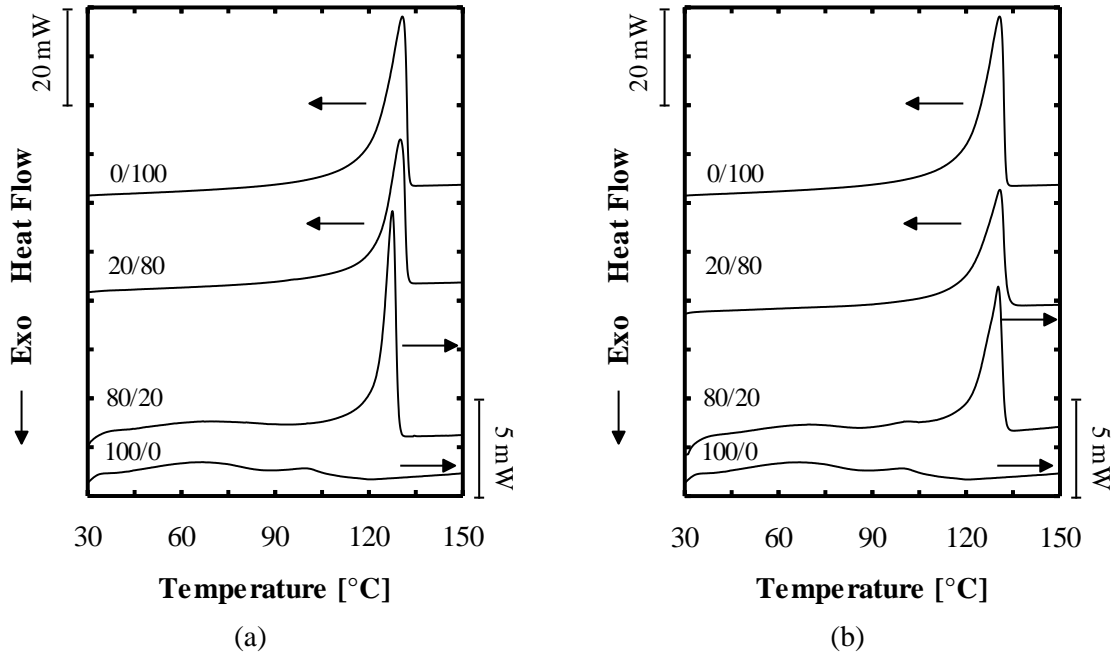


Figure 4. DSC scans of compression moulded sheets of ULDPPE/HDPE blends heated at 10 °C/min, after the controlled cooling shown in Fig 3: (a) Melt mixed blends and (b) Unmixed blends

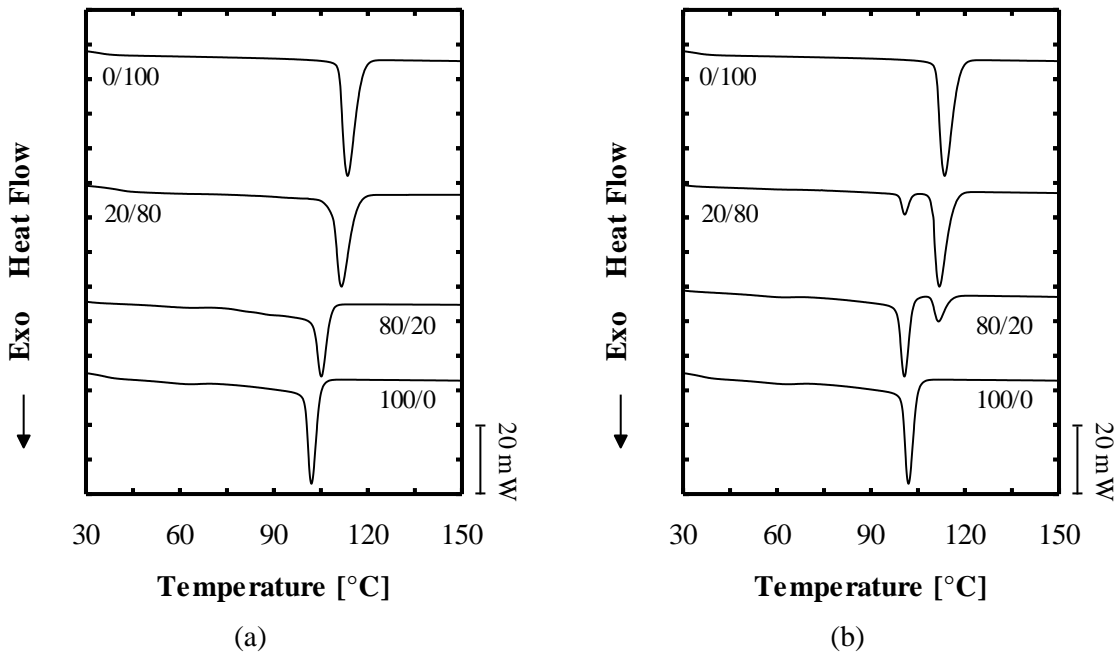


Figure 5. DSC scans of compression moulded sheets of LLDPE/PP blends cooled at 10 °C/min, from 200 °C: (a) Melt mixed blends and (b) Unmixed blends

The immiscibility of the system is evident from their melting behaviour presented in Figure 6. Their crystallization however is very peculiar in the case of the blends whose dispersed phase is the PP, i.e., the 80/20 blend. As can be gathered from Fig 5, the

expectation for an immiscible blend would be exactly the behaviour displayed by the "unmixed" blend (Fig 5b). The 80/20 melt mixed blend (Fig 5a) displays only one peak with a broad low temperature tail, where the heterogeneous

nucleation of the PP component is nearly completely suppressed as indicated by the shift of its peak crystallization temperature to lower temperatures.

This effect is due to the confinement of PP when it is well dispersed in the LLDPE matrix. If the number of droplets of PP as a dispersed phase is greater than the number of heterogeneities present in the system, fractionated crystallization occurs (10-14). The number of droplets for this composition is known (by SEM observations) to be of the order of

10^{11} particles/cm³ and polarized optical microscopy experiments have shown that the PP used here contains approximately 10^7 heterogeneities/cm³. In fact, it can be seen in Fig 5a that a phenomenon of fractionated crystallization of the PP component occurs in such a way that the PP crystallization can only start at a few degrees above the crystallization of the LLDPE matrix followed by coincident crystallization (see refs. 10-14).

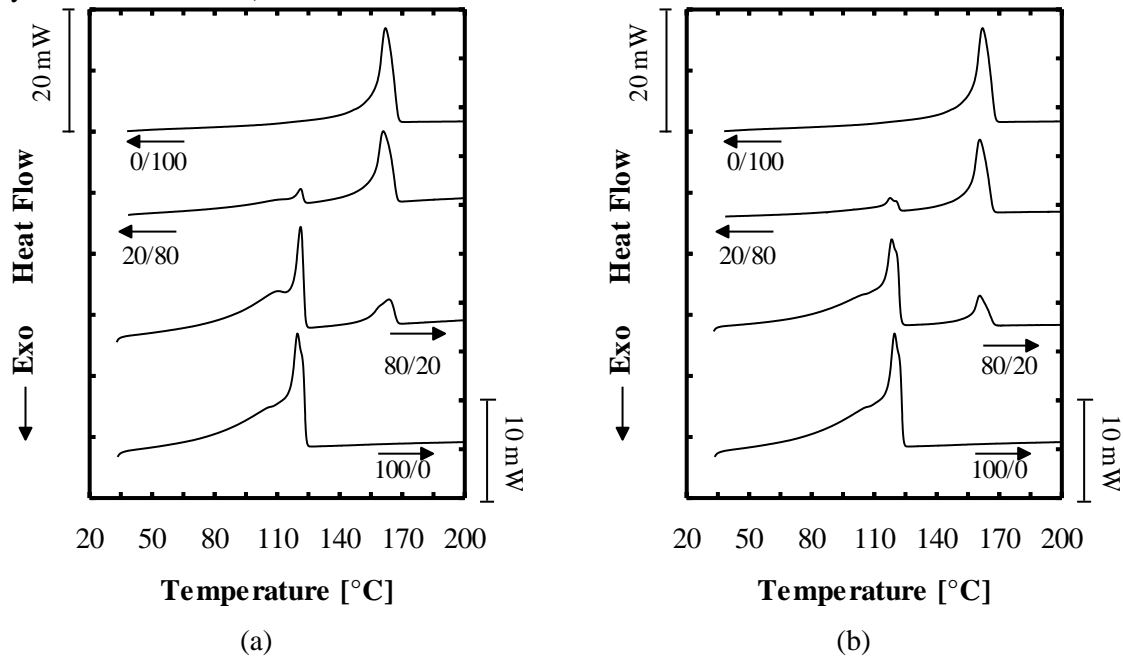


Figure 6. DSC scans of compression moulded sheets of LLDPE/PP blends heated at 10 °C/min, after the controlled cooling shown in Fig 5: (a) Melt mixed blends and (b) Unmixed blends

In the system ULDPE/PP the fractionated crystallization is even more noticeable for the composition 80/20 (compare Fig 7a and Fig 7b). The 80/20 melt mixed blend exhibits at least three low temperature exotherms well below the crystallization temperature of the PP homopolymer. Again the immiscibility of the system is demonstrated by the fact that its melting behaviour (Fig 8a) shows no qualitative differences with the melting scans of the unmixed blends (Fig 8b).

It should also be noted that the PP rich blends, and specially, the 20/80 LLDPE/PP blend, only exhibit one exotherm at temperatures that are very close to the crystallization temperature of the PP homopolymer (see Fig 5a). Such behaviour is due to the fact that the PP matrix can nucleate the dispersed PE causing a shift of its crystallization temperature in such a way that it overlaps with the PP exotherm

(this is the reason why the 20/80 LLDPE/PP exotherm for the melt mixed blend is broader than that of the PP homopolymer). For the 20/80 ULDPE/PP blend, the great difference in heat of crystallization between both components makes the signal of the ULDPE phase barely perceptible even for the unmixed blend (see Fig. 7b).

The ultimate demonstration that the peculiar crystallization behaviour of the 80/20 blends of LLDPE/PP and ULDPE/PP is due to the lack of nuclei, that induces a fractionated crystallization phenomenon, is provided by self nucleation experiments and by the addition of a nucleating agent (10, 13). Figure 9 shows that both strategies provide the PP with sufficient nuclei to start its crystallization at much higher temperatures than the PE matrices

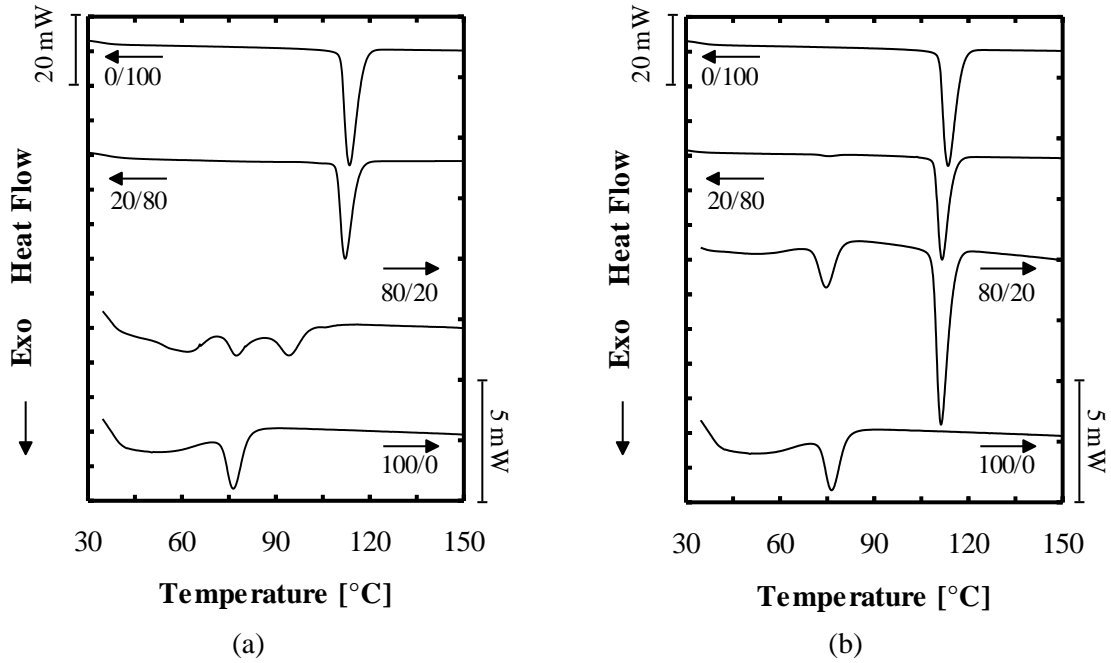


Figure 7. DSC scans of compression moulded sheets of ULDPE/PP blends cooled at 10 °C/min, from 200 °C: (a) Melt mixed blends and (b) Unmixed blends

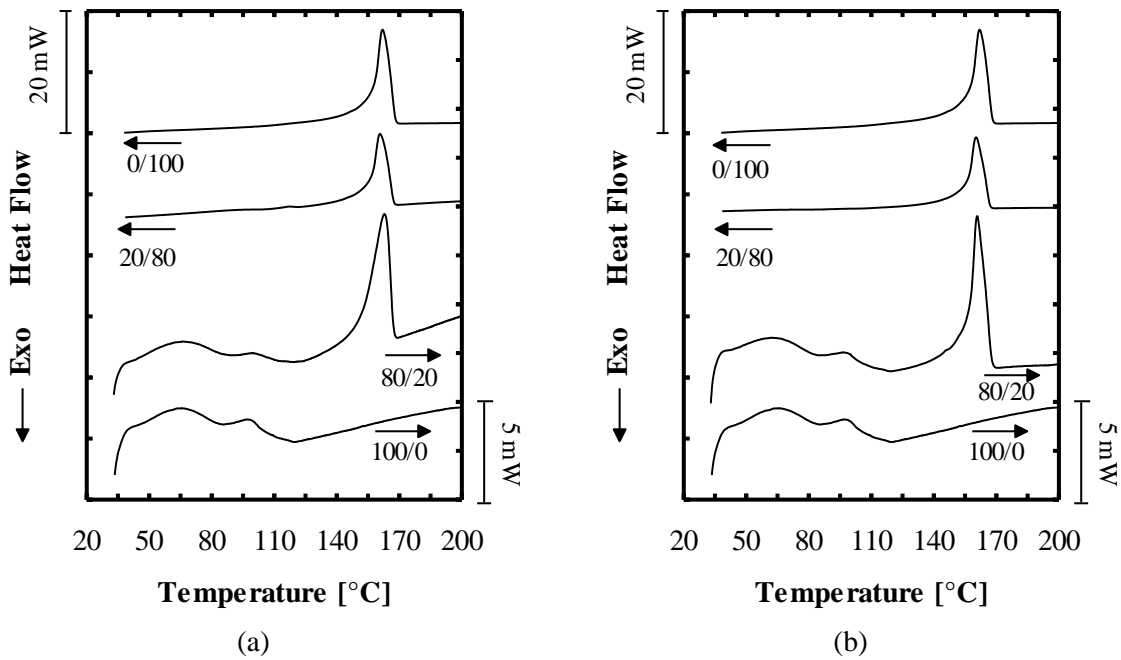


Figure 8. DSC scans of compression moulded sheets of ULDPE/PP blends heated at 10 °C/min, after the controlled cooling shown in Fig 7: (a) Melt mixed blends and (b) Unmixed blends

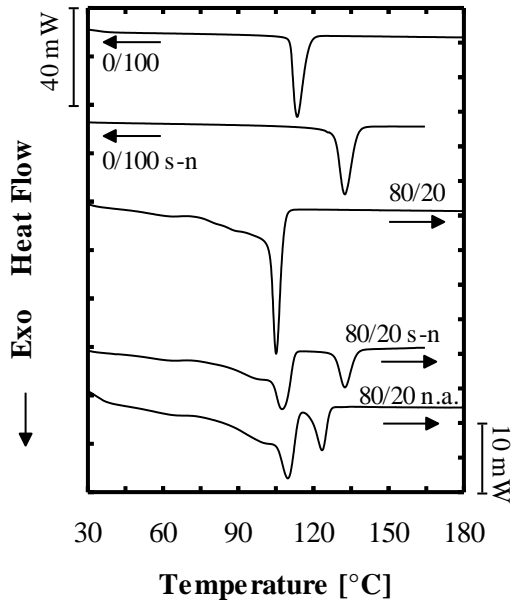
Figure 9 also demonstrates how the PP component in the blend can nucleate the LLDPE component as already discussed above. When the 80/20 blend is compared (Fig 9a) with either the self-nucleated 80/20 sample or the 80/20 with sorbitol it can clearly be seen that the LLDPE component is shifting its crystallization temperature to

temperatures higher than that of the neat LLDPE (Fig 5a). The effectiveness of the nucleating agent sorbitol in stopping the fractionated crystallization of the PP can also be demonstrated by dynamic rheological measurements as shown in Figure 10 for the first time, as far as the authors are aware.

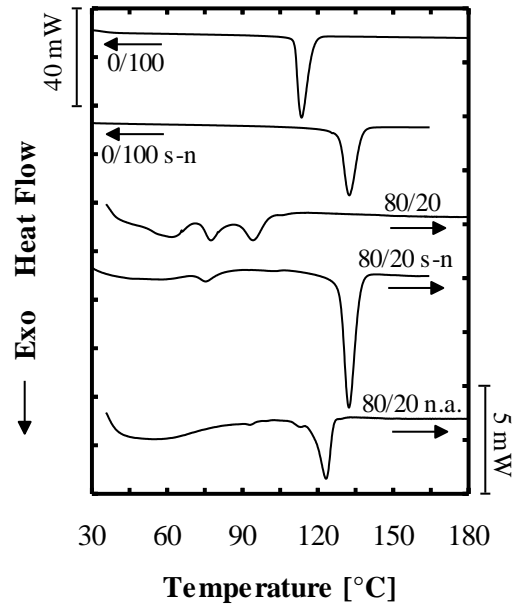
Figure 10a presents complex viscosity

measurements performed at temperatures at which both components are melted in the 80/20 LLDPE/PP

blend in view of the fractionated crystallization behaviour of the PP.

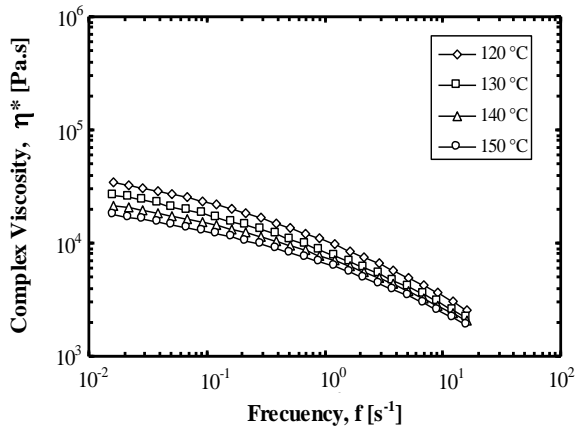


(a)

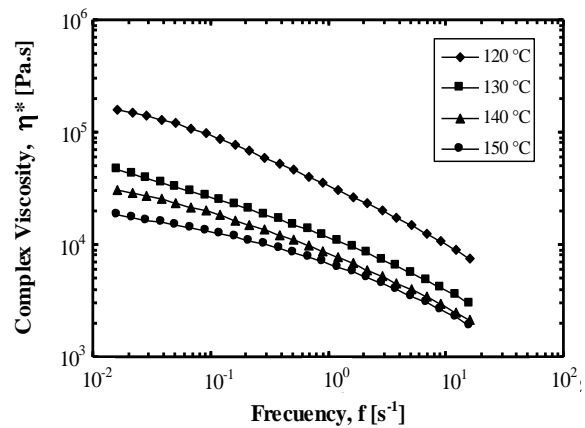


(b)

Figure 9. DSC scans of compression moulded sheets of (a) LLDPE/PP blends and (b) ULDPE/PP blends cooled at 10 °C/min, from 200 °C. s-n: self-nucleation at 164.5 °C using the method of ref. 10, and n.a.: with nucleating agent (0.1% w/w sorbitol)



(a)



(b)

Figure 10. Complex viscosity vs. Frequency, of 80/20 LLDPE/PP blends at different temperatures: (a) Without sorbitol and (b) With 0.1% sorbitol

When sorbitol is added it induces the crystallization of the PP at much higher temperatures (Fig 9a) that are in the range of the rheological measurements. Figure 10b shows how at 120 °C the complex viscosity is much greater than that for the sample without nucleating agent, since the PP has already crystallized at that temperature. The differences in complex viscosity between the samples with and without sorbitol decrease as the temperature

increase and only disappear at 150 °C when for both cases the samples are completely melted.

The mechanical properties of the blends are presented in Table I. For comparison purposes, it is also included in Table I results from ref. 15 on similar blends with Very Low Density Polyethylene (Enichem VLDPE terpolymer, $\rho = 0.900$ g/cc, 2.2 g/10 min MFI at 190 °C). The blends with HDPE are mechanically compatible and exhibit tensile

properties that conform to a simple rule of mixtures at room temperature producing an interesting material from the applications point of view. The properties can be tailored depending on the density

of the second component and blend composition in view of the partial miscibility exhibited by all the linear-branched polyethylene blends.

Table 1. Tensile and Impact Properties of blends. All samples were compression moulded at 170 °C and quenched in iced water.

<i>Blends</i>	<i>Tensile Modulus</i> [MPa] x 10 ⁻¹	<i>Yield Strain (1)</i> [%]	<i>Yield Stress (1)</i> [MPa]	<i>Break Strain</i> [%] x 10 ⁻¹	<i>Break Stress</i> [MPa]	<i>Total Impact Energy (2)</i> [J/m]x 10 ⁻¹
LLDPE/PP:						
0/100	72 ± 6	6.4 ± 0.5	33 ± 2	53 ± 4	52 ± 4	0.5 ± 0.2 (0.7 ± 0.3)
		8.3 ± 0.6	35 ± 1			
20/80	52 ± 4	6.4 ± 0.4	25 ± 1	45 ± 3	40 ± 2	1.0 ± 0.3 (0.3 ± 0.1)
		8.5 ± 0.4	27 ± 1			
80/20	24 ± 2	6.7 ± 0.3	12.1 ± 0.3	23 ± 5	18 ± 1	NB (1.7 ± 0.6)
		9 ± 1	13 ± 1			
		17 ± 3	13.5 ± 0.7			
100/0	12.3 ± 0.9	7.8 ± 0.4	7.6 ± 0.5	63 ± 5	28 ± 2	NB (7 ± 1)
		12.9 ± 0.5	8.7 ± 0.4			
		38 ± 2	9.9 ± 0.3			
VLDPE/PP:						
20/80	49 ± 4	6.3 ± 0.4	24 ± 2	47 ± 5	41 ± 4	2.1 ± 0.1 (0.9 ± 0.2)
80/20	6.9 ± 0.8	8.1 ± 0.6	3.5 ± 0.5	48 ± 4	20 ± 1	NB (2.0 ± 0.7)
100/0	5.0 ± 0.5	8.8 ± 0.8	3.0 ± 0.3	75 ± 5	30 ± 3	NB (4 ± 1)
ULDPE/PP:						
20/80	48 ± 5	6.9 ± 0.4	25 ± 1	46 ± 5	40 ± 3	6.6 ± 0.8 (0.8 ± 0.1)
80/20	4.3 ± 1.0	5.7 ± 0.4	1.8 ± 0.4	75 ± 6	13 ± 2	NB (2.1 ± 0.3)
100/0	2.7 ± 0.2	8.5 ± 0.6	1.4 ± 0.2	93 ± 5	21 ± 2	NB (5 ± 1)
High Impact PP J440	53 ± 3	6.0 ± 0.4	23 ± 2	47 ± 4	40 ± 3	6.6 ± 0.4 (0.4 ± 0.2)
		7.6 ± 0.4	25 ± 2			
LLDPE/HDPE:						
0/100	43 ± 2	7.3 ± 0.5	21 ± 1	54 ± 5	43 ± 3	-
		8.8 ± 0.8	22 ± 1			
20/80	32 ± 2	8.3 ± 0.7	18.3 ± 0.8	56 ± 5	38 ± 3	-
		9.8 ± 0.8	19.7 ± 0.9			
80/20	20.9 ± 0.8	7.1 ± 0.3	10.5 ± 0.5	63 ± 3	30 ± 3	-
		9.6 ± 0.8	11.8 ± 0.6			
VLDPE/HDPE:						
20/80	30 ± 2	8.4 ± 0.5	16.7 ± 0.8	53 ± 3	34 ± 3	-
80/20	10.9 ± 0.7	7.8 ± 0.4	6.0 ± 0.4	76 ± 3	28 ± 2	-
ULDPE/HDPE:						
20/80	25 ± 1	8.3 ± 0.6	14 ± 1	60 ± 5	34 ± 2	-
80/20	5.8 ± 0.4	8.6 ± 0.3	3.4 ± 0.3	89 ± 6	20 ± 2	-

(1) ASTM Standard D 638M, type V: First value correspond to A.1.13 Offset Yield at 1.5 %, second value correspond to first yield, third

value correspond to second yield when displayed.

(2): Instrumented Izod A Test at $T \approx 20^\circ\text{C}$. NB: No break. Values in brackets correspond to cryogenic condition at $T \approx -120^\circ\text{C}$.

A demonstration of this fact is shown in Fig. 11 where the tensile modulus of these blends is plotted as a function of the degree of crystallinity determined by density measurements (Fig 11a) and

by DSC (Fig 11b). It should be stated that the values from both determinations of crystallinity were linear functions of blend composition and followed closely the rule of mixtures.

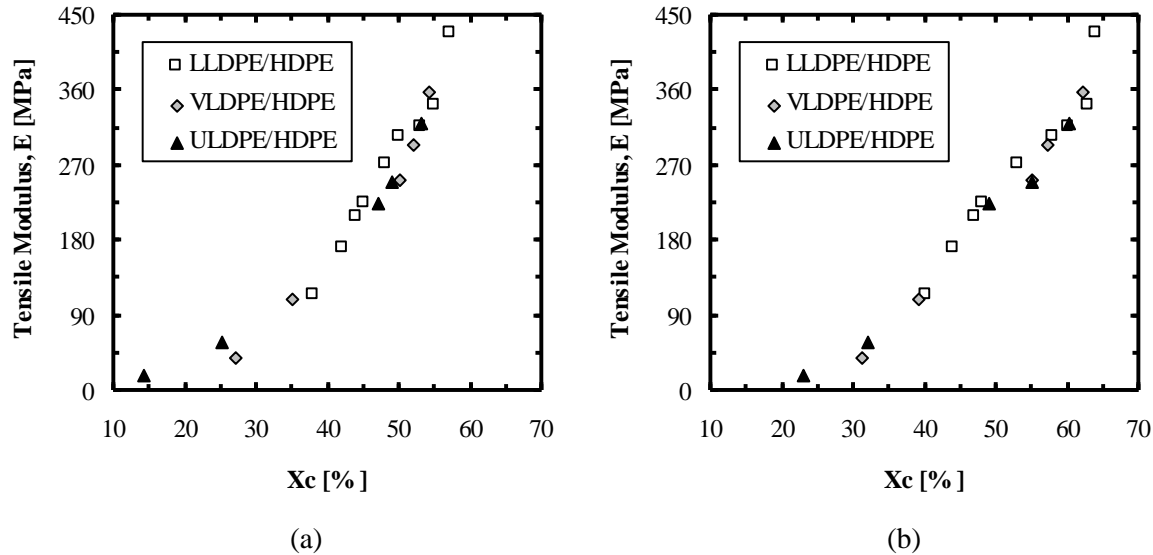


Figure 11. Tensile modulus (E) vs. degree of crystallinity (Xc) of HDPE based blends.

(a) Xc by density and (b) Xc by DSC.

In the case of the blends incorporating PP, the systems are immiscible but also somewhat mechanically compatible. Most tensile properties conform to a rule of mixtures or slight negative deviations from it except for the strain at yield. We have shown previously that in 80/20 LLDPE/PP 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 (9). Table I shows a similar effect for the VLDPE/PP and the ULDPE/PP blends. It can be seen that these blends possess a remarkably high strain at yield which must be the result of a highly effective plastic deformation mechanism. Finally, in the other end of compositions, the 20/80 PE/PP blends do not exhibit the fractionated crystallization phenomenon since as mentioned above the matrix crystallizes at higher temperatures than the dispersed phase (see Figs 1a, 3a, 5a, 7a) and is obviously capable of nucleating the dispersed phase, this constitutes an evidence of their interfacial interaction. This interaction might be responsible for the mechanical compatibility of

the blends reflected in Table I in the improvement of the impact strength with respect to pure PP at room temperature.

It is interesting to note how the impact strength of pure PP is improved with 20% addition of a branched polyethylene. Furthermore, the higher the branch content in the polyethylene (or the lower the density) the higher the impact strength obtained in the blend, a fact connected to the reduction in crystalline fraction with branch content (see Fig. 11). The 20/80 ULDPE/PP has an impact strength at room temperature that matches that of the commercial high impact PP copolymer chosen for comparison purposes. If the test temperature is lowered to -120°C the energy absorbed during impact is substantially reduced for all the materials tested since the mobility of the amorphous phases is severely restricted, a fact awaiting confirmation by dynamic mechanical testing. Even so, the blends with ULDPE exhibit higher impact resistance than the PP copolymer at very low temperatures

IV. CONCLUSION

The addition of ULDPE to HDPE and to PP produces blends that are mechanically compatible even though their miscibility is restricted. In the case of ULDPE/HDPE, the thermodynamic interaction is more pronounced and there are linear and branched fractions of both polymers capable of co-crystallization. In the case of the ULDPE/PP blends, the blends are immiscible but exhibit signs of interfacial interactions that together with morphologically induced crystallization peculiarities make the mechanical properties of the system attractive for practical applications.

V. ACKNOWLEDGMENTS

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