

# Morphology and Mechanical Properties of Blends of Linear Low Density Polyethylene and Poly(ethene-propene-1-butene)

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**ABSTRACT:** Blends of linear low density polyethylene (LLDPE) and ethene-propene-1-butene copolymer (t-PP) were obtained through mechanical mixing using a single-screw extruder with different compositions: 20, 40, 50, 60, and 80 wt % of t-PP. For this, two types of polyethylene were used: 1-hexene comonomer and 1-octene comonomer based. The same blends were prepared in a batch mixer and the torque and temperature were analyzed. The torque showed a decrease with increasing t-PP content, indicating better processability of the mixture in comparison with LLDPE.

The morphology of the blends was analyzed by SEM and showed a composition dependence. The mechanical properties of the blends were evaluated by tensile tests. The results revealed that the best properties were obtained in a 20% t-PP blend. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 1255–1261, 2006

**Key words:** blends; polyethylene; processing; mechanical properties; morphology

## INTRODUCTION

Linear low density polyethylenes (LLDPE) are a class of polyethylenes with linear chains containing only short chain branching due to the insertion of  $\alpha$ -olefin units during the copolymerization reaction of ethene with an  $\alpha$ -olefin, like 1-butene, 1-hexene, and 1-octene. Depending on the  $\alpha$ -olefin and the catalyst system used, LLDPE presents different microstructures with distinct thermal and mechanical properties. LLDPE has acquired great commercial importance, mainly in the packaging industries, because of its superior mechanical properties, compared to low density polyethylene (LDPE).<sup>1–4</sup>

The rheological properties of LLDPE differ from those of conventional LDPE, because of its linear structure, molar mass, and short chain distribution. Film extrusion lines designed for conventional LDPE can be modified to extrude LLDPE at optimum extrusion rates and to yield products with superior properties. At the low shear rates experienced during melt index measurement, LLDPE and LDPE are equally viscous. However, these resins behave differently at the higher shear rates experienced during film extrusion. LLDPE does not shear as thin as LDPE and is more viscous in the extruder. Necessary changes in screw, die, and air-ring are recommended to optimize

throughput rates, decrease power consumption, prevent heat buildup in the extruder, and permit better film production.<sup>5,6</sup>

Another way to improve the processability of LLDPE is blending it with LDPE. Blends of LDPE and LLDPE are regarded as excellent materials for film manufacture, because they combine the processability of LDPE and the good mechanical properties of LLDPE. In film industries, the bubble stability of LLDPE when extruded represents another processing problem, which is resolved by blending with LDPE.<sup>7–10</sup>

t-PP is a polypropylene random copolymer with low contents of ethene and 1-butene. Like LLDPE, the vinyl groups of comonomers are incorporated into the backbone, and the rest of the carbons of comonomer result in branches. Therefore, the crystalline phase of t-PP is due to the polypropylene fraction. Copolymerization with ethene and 1-butene causes a decrease in the melting and crystallization temperatures and in crystallinity. The mechanical properties of polypropylene are also modified by copolymerization. For example, a decrease in the modulus and yield stress and an increase in the elongation at break is observed.<sup>11</sup> These changes make this terpolymer appropriate to blend with LLDPE for industrial packaging, because these blends are easily processable with good mechanical properties.

Rana et al. prepared blends of metallocenic linear low density polyethylene (MCPE) with a high density polyethylene (HDPE), an isotactic polypropylene (i-PP), a copolymer of propene and ethene (co-PP), and a

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TABLE I  
Typical Characteristics of the Polymers used in this Study

Properties	LLDPE(H)	LLDPE(O)	t-PP
Comonomer (wt %) <sup>a</sup>	9.0% 1-hexene	10.0% 1-octene	2.0% ethene + 6.0% 1-butene
$M_w$ (g/mol) <sup>b</sup>	223000	228000	157000
$M_n$ (g/mol) <sup>b</sup>	46000	44000	37000
$M_w/M_n$	5	5	4
I.F. (g/10 min) <sup>c</sup>	1	1	6
$T_f$ (°C) <sup>d</sup>	130	127	135
$T_c$ (°C) <sup>d</sup>	107	102	93
Density (g/cm <sup>3</sup> ) <sup>e</sup>	0.920	0.920	0.910
$\chi_c$ (%) <sup>d</sup>	45	45	36

<sup>a</sup> Calculated from <sup>13</sup>C NMR data at 125°C in 1,2,4-trichlorobenzene.

<sup>b</sup> GPC at 125°C in 1,2,4-trichlorobenzene.

<sup>c</sup> ASTM-D1238 at 190°C and 2160 g.

<sup>d</sup> DSC.

<sup>e</sup> Supplied by manufacturer.

terpolymer poly(propene-*co*-ethene-*co*-1-butene)-t-PP. The results showed that the compatibility of MCPE with these polymers increases in the following order: i-PP < *co*-PP < t-PP < HDPE, indicating that t-PP is more adequate to LLDPE blends when compared with other polypropylene copolymers.<sup>12</sup>

In the present study, we compare the effect of two types of LLDPE with different microstructure, type, and distribution of the comonomer on the mechanical and morphological properties of LLDPE/t-PP blends.

The two LLDPE used to prepare blends have different types of comonomer distribution, although the total comonomer concentration in both polyethylenes was the same, as demonstrated by <sup>13</sup>C NMR analysis. LLDPE with 1-hexene as comonomer (LLDPE(H)) has higher molecular chain fraction with low quantities of comonomer than LLDPE with 1-octene as comonomer (LLDPE(O)). Previous results from X-ray diffraction, differential scanning calorimetry, and dynamic-mechanical analysis showed that these polymers are immiscible in the crystalline and amorphous phase, as viewed, but the crystallization and melting behavior of the polymers as well as the unit cell of both crystalline phases do not change. At 80 wt % of LLDPE, the crystallization of t-PP is shifted to lower temperatures and this effect is more evident for LLDPE(H)/t-PP blends. The microstructure of LLDPE influences the dynamical mechanical behavior, mainly in the temperature range of relaxations of the LLDPE crystalline phase.<sup>11</sup>

## EXPERIMENTAL

### Materials and blend preparation

The polymers used in this study were obtained from commercial sources. Some properties are listed in Table I. Two types of LLDPE synthesized by Ziegler–Natta catalysts: 1-hexene comonomer (LLDPE(H)) and

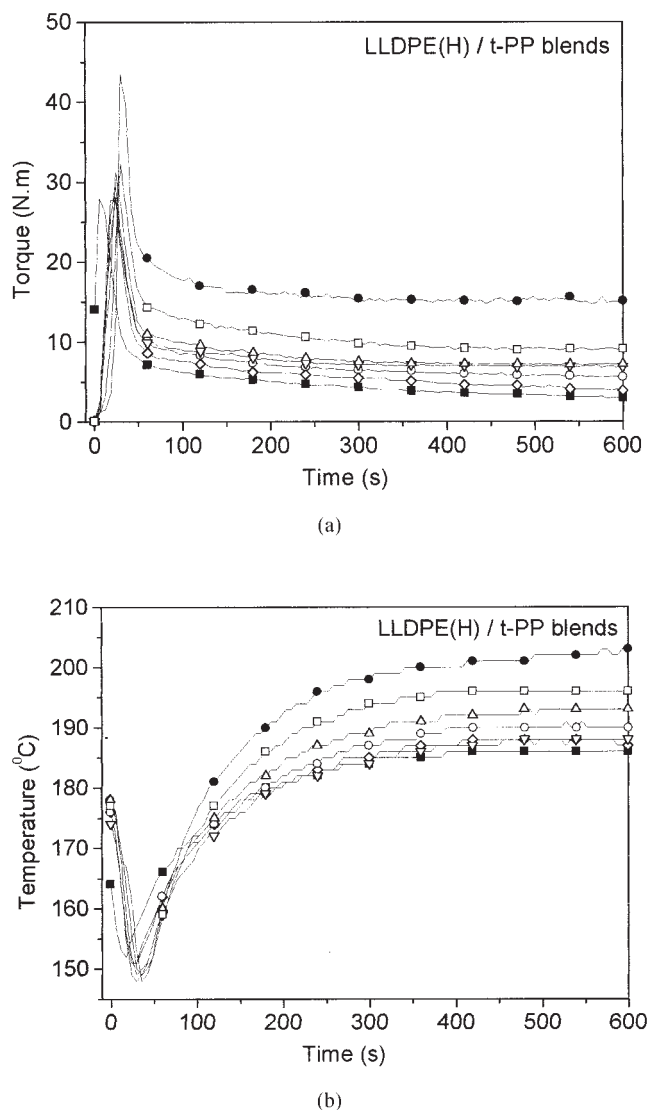
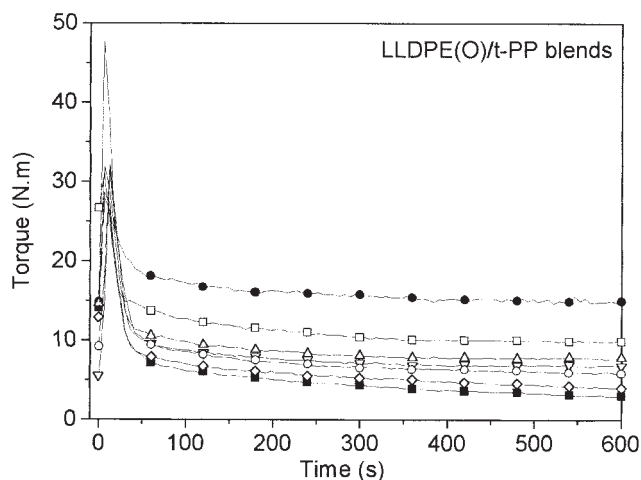
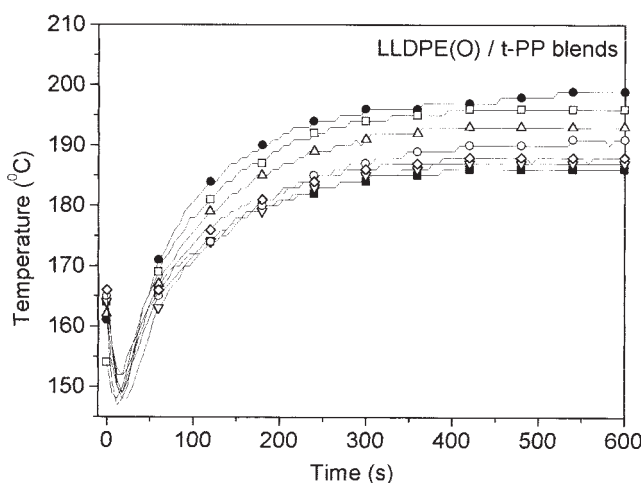


Figure 1 Typical batch mixer curves for LLDPE(H)/t-PP blends. (a) Torque–time curves and (b) Temperature–time curves. t-PP (wt %): 0(●), 20(□), 40(△), 50(▽), 60(○), 80(◇), and 100(■).



(a)



(b)

**Figure 2** Typical batch mixer curves for LLDPE(O)/t-PP blends. (a) Torque–time curves and (b) Temperature–time curves. t-PP (wt %): 0(●), 20(□), 40(△), 50(▽), 60(○), 80(◇), and 100(■).

1-octene comonomer (LLDPE(O)) were blended with poly(ethene-propene-1-butene), and t-PP. The LLDPE(H) and t-PP were supplied by Braskem (Brazil) and LLDPE(O) was supplied by Dow Plastics (USA). Five blends were prepared for this study with 20, 40, 50, 60, and 80 wt % of t-PP. The blends were prepared in a single-screw extruder, with five zones under barrel temperatures of 160, 180, 200, 205, and 215°C from the hopper to the die and a screw speed of 120 rpm. The screw has a Madock mixer and  $L/D = 32$ .

**Torque measurements**

The polymer blends were also prepared by melt-mixing in a model 600 Haake Rheomix equipped with roller blades and a mixing head, with volumetric ca-

capacity of 69 cm<sup>3</sup>. The mixing conditions were 40 rpm, 180°C, and 10 min of processing time. The components in pellet forms were premixed before being fed into the mixer. The pure polymers were also subjected to the same procedure. The investigated compositions of blends were the same as for extrusion. The melt temperature and torque were continuously recorded during the mixing period.

**Tensile testing**

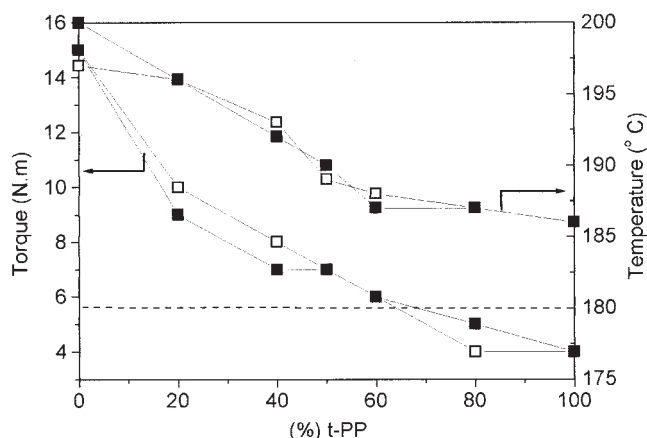
The tensile properties were evaluated using an EMIC model DL-2000 in accordance with ASTM D1708, using a cross head speed of 100 mm/min and distance between the grips of 22.9 mm. The samples were compression molded to sheets with 1.20 mm of thickness in a rectangular stainless steel mold, using a heated electric press under a pressure of 1.10 MPa and a temperature of 180°C for 5 min, then allowed to cool slowly to room temperature. All test specimens were prepared by die-cutting and conditioned prior to testing for 48 h at 50% humidity and a constant temperature of 23°C. The testing was performed under the same conditions.

**SEM**

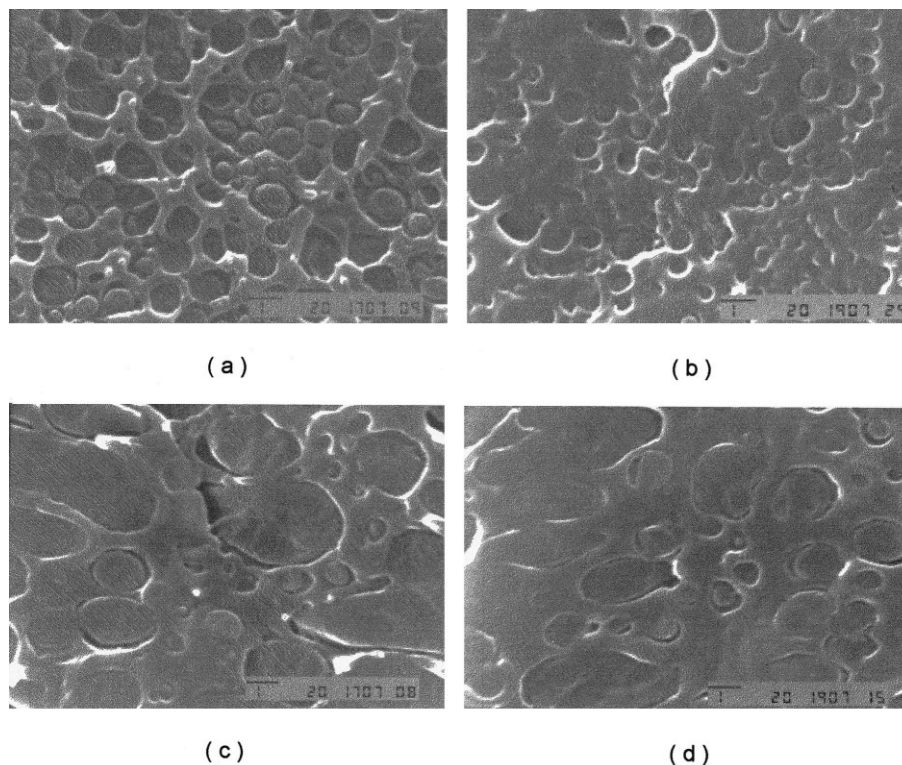
A JEOL JSM-T300 scanning electron microscope was used to examine the morphology of the blends. The microscope was operated at a voltage of 20 kV. Fractured surfaces were prepared by breaking the tensile specimens at liquid nitrogen temperature and sputtered with gold.

**RESULTS AND DISCUSSION**

To investigate polymer and blend processability, samples were made in a Haake Rheomix 600 mixer. The



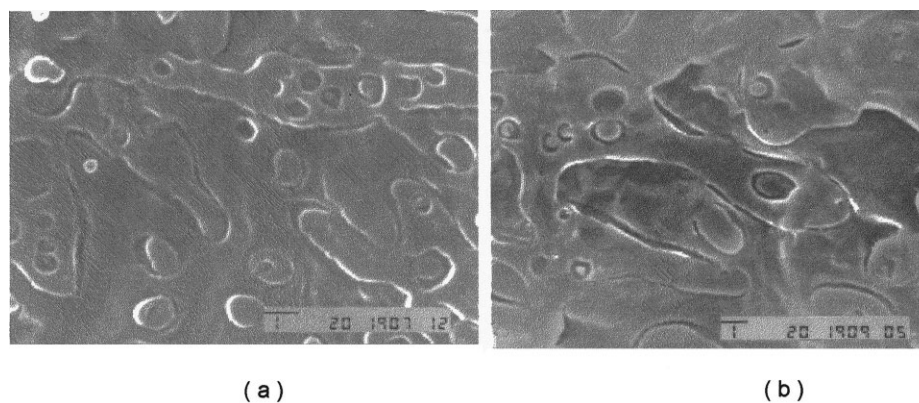
**Figure 3** Compositional dependence of torque and temperature as a function of t-PP content for (○)LLDPE(H)/t-PP and (□)LLDPE(O)/t-PP blends.



**Figure 4** Scanning electron micrographs of tensile test bar fractures of LLDPE/t-PP blends. (a) and (c) show compositions of 80/20 and 60/40 for LLDPE(H)/t-PP blends; (b) and (d) show compositions of 80/20 and 60/40 for LLDPE(O)/t-PP blends.

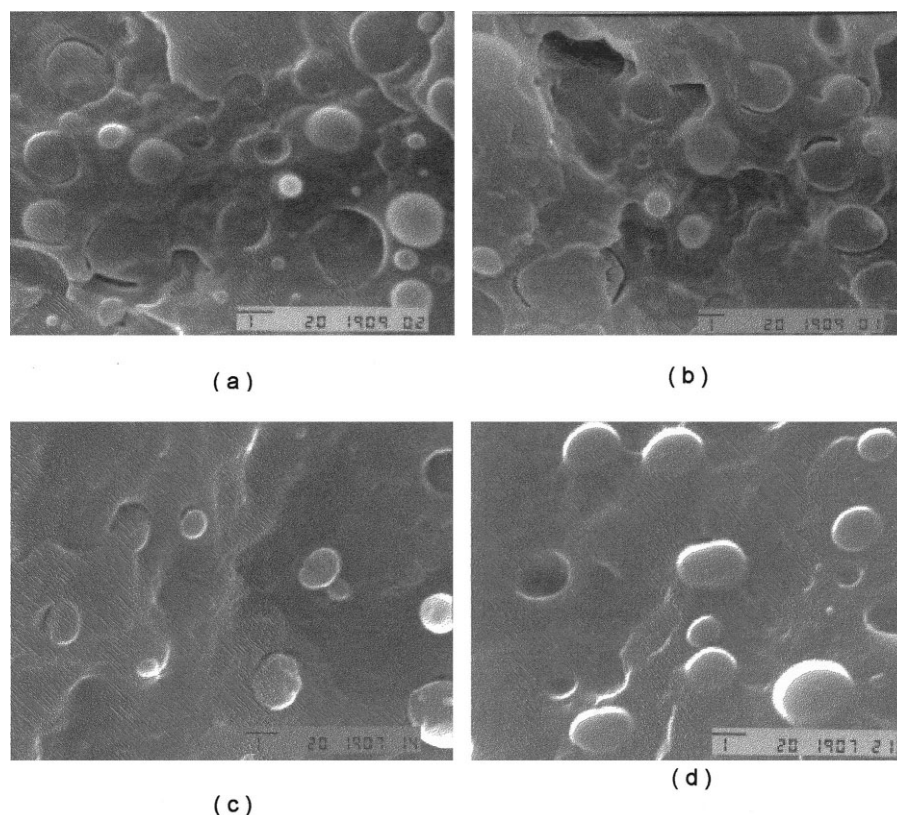
torque and temperature as a function of time are shown in Figures 1 and 2 for LLDPE(H)/t-PP and LLDPE(O)/t-PP blends. Batch mixers are usually fitted and calibrated with a torque meter. Because of the small dimensions of the mixing chamber, torque data measured by the torque meter are reasonably representative of the actual torque exerted on the polymer melt. Typical curves of torque as a function of time is shown in Figures 1(a) and 2(a). They show a region that correspond to the steady state, where equilibrium torque values are achieved and may be taken as pro-

portional to the viscosity of the system at the temperature and shear rate involved. The temperature of the mixture as a function of time also achieves a steady state, [see Figures 1(b) and 2(b)]. In this work, the torque and temperature at the equilibrium of the melt is found to decrease with an increase in the t-PP content. For most samples, the temperature in the mixing chamber is higher than the programmed temperature as a consequence of the energy dissipation due to shear. High torque and temperature are associated with higher shear, therefore leading to greater diffi-



**Figure 5** Scanning electron micrographs of tensile test bar fractures of LLDPE/t-PP 50/50 blend. (a) LLDPE(H)/t-PP and (b) LLDPE(O)/t-PP.





**Figure 6** Scanning electron micrographs of tensile test bar fractures of LLDPE/t-PP blends. (a) and (c) show compositions of 40/60 and 20/80 for LLDPE(H)/t-PP blends; (b) and (d) show compositions of 40/60 and 20/80 for LLDPE(O)/t-PP blends.

culty in the processing. The blends with 20% of t-PP show a decrease in the torque and temperature of processing compared with pure LLDPE, quite clearly indicating better processing. The t-PP makes the processing easier, with the torque and temperature decreasing and thus requiring lower energy for production.

Figure 3 shows the behavior of torque and temperature as a function of t-PP quantity in the blends. The points in Figure 3 correspond to the torque at 400 s of processing, relating to the steady state. The dashed line in the Figure 3 represent the temperature programmed in the chamber mixer, which is 180°C. LLDPE is more viscous than t-PP under the same processing conditions. The torque and temperature show

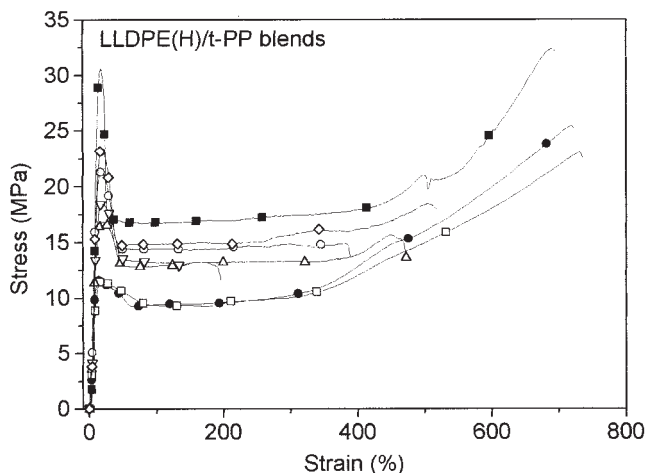
a decrease with an increase in the t-PP content in the blends, showing a better processability with increasing quantities of t-PP.

### Morphology

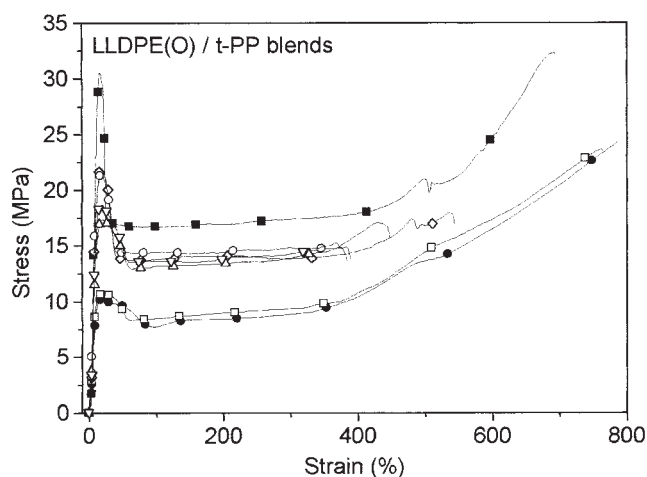
The morphology of polymer blends is mainly affected by three factors: interfacial tension, rheological properties, and blend composition. In this work, two types of LLDPE were used to prepare the blends, both with similar viscosities but different microstructures. The morphology of the blends was shown to be dependent on the composition. For all blend compositions, the systems are clearly immiscible with distinct phase separation in all compositions.

**TABLE II**  
Size of the Dispersed Phase from Several Blend Compositions

t-PP (%)	Dispersed phase	Diameter of dispersed phase (μm)	
		LLDPE(H) blends	LLDPE(O) blends
20	t-PP	0.5–1.0	0.5–1.0
40	t-PP	2.0–5.0	2.0–5.0
50	co-continuous	—	—
60	LLDPE	1.0–2.0	1.0–2.0
80	LLDPE	1.0–2.5	1.0–2.5



(a)

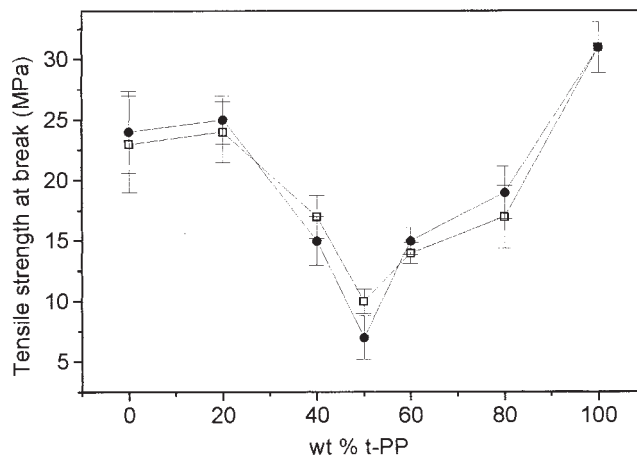


(b)

**Figure 7** Stress-Strain curves as a function of t-PP content for LLDPE/t-PP blends. (a) LLDPE(H)/t-PP and (b) LLDPE(O)/t-PP. t-PP (wt %): 0(●), 20(□), 40(△), 50(▽), 60(○), 80(◇), and 100(■).

At lower t-PP contents (20–40%), a typical morphology is spherical t-PP in the LLDPE matrix; see Figure 4. Blends containing 20 wt % of t-PP present good domain distributions as spherical particles of varying sizes dispersed within a continuous LLDPE matrix, as seen in Figure 4(a,b) for LLDPE(H)/t-PP and LLDPE(O)/t-PP blends, respectively. The domain size varies between 0.5 and 1.0  $\mu\text{m}$ . At this composition, the mechanical properties are comparable to pure LLDPE, independent of the LLDPE used. By increasing the quantity of t-PP, the sizes of the spherical particles also increase. The size distribution is very irregular with size domains of 0.5–5.0  $\mu\text{m}$ ; see Figure 4(c,d) for LLDPE(H)/t-PP and LLDPE(O)/t-PP blends, respectively.

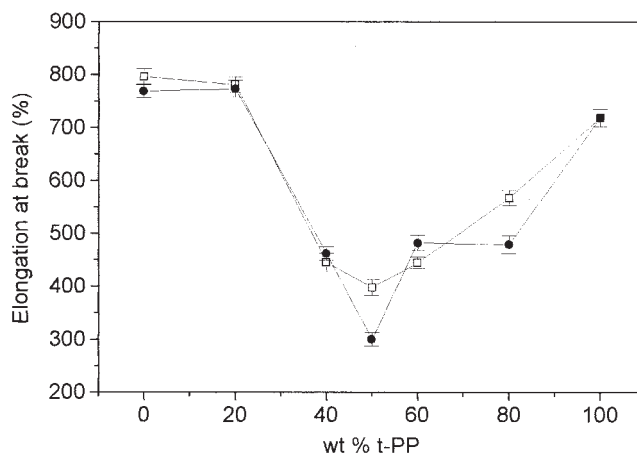
At 50% of t-PP the morphology becomes complex, suggesting a cocontinuous morphology and probably



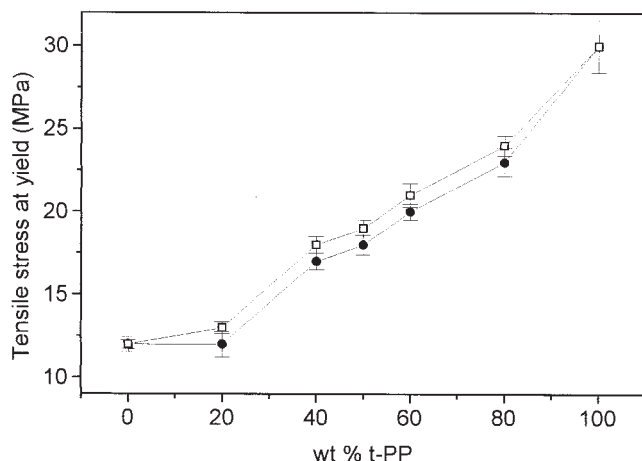
**Figure 8** Compositional dependence of elongation at break as a function of t-PP content for (●)LLDPE(H)/t-PP and (□)LLDPE(O)/t-PP blends.

close to an inversion phase, see Figure 5. The main problem when the two polymers are in equal amounts, is to identify which one is the dispersed phase and which one is the matrix. If one of them is soluble in a solvent (which is not a solvent for the other), it can be extracted and then it is easy to determine by SEM which polymer forms the matrix and which the dispersed phase in the polymer blend. In this case, both polymers are soluble in the same solvents, specifically in hot solvents, like toluene and xylene.

At higher t-PP contents, 60–80%, spherical LLDPE domains are present in the t-PP matrix, see Figure 6. At 80% of t-PP content, LLDPE shows more spherical dispersed phases with large size domains. Due to its higher viscosity, LLDPE shows a poorer dispersion in the t-PP matrix, unlike that at 20% of t-PP, which shows a better dispersion and smaller size domains.



**Figure 9** Compositional dependence of tensile strength at break as a function of t-PP content for (●)LLDPE(H)/t-PP and (□)LLDPE(O)/t-PP blends.



**Figure 10** Compositional dependence of tensile stress at yield as a function of t-PP content for (●)LLDPE(H)/t-PP and (□)LLDPE(O)/t-PP blends.

Table II shows the diameter of dispersed phases in LLDPE/t-PP blends. As observed, the diameter of dispersed phases are equal to both blends LLDPE(H)/t-PP and LLDPE(O)/t-PP when the same compositions are compared.

### Tensile properties

Representative stress-strain curves for the LLDPE(H)/t-PP and LLDPE(O)/t-PP blends are shown in Figure 7(a,b), respectively. The mechanical behavior for both LLDPE are similar. Both pure t-PP and LLDPE show high elongation;  $\epsilon = 700\text{--}800\%$ . From the data of Figure 7(a) and 7(b), the tensile strength at break, elongation at break, and tensile strength at yield as a function of t-PP wt % in the blends were obtained; see Figures 8–10, respectively.

The mechanical properties show a composition dependence. With the introduction of 20% t-PP, blends showed mechanical behavior similar to pure LLDPE. With more than 20% of t-PP the mechanical properties of blends decrease significantly. For example, the elongation at break and tensile strength, indicates immiscibility and incompatibility. Because t-PP has higher

yield stress than LLDPE, the yield stress of the blends increases linearly with t-PP content. For blends with 20% t-PP the mechanical properties, like the elongation at break, tensile strength at break, and yield stress are very close to pure LLDPE properties, with the advantage of better processability. The microstructure of LLDPE does not show any influence on the mechanical properties of the blends.

### CONCLUSIONS

Torque measurements showed that the addition of t-PP causes a decrease of viscosity, making processing easier. Blends containing 20 wt % of t-PP present mechanical properties similar to LLDPE, while blends richer in t-PP exhibit poor mechanical properties characteristic of incompatible blends. Morphological observations showed that phase inversion took place at the 50/50 (LLDPE/t-PP) composition, which exhibits a cocontinuous morphology. The microstructure of LLDPE has no influence on the blend properties. Blends containing 20 wt % of t-PP combine mechanical properties similar to LLDPE with better processability than pure LLDPE.

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