

# Use of Modified Poly( $\epsilon$ -caprolactone) in the Compatibilization of Poly( $\epsilon$ -caprolactone)/Maize Starch Blends

C. Pascente, L. Márquez, V. Balsamo, A. J. Müller

Grupo de Polímeros, Departamento de Ciencia de los Materiales, Universidad Simón Bolívar, Apartado 89000, Caracas 1080A, Venezuela

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**ABSTRACT:** In this work, the compatibilization of a poly( $\epsilon$ -caprolactone) with a number-average molecular weight of 120,000 g/mol (PCL<sup>120</sup>) and maize starch was investigated by the addition of a chemically modified poly( $\epsilon$ -caprolactone). Two types of blends were prepared by melt extrusion. In type A blends, low-molecular-weight compatibilizers were used: (1) a poly( $\epsilon$ -caprolactone) with a number-average molecular weight of 10,000 g/mol that was reacted with maleic anhydride to obtain chains terminating in carboxylic groups and (2) low-molecular-weight poly( $\epsilon$ -caprolactone)s (number-average molecular weights of 600 and 2000 g/mol) with one pendant carboxylic group within the chains. With these groups of blends, tensile testing and scanning electron microscopy demonstrated that the compatibilizers were generally effective in inducing a better dispersion for a 60/40 poly( $\epsilon$ -caprolactone)/maize starch blend

with a compatibilizer, improving the mechanical properties in comparison with uncompatibilized blends. The blends with 30% starch were not improved by the addition of compatibilizer, and this may be related to the rheology of the blends during preparation. In type B blends, high-molecular-weight compatibilizers were prepared through the grafting of variable amounts of acrylic acid or maleic anhydride to PCL<sup>120</sup> chains. The best compatibilizer action was obtained with 0.7 wt % maleic anhydride grafted to PCL<sup>120</sup> because both the dispersion and mechanical properties were further improved in comparison with uncompatibilized blends and type A blends. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 4089–4098, 2008

**Key words:** blends; biopolymers; compatibility; functionalization of polymers

## INTRODUCTION

There is growing interest in developing environmentally friendly polymeric products whose performance should be at least similar to that of conventional materials. Besides its biodegradability, poly( $\epsilon$ -caprolactone) (PCL) has the ability to form technologically useful blends with a wide variety of polymers; however, PCL has a relatively high cost and a low melting point ( $\approx 60^\circ\text{C}$ ), and these features limit its use for certain applications, such as the production of films by film blowing.<sup>1</sup> These difficulties could be overcome through the blending of PCL with starch. Starch is one of the most promising materials for biodegradable plastics because of its wide availability all over the world and its low price.<sup>2</sup> To prepare completely biodegradable blends, many researchers have blended starch with aliphatic polyesters such as PCL,<sup>3–6</sup> and even though different

methods of blend preparation have been reported (varying the starch type, using thermoplastic starch, and changing the humidity content of starch), the mechanical properties become poorer with increasing starch content in the blends. This has been attributed to poor adhesion between the hydrophobic PCL and the hydrophilic starch.

Because of the immiscibility of PCL/starch blends, compatibilization strategies should, therefore, be used to obtain products with appropriate mechanical properties. The optimum compatibilization of immiscible blends can be achieved by the addition of a small amount of a compatibilizer. The compatibilizers could be composed of block or graft copolymers or a chemically modified homopolymer. Theoretical and experimental investigations have shown that an effective compatibilizer will reduce the interfacial tension between the immiscible phases and will reduce the droplet or particle size. Such changes may have an impact on the adhesion between the phases and therefore improve the mechanical properties.<sup>7</sup> To achieve such compatibilization, two strategies can be employed for the preparation of a compatibilizing agent: the chemical modification of the starch or the chemical modification of the PCL. With respect to the first strategy, the work of Park et al.<sup>8</sup>

Correspondence to: V. Balsamo (vbalsamo@usb.ve) or A. J. Müller (amuller@usb.ve).

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can be mentioned; they prepared starch-*g*-PCL graft copolymers as compatibilizers by varying the number of PCL grafts and their length, and they concluded that the increase in the number of PCL grafts on starch has a stronger effect than changing their length. In fact, they observed that the modulus and strength of the blends decreased, whereas the elongation at break and toughness increased remarkably, with the addition of a graft copolymer in comparison with uncompatibilized PCL/starch blends. Santayanon and Wootthikanokkhan<sup>9</sup> also performed a chemical modification of starch by carrying out acylation with propionic anhydride in the presence of sodium hydroxide or triethylamine; after they blended the modified starch with PCL, an increase in the modulus and tensile properties was obtained in comparison with the blends of PCL and unmodified starch. Nevertheless, the elongation at break decreased as the propionyl content increased.

With respect to the chemical modification of PCL, more studies can be found in the literature that introduced functional groups at the ends or along the PCL chain. Thus, Avella et al.,<sup>10</sup> for example, prepared a compatibilizer by modifying a low-molecular-weight PCL on its terminal groups with pyromellitic anhydride; the addition of this compatibilizer led to an improvement of the performance of the blends without changes in their overall biodegradability.

Other authors have reported the chemical modification of PCL by grafting functional groups such as maleic anhydride (MAH),<sup>11,12</sup> acrylic acid (AA),<sup>13,14</sup> and methacrylic acid<sup>15</sup> along the chain by means of a free-radical mechanism, although not all of them have been blended with starch. Wu found that the compatibility and mechanical properties of PCL/starch composites were improved by the use of PCL-*g*-MAH<sup>11</sup> or PCL-*g*-AA<sup>14</sup> in place of PCL. Blending these materials with starch led to the formation of an ester carbonyl group, and this group was responsible for differences that resulted in a noticeable reduction of the starch phase size. Although water resistance for PCL-*g*-MAH/starch was higher than that for PCL/starch, in a soil environment, the compatibilized blend showed only a slightly lower biodegradation rate than the uncompatibilized one.

Despite the successful blending of modified PCL with starch, it should be taken into account that the use of modified PCL in place of PCL would result in a composite with a high price. It was therefore our objective to evaluate the effect of using different modified PCLs as compatibilizers in PCL/maize starch ( $St_m$ ) blends. At this point, we should mention the work of Mani and Bhattacharya,<sup>16</sup> who investigated the effect of adding MAH-functionalized polyesters as compatibilizers to polyester/starch blends, in which the polyesters were PCL, poly(butylene succinate), and a butanediol-adipate-terephthalate

copolymer. They observed in all cases that the anhydride-functionalized polyester reduced the size of the dispersed phase, thus enhancing the interaction between the two phases. To gain wider insight into the effects of the different kind of compatibilizers, we investigated the use of the following materials as compatibilizers in PCL/starch blends: PCLs modified at the ends with MAH and PCLs modified within the chain with a carboxylic group, AA groups, or MAH groups. In the last case, the effect of the MAH content was also studied.

## EXPERIMENTAL

### Preparation of the blends

Before the PCL/ $St_m$  blends were prepared, native  $St_m$  (kindly supplied by Alfonso Rivas C.A., Caracas, Venezuela) was vacuum-dried at 70°C for 72 h; after drying, the moisture content was determined with the 14.003 method of the Association of Official Analytical Chemists, which gave a value of 1.6%. A PCL with a number-average molecular weight of 120,000 g/mol (PCL<sup>120</sup>; P-787, Union Carbide, Caracas, Venezuela) was melt-extruded at 145°C. To ensure the best dispersion of the starch in the matrix, PCL/ $St_m$  blends were prepared in a laboratory-scale screw extruder (60 rpm) by being passed three times at 120°C before the addition of the compatibilizer and two times at 100°C after the compatibilizer was added.

Two series of blends were prepared (type A and type B blends) with the same procedure previously described, and their compositions are shown in Tables I and II; the compatibilizer (c) contents were established at 10 and 30% with respect to the PCL content in the blends. Type A refers to blends with low-molecular-weight compatibilizers, and type B refers to blends with high-molecular-weight compatibilizers.

### Compatibilizers

A PCL with a number-average molecular weight of 10,000 g/mol modified at the ends with MAH to obtain terminal carboxylic groups (MAH<sub>E</sub>-PCL<sup>10</sup>) was purchased from Aldrich (Caracas, Venezuela). The chemical modification was carried out with the procedure reported by Avella et al.:<sup>10</sup> they modified the ends of a molten PCL homopolymer with pyromellitic anhydride and pyridine as a catalyst. The reaction procedure is schematically shown in Scheme 1; subsequently, the products were purified with water/acetone to eliminate any anhydride traces. The presence of the carboxylic end groups was corroborated by means of <sup>1</sup>H-NMR. Low-molecular-weight PCLs with number-average molecular weights of 600 and 2000 g/mol carrying carboxylic groups within the PCL chains (HC-PCL<sup>0.6</sup> and HC-PCL<sup>2.0</sup>, respectively) were purchased from Solvay (Caracas, Venezuela).

TABLE I  
Compositions of Type A Blends Prepared for This Study

PCL <sup>120</sup> /St <sub>m</sub> /C		PCL <sup>120</sup> /St <sub>m</sub> /C	
Blend composition	Compatibilizer	Blend composition	Compatibilizer
60/40/0	—	70/30/0	—
60/40/6	MAH <sub>E</sub> -PCL <sup>10</sup>	70/30/7	MAH <sub>E</sub> -PCL <sup>10</sup>
60/40/18	MAH <sub>E</sub> -PCL <sup>10</sup>	70/30/21	MAH <sub>E</sub> -PCL <sup>10</sup>
60/40/6	HC-PCL <sup>2.0</sup>	70/30/7	HC-PCL <sup>2.0</sup>
60/40/18	HC-PCL <sup>2.0</sup>	70/30/21	HC-PCL <sup>2.0</sup>
60/40/6	HC-PCL <sup>0.6</sup>	70/30/7	HC-PCL <sup>0.6</sup>
60/40/18	HC-PCL <sup>0.6</sup>	70/30/21	HC-PCL <sup>0.6</sup>

The superscripts 120 and 10 indicate the molecular weights of the PCL, as purchased, expressed in kilograms per mole. The superscripts 2.0 and 0.6 indicate the molecular weights of the modified PCL expressed in kilograms per mole.

The graft copolymers PCL<sup>120</sup>-*g*-AA and PCL<sup>120</sup>-*g*-MAH (see Fig. 1) were prepared with P-787 as the starting material according to the procedure reported by Wu.<sup>11,14</sup> MAH and AA were grafted within the PCL chains with benzoyl peroxide as the initiator and with xylene and *o*-dichlorobenzene for the modification with AA and MAH, respectively. The reactions were carried out at 85°C for 6 h, and the products were purified. The products were purified through washing with acetone. The AA and MAH weight contents were determined through titration,<sup>17</sup> and this is indicated in Table II by the subindices in grams of MAH per 100 g of PCL.

### Characterization of the blends

#### Tensile tests

Compression-molded sheets were prepared from neat PCL and blends at 100°C in all cases. Dumb-bell-type samples were cut from the sheets to carry

out tensile tests in a JJ tensile testing machine (Caracas, Venezuela) at a deformation rate of 50 mm/min. In addition to the blends listed in Tables I and II, the mechanical behavior of 60/40/6 PCL/St<sub>m</sub>/MAH<sub>E</sub>-PCL<sup>10</sup> blends containing a plasticizer was evaluated (see Table III).

#### Scanning electron microscopy (SEM)

To evaluate the dispersion of starch in the PCL matrix, the blends were fractured in liquid nitrogen, and the fracture surfaces were gold-plated. The observation of the surfaces was performed with a Hitachi S-5000 scanning electron microscope (Caracas, Venezuela).

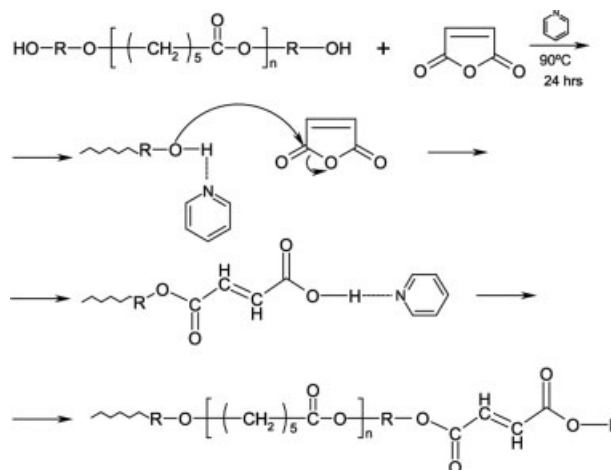
#### Differential scanning calorimetry (DSC)

Small disc samples were cut (10 ± 1 mg) from the compression-molded sheets and encapsulated in aluminum pans. A PerkinElmer DSC-7 (Caracas, Venezuela) was used to study the thermal behavior of all

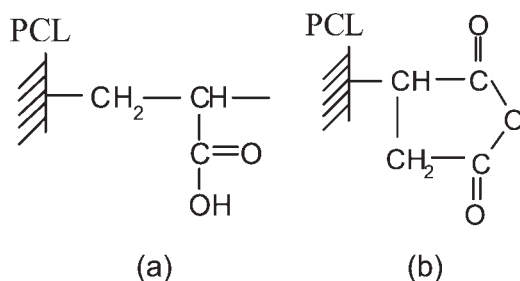
TABLE II  
Composition of Type B Blends Prepared for This Study

Blend	Compatibilizer	Blend composition
PCL <sup>120</sup> - <i>g</i> -AA <sub>6.5</sub> /St <sub>m</sub>	—	60/40/0
PCL <sup>120</sup> - <i>g</i> -AA <sub>6.5</sub> /St <sub>m</sub>	—	70/30/0
PCL <sup>120</sup> - <i>g</i> -MA <sub>0.7</sub> /St <sub>m</sub>	—	60/40/0
PCL <sup>120</sup> - <i>g</i> -MA <sub>0.7</sub> /St <sub>m</sub>	—	70/30/0
PCL <sup>120</sup> /St <sub>m</sub> /C	PCL <sup>120</sup> - <i>g</i> -AA <sub>6.5</sub> /St <sub>m</sub>	60/40/12
PCL <sup>120</sup> /St <sub>m</sub> /C	PCL <sup>120</sup> - <i>g</i> -AA <sub>6.5</sub> /St <sub>m</sub>	70/30/9
PCL <sup>120</sup> /St <sub>m</sub> /C	PCL <sup>120</sup> - <i>g</i> -MAH <sub>0.7</sub> /St <sub>m</sub>	60/40/12
PCL <sup>120</sup> /St <sub>m</sub> /C	PCL <sup>120</sup> - <i>g</i> -MAH <sub>0.7</sub> /St <sub>m</sub>	70/30/9
PCL <sup>120</sup> /St <sub>m</sub> /C	PCL <sup>120</sup> - <i>g</i> -MAH <sub>1.8</sub> /St <sub>m</sub>	60/40/12
PCL <sup>120</sup> /St <sub>m</sub> /C	PCL <sup>120</sup> - <i>g</i> -MAH <sub>1.8</sub> /St <sub>m</sub>	70/30/9
PCL <sup>120</sup> /St <sub>m</sub> /C	PCL <sup>120</sup> - <i>g</i> -MAH <sub>2.1</sub> /St <sub>m</sub>	60/40/12
PCL <sup>120</sup> /St <sub>m</sub> /C	PCL <sup>120</sup> - <i>g</i> -MAH <sub>2.1</sub> /St <sub>m</sub>	70/30/9

The superscript 120 indicates the molecular weight of the PCL, as purchased, expressed in kilograms per mole. The subscripts indicate the modification degree of the specific compatibilizer in grams of modifier per 100 g of PCL.



Scheme 1 Reaction scheme for the introduction of carboxylic functional groups at the PCL ends to obtain MAH<sub>E</sub>-PCL<sup>10</sup>.



**Figure 1** Schematic representation of the chemical structures of (a) PCL<sup>120</sup>-g-AA and (b) PCL<sup>120</sup>-g-MAH graft copolymers.

compositions under an ultrahigh-purity nitrogen atmosphere. The instrument was calibrated with hexatricontane and indium. Samples were heated up to 140°C, held at that temperature for 3 min, and cooled to 0°C at 10°C/min. Finally, they were heated again from 0 to 140°C at 10°C/min.

## RESULTS AND DISCUSSION

### Type A blends

Tensile properties such as the strength at yield, strength and elongation at break, and Young's mod-

**TABLE III**  
PCL/St<sub>m</sub>/MAH<sub>E</sub>-PCL<sup>10</sup>/Plasticizer Blends Prepared in This Study

Composition <sup>a</sup>	MAH <sub>E</sub> -PCL <sup>10</sup>	Glycerol	Sorbitol
60/40	0	0	0
60/40/6	6	0	0
60/40/6/G	6	4 <sup>b</sup>	0
60/40/6/S	6	0	4 <sup>b</sup>
60/40/6/2G	6	8 <sup>c</sup>	0
60/40/2G <sup>d</sup>	0	8 <sup>c</sup>	0

<sup>a</sup> G, glycerol; S, sorbitol.

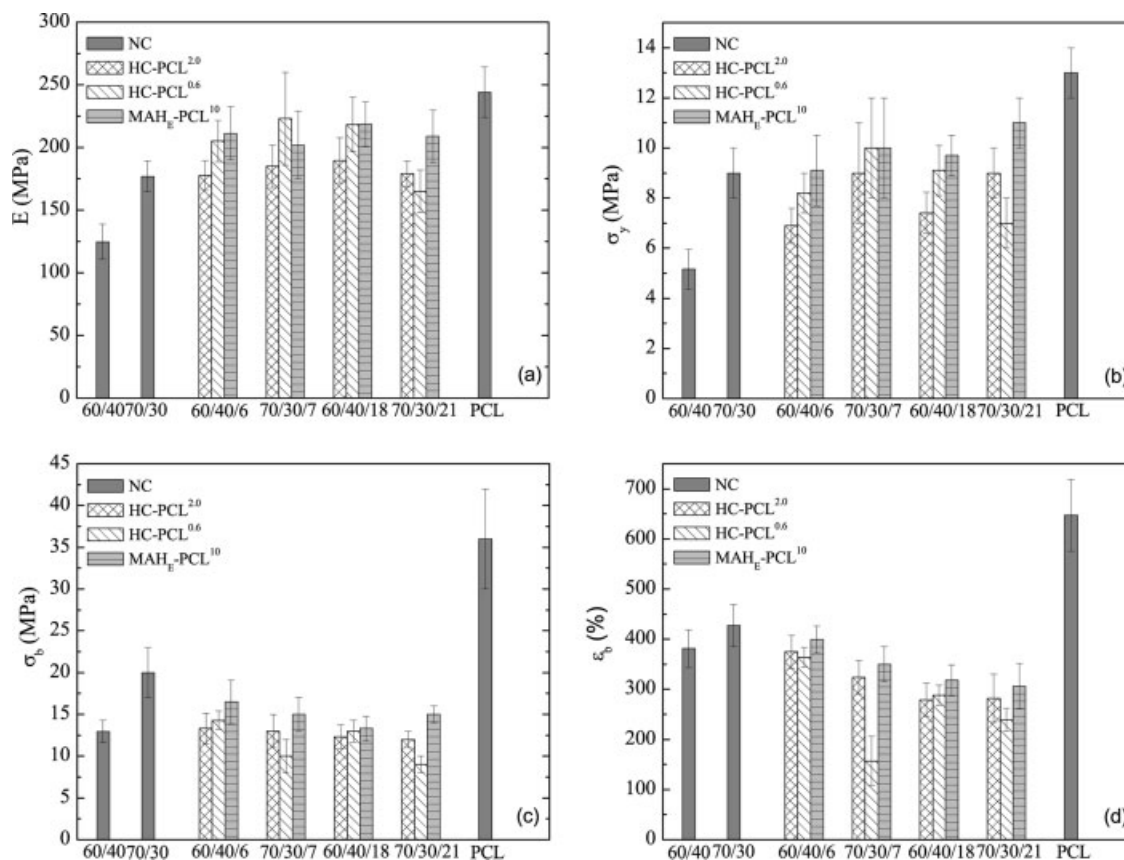
<sup>b</sup> Plasticizer/starch weight ratio = 0.1.

<sup>c</sup> Plasticizer/starch weight ratio = 0.2.

<sup>d</sup> This blend was prepared through the premixing of starch and glycerol at 90°C for 30 min before melt extrusion with PCL.

ulus were evaluated from stress–strain curves of neat PCL, PCL/St<sub>m</sub>, and PCL/St<sub>m</sub>/C blends (in blend names, C indicates a compatibilizer), and they are shown in Figure 2.

PCL exhibited its well-known behavior; that is, it was highly ductile with yielding and an elongation at break of nearly 650% at the used test rate. PCL/St<sub>m</sub> (70/30 and 60/40) exhibited a reduction of all parameters with respect to neat PCL, and the magni-



**Figure 2** (a) Young's modulus ( $E$ ), (b) stress at yield ( $\sigma_y$ ), (c) stress at break ( $\sigma_b$ ), and (d) strain at break ( $\epsilon_b$ ) of PCL/St<sub>m</sub>/C blends. NC indicates that no compatibilizer was added.

tude of the decrease increased with the starch content. The decrease in the modulus with the starch content was unexpected because it should have acted as a filler, increasing Young's modulus as previously reported in the literature.<sup>5,10,18</sup> Nevertheless, even in the literature, a variety of values has been given, and this probably depends on the different preparation methods of the blends. Thus, Panayioutou et al.<sup>19</sup> reported an increase in the modulus from 241 MPa for pure PCL to only 283 MPa for a 60/40 PCL/thermoplastic starch. To find a plausible explanation for our results, we performed experiments with the moisture content varied in the blends, but a significant difference was found only when the samples for tensile tests were immersed for 1 week in a vessel with water. In a related work,<sup>20</sup> we prepared identical blends with PCL and cassava starch and found that the mechanical properties depended on the number of passes through the mini-extruder employed to prepare the blends. After 3 passes, substantial degradation of starch occurred, and this could account for the fall in the elastic modulus. A similar situation may have happened here.

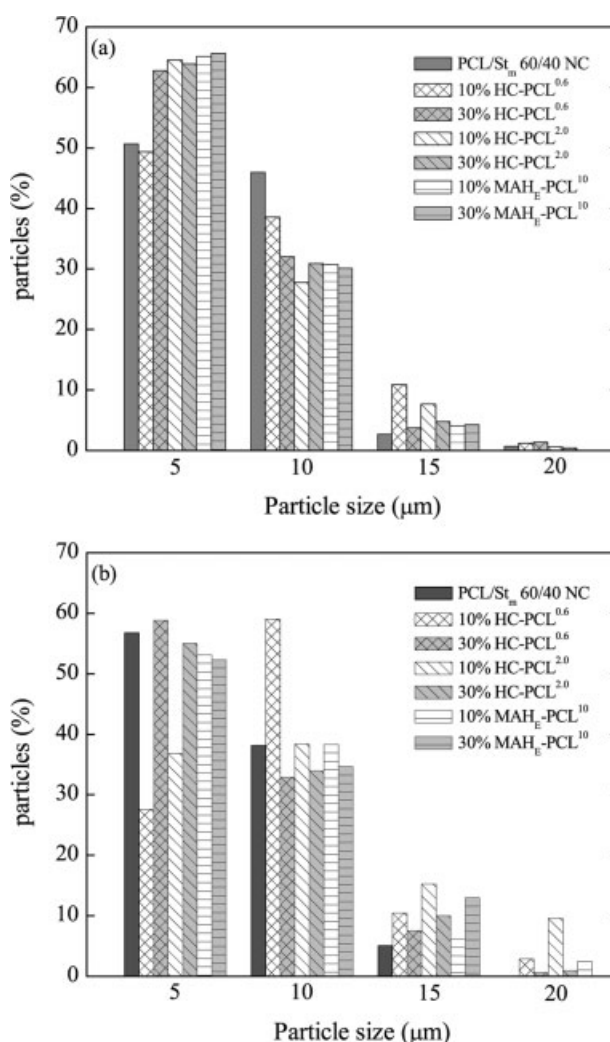
In Figure 2, it is also possible to observe that the addition of any of the compatibilizers to the 60/40 PCL/ $St_m$  blend led to an increase in the elastic modulus and stress at yield with respect to the uncompatibilized blend, the increase being slightly more marked when HC-PCL<sup>2.0</sup> and MAH<sub>E</sub>-PCL<sup>10</sup> were used. In the 60/40/6 PCL/ $St_m$ /MAH<sub>E</sub>-PCL<sup>10</sup> blend, for example, increases of  $\sim 60\%$  and  $\sim 80\%$  in the modulus and stress at yield, respectively, were observed. On the other hand, for the 70/30/C PCL/ $St_m$ /C blends, the increase was not so marked, being independent of the compatibilizer type and content.

The properties at break of the 60/40/C blends slightly increased with 10% MAH<sub>E</sub>-PCL<sup>10</sup> as the compatibilizer, but they exhibited a reduction when a 30% concentration of the compatibilizer was used. The 70/30/C blends, on the other hand, showed a small reduction of the strength and strain at break with a 10 or 30% concentration of the compatibilizer. Because the thermal behavior of the PCL fraction in the blends with and without the compatibilizer did not change in comparison with that of the neat PCL, the described behavior indicates that in the 60/40/C blends, the compatibilizer led to an increase in the interfacial adhesion between the starch granules (as discussed later) and the polymeric matrix with a corresponding increase in the toughness, especially when MAH<sub>E</sub>-PCL<sup>10</sup> was used. The improvement of the mechanical properties of the blends with MAH<sub>E</sub>-PCL<sup>10</sup> in comparison with HC-PCL<sup>2.0</sup> can be attributed to the higher molecular weight of the first compatibilizer.

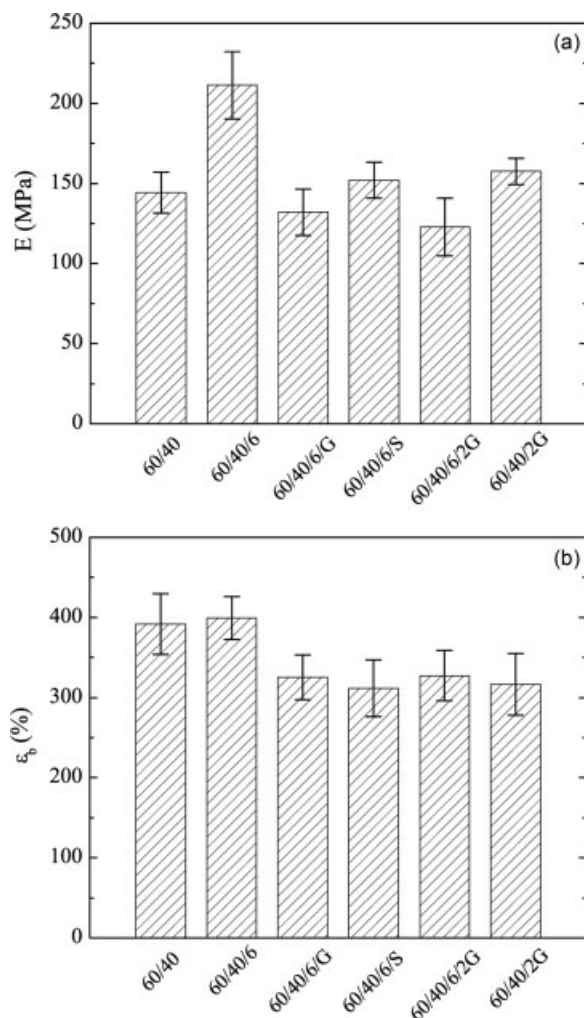
Figure 3 presents for each blend a comparison of the starch particle size distribution obtained by SEM. In the 60/40 PCL/ $St_m$  blends, the following can be

observed: for the blend without a compatibilizer,  $\sim 50\%$  of the particles were 5  $\mu m$  in size, and the addition of the different compatibilizers (with the exception of 60/40/6 PCL/ $St_m$ /HC-PCL<sup>0.6</sup>) caused an increase of this value to 60–68%. Additionally, the percentage of bigger particles decreased (particles with a size of 10  $\mu m$  decreased from ca. 58% to ca. 30%). Such changes in the particle size indicated the effect of the compatibilizer in improving starch dispersion in the PCL matrix due to the interactions between the components. This effect was more marked with the addition of MAH<sub>E</sub>-PCL<sup>10</sup> independently of its content (10 or 30%), and this was in agreement with the mechanical evaluation of the blends.

In the case of the 70/30 PCL/ $St_m$  blends, no improvement in the dispersion was detected (i.e., no particle size reduction) with the addition of any of the compatibilizers. This result can explain the poor



**Figure 3** Particle size distribution for (a) 60/40/C and (b) 70/30/C PCL/ $St_m$ /C blends. NC indicates that no compatibilizer was added.



**Figure 4** Effect of the addition of a plasticizer (G = glycerol; S = sorbitol) on (a) Young's modulus ( $E$ ) and (b) the strain at break ( $\epsilon_b$ ) of PCL/St<sub>m</sub>/MAH<sub>E</sub>-PCL blends.<sup>10</sup>

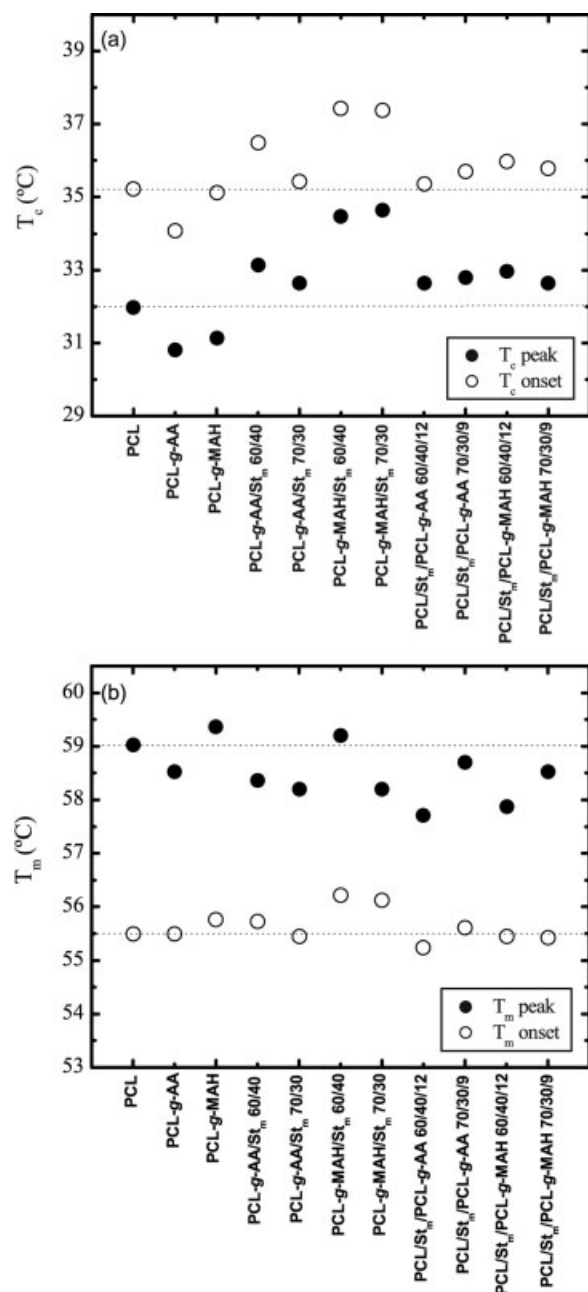
mechanical properties of this type of blend (see Fig. 2). It is possible that rheological factors may have played a role in driving the compatibilizer to the interphase only when starch was present in a 40% concentration. The shear stresses generated during melt blending increased in the PCL/starch blends as the starch content increased.

From the results reported before, in which a higher Young's modulus and stress at yield were observed, we selected the 60/40/6 PCL/St<sub>m</sub>/MAH<sub>E</sub>-PCL<sup>10</sup> blend for further studies. Thus, on the basis of previous results of other authors,<sup>19,21,22</sup> we investigated the effect of adding a plasticizer (glycerol or sorbitol) in the proportions indicated in Table III. Independently of the plasticizer used, Figure 4 shows that no improvement was obtained in the mechanical behavior of the blends. In fact, there was a slight decrease in the stress and strain at break, without significant variations in the other parameters. This was in agreement with the lack of changes

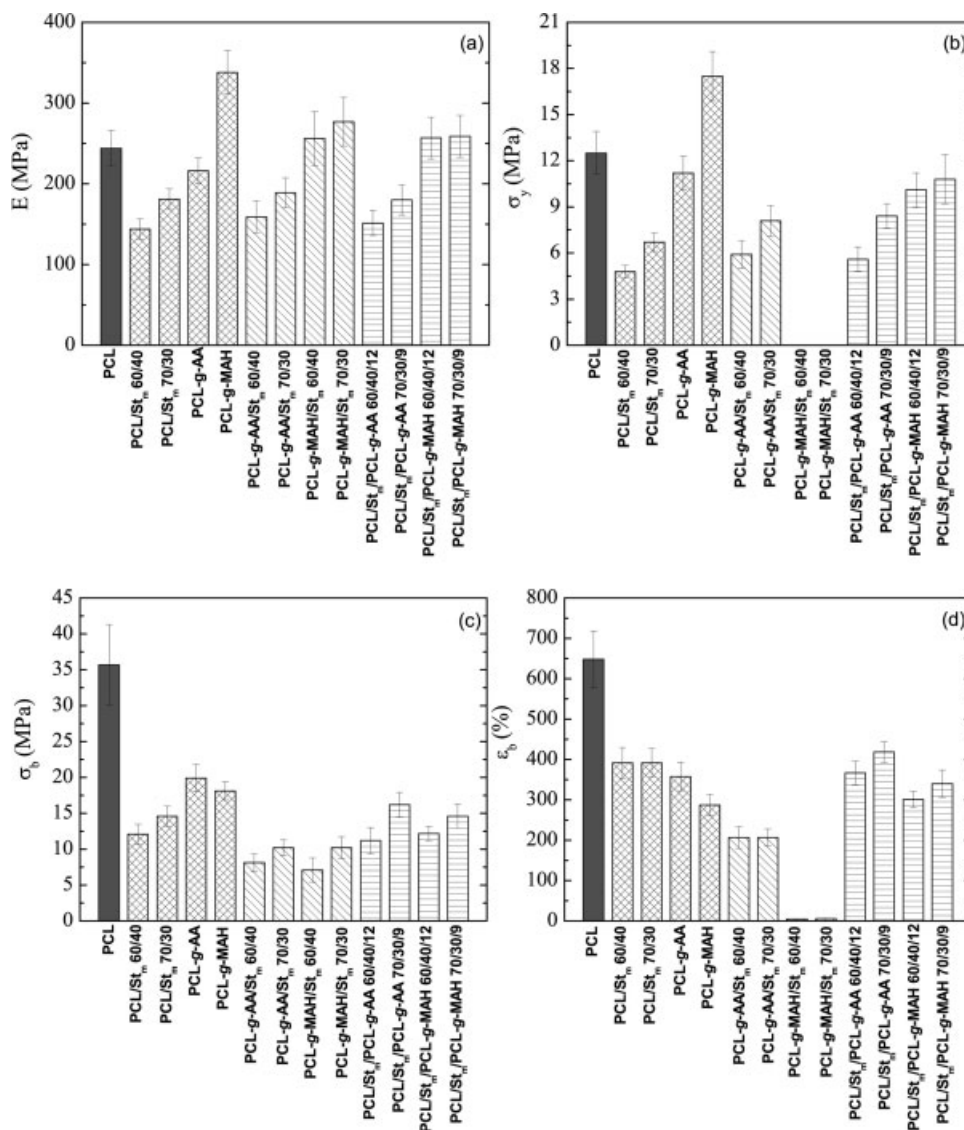
in the dispersion of starch ascertained by SEM. The 60/40/2G blend (G indicates the addition of glycerol), which was prepared by the heating of the starch and glycerol for 30 min before blending with PCL, did not show any changes either.

### Type B blends

The blends that incorporated high-molecular-weight compatibilizers (i.e., type B blends) generally yielded



**Figure 5** (a) Crystallization temperature ( $T_c$ ) and (b) melting temperature ( $T_m$ ) values obtained from the modified PCLs and their blends with starch. The PCL-g-MAH copolymer had an MAH content of 0.7%.



**Figure 6** (a) Elastic tensile modulus ( $E$ ), (b) stress at yield ( $\sigma_y$ ), (c) stress at break ( $\sigma_b$ ), and (d) strain at break ( $\epsilon_b$ ) of PCL/ $St_m$ /C and PCL/ $St_m$ /C blends. The PCL-g-MAH copolymer had an MAH content of 0.7%.

better results than type A blends; therefore, we investigated these blends in more detail. In this case, blends in which the compatibilizer was used as a matrix (C/ $St_m$  blends) were also prepared. In fact, in the following discussion, we present first the results obtained with the C/ $St_m$  blends and then those obtained with the PCL/ $St_m$ /C blends.

#### C/ $St_m$ Blends

From the DSC scans, we obtained the results plotted in Figure 5, which correspond to crystallization and melting temperatures. No significant effects can be observed as the changes were rather small in the crystallization and melting temperatures. Nevertheless, when PCL was mixed with starch, a slight nucleating effect of starch on PCL was detected

because small increases in the peak crystallization temperature of PCL were always observed when starch was present in the blends.

The variation of the mechanical properties of modified PCLs and their blends with starch is presented in Figure 6. PCL-g-AA and PCL-g-MAH exhibited a tensile behavior that varied with respect to unmodified PCL. In the case of PCL-g-AA, a slight reduction of the strength at yield and Young's modulus was appreciated in comparison with unmodified PCL; the properties at break showed a marked decrease, clear evidence of a toughness reduction in the PCL caused by the AA groups, in agreement with the results reported by Wu.<sup>14</sup>

PCL-g-MAH<sub>0.7</sub>, on the other hand, exhibited an increase in the modulus (42%) and strength at yield (46%) but a marked reduction in the strength and elongation at break (50 and 56%), and this indicated

that the material was now less tough and more fragile upon the introduction of the rigid maleic groups. In the specific case of PCL-g-MAH<sub>0.7</sub>, the values were not in agreement with those obtained by Wu<sup>11</sup> for a PCL-g-MAH with a grafting percentage of 0.98 wt %.

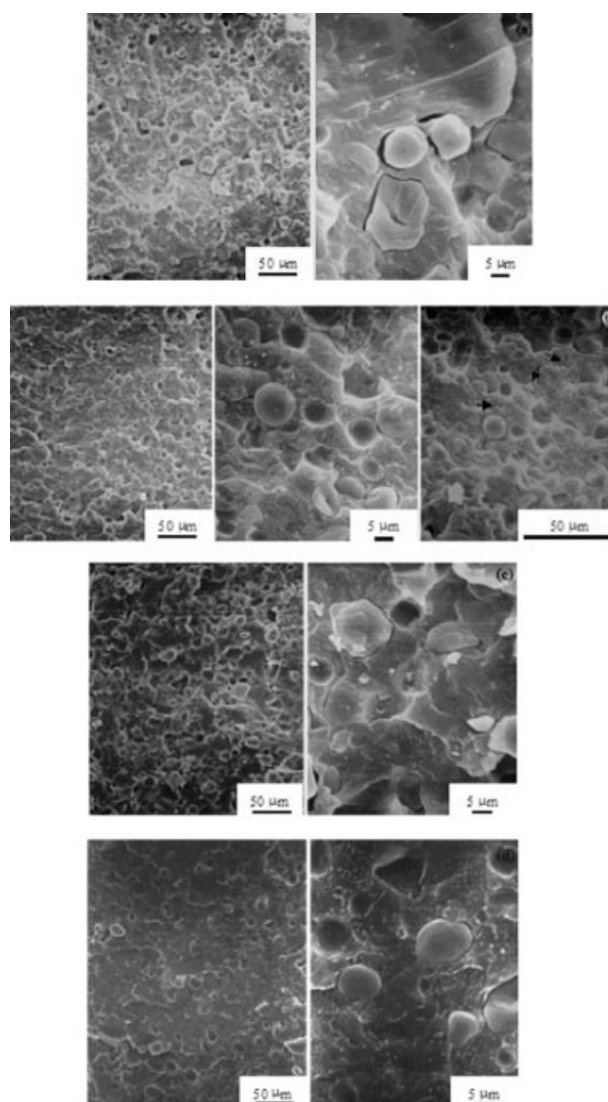
Even though, as previously discussed, PCL-g-AA<sub>6.5</sub> exhibited a decrease in the mechanical parameters in comparison with unmodified PCL, the decrease in the tensile properties with the starch content was smaller in PCL-g-AA<sub>6.5</sub>/St<sub>m</sub> than in PCL/St<sub>m</sub> (see Fig. 6). Blends prepared with PCL-g-MAH<sub>0.7</sub> as the matrix and starch as the dispersed phase (60/40 and 70/30) behaved in a very fragile fashion. Compared with PCL/St<sub>m</sub> blends, they exhibited an increase in Young's modulus and a dramatic decrease in the strength and strain at yield and break.

#### PCL/St<sub>m</sub>/C blends

From a practical point of view, it is interesting to analyze the effect of the modified PCLs as compatibilizers in PCL/St<sub>m</sub> blends. As can be appreciated in Figure 6, when PCL-g-AA<sub>6.5</sub> was used as a compatibilizer in the 60/40/12 blend, all mechanical parameters remained more or less similar to the values reported for the uncompatibilized 60/40 blend, but for the 70/30/9 composition, a slight increase in the strength at yield was observed.

A significant improvement in the toughness of the PCL/St<sub>m</sub> blends was obtained when PCL-g-MAH<sub>0.7</sub> was used as the compatibilizer. It is worth noting that the Young's modulus and strength at yield increased 78 and 110%, respectively, the strength at break remained more or less the same, and the breaking strain decreased only 23%. Therefore, an increase in the rigidity resulted along with a small decrease in the ductility, that is, a good balance in properties, which implied a good compatibilizing action of 0.7% MAH. Such increased compatibility was probably promoted by the reaction of the anhydride groups in PCL-g-MAH<sub>0.7</sub> with the hydroxyl groups of the starch.<sup>11</sup> The resulting mechanical properties were in agreement with the morphology of the blends, which was investigated by means of SEM.

If the micrographs in Figure 7 are examined, it becomes clear that in all blends investigated, the dispersed phase consisted of starch. A comparison of the morphologies obtained with both kinds of compatibilizers indicates that although starch droplets were well distributed in both cases, they apparently showed a tendency to form clusters in the blends compatibilized with PCL-g-AA<sub>6.5</sub>, whereas with PCL-g-MAH<sub>0.7</sub>, spherical particles could be clearly

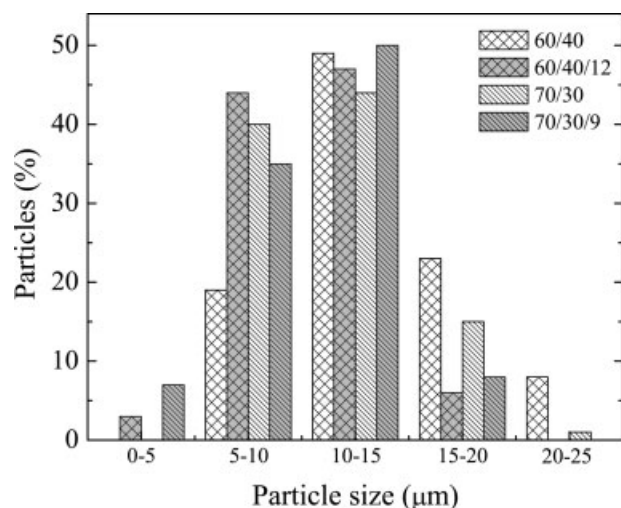


**Figure 7** SEM micrographs of (a) 60/40/12 PCL/St<sub>m</sub>/PCL-g-AA<sub>6.5</sub>, (b) 60/40/12 PCL/St<sub>m</sub>/PCL-g-MAH<sub>0.7</sub>, (c) 70/30/9 PCL/St<sub>m</sub>/PCL-g-AA<sub>6.5</sub>, and (d) 70/30/9 PCL/St<sub>m</sub>/PCL-g-MAH<sub>0.7</sub>.

identified. Micrographs corresponding to 60/40/12 PCL/St<sub>m</sub>/PCL-g-MAH<sub>0.7</sub> showed signs of deformation at the matrix/starch granule interphases, indicating that the addition of PCL-g-MAH<sub>0.7</sub> caused an enhancement of the interfacial adhesion with the consequent favorable effect on the mechanical properties.

Figure 8 plots the starch phase size of PCL/St<sub>m</sub> blends with and without a compatibilizer. The size of the starch phase increased with the starch content, and this is evident from the higher percentage of larger particles in the 60/40 blend in comparison with the 70/30 blend. On the other hand, the addition of the PCL-g-MAH<sub>0.7</sub> compatibilizer led to a reduction of the starch particle size in such a magnitude that at the ends of the histogram, the largest particle population of 20–25 μm disappeared, and a

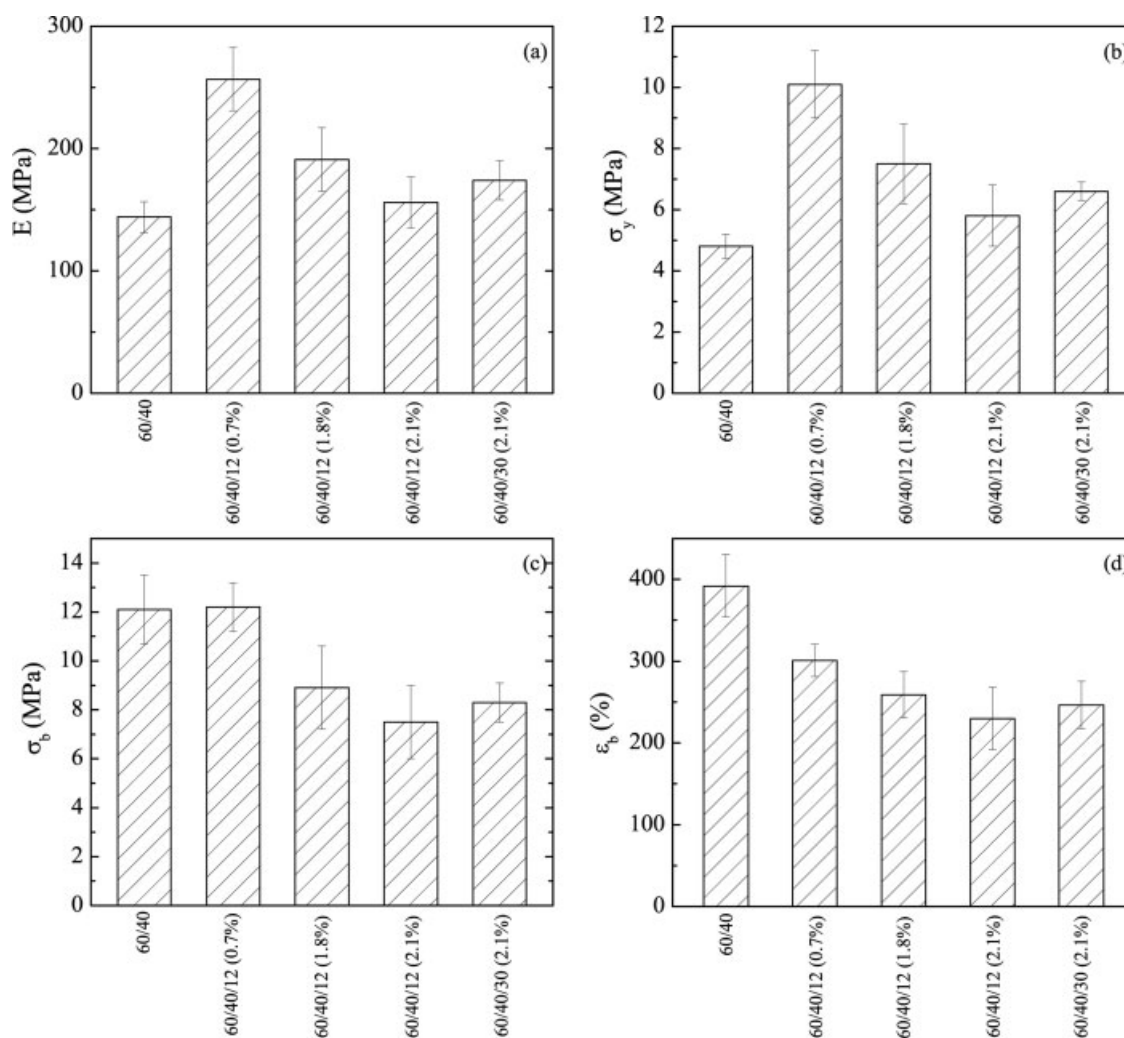




**Figure 8** Particle size distribution in PCL/ $\text{St}_m$ /PCL-g-MAH<sub>0.7</sub> blends.

population in the range of 0–5  $\mu\text{m}$  emerged. As mentioned previously, this was the result of the reduction in the interfacial tension between PCL and  $\text{St}_m$ .<sup>23</sup>

Finally, we investigated the effect of the modification degree of the PCL-g-MAH compatibilizer on the mechanical properties of 60/40 PCL/ $\text{St}_m$ /C blends. Figure 9 illustrates the Young's modulus, strength at yield, and strain at break as functions of the compatibilizer content (12 or 75%) and modification degree (0.7, 1.8, or 2.1%). As mentioned previously, the addition of PCL-g-MAH led to an increase in the mechanical parameters, especially with the compound that had only a 0.7% concentration of maleic groups. These results could be correlated with better interfacial adhesion between the two phases; the rigid maleic groups may have induced a minor ability of PCL chains to flow, giving rise to a higher ri-



**Figure 9** (a) Elastic tensile modulus ( $E$ ), (b) stress at yield ( $\sigma_y$ ), (c) stress at break ( $\sigma_b$ ), and (d) strain at break ( $\epsilon_b$ ) of PCL/ $\text{St}_m$ /PCL-g-MAH blends. The numbers in parentheses indicate the modification degrees of PCL-g-MAH.

gidity in the blend. Nevertheless, the best results were obtained with the compatibilizer containing the smallest concentration of MAH groups (0.7%). Because no variations were observed in the crystallinity degree of the PCL matrix, this indicates that there should be a balance between the compatibilizer/matrix interactions and the presence of the rigid MAH groups in the PCL chains.

### CONCLUSIONS

The compatibilization of PCL and  $St_m$  can be achieved up to a certain extent through the addition of suitable compatibilizers with chemically modified PCL chains. In the case of the low-molecular-weight compatibilizers employed here, the best balance of properties was obtained when  $MAH_E-PCL^{10}$  was employed as a compatibilizer for the 60/40 PCL/ $St_m$  blend. No effect was found on the 70/30 blends upon low-molecular-weight compatibilizer addition, presumably because the blend rheology did not promote an interfacial action of the compatibilizer (in fact, no improvement in dispersion in comparison with uncompatibilized blends was obtained). The improvement of the mechanical properties when  $MAH_E-PCL^{10}$  was used could be attributed to the enhancement of the interfacial adhesion between the starch granules and the polymeric matrix, as evidenced by a reduction of the starch particle size.

High-molecular-weight compatibilizers proved to be more effective, and in particular, a significant improvement in toughness was achieved when 0.7% MAH-grafted  $PCL^{120}$  was added to the PCL/ $St_m$  blends. Because no significant changes were observed in the thermal behavior of the components, it can be concluded that the mechanical properties resulted from a suitable balance between the functional group interactions and the rigidity of the added compatibilizer.

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