

Comparison of Sorbitol and Glycerol as Plasticizers for Thermoplastic Starch in TPS/PLA Blends

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ABSTRACT: This article investigates the structure and properties of thermoplastic starch/PLA blends where the TPS phase is plasticized by sorbitol, glycerol, and glycerol/sorbitol mixtures. The blends were prepared using a twin-screw extruder where starch gelatinization, water removal, and dispersion of TPS into a PLA matrix were carried out sequentially. The plasticizers were added to starch in the first stage of the extruder to allow complete starch gelatinization. The PLA was added at mid-extruder and thoroughly mixed with the TPS. The plasticizer concentration was varied from 30 to 42% and the TPS content was varied from 27 to 60% on a weight basis. In all investigated blends,

the PLA formed the continuous phase and the TPS was the dispersed phase. The viscosity, blend morphology, tensile mechanical properties as well as the thermal properties of the materials were measured. It was found that the glycerol/sorbitol ratio has an important effect on the blend properties. Finer blend morphologies, higher tensile strength and modulus but lower crystallization rate were found for the sorbitol plasticized blends. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 2439–2448, 2011

Key words: thermoplastics starch; poly(lactic acid); blends; sorbitol; glycerol

INTRODUCTION

Thermoplastic starch (TPS) and polylactic acid (PLA) are two biobased and biodegradable polymers that are increasingly being used for the replacement of petrochemically-based polymers. PLA is an aliphatic polyester. It is often compared to PET because of its transparency, good stretchability, and low crystallization rate. It is used to fabricate biaxially oriented films, thermoformed containers, and stretch-blown bottles.¹ PLA has good barrier properties to aromas but has higher permeability to carbon dioxide, oxygen, and water vapor.^{1,2} TPS is a material obtained by destroying the crystalline structure of native starch in presence of a plasticizer (i.e., the so-called gelatinization process). In turn, the nature and concentration of this plasticizer governs, to a great extent, the rheological and mechanical properties of the TPS. Water is a strong plasticizer for starch, but for material applications, higher boiling point plasticizers are preferred because they improve the material stability and water resistance. Thermoplastic

starch has low oxygen permeability and thus could potentially play an oxygen barrier role in biodegradable packaging.^{3,4} Because of its hygroscopic nature however, the TPS must be blended with another polymer to produce useful materials for packaging and industrial applications. The addition of dry-starch to PLA to form composites has been investigated but generally leads to very brittle materials.^{5–8} The addition of starch in its thermoplastic state is more promising since it can deform under flow leading to much finer dispersions. Adding TPS into a PLA matrix can also decrease the material cost and increase its biodegradation rate. The first reports on noncompatibilized TPS/PLA blends showed only poor and nonhomogeneous TPS dispersions and poor mechanical properties due to the lack of interfacial compatibility between the PLA and TPS.⁹ More finely and homogeneously dispersed PLA/TPS blends were achieved by using a compatibilization strategy that involved the use of maleic anhydride grafted PLA.¹⁰ This finding has opened the path to the biaxial stretching of compatibilized PLA/TPS blends for the production of biaxially oriented films¹¹ and to the production of low-density foams.¹²

Common TPS plasticizers include water, polyols such as glycerol and sorbitol and amide functionalized chemicals such as urea, formamide, and ethylene-bisformamide. Recently, the combination of

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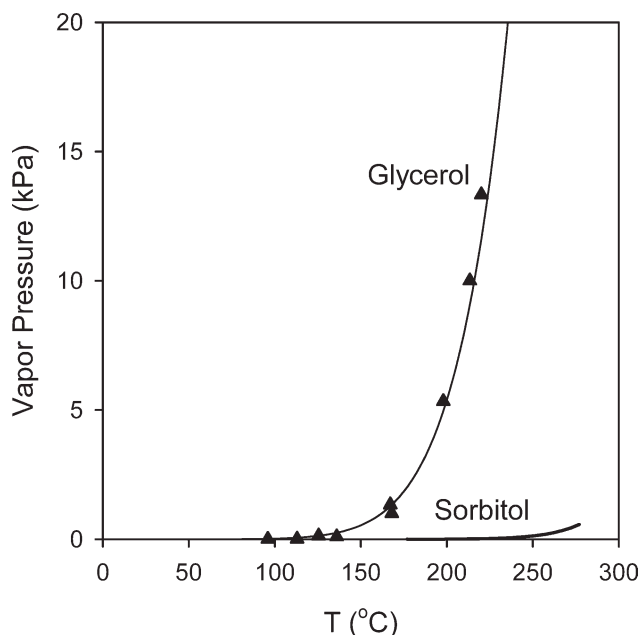


Figure 1 Vapor pressure of sorbitol and glycerol. (Data for sorbitol is based on the equation from Ref. 19 and data for glycerol is from Ref. 20).

different plasticizers was investigated as a means of overcoming or reducing problems such as the starch retrogradation, long-term plasticizer migration, and TPS embrittlement. Investigated combinations include formamide/urea,¹³ ethylene-bisformamide/sorbitol,^{14,15} sorbitol/glycerol,¹⁶ and glycerol/maltose.¹⁷ The use of plasticizer mixtures may also open the possibility of tuning the water resistance and tensile properties of the material.

In this study, we will concentrate on sorbitol and glycerol as plasticizers for TPS. Glycerol and sorbitol are both FDA-approved as food additives, and are plasticizers known to strongly interact with starch at the molecular scale by forming hydrogen bonds with the starch (i.e., amylose) macromolecules. The effect of glycerol and sorbitol on the glass transition temperature (T_g) of starch was thoroughly investigated by Lourdin et al.¹⁸ using DSC analysis. It was shown that both plasticizers can decrease the T_g of the TPS and that they are therefore effective plasticizers for starch. For example, the T_g of starch with 15% moisture and 30% plasticizer was decreased from around 87 to 25°C for glycerol and to 35°C for sorbitol. Similar observations were also reported by Yang et al.¹⁴ On the basis of DMA analysis, they reported that the T_g for the sorbitol-plasticized TPS was decreased to around 60°C, comparing with the value of 38°C for the glycerol plasticized TPS at the same weight content of 30%. One advantage of sorbitol during blend preparation is that it has a lower volatility; sorbitol has a melting point of 95°C compared to 18°C for glycerol. Figure 1 compares

the reported vapor pressure of sorbitol¹⁹ and glycerol²⁰ as a function of temperature. Above 200°C, the vapor pressure of glycerol increases dramatically following an exponential growth while the vapor pressure of sorbitol remains almost negligible. This is an advantage in terms of limiting plasticizer losses and improving the thermal stability of the material. The use of sorbitol is also expected to improve water resistance as well as tensile properties. Yang et al.¹⁴ reported that the equilibrium moisture content of sorbitol plasticized TPS was much lower than that of glycerol plasticized ones. The sorbitol plasticized TPS also exhibited a higher decomposition temperature. The stronger starch–sorbitol interaction was also believed to reduce water absorption and thus increase the TPS's water resistance.

Unfortunately the use of sorbitol as plasticizer for starch is limited by its tendency to migrate to the part surface and by its recrystallization over time. The materials thus eventually lose their homogeneity and become brittle. According to Krogars et al., the combination of sorbitol and glycerol effectively improved the stability of solution cast TPS films and limited sorbitol migration.¹⁶

The blending of TPS into a hydrophobic polymer matrix, undoubtedly limits the migration of the plasticizer to the surface. Ke et al.²¹ has investigated blends of PLA and up to 40% TPS plasticized by adding 5–25% sorbitol. The resulting morphology was very coarse, with TPS dispersed phase size around 20 μm , roughly the same size as the dry-starch particles. The tensile properties of the composites were highly deteriorated in comparison to the pure PLA. It is possible that the low plasticization level used may not have provided sufficient fluidity to the TPS phase. A second factor is that the PLA, starch, and sorbitol were dry-mixed and fed together into a twin screw extruder. Therefore, part of the sorbitol may have been incorporated into the PLA phase and thus further reduced the available plasticizer concentration for starch gelatinization prior to TPS/PLA mixing.

By contrast with earlier reports, the starch plasticization/gelatinization, water devolatilization, and PLA/TPS mixing were performed in sequence in this study. The purpose of the investigation was to determine if finer TPS dispersions and better mechanical properties can be achieved using the sequential process and to evaluate the potential of sorbitol/glycerol combinations for TPS plasticization in TPS/PLA blends. Blend rheology, differential scanning calorimetry, thermogravimetric analysis, X-ray diffraction, blend morphology observation by electronic microscopy, and tensile mechanical testing were performed to compare the potential of glycerol, sorbitol, and glycerol/sorbitol mixtures as plasticizers in the TPS/PLA blends.

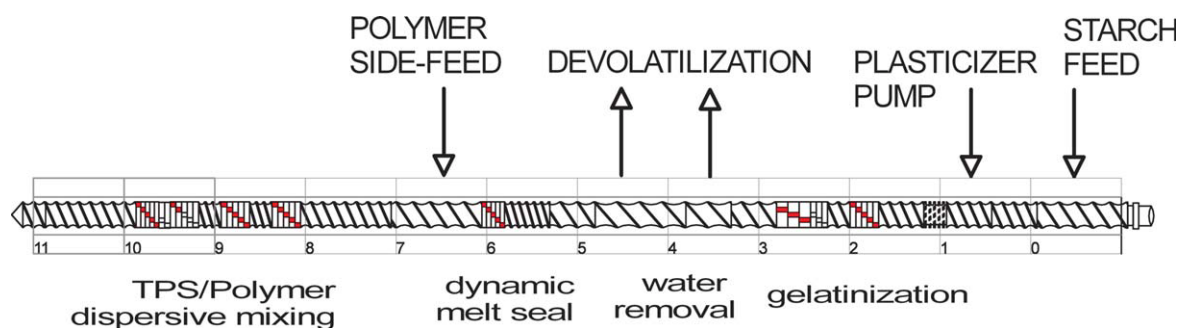


Figure 2 Process configuration for TPS/polymer blending. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

EXPERIMENTAL

Materials

The poly(lactic acid), supplied by NatureWorks, was a semicrystalline grade (PLA 4032D) comprising around 2% D-LA. Wheat starch, Supergel 1203, was provided by ADM-Ogilvy. The reactive modification of PLA was performed using Maleic anhydride (95% pure) 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.¹⁰ According to literature, the grafting level using this technique is around 0.5%.²²

D-Sorbitol was obtained from Aldrich Chemical Company with a purity of 98%. The glycerol was a 99.5% pure USP grade supplied by Mat Laboratories.

Sample preparation

PLA/TPS blends were prepared on a Leistritz 34-mm corotating twin-screw extruder with an L/D ratio of 42 using a sequence of twin-screw operation that was successfully used for polyethylene/TPS blends²³ and that is also described in patent literature.²⁴ The process and screw configuration are shown in Figure 2. The screw configuration was the result of trial and error optimization to provide enough mixing for starch gelatinization and TPS/PLA blending and at the same time to minimize degradation. The first half of the extruder was dedicated to starch gelatinization. The starch and sorbitol were introduced in the primary feed hopper. Glycerol was pumped downstream. The first mixing zone was used to gelatinize the starch. The material then entered a devolatilization zone to remove the free-water from the TPS. The PLA was introduced in the second half of the extruder. It was mixed with the TPS phase using a kneading section. For compatibilized blends, 20 wt % of the PLA was substituted

by maleic anhydride grafted PLA (PLAg). The PLA and PLAG were simply dry-blended prior to extrusion. The sorbitol/glycerol ratio was varied from 0 : 36, 12 : 24, 24 : 12, 36 : 0, maintaining a total plasticizer content of 36% in TPS on a weight basis. 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 screw rotation speed was set to 100 rpm and the mixtures were extruded at a rate of 10 kg h⁻¹ through a two-strand die. The TPS content in most blends was set to 27 wt % but blends with 42 and 60 wt % of sorbitol plasticized TPS were also produced to evaluate the effect of sorbitol-TPS concentration on the blend morphology. The strands 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.

In addition to PLA/TPS blends, pure TPS bands plasticized with glycerol and sorbitol were produced in conditions similar to those existing in the gelatinization portion of the compounding process. The purpose was to assess the structure of the TPS at the end of the gelatinization zone, prior to its mixing with PLA. The TPS was therefore produced using a shorter screw configuration comprising only barrel sections 0 to 7 (see Fig. 2) corresponding to an L/D ratio of 28. A slit die (30 mm × 1 mm) was mounted at the end of the extruder to produce rectangular TPS bands. The bands were supported on a conveyer belt after die exit and air-cooled over a conveyer length of 5 m. The extruded bands were collected and sealed in plastic bags for 24 h and then subjected to XRD analysis and tensile testing.

Rheology testing

The rheological properties of 27%TPS/PLA blends with various plasticizer 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 sweep were carried out to determine the complex viscosity over a frequency ranging from 0.1 to 100 rad s⁻¹. 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.

Gelatinization

Wide-angle X-ray diffraction measurements were carried out directly on the pure TPS bands. The diffraction patterns were obtained with a D-8 X-ray diffractometer (Bruker). The samples were exposed to the X-ray beam with the X-ray generators running at 40 kV and 40 mA. The scanning was carried out at a rate of 0.035°/s in the angular region (2θ) of 2°–40°.

Thermogravimetric analysis (TGA)

TGA was carried out on 50-mg samples using a Setaram thermogravimetric analyzer. The samples were heated from 25 to 450°C in a nitrogen environment at a rate of 10°C min⁻¹.

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⁻¹, kept in the molten state for 2 min to erase prior thermal history and then cooled at –10°C min⁻¹ 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⁻¹ to assess the crystallization behavior upon heating.

Morphological characterization

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⁻¹ according to ASTM D638. The samples were injection molded Standard Type I samples with a

thickness of 3.1 mm. These were sealed in plastic bags after injection and then conditioned at room temperature for 24 h prior to testing. For each of the materials, a minimum of five samples were tested and the average values with standard deviation were reported.

RESULTS AND DISCUSSION

Rheology of PLA/TPS blends

The viscosity at 180°C of compatibilized 27% TPS/PLA blends with various glycerol/sorbitol ratio is presented in Figure 3. The total plasticizer content (glycerol + sorbitol) in the TPS phase was maintained at a level of 36%. The blends with TPS plasticized with glycerol alone had the lowest shear viscosity with a zero-shear viscosity around 2 kPa s⁻¹, a three-fold decrease in comparison to the virgin PLA. As glycerol was progressively substituted by sorbitol, the blend viscosity increased. For the material with the TPS solely plasticized with sorbitol, the blend viscosity was similar to that of the virgin PLA. Unfortunately, direct viscosity measurements of pure TPS in oscillatory shear at 180°C (and atmospheric pressure) were not possible due to plasticizer evaporation and change in residual humidity during the test. It is interesting to postulate on the possible reasons for the large difference in viscosity associated with the selection of the plasticizer. In a blend with a nodular morphology, the rheological properties are expected to be in closer relation with the properties of the matrix than with those of the

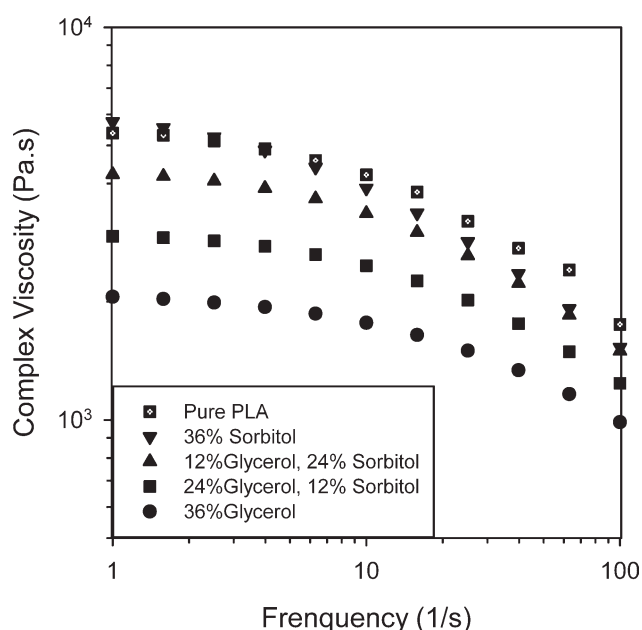


Figure 3 Complex viscosity of 27% TPS/PLA blends with different sorbitol/glycerol ratio as a function of oscillation frequency.

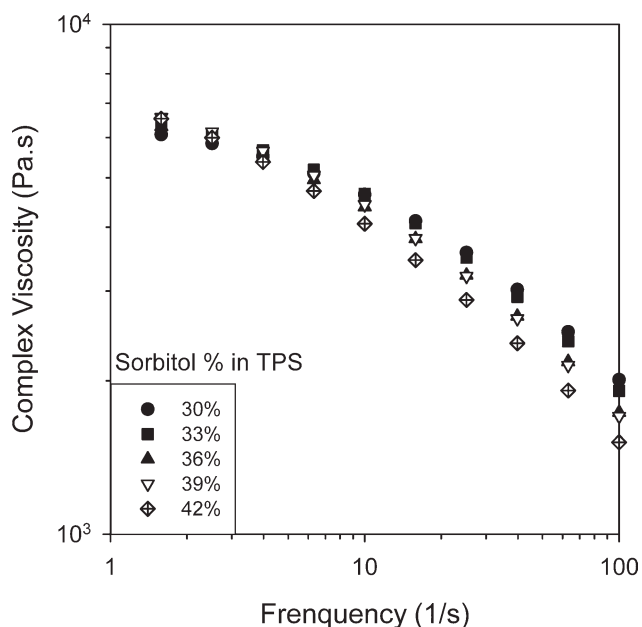


Figure 4 Complex viscosity of 27% TPS/PLA blends with different sorbitol content as a function of oscillation frequency.

dispersed phase. The chain scission of PLA is one potential cause for the large viscosity reduction. However, in independent control experiments, the viscosity of extruded PLA was found to be nearly identical to that of the virgin resin. Another potential reason for viscosity depression in blends with glycerol-TPS could be plasticizer transfer from the TPS phase to the PLA phase. We will further discuss this topic after examination of the blend morphology.

The effect of the sorbitol content on the PLA/TPS blend viscosity is presented in Figure 4. The sorbitol content was varied from 30 to 42%. The viscosity data did not fully reach the zero-shear plateau region in the investigated shear-rate range but it could be inferred from the shape of the viscosity curves that the extrapolated plateau values would not vary widely with sorbitol content. On the other hand, at high oscillation frequency, the more highly plasticized blends exhibited lower viscosities and more shear-thinning (i.e., greater slope).

Thermal stability

One potential drawback with the use of TPS is the potential evaporation of the plasticizer at elevated temperature which leads to changes in mechanical properties. Sorbitol could hold a clear advantage over glycerol in that respects as shown earlier with the vapor pressure data. This was verified using thermogravimetric analysis between 25 and 450°C. The TGA results for 27% TPS/PLA blends are presented in Figure 5. The compared blends comprised

a total of 36% of either sorbitol, glycerol or a 24 : 12 sorbitol : glycerol mixture in the TPS phase. There were no observable weight loss below 200°C and most of the weight loss occurred in the 300–400°C range. The three materials exhibited a similar behavior but the stability was greater for the sorbitol plasticized materials. The embedded graph shows $T_{5\%}$ defined as the temperature for a weight loss of 5% and used as a plasticizer loss indicator. The $T_{5\%}$ increased from 287°C for the glycerol plasticized blends up to 308°C for the sorbitol plasticized one. The increased thermal stability for sorbitol plasticized blends can be associated to its lower volatility but could also be linked to stronger plasticizer-starch interactions.

Blend morphology

The blend morphology is presented in Figure 6 for uncompatibilized and compatibilized blends. The compatibilized blends were obtained by substituting 20% of the virgin PLA by maleic anhydride grafted PLA. A very coarse morphology with particles ranging from 5 to 30 μm was obtained for the non-compatibilized glycerol plasticized blends. As found in previous work,¹⁰ the dispersed phase size for the same blend was reduced to the 1- to 3- μm range in the compatibilized case. Surprisingly, as the glycerol was substituted by increasing levels of sorbitol, the particle size in the uncompatibilized blends progressively decreased to the 1- to 2- μm range and the particles became more spherical and more homogeneously distributed. In the compatibilized case, the

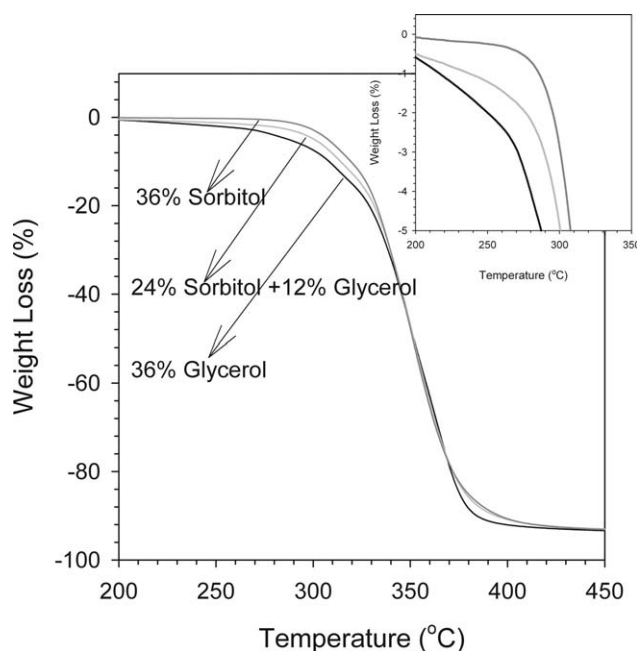


Figure 5 TGA curves for 27% TPS/PLA blends with different sorbitol/glycerol ratios.

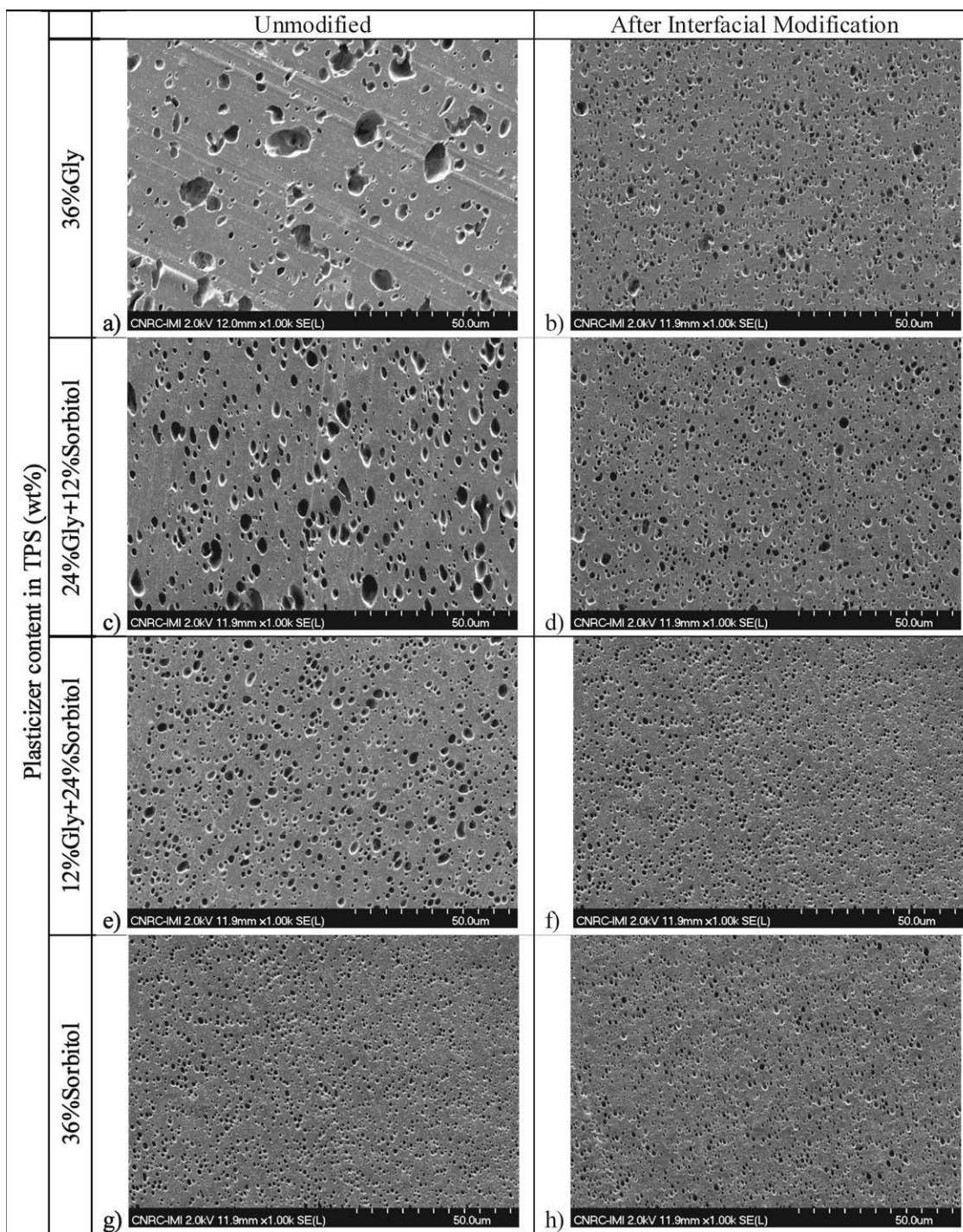


Figure 6 Effect of different sorbitol/glycerol ratio on the morphology of 27% TPS/PLA blends.

glycerol plasticized TPS dispersions was already finer but substitution of glycerol by sorbitol further reduced the particle size and improved the distribution homogeneity.

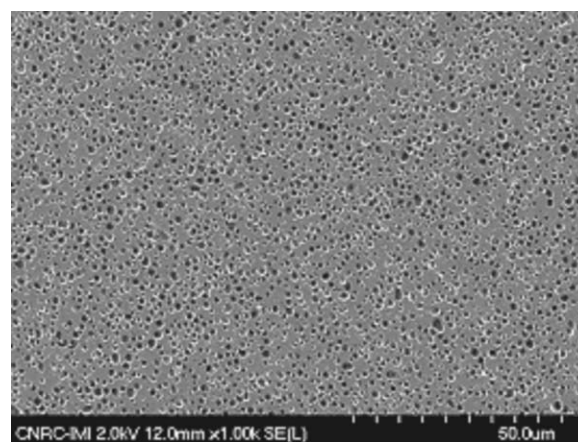
The dispersed phase size reduction with the substitution of glycerol by sorbitol was unexpected. In general, the dispersed phase size of a blend is in close relation with the blends interfacial tension and all compatibilization strategies aim at reducing the

interfacial tension and at minimizing the coalescence of the dispersed phase. It is unlikely that the plasticizer substitution would dramatically change the TPS surface properties. Therefore, a more likely explanation may come from a change in the viscosity ratio between the dispersed TPS phase and the PLA matrix. In the case of the glycerol-TPS, it was noted in Figure 3 that the substitution of glycerol by sorbitol in the TPS increased significantly the blends

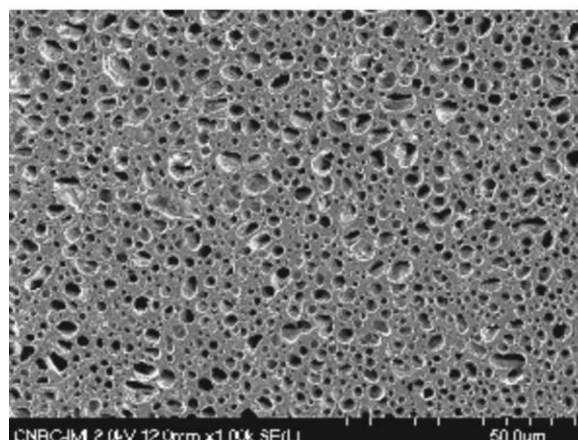
viscosity. As mentioned earlier, this change cannot be explained by changes in the TPS viscosity alone since the viscosity of blend with a nodular dispersion is typically governed by the blend's matrix properties. Therefore, it is likely that the lower viscosity with the glycerol-TPS came from a plasticizer transfer from the TPS to the PLA. The rheological consequences of such a transfer are a decrease in matrix viscosity and, more importantly, a dramatic increase in the viscosity of the dispersed TPS phase. These two effects both lead to a higher viscosity ratio. Even in absence of significant interfacial forces, polymer blends with high viscosity ratios are known to be more difficult to disperse than blends with well matched viscosity leading to coarser morphologies.²⁵ The lack of sorbitol migration was also supported by very weak effect of plasticizer concentration on the blend rheology presented in Figure 4. The blend morphology obtained in the investigated sorbitol concentration range, between 30 and 42%, (not shown for conciseness) were nearly identical to the one reported in Figure 6(g). Thus, as for the viscosity, the blend morphology was not dependant on the sorbitol level and remained in all cases much finer than for the glycerol-plasticized materials. The rheological measurements in combination with the morphological observation therefore support the hypothesis that plasticizer transfer is more significant when using glycerol-plasticized TPS leading to coarser morphologies than in the case of sorbitol-plasticized TPS.

All the above results were using a TPS content of 27%. The finding of finely dispersed sorbitol-TPS in absence of interfacial modifier was clearly unexpected. Blends with 42 and 60 wt % TPS were prepared to verify if this fine dispersion could be maintained over a large TPS concentration range. The blend morphologies are presented in Figure 7. For the 42% blend, the particle size remained surprisingly fine, below 2 μm , almost similar to the 27% blend. For the 60 wt % blend, particles became larger, in the 5- to 7- μm range, but remained spherical and homogeneously distributed. There was also no indication of phase inversion (to a TPS matrix). By contrast, much coarser blend morphologies with large and irregularly shaped particles were found in earlier work for uncompatibilized blends comprising glycerol-TPS at the same concentration.¹⁰

It is noteworthy that the blend morphologies reported in this work are much finer than those reported by Ke et al.²¹ for 40% sorbitol-TPS/PLA blends. One obvious reason is that the investigated sorbitol concentration range in this study, 30–42%, was higher than the one explored by Ke et al. (5–25%). This lowers the TPS viscosity and improves its dispersability. Another factor may also be the sequential process operations used in this study



a) 42% TPS



b) 60% TPS

Figure 7 Effect of TPS content on the sorbitol-TPS/PLA blend morphology.

which enables complete starch gelatinization before the TPS is mixed with the PLA. X-ray diffraction was used to detect changes in the crystalline and ordered structures of starch upon processing and as a way to ensure that complete gelatinization was achieved at the end of the compounding process.^{26,27} Figure 8 shows the X-ray diffraction pattern as a function of angle 2θ for the pure TPS bands plasticized with 36% glycerol or 30–39 wt % sorbitol. The peaks observed around 15° , 18° , and 23° for the native wheat starch controls correspond to those expected from the A-type crystalline structures. These peaks have totally disappeared after processing in the first gelatinization section regardless of the plasticizer type and plasticizer contents. New peaks at 13.5° , 19° , and 21° have appeared for the gelatinized starches indicative of the V-type structure, a new structure formed by the complexing of plasticizers with amylose.²⁷ Therefore, in all conditions, the sequential process used in this study enabled complete gelatinization prior to the point of contact with PLA at mid-extruder.

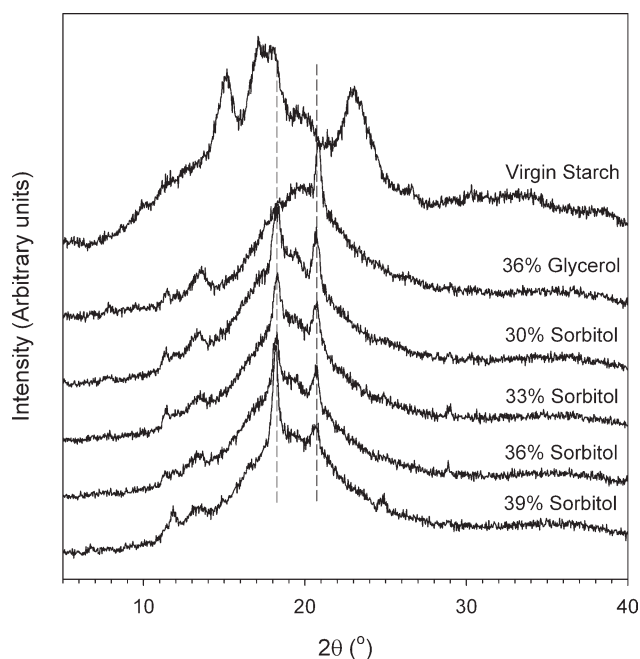


Figure 8 X-ray diffraction intensity for TPS plasticized with glycerol and sorbitol at a process temperature of 140°C.

Tensile characterization

Figure 9 compares the tensile strength and modulus of the sorbitol and glycerol plasticized TPS. As the plasticizer content increased from 33 to 39%, the tensile modulus and strength for sorbitol plasticized TPS remained relatively stable, with a high tensile strength over 20 MPa, and a high tensile modulus around 3 GPa. However, for the glycerol plasticized TPS, the tensile strength had a lower value of 17 MPa, and a lower tensile modulus around 1 GPa

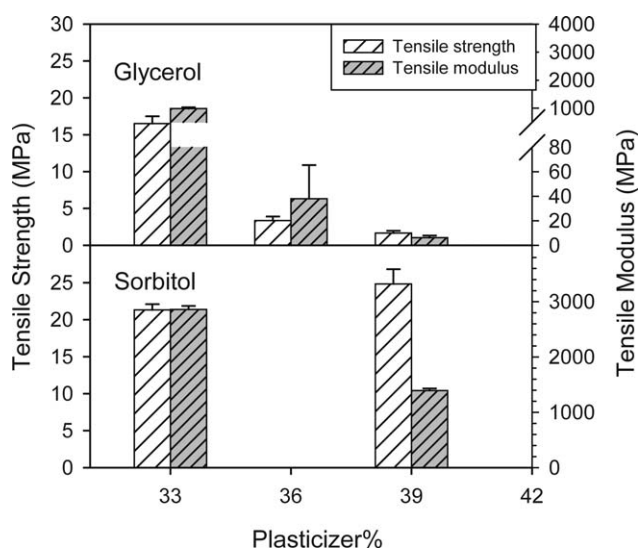


Figure 9 Comparison of tensile strength and modulus for sorbitol and glycerol plasticized TPS.

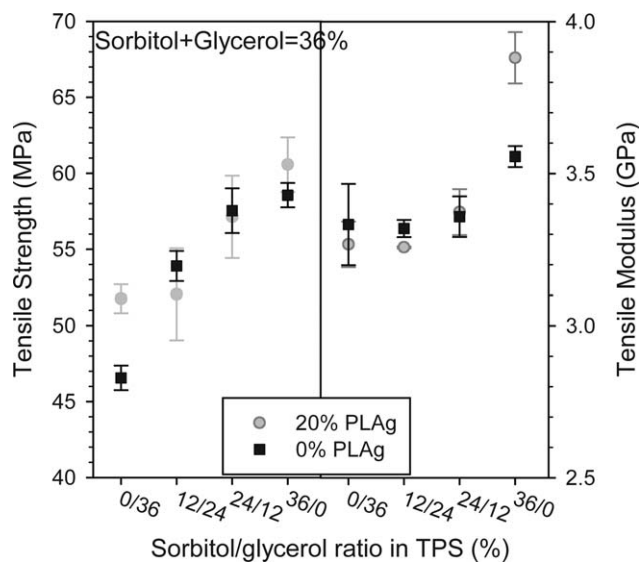


Figure 10 Effect of the sorbitol/glycerol ratio on the tensile strength and modulus of the 27% TPS/PLA blends.

at 33% glycerol content. As the glycerol content was increased above 36%, the tensile strength decreased dramatically, down to values as low as 5 MPa and the modulus was reduced below 20 MPa. Figure 10 shows the tensile properties of the 27% TPS/PLA blends and in particular the effect of glycerol substitution by sorbitol on the tensile strength and modulus. The total plasticizer level in the TPS was maintained at 36% in all blends. As expected from the results obtained on pure TPS, the tensile strength increased as glycerol was progressively substituted by sorbitol. The tensile strength increases from 47 MPa for glycerol plasticized blend to 59 MPa for sorbitol (complete substitution) plasticized blend. The modulus was also increased from around 3.3 GPa, for the glycerol-plasticized blend to 3.5 GPa for the uncompatibilized sorbitol plasticized blends. The lower plasticizer transfer discussed earlier, the finer morphology observed with sorbitol and the intrinsically higher sorbitol-TPS strength therefore had clear benefits in terms of material rigidity and strength. The compatibilization of sorbitol-plasticized blend using PLAG increased the modulus and strength to 3.9 GPa and 60 MPa, respectively. Thus, the lowering of the interfacial tension and the improvement in interfacial adhesion have further contributed to the property increase. These values were very close to those measured for pure PLA (3.7 GPa and 69 MPa, respectively). In terms of ultimate properties, all materials exhibited low elongations at break as expected from the brittle nature of PLA. All values were between 4 and 4.7% and did not present any significant trend as a function of glycerol substitution.

Figure 11 presents the tensile strength and modulus as a function of sorbitol content in 27% TPS/

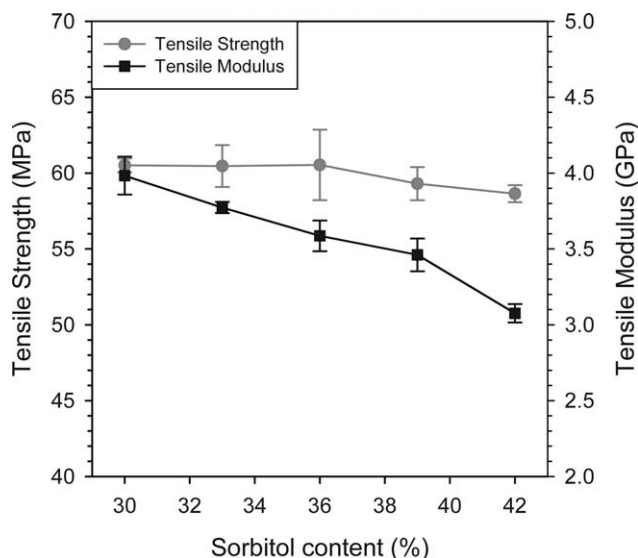


Figure 11 Effect of the sorbitol content on the tensile strength and modulus of the 27% TPS/PLA blends.

PLA blends. The tensile strength remained around 60 MPa in the whole sorbitol content investigated. The tensile modulus decreased slightly from 3.9 to around 3.0 GPa as the sorbitol content was pushed up to 42%. The relatively weak effect of the sorbitol is another argument supporting that sorbitol does not tend to migrate to the matrix.

The effect of the TPS content on the blend's tensile properties was also investigated and is reported in Figure 12. The plasticizer content in the TPS phase was set to 36%. Surprisingly, for sorbitol-TPS/PLA blends, the tensile modulus increased slightly from 3.6 to 3.9 GPa, and the tensile strength

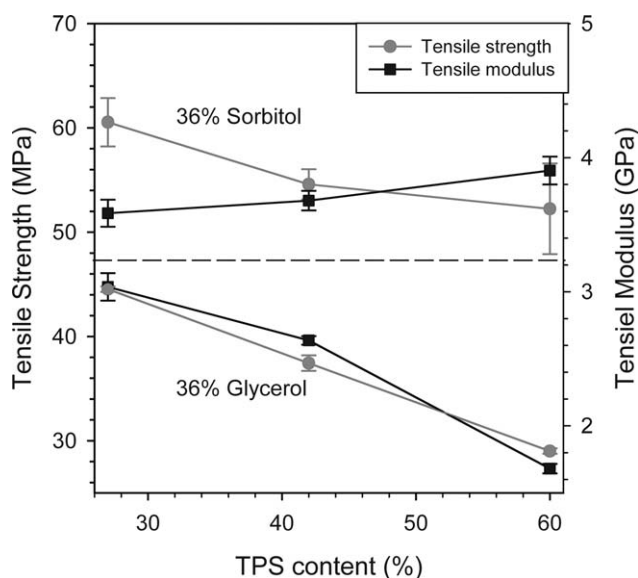


Figure 12 Effect of the TPS content on the tensile strength and modulus of the TPS/PLA blends.

decreased slightly from 60 to 52 MPa, as the TPS content increased from 27 to 60%. By contrast, the tensile strength of glycerol-TPS/PLA blends decreased from 44 to 27 MPa, and the tensile modulus decreased from 2.8 to 1.8 MPa over the same TPS content.¹⁰ The higher tensile strength and modulus for sorbitol-TPS/PLA blends are directly linked to the high tensile properties of sorbitol-TPS discussed in Figure 9.

Thermal analysis

In many applications, PLA crystallization is desired to improve thermal resistance.²⁸ Amorphous PLA has a T_g around 56°C, and this limits its use at higher temperature unless it can be crystallized. It has been reported that the presence of the glycerol-TPS phase increases the crystallization rate of PLA.²⁹ In this study, the effect of the TPS plasticizer on the crystallization of PLA was investigated in non-isothermal conditions. Figure 13 presents the DSC thermograms for blends comprising 27% TPS for various levels of glycerol substitution by sorbitol at a total plasticizer content of 36%. The thermal history of all materials was erased through a first heating run. The materials did not exhibit any crystallization peaks upon cooling at $-10^\circ\text{C min}^{-1}$. The presented data is for a second heating run carried out at a heating rate of $20^\circ\text{C min}^{-1}$. All formulations crystallized to their maximum crystallinity upon heating. The glycerol plasticized blend showed the lowest peak crystallization temperature upon heating, $T_{c,hr}$ around 112°C, and thus had the highest

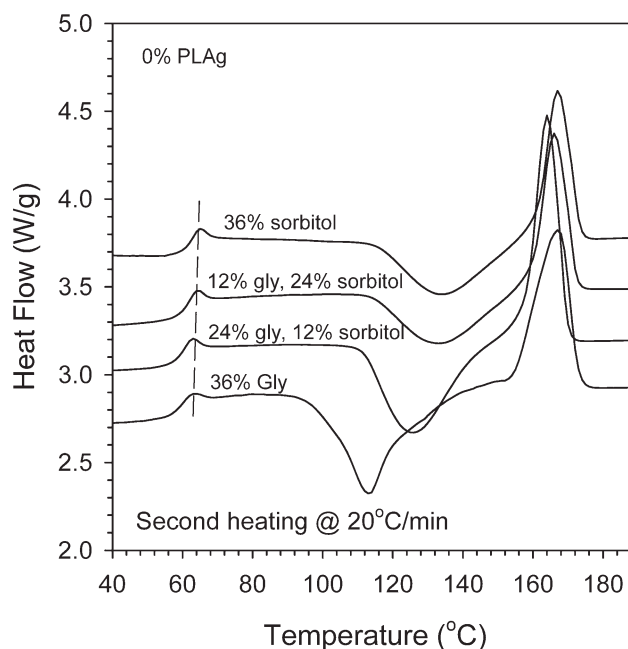


Figure 13 DSC thermograms for 27% TPS/PLA plasticized with different sorbitol/glycerol ratio.

crystallization rate. As the substitution of glycerol by sorbitol increased from 0 to 100%, the $T_{c,h}$ increased to 128°C. Obviously, the sorbitol plasticized TPS was less effective in promoting PLA crystallization. In earlier work, it was postulated that the increased crystallization rate in glycerol-TPS/PLA blends was associated to a nucleating effect of the TPS phase.²⁹ In light of the current results, it seems more likely that the crystallization rate improvement in TPS/PLA is coming from glycerol migration which increases the PLA chain mobility in the crystallization temperature range.

CONCLUSIONS

The use of glycerol and sorbitol as TPS plasticizers in TPS/PLA blends has been investigated. It was found that the sorbitol-plasticized TPS phase can be more finely dispersed and more uniformly distributed in the PLA matrix even in absence of any compatibilization. The sorbitol plasticized TPS/PLA blends exhibited much higher tensile strength and modulus. It was also shown to be less volatile in thermogravimetric measurements. It was postulated that much of the differences in the use of the two plasticizers lied in their affinity for the PLA phase. Rheological, morphological, and mechanical properties observations all inferred that glycerol was more prone to transfer from the TPS to the PLA phase than sorbitol. In the melt phase, this plasticizer migration leads to a higher viscosity ratio between the dispersed TPS phase and the PLA matrix, which in turn lead to coarser blend morphologies. In the solid state, the plasticizer transfer to the matrix lead to lower tensile strength and modulus but to a higher crystallization rate upon heating due to higher chain mobility.

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