

# Effect of Chain Extension on the Properties of PLA/TPS Blends

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**ABSTRACT:** Multifunctional Epoxy-based copolymers can be used as chain-extender (CE) to increase the molecular weight and create branching in polylactides (PLA). In this study, the effect of a multifunctional epoxy-acrylic-styrene copolymer on the properties of PLA/Thermoplastic Starch (PLA/TPS) blends was investigated. The PLA/TPS blends were prepared by twin-screw extrusion. The dry-starch and plasticizers were mixed together in the first half of the extruder to complete starch gelatinization. Water was removed by devolatilization at mid-extruder and the PLA matrix was mixed with the water-free TPS in the latter portion of the compounding process. The standard blends comprised 27% TPS in the PLA matrix. The TPS phase itself comprised 36% plasticizer in the form of glycerol or sorbitol. A maleic anhydride grafted PLA (PLAg) was also used in selected blends to examine the effect of interfacial modification on the morphology of chain-extended blends. The blends were injection molded

into standard test bars and their tensile properties were measured. Differential scanning calorimetry was carried out to examine the effect of chain extension on PLA's ability to crystallize. Oscillatory-shear rheology was used to monitor changes in blend viscosity. Finally, scanning electron microscopy on microtomed and acid-etched samples was carried out to assess the blend morphology. It was found that the combination of interfacial modification and chain-extension strategies led to greatly improved ductility. The viscosity of the PLA/TPS blends was also dramatically increased by adding a small amount of epoxy-based chain extender. This is of great interest for polymer processing techniques (such as foaming or film blowing) that require high melt strength. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 134–141, 2011

**Key words:** thermoplastics starch; polylactide; blends; glycerol; sorbitol; chain extender

## INTRODUCTION

Poly(lactide) (PLA) is a synthetic polymer that can be produced using a renewable biobased feedstock.<sup>1–4</sup> Blending starch, a natural mixture of polysaccharides, into PLA could provide an opportunity to reduce material cost and increase the biodegradation rate of PLA.<sup>2,4</sup> Unfortunately, PLA/starch composites are extremely brittle because of the coarse structure and lack of interfacial adhesion.<sup>2,4,5</sup> One way around this problem is to plasticize and gelatinize starch prior to mixing with PLA. The gelatinized starch, also called thermoplastic starch (TPS), can be deformed and dispersed under flow resulting in a dispersed phase that is finer than the original dry-starch particles. In general, however, this does

not significantly improve the blend ductility unless the blend is compatibilized. It was shown that for glycerol-plasticized TPS dispersed into PLA, the addition of maleic anhydride grafted PLA led to much finer blend morphologies, in the 2–5 micron range, to improved mechanical performance<sup>6</sup> and to improved processability.<sup>7,8</sup> More recently, it was shown that the use of sorbitol or of sorbitol/glycerol mixtures as plasticizers for the TPS further increased the tensile strength and modulus and reduced the dispersed TPS minor phase size even without the use of maleated PLA.<sup>9</sup> Surprisingly, the TPS remained finely dispersed with dimensions below 5 microns even when the TPS content was increased to 60%.

In general, it is difficult to foam PLA using a continuous extrusion process because it has a relatively low melt strength.<sup>10,11</sup> This limitation is directly related with the linear structure of PLA. Small molecular weight chain extenders can be used to increase molecular weight of polymers, especially condensation polymers, through chain-ends reactions. The use of polymeric and multifunctional chain extenders can also provide a means toward

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branching of linear materials. This is especially useful to increase the molecular weight and melt strength and was also shown to create strain-hardening under elongation.<sup>10–12</sup> However, the effect of PLA chain-extenders on the properties of PLA/TPS blends has not been investigated and reported yet.

The solid-state properties of PLA/TPS blends are controlled by the phase size and intrinsic properties of the dispersed TPS phase and by interfacial adhesion. In particular, the TPS behavior can range from that of a ductile elastomer-like material to that of a rigid and brittle material simply by changing the plasticizer type and content in the TPS phase. For example, when increasing glycerol concentration from 33 to 39 wt %, the TPS tensile modulus changes from around 1000 MPa to 10 MPa.<sup>9</sup> Obviously, the tensile elongation follows the inverse trend going from 100 to 500% to as low as 5–10%. One problem with glycerol plasticization in PLA/TPS blends is that that material viscosity is greatly reduced compared with the matrix material. This has been explained by plasticizer migration to the PLA phase as well as by chain-scission due to PLA hydrolysis during compounding. This limits the use of these blends in applications, such as foaming, sheet extrusion, thermoforming where sufficient “melt strength” is necessary during the forming operation. The addition of a chain extender into PLA/TPS blends during processing could potentially alleviate this problem.

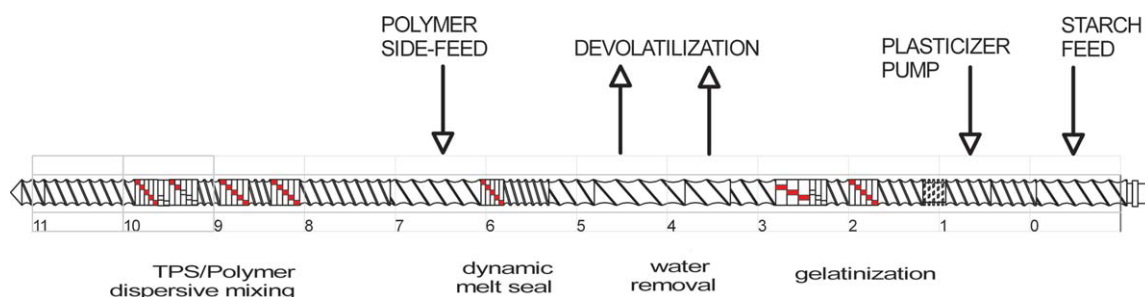
The compatibilization strategy is another important issue in the production of PLA/TPS blends. PLA and TPS have a high interfacial tension in the melt-state leading to very coarse blend structures. In addition the two materials do not inherently have good interfacial adhesion in the solid-state. The use of a compatibilizer is therefore required. The use of a block copolymer comprising blocks miscible with each of the immiscible phase is a conventional strategy to compatibilize blends. Even though this can be made by adding a premade block copolymer, in practice the formation of the copolymer is made *in situ* during the compounding step. For example, in the case of PLA/TPS blends, this is carried out by adding some maleic anhydride grafted PLA.<sup>6</sup> The anhydride groups react with starch amylose chains to form a graft copolymer that will act as an emulsifier for the blend. This approach has the advantage that the graft or block copolymer is formed directly at the interface and removes the need to prepare and purify a premade block copolymer. The efficiency of the compatibilization largely depends on the diffusion of the reactive component migrating to the interface and to the chain entanglement between the modifier and the pure phases in the interfacial region. Theoretically, only a few percent of block copolymer modifier is needed to cover the interface

and enable a significant reduction in dispersed phase size at the end of the compounding process. An additional requirement to produce blends with good mechanical performance is to obtain molecular entanglement between each blocks of the copolymer and the phase with which it is miscible.<sup>13–15</sup> In more formal terms, the molecular weight of each block must exceed the critical molecular weight for entanglement of the polymer being compatibilized. In a previous study on PLA/TPS blends, it was noted that successful TPS dispersed phase size reduction was not always followed by a dramatic improvement in mechanical properties.<sup>6</sup> Since the maleation step significantly decreases the PLA molecular weight and since the shortest grafted PLA chains will diffuse more readily to the interface, it may be possible to improve the blends mechanical properties through chain extension of the grafted species or through chain-end reaction between unmodified PLA and maleated PLA. In this study, the addition of an epoxy base copolymer (chain extender) to compatibilized and noncompatibilized PLA/TPS blends will be investigated. In particular, the melt rheology, the blend morphology, and the thermomechanical properties will be examined.

## EXPERIMENTAL

### Materials

The polylactide, PLA 4032D supplied by NatureWorks, was a semicrystalline grade comprising around 2% D-LA. Wheat starch, Supergel 1203, was provided by ADM -Ogilvy. The reactive modification of PLA was performed using 95% pure maleic anhydride and 0.25% of a peroxide initiator [2,5-dimethyl-2,5-di(*tert*-butylperoxy) hexane] (Luperox® 101 or L101) obtained from Aldrich Chemical Company. The peroxide initiator was adsorbed on a silica support with an effective content of 45%. The maleic anhydride grafted PLA was prepared according to the method described in an earlier work.<sup>6</sup> According to literature, the grafting level using this technique is around 0.5%.<sup>16</sup> The chain-extender (CE) was a commercially available epoxy-styrene-acrylic copolymer.<sup>10</sup> The active copolymer was obtained in the form of concentrate in a PLA base. It is commercially available from Clariant under trade name CESA-Extend OMAN698493. The epoxy groups in the chain-extender can react with the carboxyl end-groups of PLA. Since the chain-extender has multiple reaction sites, branching as well as chain extension can be expected. The plasticizers were 98% pure D-sorbitol, obtained from Aldrich Chemical Company and a 99.5% pure USP grade glycerol supplied by Mat Laboratories.



**Figure 1** Process configuration for PLA/TPS blending. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

### Sample preparation

PLA/TPS blends were prepared on a Leistritz 34 mm co-rotating twin-screw extruder with an L/D ratio of 42 using a sequence of twin-screw operation shown in Figure 1. The first half of the extruder was dedicated to starch gelatinization. Starch and sorbitol were fed in a dry powder form. In a separate stream, glycerol and water were added to starch through the plasticizer injection port. The water was used as a “temporary” plasticizer to enhance the gelatinization rate and decrease starch degradation. It was removed by devolatilization in a subsequent extruder portion to provide a TPS. The second part of the extruder was used to mix the TPS with the PLA. When used, the maleic anhydride grafted PLA (PLAg) and/or the chain extender were dry-mixed with PLA before extrusion. In that case of compatibilized blends, 20 wt % PLA was substituted by PLAG. For glycerol plasticized TPS, the water/glycerol ratio was kept at 0.1/1. In all cases, the TPS contents in PLA were kept at 27% and the plasticizer contents in TPS (either glycerol or sorbitol) were fixed at 36%. The extruder temperature was set to 140°C for the first half of the extruder dedicated to starch gelatinization and water removal. In the second extruder portion dedicated to PLA/TPS mixing, the extruder temperature was set to 180°C. The mixtures were extruded at a rate of 10 kg/h using a rotation speed of 100 rpm. Strands produced using a 2-strand die were water-cooled and pelletized. The PLA and PLAG were dried prior to compounding in a desiccating dryer at 60°C for at least 24 h and the compounded pellets were dried again at the same conditions prior to injection molding and to subsequent analysis.

### Rheology

The rheological properties of PLA/TPS with various CE contents were measured in dynamic mode at 180°C using a rotational rheometer in plate-plate geometry. The complex viscosity was monitored over time to verify the thermal stability of the samples. Frequency sweeps were carried out to determine the complex viscosity over a frequency ranging from 0.1

to 100 rad/s. Care was taken to dry the samples prior to testing and to keep them under a nitrogen blanket during testing to minimize oxidation and to maintain a dry environment.

### Differential scanning calorimetry (DSC)

The crystallization kinetics was investigated using a Perkin-Elmer DSC 7 system. The DSC was calibrated using the melting temperature and enthalpy of indium. For nonisothermal crystallization, samples were heated from 20 to 200°C at 20°C/min, kept in the molten state for 2 min to erase prior thermal history and then cooled at -10°C/min down to 20°C to evaluate their ability to crystallize upon cooling. Subsequently, the samples were heated back to 200°C at a rate of 20°C/min to assess the crystallization behavior upon heating.

### Blend Morphology

The blend morphology was assessed by observation of microtomed surfaces using scanning electron microscopy (SEM). The microtoming was carried out at room temperature using a diamond knife and the surfaces were subsequently treated with hydrochloric acid (HCl, 6N) for 3 h to selectively dissolve the TPS phase.

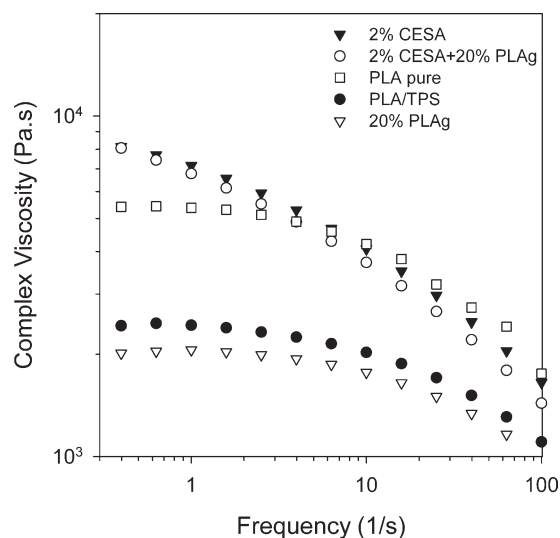
### Tensile characterization

The tensile testing was carried out at a rate of 5 mm/min according to ASTM D638 on injection molded standard type I dog-bone shaped samples with a thickness of 3.1 mm. These samples were sealed in plastic bags after injection and then conditioned at room temperature for 24 h before testing. For each material, a minimum of 5 samples were tested and the average values with standard deviation were reported.

## RESULTS AND DISCUSSION

### Rheology

The first and most obvious sign of effective chain-extension was the increase of polymer melt viscosity. Figure 2 compares the viscosity at 180°C of PLA and



**Figure 2** Effects of adding CESA and PLAg on the complex viscosity of glycerol plasticized PLA/TPS blends.

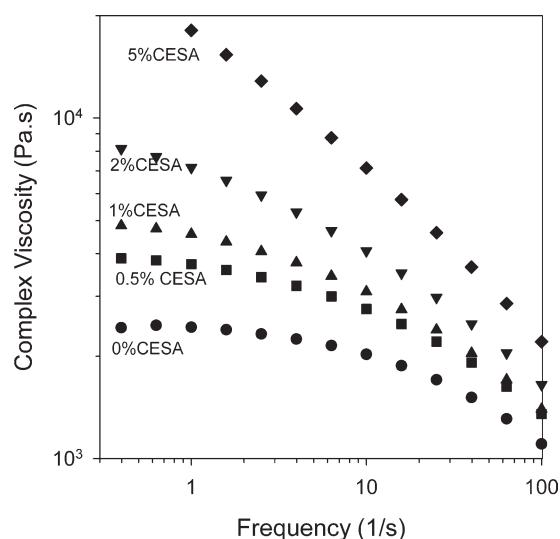
PLA/TPS blend with varying concentrations of chain-extender and maleated compatibilizer. The glycerol concentration (on the basis of the TPS phase) in this data was set to 36 wt %. The virgin PLA exhibited a Newtonian viscosity plateau around 6 kPa.s and suffered a threefold reduction in plateau viscosity when blended either with the grafted PLA or with the TPS. When 2% CE was added to the PLA/TPS blend however, the viscosity was dramatically increased. The Newtonian plateau was pushed to lower oscillation frequency (below the investigated range), and to values probably in excess of 10 kPa.s. The blends also exhibited more shear-thinning compared to pure PLA. This lead to viscosities that are below that of pure PLA at high frequency. It is noteworthy that for the same molecular weight,

branched polymers exhibit more shear thinning.<sup>17</sup> Thus, the current observations are in line with expectations.

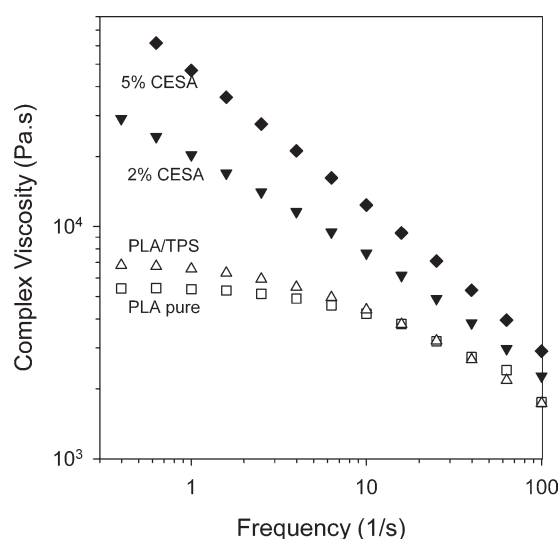
The effect of CE contents on the viscosity of the glycerol plasticized PLA/TPS blends is shown in Figure 3. Addition of only 0.5% CE increased the plateau viscosity from 2.4 kPa.s to 4.0 kPa.s. The viscosity continued to increase as CE content was increased to 2 and 5 wt %. For concentrations above 2 wt %, the Newtonian Plateau was pushed to frequencies below our observation range but that can be estimated in the order of  $10^4$  Pa·s for 2 wt % and  $10^5$  Pa·s for 5 wt %.

In a previous study using the same chain-extender up to 2 wt % but mixing with an internal mixer, the viscosity of PLA first increased with CE content and then levelled off at a level around 1.4 wt% CE.<sup>11</sup> Because it is more difficult to protect the material from humidity in an internal mixer (at atmospheric pressure), this was possibly an equilibrium value imposed by simultaneous chain branching through chain-end reaction and chain scission through random hydrolysis reaction. When mixing in a twin screw extruder, the same authors had not found a similar limit (in the 0–2 wt % CE range). In the current study, we see that further viscosity increase can be obtained by pushing the CE concentration to 5 wt %. This could be useful if the chain extension is carried out *in situ* near the end of the forming process but may lead to unprocessable material otherwise.

It was shown in a previous study that sorbitol-TPS could be much finely dispersed in PLA and that the use of sorbitol led to more viscous melt viscosity and higher modulus and tensile strength in the solid state.<sup>9</sup> It was therefore interesting to investigate the effect of CE addition on the viscosity of sorbitol plasticized PLA/TPS blends. Results are presented in Figure 4.

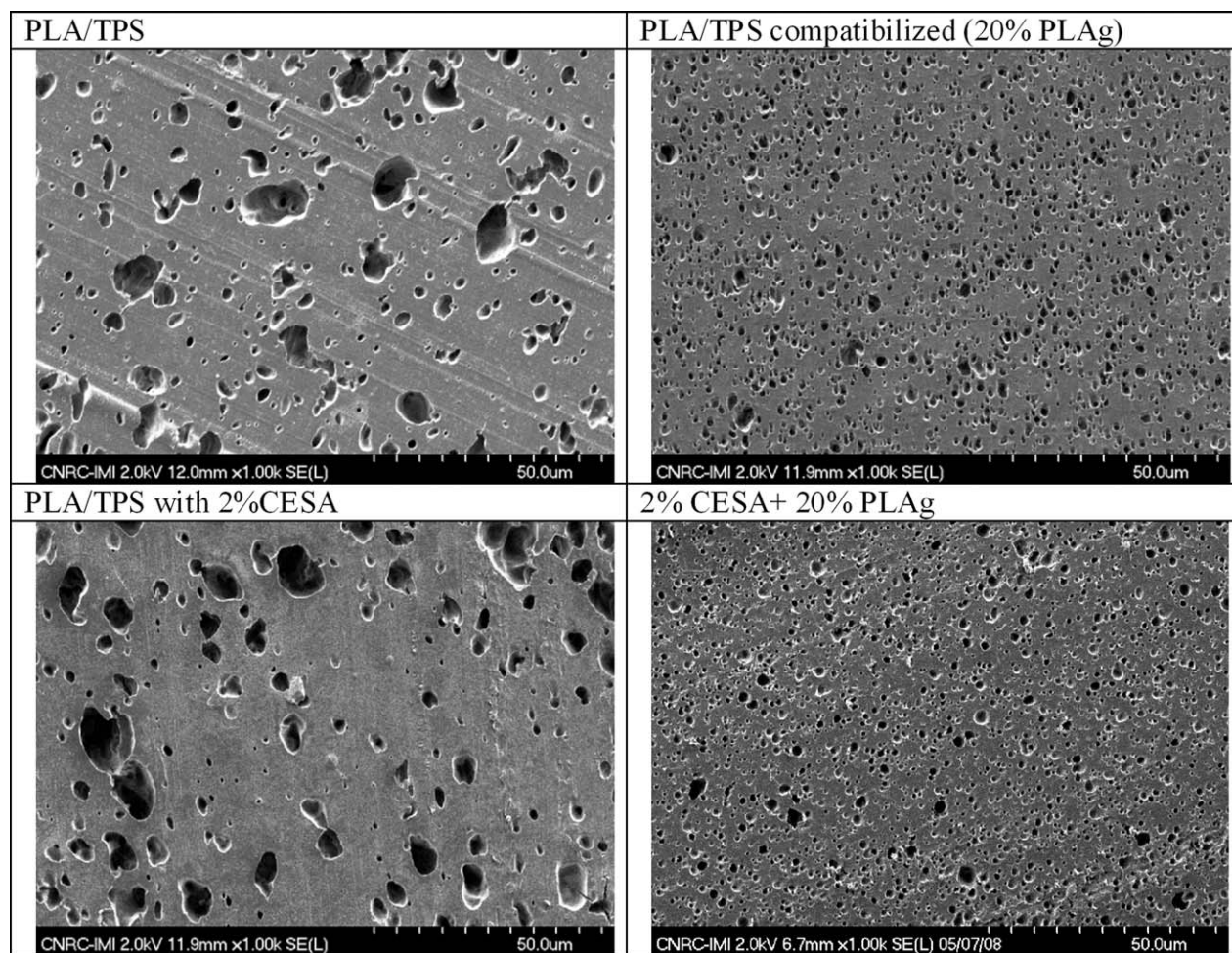


**Figure 3** Complex viscosity of glycerol plasticized PLA/TPS blends with different CESA contents.



**Figure 4** Complex viscosity of sorbitol plasticized PLA/TPS blends with different CESA contents.





**Figure 5** Effect of CESA on the morphology of glycerol plasticized PLA/TPS blends.

The shear viscosity of the blends was comparable with that of pure PLA. By adding 2 and 5% of the chain extender into the blends, the viscosity at shear rate of  $1 \text{ s}^{-1}$  was increased by factors of 5 and 10 relative to the viscosity of pure PLA. The same as the glycerol plasticized blends, there were no Newtonian Plateau at low shear rates.

### Blend morphology

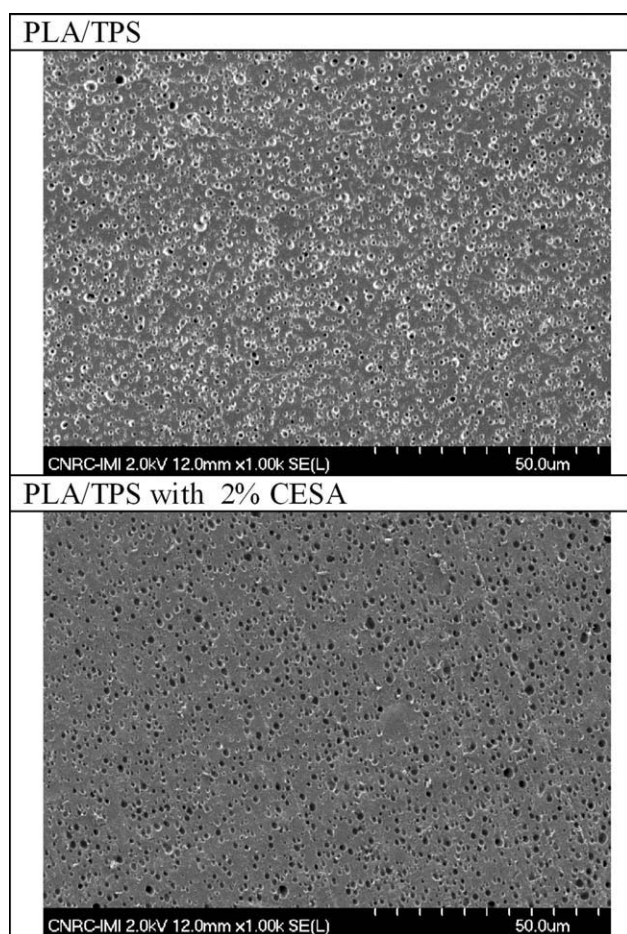
SEM micrographs of glycerol-PLA/TPS blends are presented in Figure 5. The TPS phase has been selectively dissolved before observation, and therefore, appears as the darker phase in the micrographs. For glycerol plasticized TPS, a very coarse dispersion was obtained for noncompatibilized blends with particles ranging from 5 to 30  $\mu\text{m}$ . The dispersed phase size was reduced to 1–3  $\mu\text{m}$  for the compatibilized blends, in agreement with previously reported results.<sup>6</sup> It was interesting to investigate if the epoxy-based chain-extender could interact with the hydroxyl moieties present on the starch macromolecules, and thus, play a role at the blend's interface. However, the micrographs comprising 2% CE were nearly identical

to their compatibilized and noncompatibilized counterparts without the chain extender. It is therefore safe to say that the chain extender strictly reacts with PLA chain-end and does not create any graft copolymer of PLA with starch amylose/amylopectin macromolecules. Similar morphological observations were made with 0.5 and 5% CE (not shown).

Figure 6 presents similar results but for sorbitol plasticized TPS dispersed in PLA. As reported previously, the use of sorbitol instead of glycerol as TPS plasticizer enables a dramatic reduction in TPS dispersed phase size.<sup>9</sup> The TPS particle diameter were in the 1–2  $\mu\text{m}$  range and were more spherical and better distributed than in the glycerol-PLA/TPS blends. In this case, the use of the compatibilizer did not further decrease the TPS phase size. Also as observed in Figure 5, the addition of the CE did not modify the blend morphology.

### Tensile characterization

The tensile properties of the blends are shown in Table I. The tensile stress of the glycerol plasticized



**Figure 6** Effect of CESA on the morphology of sorbitol plasticized PLA/TPS blends.

materials was in the 40–50 MPa range, whereas the modulus was in the 2.7 to 3.3 GPa range. There was no significant difference with chain extender or compatibilizer addition. Similarly, the elongation at break did not vary widely and was within the 4–5% elongation range. The only exception is the blend with both the chain extender and the PLAG which suddenly exhibited dramatically increased elongation. This particular feature is related to the ability

of the material to deform through a necking mechanism after the yield point. It may be related to the improved chain entanglement and better bonding through an increase in molecular weight of the PLAG modifier by using the chain extender, which improves the stress transfer between PLA and the ductile TPS with 36% glycerol.<sup>6</sup> The sorbitol plasticized blends exhibited significantly higher tensile strength and modulus values than the glycerol ones with values respectively, around 61 MPa and 3.5 GPa. Again, no significant differences were observed between the samples with and without the chain extender. Low elongations in the 4–5% range were also obtained for these blends.

### Thermal analysis

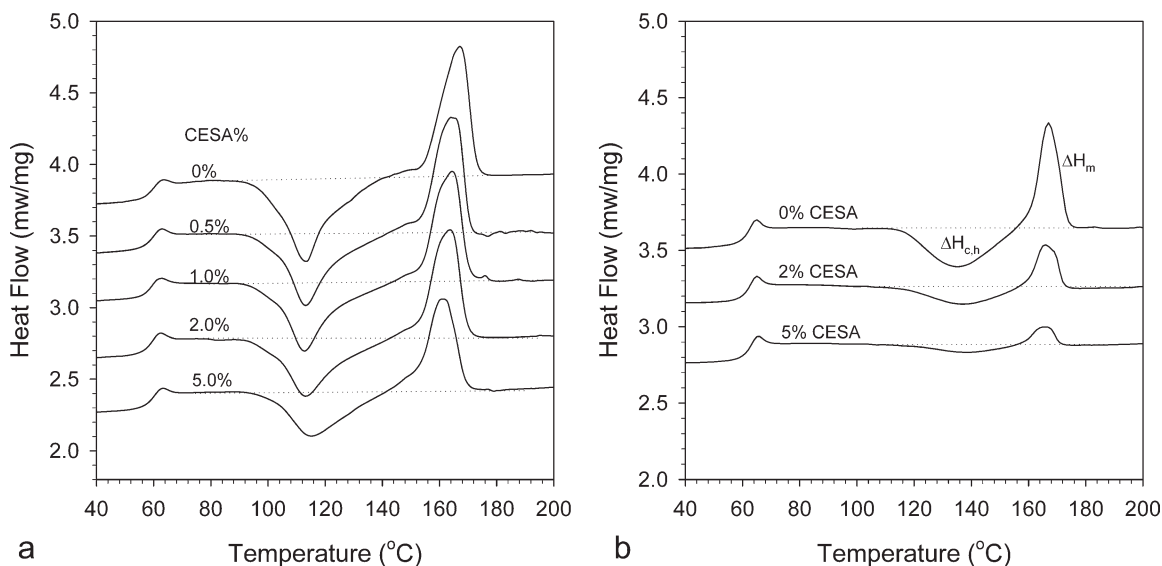
The thermal analysis for the PLA/TPS blends is shown in Figure 7 and the thermal data is summarized in Table II. The thermal data was based on the second heating run. Thus, a first heating/cooling cycle was used to eliminate process history effects and compare all samples on an equal basis. It is noteworthy that there was no significant crystallization upon cooling (before the second heating run).<sup>18</sup> Upon reheating, the samples thus showed strong crystallization exotherms between 90 and 140°C followed by complete melting of the formed crystallites between 145 and 175°C. Figure 7(a) shows the effect of CESA on crystallization of glycerol-PLA/TPS blends. For PLA/TPS blends without chain extender, the melting enthalpy was estimated at 43 J/g corresponding to 46% crystallinity based on a pure PLA melting enthalpy of 93 J/g.<sup>19</sup> The addition of the chain extender decreased the melting enthalpy progressively down to around 31 J/g for 5% CE. The lowering of the crystalline content is expected as some of the PLA chains will end up in grafted structures with multiple PLA chains attached to a single chain extender molecule. The increase of the material viscosity will also tend to slow the crystallization rate leading to lower final crystallinity if

**TABLE I**  
Tensile Properties for PLA/TPS Blends

Plasticizer	CE (wt %)	PLAg (wt %)	Strength <sup>a</sup> (MPa)	Modulus <sup>a</sup> (GPa)	Elongation at break <sup>a</sup> (%)
Glycerol	0	0	46.6 (0.8)	3.32 (0.13)	4.0 (0.19)
	0	20	50.9 (0.6)	3.16 (0.06)	4.7 (0.14)
	0.5	0	47.7 (0.8)	3.09 (0.05)	4.4 (0.22)
	1.0	0	49.5 (0.9)	3.09 (0.01)	4.6 (0.16)
	2.0	0	47.3 (0.7)	3.13 (0.06)	4.2 (0.12)
	5.0	0	50.8 (0.6)	3.17 (0.09)	4.8 (0.17)
	2.0	20	46.6 (2.9)	2.77 (0.15)	339 (10)
	Sorbitol	0.0	0	60.5 (2.3)	3.59 (0.10)
	2.0	0	62.8 (0.7)	3.47 (0.06)	5.2 (0.15)
	5.0	0	62.4 (1.3)	3.51 (0.14)	5.3 (0.22)

<sup>a</sup> Standard deviation given between parenthesis.





**Figure 7** (a) Effect of CESA on crystallization of glycerol plasticized PLA/TPS blends; (b) Effect of CESA on crystallization of sorbitol plasticized PLA/TPS blends.

crystallization cannot proceed to completion upon heating. Figure 7(b) shows the effect of CESA on crystallization of sorbitol-PLA/TPS blends. The sorbitol plasticized blends exhibited much lower crystalline content. The addition of the chain extender further decreased the attained crystallinity. Similar arguments can be used to explain the lowering of the crystallinity content.

## CONCLUSIONS

The effect of chain extension on the morphology and on the mechanical and thermal properties of PLA/TPS blends was investigated. The use of a styrene-acrylic-epoxy oligomer can effectively increase the viscosity of PLA/TPS blends. This can potentially compensate for any PLA molecular weight loss due to the presence of residual water in TPS during compounding or to the viscosity drop encountered when using the lower molecular weight grafted resins as

blend compatibilizers. Thus, chain extension enables the fine tuning of the material rheology in terms of specific viscosity or melt strength. It should therefore be possible to fulfill the rheological requirements of a wide range of polymer processing techniques. In the investigated materials however, chain extension resulted in relatively minor differences in tensile mechanical properties or in PLA/TPS blend morphology. This indicates that the chain extender played effectively its role in terms of linking PLA end groups but did not play any particular interfacial role. The combination of interfacial modification and chain-extension strategies led to greatly improved ductility, probably because of the improved PLA molecular weight and chain entanglement at the interface, which improves the stress transfer between PLA and the ductile glycerol-TPS phase.

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**TABLE II**  
Thermal Transitions of TPS/PLA Blends  
with Chain Extender

Plasticizer	CE (wt %)	$T_g$ (°C)	$T_m$ (°C)	$\Delta H_m$ (J/g)
Glycerol	0	58.5	167.2	43.5
	0.5	58.3	163.9	37.1
	1	57.6	164.5	36.6
	2	57.9	163.7	35.8
	5	58.5	161.4	31.3
Sorbitol	0	60.8	166.9	24.9
	2	61.3	165.8	11.2
	5	61.5	165.8	4.4

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