

# Use of Functionalized Metallocene Copolymers from Ethylene and Polar Olefins as Compatibilizers for Low-Density-Polyethylene/Starch and Low-Density-Polyethylene/Dextran Blends

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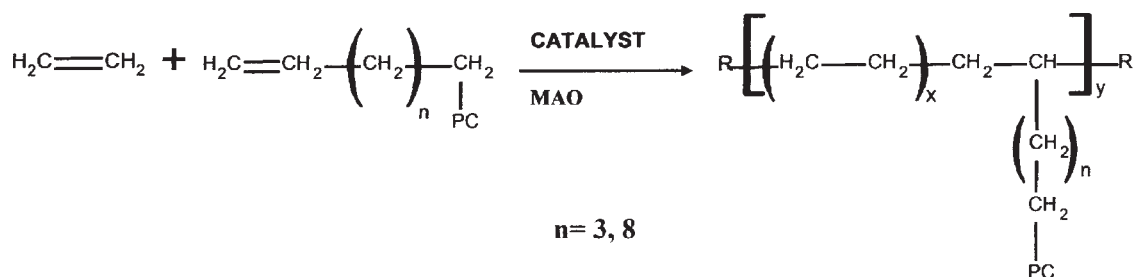
**Keywords:** blends; compatibilizers; dextran; low-density polyethylene; metallocene copolymers; starch

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## Introduction

Plastic materials are of great importance owing to their versatility, processability, and the wide range of applications of their manufactured products.<sup>[1]</sup> Polyolefins constituted the majority of this industry production. Low-density polyethylene (LDPE) is widely employed in agriculture in film form, generating a large amount of waste material. In spite of

the low cost of production of polyolefins and their good mechanical properties, their nonbiodegradable nature causes waste-disposal problems leading to acute pollution problems.<sup>[2]</sup> At present much research is being carried out on the recycling of polymers as an environmental solution to pollution, but only 1% of the plastic produced worldwide is recycled.<sup>[1]</sup> These problems have led to the development of biodegradable plastics.



Scheme 1. Copolymerization reaction of ethylene with protected hydroxyl groups (PC) of the comonomers 10-undecen-1-ol or 5-hexene-1-ol.

Starch, cellulose, gluten, gelatin, and chitin have all received attention as possible biodegradable polymers.<sup>[3]</sup> Starch is an inexpensive abundant and renewable biopolymer produced by many plants as a storage polymer. It is composed of glucose monomers joined by  $\alpha$ -(1-4) linkages. However, it has poor mechanical and processing properties and is unsuitable for most uses in the plastic industry.<sup>[4]</sup>

Blending of polyolefins with starch can overcome these problems and increase the biodegradability of the resulting material.<sup>[5]</sup> Polyolefins are immiscible with starch and other natural polymers of polar nature. The morphology of their blends or composites is characterized by a total lack of adhesion between the starch granules and the polyolefin matrix, producing a material with poor mechanical properties.<sup>[6]</sup> To overcome the incompatibility between the phases, which are a result of the different polar characters of natural

polymers and the LDPE, compatibilizers should be incorporated into the mixture. Copolymers such as poly(ethylene-1-octene) elastomer, polyoxyethylene grafted with maleic anhydride (POE-*g*-maleic anhydride),<sup>[4]</sup> polyethylene grafted with maleic anhydride,<sup>[1,5]</sup> oxidized polyethylene (OPE),<sup>[7]</sup> poly[ethylene-*co*-(methacrylic acid)],<sup>[8]</sup> and poly[ethylene-*co*-(acrylic acid)]<sup>[9]</sup> have been used to enhance the adhesion between polyethylene and starch in polyethylene/starch blends. On the other hand, dextran is a natural polymer composed of glucose monomer units joined mainly by  $\alpha$ -(1-6) linkages with some branching with  $\alpha$ -(1-4) linkage. Although the properties of poly(acrylic acid)/dextran blends has been studied,<sup>[10]</sup> we have found no reports on the use of functionalized metallocene polyolefins as compatibilizers in dextran blends.

The aim of this work was to study the use of metallocene-synthesized copolymers of ethylene and  $\alpha$ -olefins containing

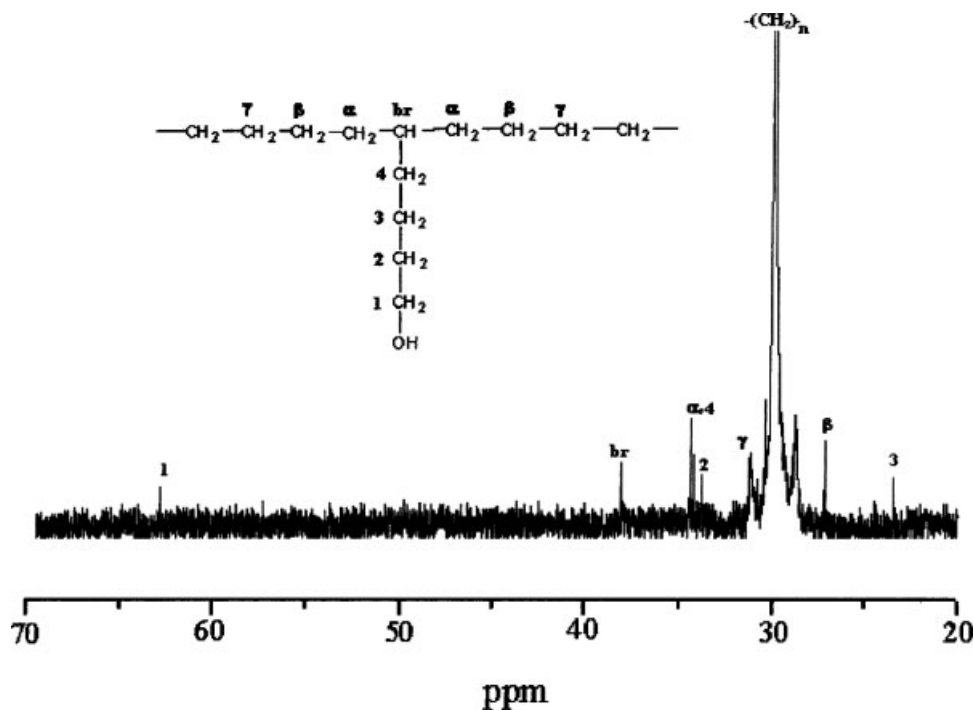


Figure 1. <sup>13</sup>C NMR spectrum and schematic structure of poly[ethylene-*co*-(5-hexene-1-ol)].

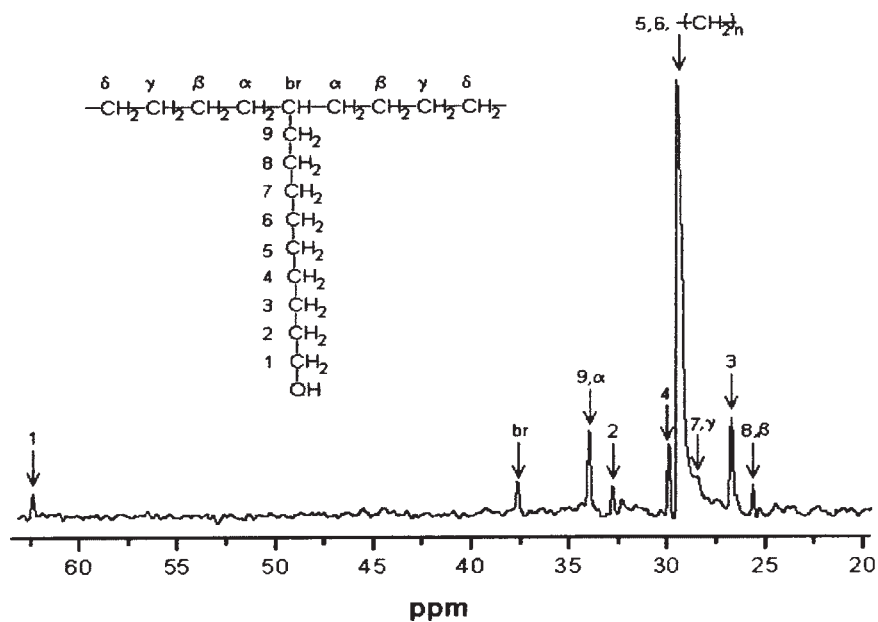


Figure 2.  $^{13}\text{C}$  NMR spectrum and schematic structure of poly[ethylene-co-(10-undecen-1-ol)].

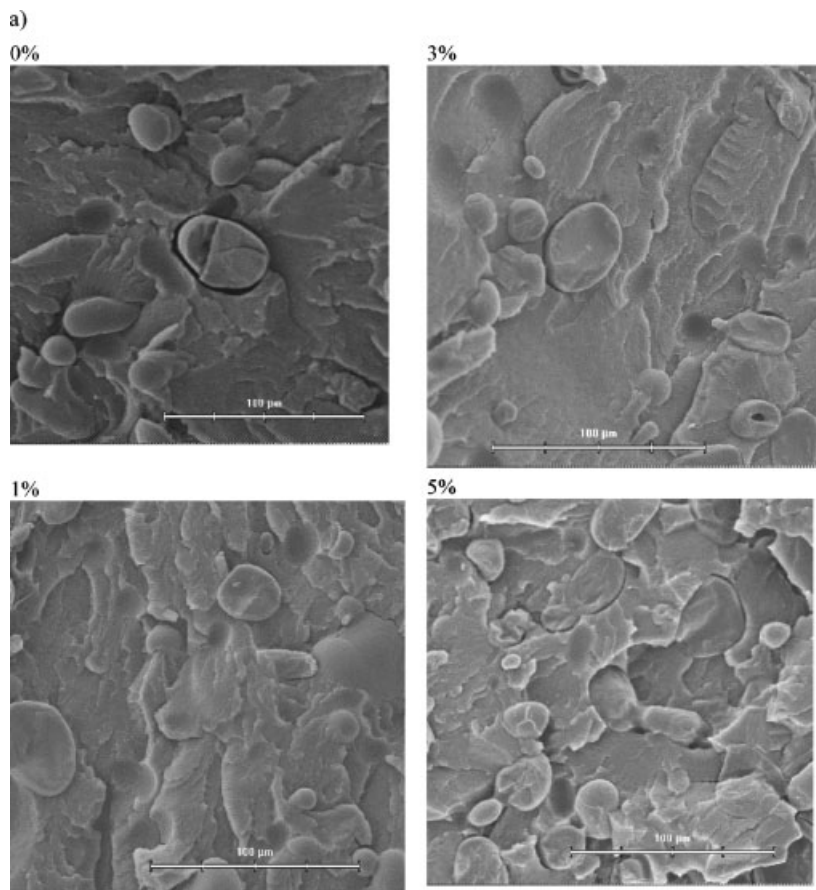


Figure 3. Scanning electron micrographs of 70:30 wt.-% LDPE/starch unmodified blends and modified blends with the addition of 1, 3, or 5 wt.-% of (a) poly[ethylene-co-(5-hexen-1-ol)] and (b) poly[ethylene-co-(10-undecen-1-ol)] as compatibilizers. The micrographs are shown at a magnification of  $670\times$  (bar size = 100  $\mu\text{m}$ ).

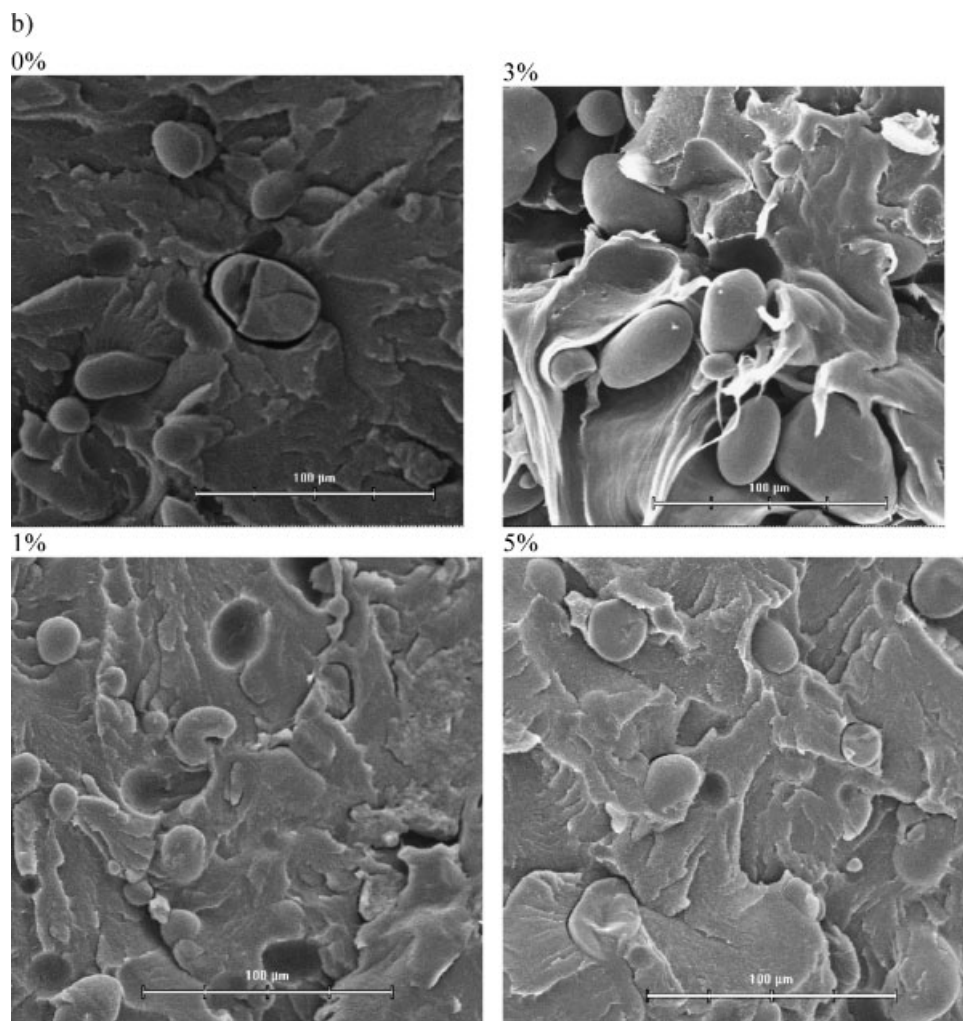


Figure 3. (Continued)

polar functional groups, namely poly[ethylene-*co*-(10-undecen-1-ol)] and poly[ethylene-*co*-(5-hexen-1-ol)] as compatibilizers in LDPE/starch and LDPE/dextran blends. The compatibilizing effect of these copolymers was studied by tensile mechanical testing, DSC, and scanning electron microscopy (SEM).

## Experimental Part

### Materials

LDPE Trithene Jx-7300 was provided by Polyfibra S. A., Chile with a melt flow index of 2.2–2.9 at 190 °C · (5 kg)<sup>-1</sup>. Poly[ethylene-*co*-(10-undecen-1-ol)] and poly[ethylene-*co*-

Table 1. Influence of the amount of compatibilizers on the elastic modulus ( $E$ ), tensile strength ( $\sigma$ ), elongation at break ( $\epsilon$ ), melting temperature ( $T_m$ ), and crystallization temperature ( $T_c$ ) of 70:30 wt.-% LDPE/starch blends.

| Compatibilizer                               | LDPE:compatibilizer:<br>starch | $E$      | $\sigma$   | $\epsilon$ | $T_m$ | $T_c$  |
|--|--------------------------------|----------|------------|------------|-------|--------|
|  |                                |          |            |            |       |        |
| –  | 100:0:0                        | 250 ± 9  | 12.1 ± 0.1 | 68 ± 3     | 110   | 94     |
| –  | 70:0:30                        | 339 ± 6  | 11.4 ± 0.3 | 6 ± 1      | 109   | 94     |
| Poly[ethylene- <i>co</i> -(10-undecen-1-ol)] | 69.5:1:29.5                    | 302 ± 4  | 10.0 ± 0.2 | 8 ± 1      | 110   | 96     |
|  | 68.5:3:28.5                    | 350 ± 15 | 11.6 ± 0.2 | 7 ± 1      | 109   | 99     |
|  | 67.5:5:27.5                    | 361 ± 6  | 12.2 ± 0.3 | 7 ± 1      | 107   | 100    |
| Poly[ethylene- <i>co</i> -(5-hexen-1-ol)]    | 69.5:1:29.5                    | 316 ± 3  | 11.0 ± 0.3 | 7 ± 1      | 109   | 97     |
|  | 68.5:3:28.5                    | 348 ± 12 | 12.0 ± 0.8 | 7 ± 1      | 108   | 100    |
|  | 67.5:5:27.5                    | 389 ± 11 | 12.3 ± 1.3 | 7 ± 1      | 107   | 95/103 |

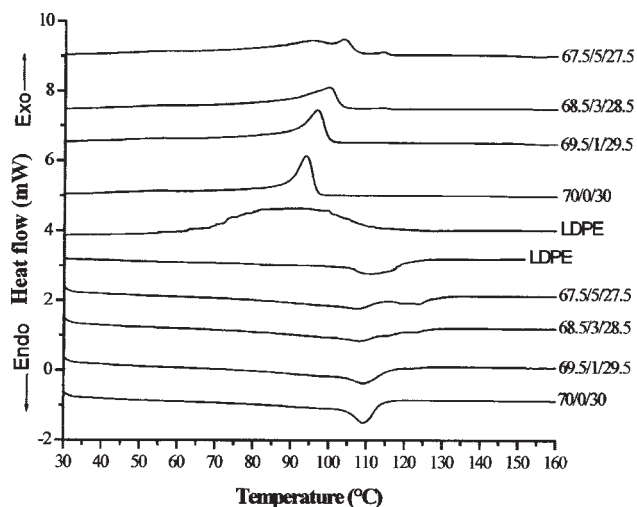


Figure 4. DSC thermograms of LDPE, noncompatibilized 70:30 wt.-% LDPE/starch blend, and compatibilized 70:30 wt.-% LDPE/starch blends containing either 1, 3, or 5 wt.-% of poly[ethylene-*co*-(5-hexen-1-ol)] as compatibilizer.

(5-hexen-1-ol)] were synthesized from ethylene (AGA) with 10-undecen-1-ol or 5-hexen-1-ol (Aldrich) by using the  $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$  metallocene catalysts. These copolymers contained 1.1 and 0.8 mol-% of the polar comonomer, respectively, as determined by  $^{13}\text{C}$  NMR. Soluble nonplasticized starch powder was supplied by Aldrich. Raw nonplasticized dextran sample was supplied by the ICIDCA Institute, Cuba and was used after its purification by repeated dissolution in water and precipitation in ethanol, drying under vacuum at room temperature, and finally milling to 45  $\mu\text{m}$  particles. Both starch and dextran were dried under vacuum at room temperature to constant weight before use.

#### Copolymer Preparation

The copolymerization reaction (represented in Scheme 1) was performed with ethylene at a pressure of 2 bar in a 600 ml Parr glass reactor using toluene as solvent. The cocatalyst, methylaluminumoxane (MAO) was added as a moisture and oxygen scavenger in a weight ratio of Al:Zr = 1000 after the addition of the protected monomer. A suspension containing the catalyst preactivated with the cocatalyst (MAO) was injected into the reactor by syringe. The reactor was then pressurized and the polymerization was continued for 30 min. At the end of the polymerization, a solution of HCl/methanol was added in order to decompose the unreacted cocatalyst. The copolymer was

separated from the reaction mixture by filtration, washed with methanol, and dried in a vacuum at 60 °C.<sup>[11–13]</sup> The employed concentrations of the comonomers (10-undecen-1-ol and 5-hexen-1-ol) were  $1.7 \times 10^{-1} \text{ mol} \cdot \text{L}^{-1}$ . Composition of these copolymers were determined by  $^{13}\text{C}$  NMR studies as shown in Figure 1 and 2. More detailed information can be found in ref.<sup>[14]</sup>

#### Blend Preparation

A Brabender Plasticorder was employed to prepare the blends under a stream of nitrogen. The mixtures were prepared at 150 °C and 70 rpm for 7 min. 90:10 wt.-% LDPE/starch blends and 90:10 wt.-% LDPE/dextran blends were modified by using 3 wt.-% of poly[ethylene-*co*-(10-undecen-1-ol)] as compatibilizer. 1, 3, or 5 wt.-% of either poly[ethylene-*co*-(5-hexen-1-ol)] or poly[ethylene-*co*-(10-undecen-1-ol)] copolymers were added to the 70:30 wt.-% LDPE/starch blends. LDPE/dextran 70:30 wt.-% blends were elaborated and modified by adding 3 wt.-% of either poly[ethylene-*co*-(5-hexen-1-ol)] or poly[ethylene-*co*-(10-undecen-1-ol)] copolymers as compatibilizers.

#### Mechanical Properties

Tensile strength ( $\sigma$ ), tensile modulus ( $E$ ), and elongation at break ( $\epsilon$ ) were measured using a dynamometer model HP D-500 according to the ASTM D638 method. After melt mixing, the blend was cut into small pieces and then pressed at 190 °C and 50 psi to obtain laminates from which test specimens were cut for the tensile testing according to ASTM D638. The tensile measurements were carried out for five specimens from each sample which were 1.5 mm thick, 12 mm wide, and 120 mm long. The crosshead speed was 50  $\text{mm} \cdot \text{min}^{-1}$  and the measurements were carried out on five specimens for each sample previously conditioned at 26 °C and at 30% relative humidity for 24 h, and the results were averaged to obtain a mean value.

#### SEM

Specimens were fractured after freezing in liquid nitrogen and the fractured surfaces, after coating with gold, were observed with a Tesla model BS 343A scanning electron microscope.

#### DSC

Thermal analysis was carried out under nonisothermal conditions by using a DSC model 2920 from TA Instruments. The

Table 2. Influence of the addition of 3 wt.-% of poly[ethylene-*co*-(10-undecen-1-ol)] as compatibilizer on the elastic modulus ( $E$ ), tensile strength ( $\sigma$ ), elongation at break ( $\epsilon$ ), melting temperature ( $T_m$ ) and crystallization temperature ( $T_c$ ) of 90:10 wt.-% LDPE/starch blends.

| Compatibilizer                               | LDPE:compatibilizer:<br>starch | $E$      | $\sigma$   | $\epsilon$ | $T_m$ | $T_c$ |
|--|--------------------------------|----------|------------|------------|-------|-------|
|  |                                |          |            |            |       |       |
| –  | 100:0:0                        | 250 ± 9  | 12.1 ± 0.1 | 68 ± 3     | 110   | 94    |
| –  | 90:0:10                        | 207 ± 5  | 10.2 ± 0.2 | 32 ± 11    | 110   | 94    |
| Poly[ethylene- <i>co</i> -(10-undecen-1-ol)] | 88.5:3:8.5                     | 211 ± 10 | 11.1 ± 1.2 | 21 ± 11    | 110   | 95    |



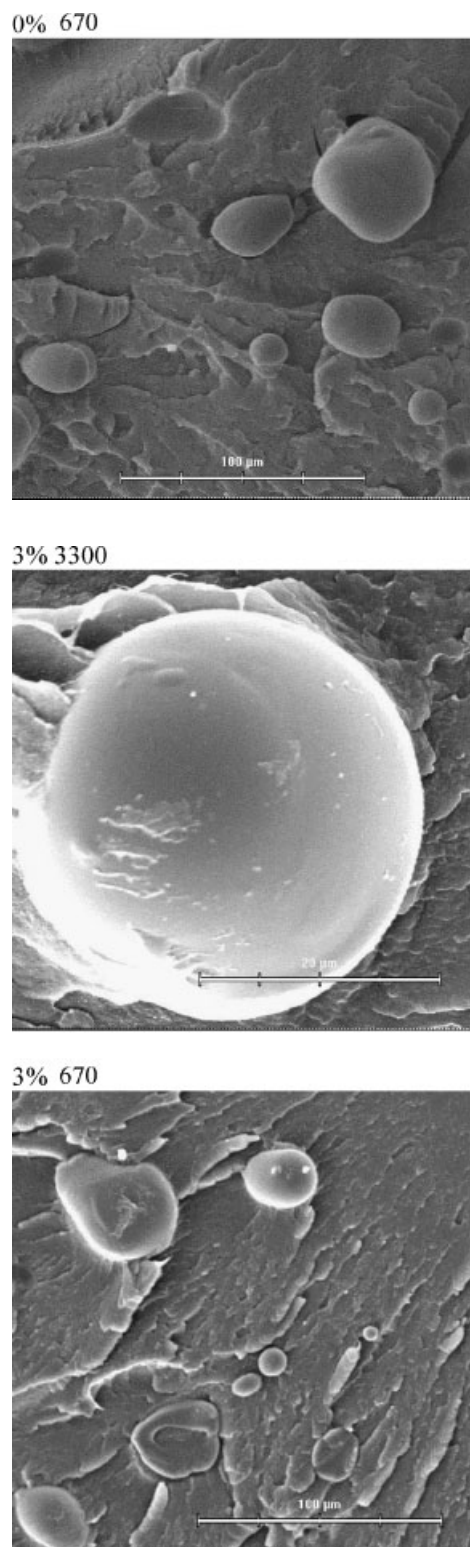


Figure 5. SEM micrographs of unmodified and modified 90:10 wt.-% blends with the addition of 3 wt.-% of poly[ethylene-*co*-(10-undecen-1-ol)] as compatibilizer. SEM micrographs are shown at a magnification of 670 $\times$  (bar size = 100  $\mu\text{m}$ ) and 3300 $\times$  (bar size = 20  $\mu\text{m}$ ).

instrument was calibrated with an indium standard. Samples of about 8 mg were melted at 160  $^{\circ}\text{C}$  and were kept at this temperature for 10 min in order to eliminate any previous thermal history in the material. Then they were cooled down 30  $^{\circ}\text{C}$  at 10  $^{\circ}\text{C} \cdot \text{min}^{-1}$  in order to determine the crystallization temperature ( $T_c$ ). The sample was then heated to 160  $^{\circ}\text{C}$  at 10  $^{\circ}\text{C} \cdot \text{min}^{-1}$  to obtain the melting temperature ( $T_m$ ).

## Results and Discussion

### 70:30 wt.-% LDPE/Starch Blends

Figure 3 shows the SEM micrographs taken of the 70:30 wt.-% LDPE/starch unmodified blend and modified blends with 1, 3, or 5 wt.-% of either poly[ethylene-*co*-(5-hexen-1-ol)] or poly[ethylene-*co*-(10-undecen-1-ol)] copolymers as compatibilizers. The increase in the percentage of compatibilizer causes a greater amount of starch granules to remain in the interface after fracture. This could indicate a better adhesion between the blend components. This can especially be appreciated when a higher percentage of the copolymer was used as blend compatibilizer.

The mechanical properties of unmodified and modified 70:30 wt.-% LDPE/starch blends are shown in Table 1. The tensile mechanical tests of these blends revealed that the addition of 1 wt.-% of both compatibilizers produce a slight decrease in the elastic modulus and the tensile strength and a large decrease in the elongation at break compared with those of LDPE. However, when the amount of copolymer added to the blend was increased to either 3 or 5 wt.-%, the tensile strength, elastic modulus, and elongation at break increased slightly, as compared with those of unmodified blend. This is most probably a result of the increase of interfacial adhesion between starch and LDPE promoted by greater amount of compatibilizer present in the interface.

As can be seen from Table 1 and Figure 4, the DSC thermal analysis shows a shift to slightly higher  $T_c$ s. It is probable that the compatibilizers act as nucleating agents for LDPE in the compatibilized blends. The same behavior was observed when 5 wt.-% of either copolymer was added to the blend as compatibilizer, leading apparently to phase segregation. Most likely the copolymer is not only located in the interface, as is expected for a compatibilizer, but is also present in the form of small droplets dispersed in the LDPE continuous phase. However, the corresponding SEM micrographs shown in Figure 3 show no direct evidence for this assumption.

### 90:10 wt.-% LDPE/Starch Blends

Table 2 shows the mechanical properties of LDPE and 90:10 wt.-% LDPE/starch unmodified and modified blends with 3 wt.-% of poly[ethylene-*co*-(10-undecen-1-ol)] as compatibilizer. Both the modulus and tensile strength of LDPE decrease on addition of starch for blends without compatibilizer. The decreases of both the modulus and

Table 3. Influence of the addition of 3 wt.-% of poly[ethylene-*co*-(10-undecen-1-ol)] as compatibilizer on the elastic modulus ( $E$ ), tensile strength ( $\sigma$ ), elongation at break ( $\varepsilon$ ), melting temperature ( $T_m$ ), and crystallization temperature ( $T_c$ ) of 90:10 wt.-% LDPE/dextran blends.

| Compatibilizer                               | LDPE:compatibilizer:<br>dextran | $E$      | $\sigma$   | $\varepsilon$ | $T_m$ | $T_c$ |
|--|---------------------------------|----------|------------|---------------|-------|-------|
|  |                                 |          |            |               |       |       |
| –  | 100:0:0                         | 250 ± 9  | 12.1 ± 0.1 | 68 ± 3        | 110   | 94    |
| –  | 90:0:10                         | 232 ± 8  | 11.0 ± 0.2 | 26 ± 1        | 110   | 94    |
| Poly[ethylene- <i>co</i> -(10-undecen-1-ol)] | 88.5:3:8.5                      | 231 ± 13 | 11.6 ± 0.5 | 25 ± 2        | 109   | 95    |

tensile strength are due to the incompatibility of starch with LDPE. However, a small increase in modulus and tensile strength without a change in the stiffness, as well as a small increase in the  $T_c$  of LDPE was observed for the blend

containing 3 wt.-% of poly[ethylene-*co*-(10-undecen-1-ol)] as compatibilizer, indicating the compatibilizing effect of this copolymer. The existence of a better phase adhesion between the LDPE matrix and the starch granules, through

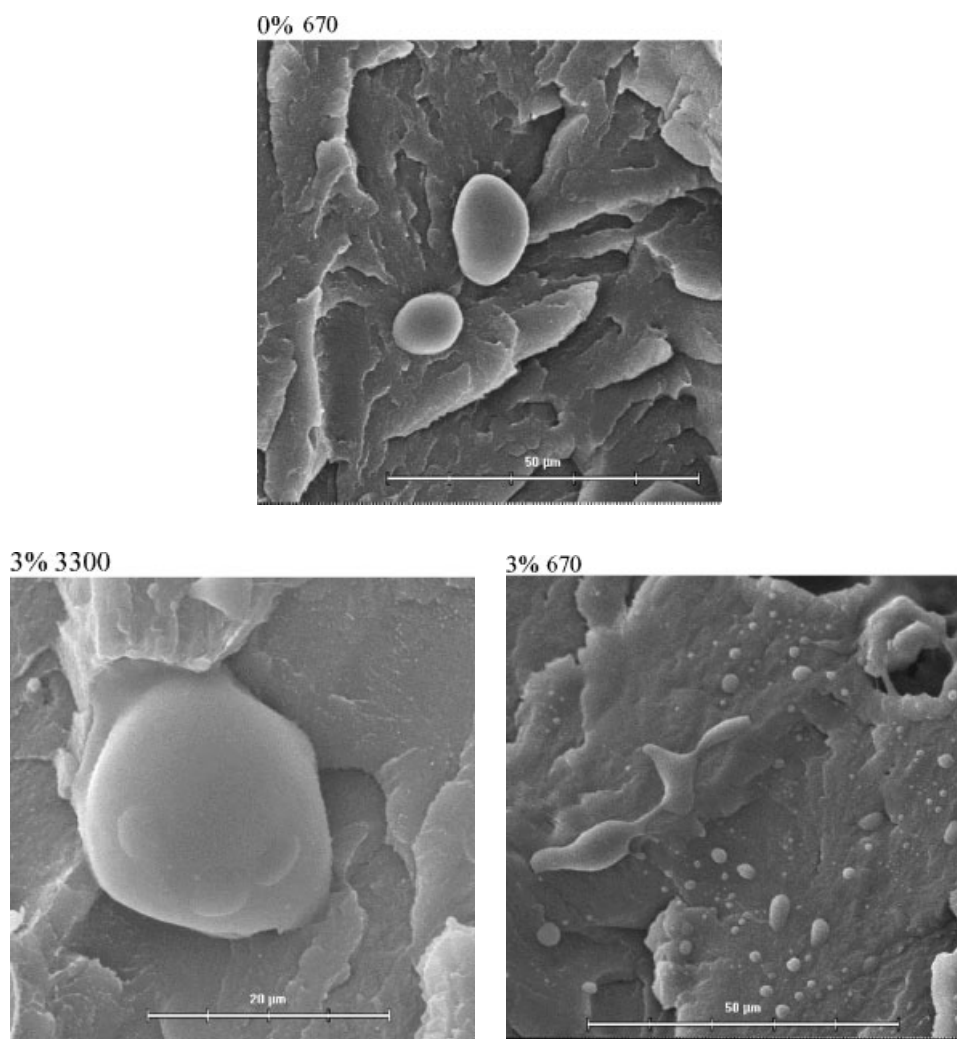


Figure 6. SEM micrographs of unmodified 90:10 wt.-% LDPE/dextran blend (magnification 670 $\times$ ) and modified blend with the addition of 3 wt.-% of poly[ethylene-*co*-(10-undecen-1-ol)] as compatibilizer. SEM micrographs of the modified blend are shown at a magnification of 1700 $\times$  (bar size = 50  $\mu$ m) and 3300 $\times$  (bar size = 20  $\mu$ m).

hydrogen-bond interactions of hydroxyl groups of starch and those of the compatibilizer, compared with that of the unmodified blend, can be seen in the magnified scanning electron micrographs shown in Figure 5. It can be seen from this figure that the starch particles seem to be coated by continuous LDPE phase. DSC studies revealed that the crystallization temperature of LDPE in the blend was slightly increased by addition of the compatibilizer. This is probably a result of the fact that the compatibilizer can act as a nucleating agent for the crystallization of LDPE.

#### 90:10 wt.-% LDPE/Dextran Blends

Unmodified and modified LDPE/dextran blends showed similar mechanical and thermal properties as those of the 90:10 wt.-% LDPE/starch blends, as shown in Table 3 and 2, respectively. Again, both modulus and tensile strength of LDPE decrease on addition of dextran for the blend without compatibilizer. The decreases of both modulus and tensile strength are due to the incompatibility of starch with LDPE. However, no variation in modulus and tensile strength without a change in the stiffness as well as small increase in crystallization temperature of LDPE was observed for blends containing 3 wt.-% of poly[ethylene-co-(10-undecen-1-ol)] as compatibilizer, indicating the compatibilizing effect of this copolymer. There was better phase adhesion between the LDPE matrix and the starch granules, through hydrogen-bond interactions of hydroxyl groups of starch and those of compatibilizer, compared with the unmodified blend. DSC studies revealed that the crystallization temperature of LDPE in the blend was slightly increased by addition of the compatibilizer. This is probably a result of the fact that the compatibilizer can act as nucleating agent for the crystallization of LDPE.

On the other hand, morphological study of both unmodified and modified 90:10 wt.-% LDPE/dextran blends showed that higher dispersion of the dextran in the continuous LDPE as well as an increase in phase cocontinuity is obtained when 3 wt.-% of poly[ethylene-co-(10-undecen-1-ol)] as compatibilizer was added to the blend. This was confirmed by examining the SEM micrographs shown in

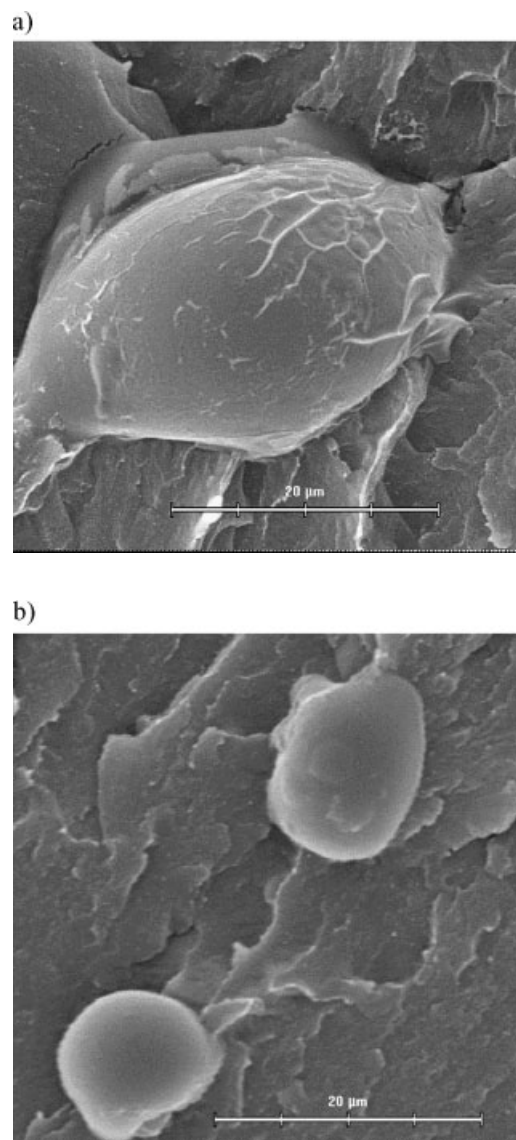


Figure 7. SEM micrographs, taken at 3300 $\times$  magnification (bar size = 20  $\mu\text{m}$ ), of 70:30 wt.-% LDPE/dextran unmodified blends and modified blends with the addition of (a) 3 wt.-% of poly[ethylene-co-(5-hexen-1-ol)] or (b) 3 wt.-% of poly[ethylene-co-(10-undecen-1-ol)] as blend compatibilizers.

Table 4. Influence of the addition of 3 wt.-% of either poly[ethylene-co-(10-undecen-1-ol)] or poly[ethylene-co-(5-hexen-1-ol)] as compatibilizers on the elastic modulus ( $E$ ), tensile strength ( $\sigma$ ), elongation at break ( $\epsilon$ ), melting temperature ( $T_m$ ) and crystallization temperature ( $T_c$ ) of 70:30 wt.-% LDPE/dextran blends.

| Compatibilizer                      | LDPE:compatibilizer:<br>dextran | $E$          | $\sigma$       | $\epsilon$ | $T_m$ | $T_c$ |
|-------------------------------------|---------------------------------|--------------|----------------|------------|-------|-------|
|                                     | wt.-%                           |              |                |            |       |       |
| –                                   | 100:0:0                         | 250 $\pm$ 9  | 12.1 $\pm$ 0.1 | 68 $\pm$ 3 | 110   | 94    |
| –                                   | 70:0:30                         | 307 $\pm$ 12 | 9.5 $\pm$ 0.3  | 6 $\pm$ 1  | 109   | 94    |
| Poly[ethylene-co-(10-undecen-1-ol)] | 68.5:3:28.5                     | 290 $\pm$ 20 | 11.4 $\pm$ 0.1 | 7 $\pm$ 1  | 110   | 96    |
| Poly[ethylene-co-(5-hexen-1-ol)]    | 68.5:3:28.5                     | 355 $\pm$ 16 | 10.9 $\pm$ 0.4 | 6 $\pm$ 1  | 109   | 99    |



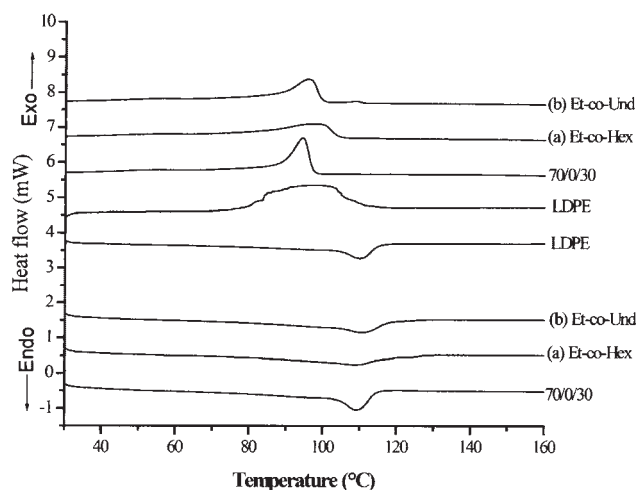


Figure 8. DSC thermograms of LDPE, 70:30 wt.-% LDPE/dextran uncompatibilized blend and compatibilized 70:30 wt.-% LDPE/dextran blends containing 3 wt.-% by weight of either poly[ethylene-*co*-(5-hexen-1-ol)] (Et-co-Hex) (a) or poly[ethylene-*co*-(10-undecen-1-ol)] (Et-co-Und) (b) as compatibilizer.

Figure 6, where a finer dispersion of dextran particles in the continuous LDPE phase is observed. It can also be seen in the magnified SEM micrographs in Figure 6 that the starch particles in the compatibilized blend are embedded in the continuous LDPE phase. This result indicates that the addition of poly[ethylene-*co*-(10-undecen-1-ol)] improves the blend compatibility through possible hydrogen-bond formation between functional groups of the compatibilizer and those of dextran.

#### 70:30 wt.-% LDPE/Dextran Blends

The influence of the addition of both poly[ethylene-*co*-(10-undecen-1-ol)] and poly[ethylene-*co*-(5-hexen-1-ol)] copolymers as compatibilizers on the compatibility and properties of 70:30 wt.-% LDPE/dextran blends was also studied. The morphological studies carried out by SEM (Figure 7) showed an apparent increase in the size of dextran particles on mixing with LDPE when 3 wt.-% of either poly[ethylene-*co*-(5-hexen-1-ol)] or poly[ethylene-*co*-(10-undecen-1-ol)] was used as blend compatibilizer. SEM analysis also showed that the addition of poly[ethylene-*co*-(5-hexen-1-ol)] as compatibilizer to the blend promoted the interfacial adhesion between dextran and the continuous LDPE phase, as seen in Figure 7. The compatibilizer seems to coat the dextran granules improving the adhesion with the LDPE phase in the modified blend than the unmodified blend without compatibilizer.

The results of the mechanical tests carried out on 70:30 wt.-% LDPE/dextran blends are shown in Table 4. The mechanical properties of the blends were found to depend on the compatibilizer used. An increase in tensile modulus

and a slight decrease in tensile strength was observed when poly[ethylene-*co*-(5-hexen-1-ol)] was added to 70:30 wt.-% LDPE/dextran blend, whereas the addition of poly[ethylene-*co*-(10-undecen-1-ol)] as compatibilizer resulted in obtaining a less rigid material. However, the addition of compatibilizers did not affect the elongation at break of the blends. An increase in  $T_c$  values was also observed in this case from DSC studies shown in Table 4 and Figure 8. An increase of  $T_c$  values observed when either poly[ethylene-*co*-(5-hexen-1-ol)] or poly[ethylene-*co*-(10-undecen-1-ol)] were used as blend compatibilizers could be due to the effect of the compatibilizer acting as a nucleating agent for the crystallization of LDPE.

## Conclusion

The compatibilizing effect of poly[ethylene-*co*-(1-hexen-1-ol)] and poly[ethylene-*co*-(1-undecen-1-ol)] in blends of LDPE/starch and LDPE/dextran was demonstrated by mechanical, thermal, and SEM studies. SEM micrographs showed an enhanced interfacial adhesion and a decrease in particle size of starch or dextran with some degree of phase cocontinuity when these functionalized copolymers were used as blend compatibilizers. The tensile strength and the elastic modulus of both types of blends increased slightly when 3–5 wt.-% of either copolymer was added as a compatibilizer to the blend. Crystallization temperature ( $T_c$ ) of LDPE, determined by DSC, was shifted to slightly higher temperature as a consequence of the addition of the compatibilizers. The existence of phase segregation was also revealed by thermal analysis when 5 wt.-% of the copolymers were used as blend modifiers.

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