

Influence of Phase Structure on Impact Toughening of Isotactic Polypropylene by Metallocene-Catalyzed Linear Low-Density Polyethylene

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ABSTRACT: In the present study isotactic polypropylene (PP) and metallocene-catalyzed linear low-density polyethylene (mLLDPE) were blended together to obtain thermoplastic materials (compositions) with improved toughness. Structure–property relationships were determined for these compositions with the help of scanning electron microscopy (SEM). Special emphasis was made on tracing the morphological features that led to the optimum mechanical performance. A co-continuous type of structure was found to have much superior toughness as compared to a dispersed-matrix structural type, for blends comprised of the same components (PP and mLLDPE). The study showed the fascinating possibility of creating toughened PP blends by inducing a co-continuous structure. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 1011–1018, 2000

Key words: toughness; co-continuity; polymer blends

INTRODUCTION

Foremost among the physical properties of practical importance are stiffness and toughness. In pure polymers, they are generally inversely proportional to each other; that is toughness always decreases dramatically with increasing stiffness. Blending makes it possible to enhance toughness without a reduction in stiffness.

The properties of a conventional rubber/rigid polymer blend (a dispersed-matrix blend) are balanced, and the significant improvement in impact strength is offset by only a small reduction in modulus and tensile strength.^{1,2} The reduction of

stiffness is nearly proportional with the amount of the rubbery phase. In these systems, the high modulus brittle polymer remains as a matrix; whereas, the soft incorporated rubber particles serve as stress concentrators.

There is another major morphological type of two-phase system depending on the continuity of the phases: co-continuous. In a co-continuous type of morphology, two immiscible phases commingle in such a way that each phase remains continuously connected throughout the bulk of the blend.³ Thus, each component shares in the load-bearing process directly without the need for transferring the stress across a phase boundary, as in classical dispersed-matrix blends. The co-continuous morphology gives the optimum contribution from each phase in all directions without stringent requirements for adhesion between phases.³

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Pairs of polymer materials with a viscosity ratio ranging from 1 to 4 at the processing temperature and the processing range of shear rates would potentially provide either a co-continuous or a fine dispersed-matrix type of structure.^{3–25} Isotactic PP and mLLDPE were shown to satisfy this requirement.²⁶

The objective of this article is to define the range of PP/mLLDPE compositions with improved balance of stiffness–toughness properties and to show how this range relates to the structure of the compositions (i.e., to establish structure–property relationships).

EXPERIMENTAL

Materials

The materials used in the blends were: a grade of isotactic PP—GWM 22—with MFI = 4 [g/10 min], (2.16 kg, 230°C), provided by former ICI Australia (presently “ORICA”) and a grade of metallocene-catalyzed ethylene-octene copolymer ENGAGE EG 8200, referred to as mLLDPE, with MFI = 5 [g/10 min], (2.16 kg, 190°C), supplied by Dow Plastics (Dow Chemical).

Blends and Samples Preparation

Blends with weight ratio 90/10, 80/20, 70/30, 60/40, 50/50, and 40/60 of PP with mLLDPE were prepared using a Brabender twin screw compounding extruder DSK 42/7. The barrel temperature was set at 220°C for all zones. The screw speed applied was 120 rpm (2 rev/s).

Test pieces of the blends were prepared on a Remtron injection moulding machine. Screw speed was set at 100 rpm (maximal), injection velocity at 100 mm/s, and barrel temperature at 220°C for all zones.

Mechanical Characterization

Values of Young’s modulus from tensile testing were used to characterize the stiffness of the blends. Testing of the samples was performed using an Instron 4467 tensile testing machine according to ASTM D 638-87b.

Values of impact strength from notched Izod impact testing were chosen to characterize the toughness of the PP/mLLDPE blends. Testing was carried out using a Davenport Izod impact tester according to ASTM D 256-93a.

Microstructural Characterization

The morphology of the materials and their blends was observed by scanning electron microscopy (SEM) with a JEOL JSM 840 A scanning electron microscope. Two types of fracture surfaces were studied:

1. Cryofractured surfaces were prepared by immersing impact test bars in liquid nitrogen for 10 min, followed by mechanical fracture.
2. Surfaces of samples were fractured in Izod impact tests at room temperature.

The final step in samples preparation was a vacuum coating with gold using a DYNAVAC sputter coater. To minimize damage of fractured surfaces, caused by overheating of samples,²⁷ the periods of applying voltage (5 s) alternated with pauses of similar length. The number of repetition—voltage-pause—was 40.

For surfaces obtained at the room temperature, the beam voltage was set at 10 kV and the working distance at 15 mm. For cryofractured surfaces, the test parameters were 20 kV and 25 mm, correspondingly. These set-ups were the most suitable for the surfaces studied. The aim was to get a compromise between the best possible resolution and the maximal depth of field.

Analysis of the Micrographs

A manual method of analysis was undertaken. Micrographs of cryogenically fractured surfaces were analysed by “point counting” using the procedure described in Pickering.²⁸ According to that author, the volume fraction of a phase is equal to: (1) the area fraction in a random planar section; (2) the linear fraction in a random linear line through the three dimensional microstructure; and (3) the fraction of randomly distributed points that lie within that particular phase:

$$V_f = \frac{V_\alpha}{V} = A_f = \frac{A_\alpha}{A} = L_f = \frac{L_\alpha}{L} = P_f = \frac{P_\alpha}{P} \quad (1)$$

where V_f is the volume fraction of α -phase, V_α is the volume of α -phase in the specimen, V is the total volume of the specimen, A_f is the areal fraction of α -phase, A_α is the area of α -phase in a random planar section, A is the total area of the random planar section, L_f is the linear fraction of α -phase, L_α is the line fraction of α -phase in a

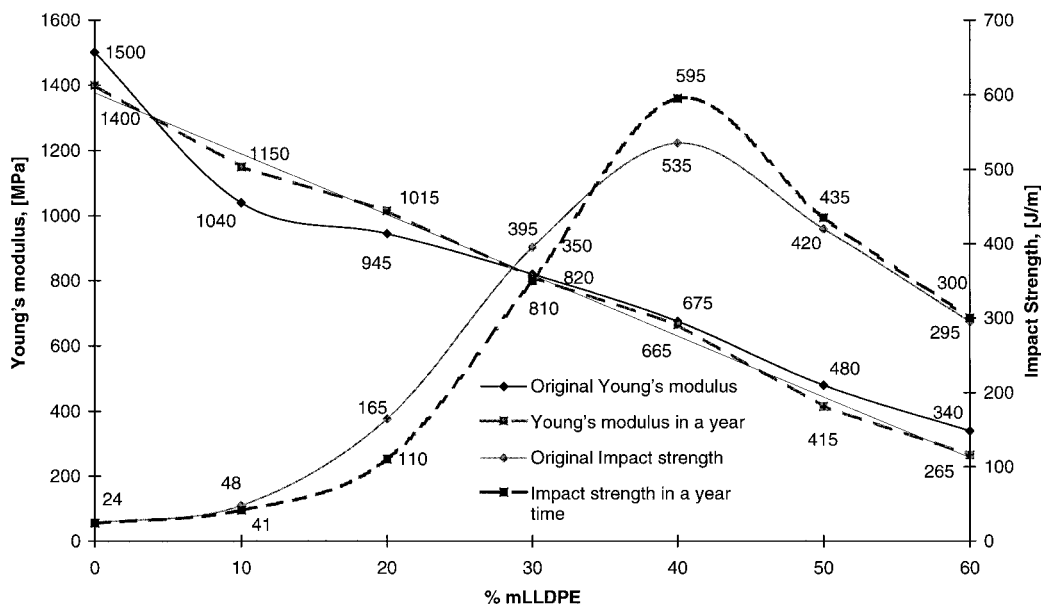


Figure 1 Influence of Composition on Stiffness/Toughness Properties PP/mLLDPE Blends.

random linear line, L is the total length of the random linear line, P_f is the point fraction of α -phase, P_α is the number of random points falling in the α -phase, and P is the total number of random points. This analysis assumes that the minor phase has a shape close to spherical.

In this study, the point fraction was calculated. A transparent rectangular grid having approximately 300 points with spacing corresponding to $0.5 \mu\text{m}$ was used. The grid was placed on the micrograph, and the fraction of grid points falling within boundaries of the circles (dispersed phase) was determined by manual counting. The accuracy of areal fraction measurements using the applied random two-dimensional (2-D) point count was given as 16% in the above-mentioned monograph.²⁸

RESULTS AND DISCUSSION

Mechanical Testing

Tensile (Instron) and notched impact (Izod) tests were conducted on the injection-molded pieces of the pure PP and its blends with 10, 20, 30, 40, 50, and 60% of mLLDPE. It is generally known that structure and mechanical properties of immiscible polymer blends might undergo changes over time. It has also been reported that blends of isotactic PP with mLLDPE from Dow Chemical

are immiscible.²⁹ Hence, mechanical tests were conducted twice: first, 1 week after the samples' preparation, and second, 1 year later.

The changes the blends have undergone over time are shown in Figure 1. They are as follows.

1. For all compositions and for the pure conventional PP, the changes to the values of Young's modulus were insignificant.
2. For the composition with 20% of mLLDPE, there was a decrease of about one third in the values of Notched Izod impact strength from the original value. For the other compositions the variations were not significant.

The changes in values of the impact strength and Young's modulus for the 80PP/20mLLDPE composition indicate that some morphological/structural changes occurred in this blend. The change in values of impact strength is more pronounced, which is as expected: the notched pendulum impact test, used in the present study, was found to be especially sensitive, even to a small variation in structure.³⁰

One possible reason for changes in mechanical properties (i.e., structure) of the blends might be presence of potential partial solubility of mLLDPE in PP, with a further phase separation over time. Partial solubility of LLDPE in PP was re-

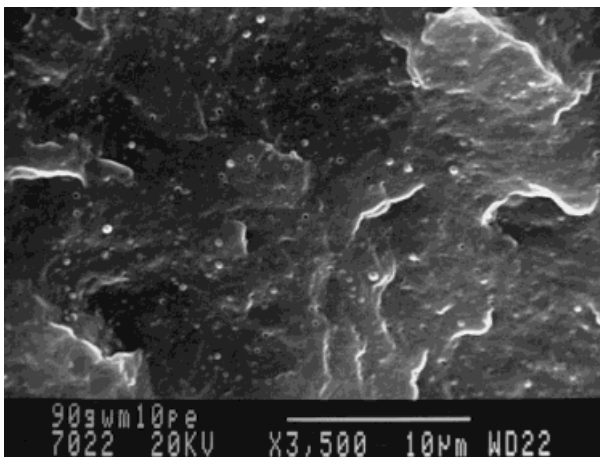


Figure 2 SEM Image of a Cryofractured 90PP/10mLLDPE Specimen, $\times 3500$.

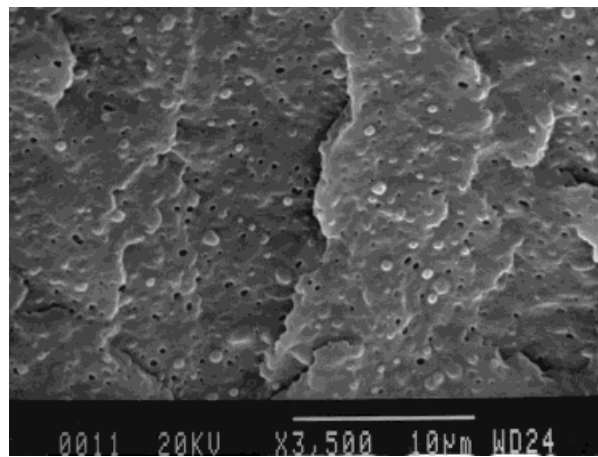


Figure 3 SEM Image of a Cryofractured 80PP/20mLLDPE Specimen, $\times 3500$.

ported by Dumoulin.^{31,32} Solubility in the melt for the same polymers was claimed by Rasoul.³³

Figure 1 also shows a linear reduction in stiffness and a nonlinear increase in toughness for the blends studied. The values of Young's Modulus for blends are additive, which is expected. Similar results were reported by Rasoul³³ for unfilled blends of PP with LLDPE. "Additivity" in values of Young's modulus, yield stress, strain at yield, and strain at break was also reported by Dumoulin³⁴ for blends of PP with LLDPE with various viscosity ratios of the components.

The impact strength grows slowly with an increase of mLLDPE phase up to a certain concentration (about 15–25%), and it starts to rise dramatically with the further increase of mLLDPE content in the blend. There is a pronounced maximum at 40% of mLLDPE. The underlying reasons for the synergistic improvement of impact strength in these systems was found by further morphological experiments, and in particular, by an SEM study.

SEM Study

SEM of Cryofractured Surfaces

A distinct two-phase structure is shown for compositions with 10–30% of mLLDPE in Figures (micrographs) 2–4. For all of these compositions, particles of mLLDPE are dispersed within a continuous matrix of polypropylene. The fracture surfaces exhibit both dispersed particles and holes (voids), where particles have been pulled out and are on the other fracture face.

Dispersed mLLDPE particles are 0.3–1.0 μm in size. This size was reported as a preferred size range for toughening blends with a ductile polymer matrix.² The apparent size of the dispersed particles seems to be larger with increasing mLLDPE content in the composition (see Table I).

The size of dispersed particles of LLDPE was found to increase with the increase in the proportion of LLDPE in LLDPE/PP blends.³⁵ A change of polydispersity toward a higher ratio of large particles with increasing concentration of the second polyolefin component (LDPE, EPR, EPDM, and PiB) in the PP blends was also reported by Bartczak.³⁶ Generally, in PP/PE blends, representing a two-phase system, the size of the dispersed domains increases with an increase in con-

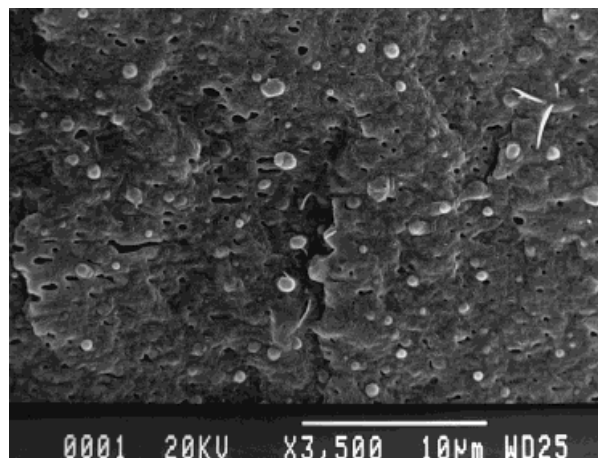


Figure 4 SEM Image of a Cryofractured 70PP/30mLLDPE Specimen, $\times 3500$.

Table I Influence of Composition on the Dispersed Particle Size and the Areal Fraction of the Dispersed Phase

Composition	Dispersed Particles Size, μm	Areal Fraction of the Dispersed Phase, %
90PP/10mLLDPE	~ 0.3	~ 3.0
80PP/20mLLDPE	~ 0.6	~ 4.5
70PP/30mLLDPE	~ 1.0	~ 7.0

tent of the dispersed phase, because the probability of the domains' coalescence becomes higher.³⁷

The fracture surfaces were analyzed for apparent fraction of mLLDPE content. The areal fraction of the dispersed phase was considered to be equal to the point/volume fraction and was calculated as described in section Micrograph Analysis. The data showing the influence of composition on the areal fraction of the dispersed phase are also presented in Table I.

The assumption was made that the volume (mass) fraction of a phase is equal to the areal fraction in a random planar section. From Table I, the areal fraction of the dispersed phase is in three to four times lower than expected.

These results contradict those of Liu and Truss,³⁸ who studied cryofractured surfaces of PP/LLDPE blends. The authors used specimens prepared from single-screw extruded sheets. According to Liu and Truss, the areal fraction of the dispersed phase found on the fracture surfaces seemed to be higher than expected for all blends. On the other hand, Dumoulin³¹ reported that the areal fraction of the dispersed phase was less than expected for PP/LLDPE blends prepared by injection moulding. He explained this discrepancy between the expected and the observed results by the presence of some partial miscibility in PP/LLDPE system. This miscibility was induced by the "extreme" conditions (high shear rates and high pressure) experienced by the blends during the injection moulding process.³¹

The difference between the calculated areal fraction and the actual amount of mLLDPE is interesting. Because the samples were prepared by injection molding, an equilibrium thermodynamic model cannot be applied. Rather, it may be supposed that a portion of mLLDPE can be found within the spherulites of iPP, as it has been shown in the recent article of Cser et al.³⁹ The

presence of the low crystallizable material (rubbers or LDPE) in interspherulitic and intraspherulitic regions of iPP was also claimed in studies on crystallization kinetic of iPP under isothermal conditions by a number of authors.^{37,40,41} Also, a further possible hypothesis is that the mLLDPE is partially miscible in the amorphous part of the PP. This hypothesis was later studied and is reported by Kukaleva et al.⁴²

For compositions with 40% (Fig. 5) and more of mLLDPE, both PP and mLLDPE phases are highly interconnected. The phase boundaries are diffuse. Only an insignificant number of dispersed particles can be distinguished. These rare particles might be either the PP or mLLDPE.

Overall, SEMs of cryofractured surfaces showed an important fact: there is a shortage in the dispersed particles for the system analyzed. This means that the blends studied do not have a "proper" dispersed-matrix type of structure.

SEM of the Fractured Surfaces

The following SEM study was performed on the specimens' fracture surfaces broken during notched Izod impact testing, conducted at room temperature. The fracture surfaces of the blends with 10, 20, 30, and 40% of mLLDPE are shown in Figures 6–9. For the composition with 40% of mLLDPE, the break was hinged, and great care was taken to ensure that the analyzed part of the surface was the "loose" part of the fractured specimen. For the compositions with 50 and 60% of mLLDPE, it was impossible to induce a brittle type of break, and, consequently, no pictures were

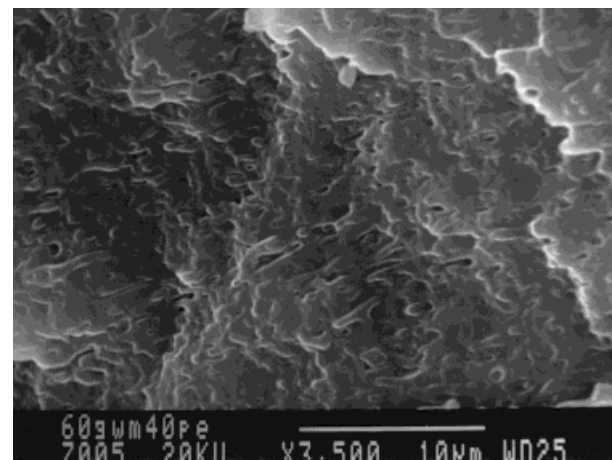


Figure 5 SEM Image of a Cryofractured 60PP/40mLLDPE Specimen, $\times 3500$.

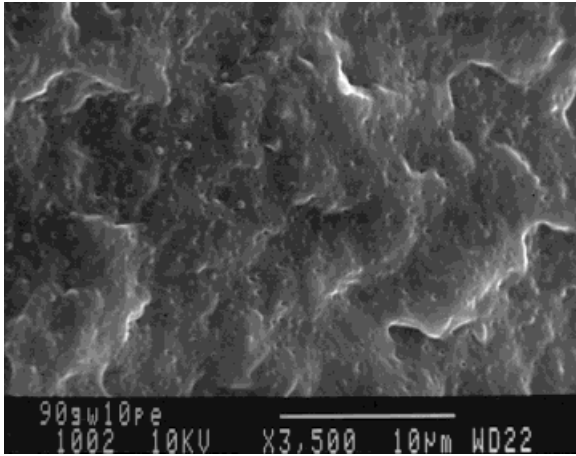


Figure 6 SEM Micrograph of a Fractured 90PP/10mLLDPE Specimen, $\times 3500$.

taken. Within the concentrations range of the mLLDPE phase from 10 to 40%, a radical change in the blends' structure occurs. The outline of this change is given below.

Blends with 10% mLLDPE. Figure 6 shows that a blend with 10% mLLDPE has a typical dispersed-matrix type of structure. The size of the uniformly distributed dispersed particles is homogeneous and approximately equal to $0.3 \mu\text{m}$. The fracture surface of the composition looks similar to the cryofractured surface of the same blend.

Blends with 20% mLLDPE. The fracture surface of the 80/20 blend (Fig. 7) also looks like the fracture surface of a traditional dispersed-matrix

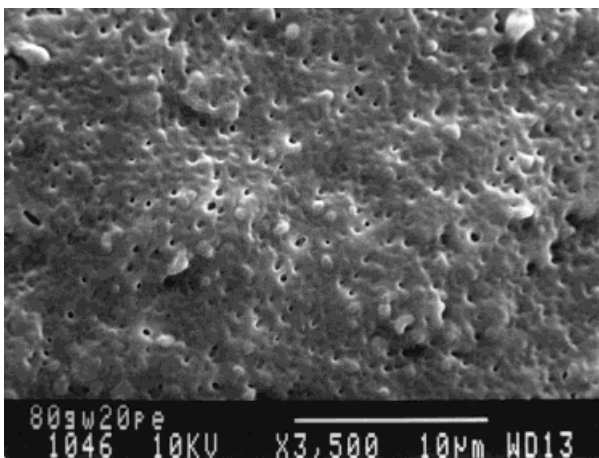


Figure 7 SEM Micrograph of a Fractured 80PP/20mLLDPE Specimen, $\times 3500$.

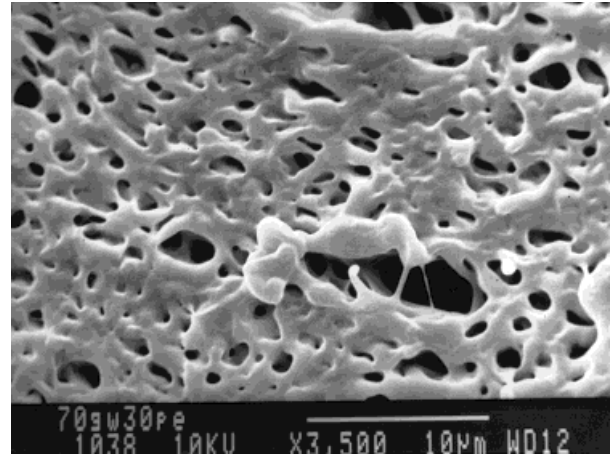


Figure 8 SEM Micrograph of a Fractured 70PP/30mLLDPE Specimen, $\times 3500$.

blend: the area is covered by hollows of a round shape from where the particles were pulled, with an insignificant amount of dispersed particles left on the surface. The size of the particles is about $0.6 \mu\text{m}$. The main difference between the fracture surface obtained at room temperature (Fig. 7) and the cryofractured one (Fig. 3) is that the matrix material—*isotactic PP*—demonstrates some ductility typical of a semicrystalline polymer at room temperature and does not do so at the temperature of liquid nitrogen. This ductility in the room temperature micrograph is apparent as blunt edges.

Blends with 30% mLLDPE. Figure 8 shows a three-dimensional (3-D) co-continuous structure

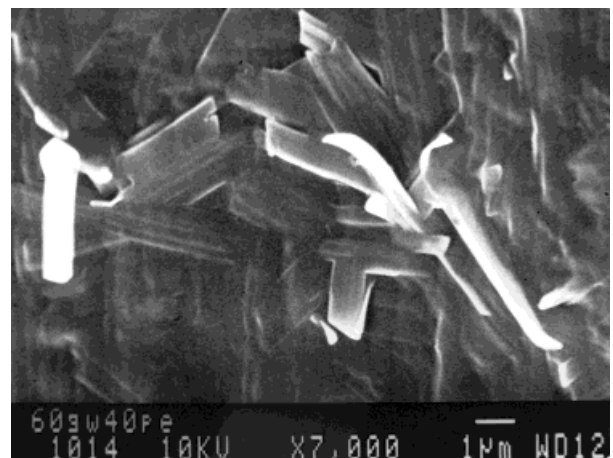


Figure 9 SEM Micrograph of a Fractured 60PP/40mLLDPE Specimen, $\times 7000$.

for the composition with 30% of the mLLDPE phase. The change in structure is considerable as compared to the composition with 20% mLLDPE (Fig. 7). It corresponds to the dramatic increase of impact strength seen for the same blend (Mechanical Testing section, Fig. 1). It seems likely that there is a direct relationship between the value of impact strength of the sample and the formation of co-continuity.

The dimensions of the mLLDPE phase, which was pulled out during the break, and, correspondingly, the dimensions of the "tunnels" left in the polypropylene matrix, are of the order of 2–8 μm . However, the dimensions of the dispersed phase were found to be about 1 μm from the analysis of the cryofractured surfaces of the same blend (SEM of Cryofractured surfaces section, Fig. 4).

The discrepancy in the dispersed phase dimensions might be explained by the following hypothesis:

1. The structure of the blend with 30% of mLLDPE is a combination of two structural types: dispersed-matrix, which was shown by cryofracture; and co-continuous, which became evident in the room temperature break.
2. Both of the phases were in a brittle glassy state at the temperature of liquid nitrogen and became more ductile at room temperature. Pictures of the fractured surfaces, induced at room temperature, show some ductility of PP matrix. Thus, at room temperature, it was feasible for the propagating crack to go "around" dispersed particles, not "through" them. On the other hand, a crack cannot go "around" the mLLDPE phase, which is continuous throughout the bulk of the blend, so yielding and pullout will occur, increasing apparent phase dimensions. The ductility of PP matrix at room temperature together with spatial continuity of mLLDPE phase in the bulk were the reasons for the great distortions (seen as deep "tunnels" of a large diameter in the micrographs) of the matrix and, consequently, for the large amount of energy required to "break" such a system.

The influence of the spherulitic structure of mLLDPE/iPP blends on their physical performance and relationships of the spherulitic structure and co-continuity are discussed in our later work.⁴³

Blends with 40% mLLDPE. Figure 9 shows unparalleled dramatic structural change for the compositions with 40% of the mLLDPE phase. The fracture surfaces of the blend shows neither dispersed-matrix nor co-continuous types of structure. The area shown in the micrograph is characterized by hard, brittle lamellae on a micrometre scale. There is no obvious explanation for such a change, and no literature on the subject has been found. It is clear that the SEM of fracture surfaces cannot clarify the phenomena and that further research is required.

CONCLUSIONS

There is a structural change in the iPP/mLLDPE blends, depending upon composition. The study conducted showed that up to a "concentration threshold," the blends belong to the dispersed-matrix structural type. With a further increase of mLLDPE content in the blends, the dispersed-matrix structure transforms to a co-continuous structure. It is also possible that the systems have a complex structure comprised of dispersed-matrix and co-continuous. In either case, it seems that it is the "contribution" of the co-continuity in the total structure that provides the improved toughness seen in the blends. A co-continuous type of structure has a much superior toughness as compared to a dispersed-matrix structural type, even for the blends comprised of the same components.

A unique structure, different from dispersed-matrix and co-continuous structures, was seen on a further increase of mLLDPE content in the blends. The structure was described as "lamellae," and it has not been previously reported.

Overall, the present study extends the traditional theory of rubber toughening of polymer blends. It shows the exciting possibility of creating toughened PP blends by inducing a co-continuous structure.

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