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PROPERTIES OF POLY (LACTIC ACID) AND THERMOPLASTIC STARCH BLENDS

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Abstract -Blending starch with poly (lactic acid) (PLA) is one of the most promising efforts because starch is an abundant and cheap biopolymer and PLA is biodegradable with good mechanical properties. Different plasticizers are used and compared in order to best plasticize the starch. Polymer blends of PLA and thermoplastic wheat starch at various ratios are prepared by using a laboratory-scale twin screw extruder and compression molding. The thermal and mechanical properties as well as the morphology of the blends are studied. Starch and PLA are immiscible polymers. Copolymer of Amylose-g-PLA is prepared ex-situ in order to improve the properties of the blends. The grafting polymerization of PLA onto the amylose is done in three steps. In the first step, in order to limit and control the number of grafting chains, the amylose is partially silylated. The second step is the ring opening polymerization of lactide onto the remaining OH groups of the amylose and the last step is to deprotect the silylether groups. The number and chain length of the grafted PLA are varied. Three different structures of amylose-g-PLA are synthesized: (a) limited number but long chains of PLA grafts; (b) higher number but shorter chains of PLA grafts (the number and the length of the grafts are chosen in a way to have the same mass fraction of PLA in these two copolymers); (c) high grafting percentage of amylose and long chains of PLA.

Introduction

The development of synthetic polymers using monomers from natural resources provides a new direction to develop biodegradable polymers from renewable resources. One of the most promising polymers in this regard is PLA, because it is made from agricultural products and is readily biodegradable.

Blending starch with PLA is a route to reduce raw material costs, energy consumption and also to increase its rate of biodegradation.

Starch is one of the most promising natural polymers because of its inherent biodegradability, overwhelming abundance and its annual renewal (Blanshard, 1987). Native starch is usually in a granular form in which the polymer molecules are hydrogen bonded and aligned radially. Starch alone in a dry state is not considered a true thermoplastic in the sense that it would be degraded upon heating rather than melt on its own. However, in the presence of a plasticizer, starch would

behave as a thermoplastic (Simmons and Thomas, 1995)

The common plasticizers are usually water, glycerol or other polyols (Sorbitol, PEG,...) (Poutanen, 1996). Glycerol and sorbitol are polyhydric alcohols that are miscible with starch and are good plasticizers to starch (Yu et al., 1998; Lawton and Fanta, 1994; Arvanitoyannis et al., 1998). Some hydroxyl groups of glycerol and sorbitol were expected to interact with the ester group from PLA in some degree, such a hydrogen bonding (Ke and Sun, 2001).

Other components such as those containing nitrogen (Urea, ammonium derived, amines,...) can be used. (Kazuo et al., 1998; Stepto and Tomka, 1987). These plasticized starches are commonly called “thermoplastic starches” or TPS. (Shogren, 1993).

Glycerol appears to be a less effective plasticizer than water (Forssell et al. 1997) However, Perry and Donald (2000) have shown that gelatinization proceeds even when no water is present: there is no chemical requirement for water, the only requirement being

mobility, induced by some low molecular weight plasticizer.

However, without water the temperature for the onset of gelatinization by glycerol increased (Nashed et al., 2003; Tan et al., 2004). Upon heating, starch granules become solvated, with the amorphous regions of the plasticized starch granule. This transformation of granular starch into a thermoplastic-like material allows it to be processed in a similar fashion to conventional polymers. At glycerol contents in the TPS lower than 10-15%, the plasticization leads to reduced mechanical properties (Lourdin et al., 1997). A more effective plasticization can be obtained at higher glycerol contents, in a range where glycerol demixing can occur in the thermoplastic starch. Thermoplastic starch itself is characterized by moisture sensitivity and weak mechanical properties as compared with other thermoplastic polymers. Blends of other polymers with thermoplastic starch represent an important route to overcome these limitations (Sarazin et al., 2008).

Martin and Ave'rous (2001) were the first to study TPS/PLA blends. They observed that the modulus of the blends decreased when the TPS fraction increased. In comparison to the pure TPS and PLA materials, all the blends showed a marked decrease in the elongation at break, tensile strength and impact resistance. They explained the poor mechanical properties by the lack of affinity between the two phases.

The type and quantity of the plasticizer influence the properties of the blends of TPS with PLA. Different plasticization strategies are compared in this work.

Polymer compatibility is an important factor in the development of polymer blends. Compatibility is critical in governing the morphology of the blend and, therefore, the final-state physical and mechanical properties of the system. One of the major governing factors that control the compatibility in polymer blends is interfacial tension (Vanoene, 1972).

One of the ways of improving the compatibility is the addition of a compatibilizer. The copolymer amylose-g-PLA with different structures is synthesized by a three step grafting strategy (Ouhib et al., 2009).

Experimental

Materials

PLA was purchased from Naturplast (France) the weight-average molecular weight was about 160,000~220,000 Da. The concentration of D-(—)-isomer was 12.0±1.0%. Wheat starch (10% moisture) was obtained from Sigma-Aldrich. The amylose and amylopectine contents were, respectively, 25 and 75%. The glycerol (purity) and D-Sorbitol were supplied by Aldrich. Native amylose from potatoes was purchased from Fluka, N,O-bis-(trimethylsilyl) acetamide (BSA) and stannous octoate (SnOct₂) were purchased from Sigma-Aldrich.

Samples Preparation

Thermoplastic starch was prepared according to the following procedure. Native starch was weighted and introduced in a turbo-mixer. Glycerol was then added and dispersed at high speed to obtain a homogeneous dispersion. The mixture was then placed in a vented oven at 170°C for 45 min and occasionally stirred, allowing vaporization of water and diffusion of glycerol into the starch granule. After cooling, the proper amount of water and sorbitol was added to the mixture that was once more dispersed at high speed. The powder was then extruded in a 15 cm³ compounding system (DSM research; Netherlands) at 165°C for 5 min and a rotation speed of 60 rpm. The extruder has a screw length of 150 mm, a L/D of 18, and a net capacity of 15 cm³. To obtain the desired specimen samples for various measurements and analysis, the molten composite materials were transferred after extrusion in a preheated cylinder to a mini-injection-molder, which was preset with the desired temperature (165°C). The mold temperature is 40°C. Injection molded samples were placed in sealed polyethylene bags in order to prevent moisture absorption.

	Water (%)	Glycerol (%)	Citric Acid (%)	Sorbitol (%)
TPS1	12	18	--	--
TPS2	12	18	3	--
TPS3	--	30	--	--
TPS4	--	15	--	15
TPS5	--	--	--	30

Table 1. Composition of different TPS

Scanning electron microscopy

Microstructures of the fractured samples were observed by using a scanning electron microscope (SEM) (JSM-6490-LV-JEOL-Japan). The surface of the samples was gold-plated.

In order to observe the starch phase, the sample was stored for 24h in a chloroform solvent to remove the PLA phase. For blends containing 20%TPS, the starch phase was removed by 5h storage in HCl (1N). The "skeleton" removed after the extraction is dried under vacuum for one day at 40°C and was then observed by SEM.

Mechanical properties of blends

Samples were prepared by injection molding. Tensile testing was done on mechanical tensile tester (Instron-Appolor). A crosshead speed of 10 mm/min is used. 5 samples of each blend composition were tested after one week period conditioning in sealed polyethylene bags. Results from 5 specimens were averaged.

Wide-Angle X-ray Diffraction

X-ray diffraction analysis was performed in a MiniFlex II-Rigaku diffractometer operating at 30 kV, 15 mA

and over a scattering angle (2θ) range of 10° - 30° at 2° per minute.

Contact angle measurement

Contact angle measurements were carried out with a OCA 15 goniometre. A droplet was deposited onto the surface of a dumbbell form samples prepared by injection for traction test.

Water and diiodmethane were used as test liquids because of their different polarities. The evolution of the droplet shape was recorded during 80s. A CCD video camera and image analysis software were used to determine the contact angle evolution.

The theoretical work of adhesion between polymers in solid state (w_{12}) which is the work required to reversibly separate two bulk phases can be calculated by contact angle measurement (1). First of all, the surface energies of solid materials are determined via contact angle measurement using the sessile drop method and two probe liquids. Wu's method (1982), practically adapted to our low energy systems, allow the calculation of the polar (γ^p) and dispersive component (γ^d) of the surface energies (2).

The harmonic mean equation is used to calculate the theoretical work of adhesion between two polymers TPS and PLA.

$$W_{12} = \frac{4\gamma_1^d \gamma_2^d}{\gamma_1^d + \gamma_2^d} + \frac{4\gamma_1^p \gamma_2^p}{\gamma_1^p + \gamma_2^p} \quad (1)$$

$$\gamma_L(1 + \cos\theta) = 2\sqrt{\gamma_S^d \gamma_L^d} + 2\sqrt{\gamma_S^p \gamma_L^p} \quad (2)$$

	Surface tension (γ_L) mJ.m ⁻²	Disperse part (γ_L^d) mJ.m ⁻²	Polar part (γ_L^p) mJ.m ⁻²
Diiodmethane	50,8	48,5	2,3
water	72,8	26	46,8

Table 2 - Test liquids used for the determination of the surface free energy of solids

Results and Discussion

Starch plasticization

The force exercised by the microcompounder for the extrusion of different types of TPS (6 gram of each sample) is shown in Figure 1.

The force is an indication of the viscosity of the polymer. TPS1 and TPS5 have the highest viscosities. The high viscosity of TPS1 can be explained by the evaporation of water during the extrusion. The sample after the extrusion contains 1% of water. TPS5 contains no water and glycerol but 30% of sorbitol. The melting temperature of sorbitol is 90°C and it has less mobility than water and glycerol (bigger molecules) and so higher viscosity during the extrusion.

The low viscosity of TPS2 is due to the acid hydrolyze of starch in presence of citric acid.

Plasticization of starch is the disruption of granular starch and the transformation of the semi-crystalline granule into a homogenous, rather amorphous material with the destruction of hydrogen bonds between the macromolecules.

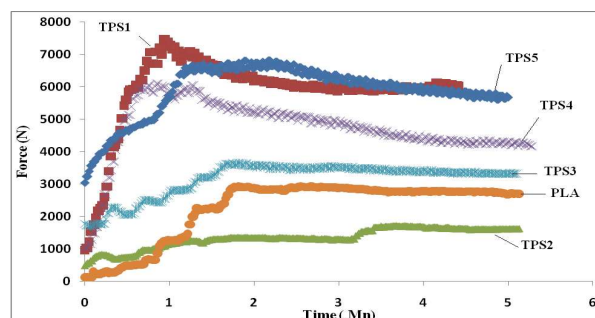


Figure 1. Force versus time for 6 gr of each TPS sample

The extrusion conditions used for the plasticization of starch are adequate for disruption of the granular starch. The fragile fracture surface analysis obtained by SEM showed a smooth surface, typical of homogeneous amorphous materials (Figure 2).

The mechanical properties (tensile strength, elongation at break) of different TPS samples were shown in figure 3. A brittle characteristic is seen in TPS1 and TPS2. TPS3 and TPS4 exhibit a "plastic behavior" plateau. Introduction of 30% glycerol led to a decrease of the tensile strength but the elongation at break increased. Generally one of the primary functions of a plasticizer is to improve the elongation at break and toughness; however this has to be achieved at the expense of tensile strength. Therefore this tendency is the same as a typical effect of plasticizer.

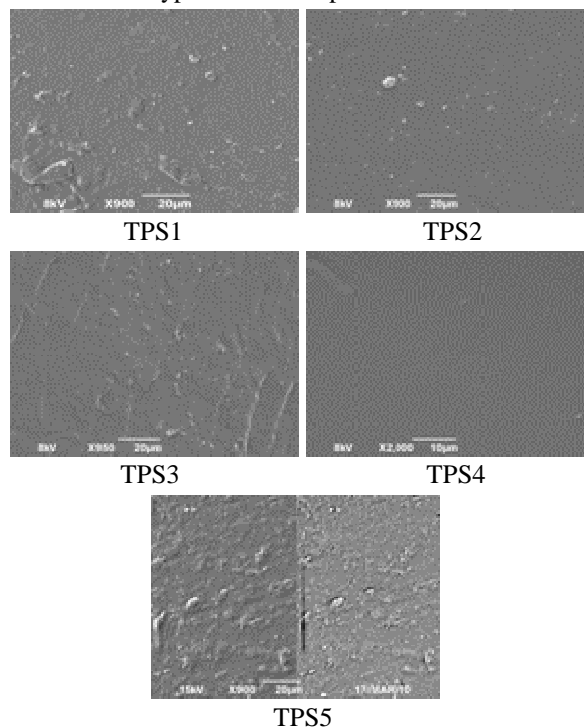


Figure 2. SEM Images of different TPS

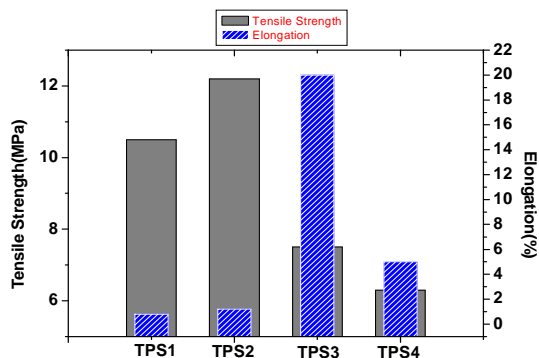


Figure 3. Comparison of mechanical properties of different TPS

X ray diffraction patterns of different TPS shows a typical V_a type patterns (Figure 4). V_a -type diffraction pattern of starch appears by a transformation from the A-type under extrusion at conditions of high temperature and pressure. For pure wheat starch, single peaks at 2θ of 14.88 and 22.54 and double peaks at 16.88 and 17.78 were observed (Figure 4). This pattern correspond to the typical A type X-ray diffraction pattern of wheat starch.

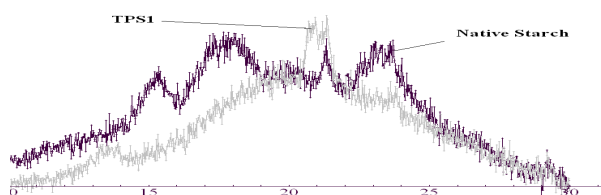


Figure 4. In black TPS1 after one week and in gray native starch (X-axis is 2θ)

All TPS samples have a V_a type pattern (Figure 5). The peaks of V_a pattern have been related to the presence of lipids in wheat starch granules, which have the ability to form complexes with amylose. The size of starch crystalline domains in TPS can typically be in order of 15-30 \AA . (Rodriguez-Gonzalez et al., 2004) For TPS, the areas of the peaks which correspond to the crystalline region decreased in comparison with pure starch, which led to the decrease of crystallinity. Citric Acid in TPS2 increases the crystallinity of TPS. Citric acid decrease the molecular weight of starch by hydrolyses acid (Wang et al., 2007). Shorter chains of starch would move easier and the crystallization is enhanced.

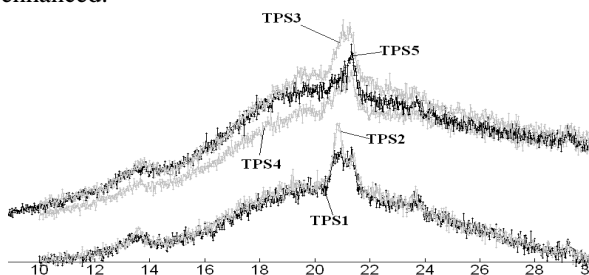


Figure 5. Different types of TPS after extrusion (X-axis is 2θ)

Polymer Blends

Plasticization and blending of starch with PLA must be done in two steps. A one step extrusion of PLA and starch with the introduction of plasticizers simultaneously in the extruder doesn't provide necessary shear for the fracture of the granule surface. As it can be seen on figure 6, many starch granules were obviously not plasticized.

So a two step extrusion is chosen. Starch is first plasticized as it has been explained earlier and after extrusion is ground in powder. PLA is dried for 5 hours at 40°C under vacuum in order to eliminate the water. Different TPS/PLA blends are prepared and introduced in the extruder at 165°C for 5 minutes and a screw speed of 60 rpm. In the two steps blending, the granules of starch are disappeared as it is shown in Figure 7.

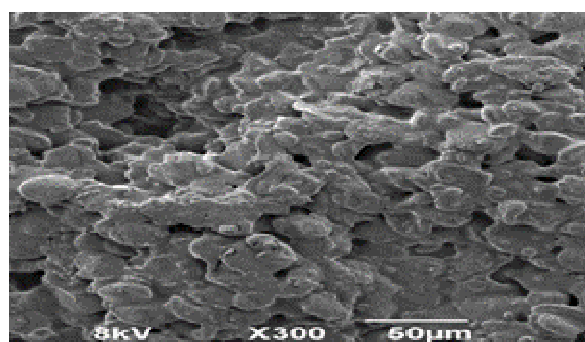


Figure 6. 50% TPS1-50%PLA- one step extrusion

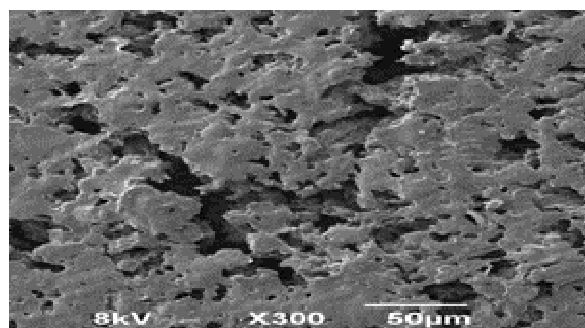


Figure 7. 50% TPS1-50%PLA- two step extrusion

The tensile strength and elongation at break of 40/60; 50/50 and 60/40 TPS/PLA blends are compared on Figures 8 and 9. Compared with the mechanical properties of pure PLA (60MPa the tensile strength and 7% of elongation), those of TPS/PLA blend decreased dramatically, especially the tensile strength, which could be ascribed to the poor interfacial adhesion between two polymer phases.

It is expected that coarse blend dispersions will lead to premature failure because the larger dispersed particles act as defects that initiate cracks in the material. The improved dispersion in the blends is therefore expected to enhance the material ductility but the magnitude of this improvement is points to a change in fracture behavior similar to that observed in rubber-toughened materials. Improvement in solid-state adhesion

between the TPS and PLA is another factor that may improve the elongation at break. Even though the TPS is the most ductile component of the blend, the elongation at break decreases with the TPS content. This is further indication that the presence of the TPS phase is changing the fracture mechanics of the material leading to a synergistic effect, (Huneault and Li, 2007).

Addition of 3% Citric Acid improves the tensile strength of the blends slightly. This improvement is due to the ester linkage between citric acid and starch and therefore the modification of the interfacial adhesion between TPS and PLA. The ester linkage between citric acid on starch (1740 cm^{-1}) is shown on Figure 10.

TPS3 contains higher residual plasticizer (30% glycerol) than TPS1 (18% glycerol) because of total evaporation of water during extrusion but these two have similar tensile strengths. This can be explained by a better dispersion of the TPS in the matrix in TPS3 as it can be seen in the Figure 11. The morphology analysis couldn't be done on the blends of TPS2/PLA because these blends are very sensitive to the extraction of PLA by chloroform.

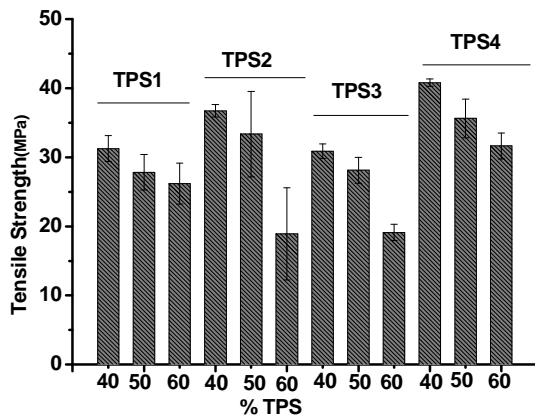


Figure 8. Tensile strength (Mpa) of 40/60, 50/50 and 60/40 TPS/PLA blends

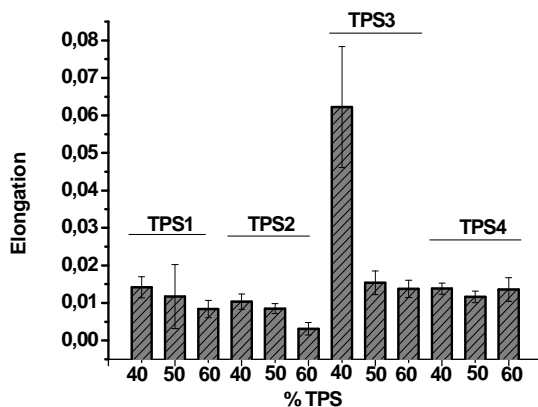


Figure 9. Elongation at break of 40/60, 50/50 and 60/40 TPS/PLA blends

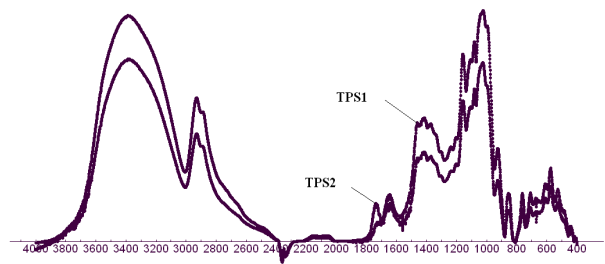


Figure 10. Influence of citric acid on the Starch (X-axis is wave number (cm^{-1}))

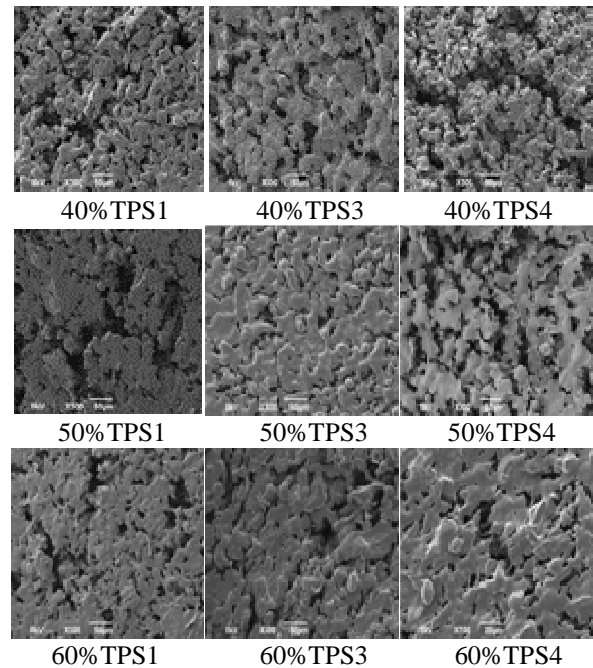


Figure 11. SEM images of 40-50-60% of TPS after extraction of PLA with chloroform

TPS4 shows the highest tensile strength comparing to the other TPS/PLA blends. Sorbitol seems to improve the adhesion of PLA and starch. The theoretical adhesion force calculated between different TPS and PLA pairs (Figure 12) shows stronger interaction between TPS4 and PLA.

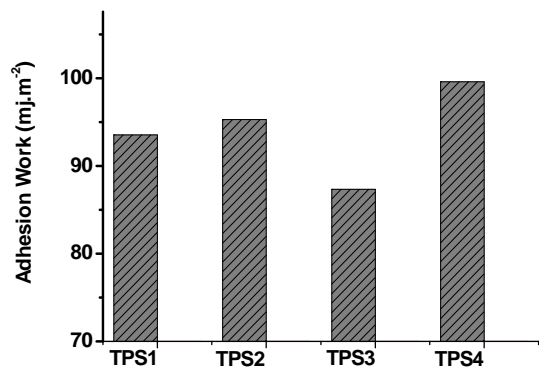


Figure 12. Adhesion work of TPS and PLA

As it was observed in Figure 11, we are in the co-continuity region of TPS for 40-60% of TPS and study

of the improvement of the dispersion by addition of a compatibilizer can hardly be observed. So lower quantities of TPS are chosen. TPS1 have a high viscosity during the extrusion and the water present during the extrusion might contribute to hydrolyze and degradation of PLA. This degradation might be more important in TPS2 because of the citric acid.

TPS3, TPS4 and TPS5 are chosen for study of the influence of compatibilizer.

Blends of TPS/PLA containing 20% TPS and 80% PLA are prepared with the same blending procedure used earlier.

In Figure 13, the mechanical properties of these blends are compared. By replacing 15% of glycerol of TPS3 (30% glycerol) by 15% sorbitol (TPS4), the tensile strength is increased by 30% and it approaches the tensile strength of the pure PLA. Figure 14 shows the FTIR spectra of the blends of TPS/PLA. For TPS5 we can observe a higher peak at 2924 cm^{-1} . This peak corresponds to the stretching of CH_3 group of PLA.

Good dispersion and mechanical properties of TPS/PLA when sorbitol is used as plasticizer can be explained by interaction of sorbitol with PLA. The elongation at break is decreased dramatically by adding TPS to the blend. TPS3 has the best elongation at break but it is less than the elongation of pure PLA.

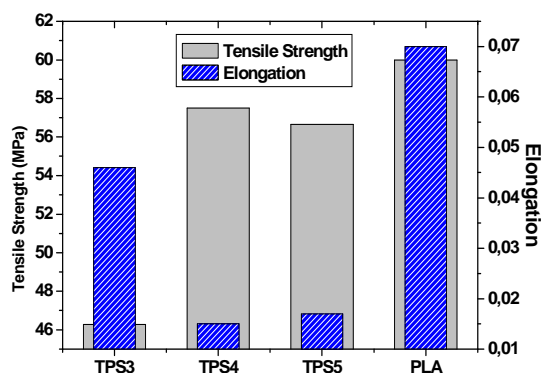


Figure 13. Tensile strength and elongation at break of 80/20 PLA/TPS blends

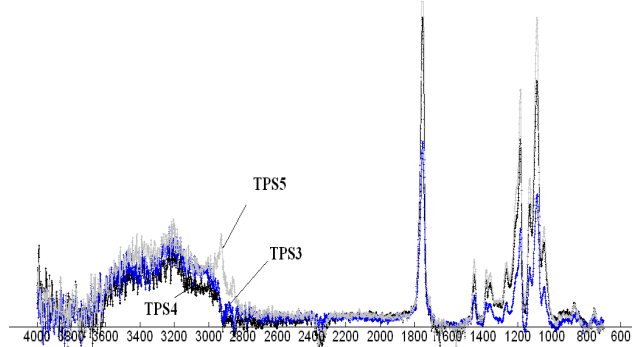
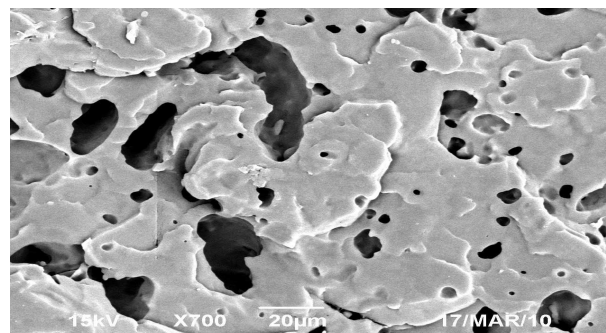
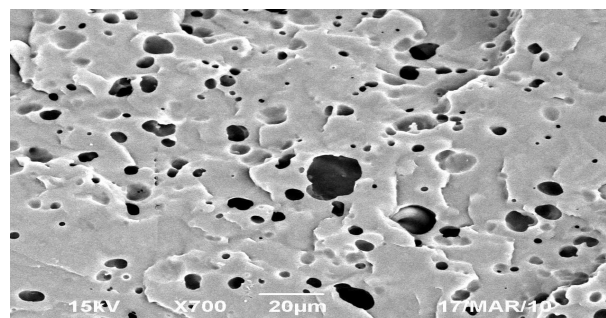


Figure 14. FTIR spectra of 80/20 PLA/TPS blends (X-axis is wave number (cm^{-1}))

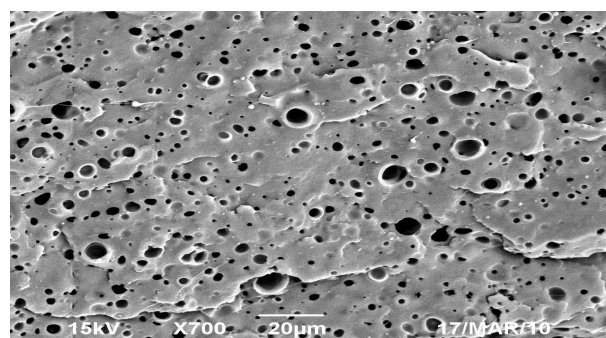
SEM images of blends of 80/20 of PLA/TPS (Figure 15) demonstrate the efficiency of sorbitol for decreasing the size of the dispersed phase.



80%PLA-20%TPS3 (30%glycerol)



80%PLA-20%TPS4 (15%glycerol-15%sorbitol)



80%PLA-20%TPS5 (30%sorbitol)

Figure 15. SEM images of 80/20 blends of PLA/TPS

Copolymer Amylose-g-PLA

The method used in this work to improve the compatibility between PLA and TPS is the addition of copolymer Amylose-g-PLA.

This copolymer amylose-g-PLA is synthesized ex-situ by the procedure explained by Ouhib et al. (2008).

In order to control the structure, the copolymer is synthesized through a three-steps procedure (Figure 16): (i) partial silylation of the hydroxyl groups carried by amylose chains with N,O-bis-(trimethylsilyl) acetamide (BSA) as a silylation agent ; (ii) ring-opening polymerization (ROP) of D,L-lactide initiated from all the remaining hydroxyl groups on the partially silylated polysaccharide; and (iii) silylether deprotection under mild conditions.

Interface modification in polymer blends is expected to decrease interfacial tension in the melt phase leading to a smaller segregation scale and to improve interfacial adhesion in the solid state.

The stable location of the copolymer at the interface essentially depends on its molecular weight (Israels et

al., 1995; Matos, et al., 1995), architecture, chemical composition (Cigana et al., 1996), as well as the number of blocks (Cigana and Favis, 1998).

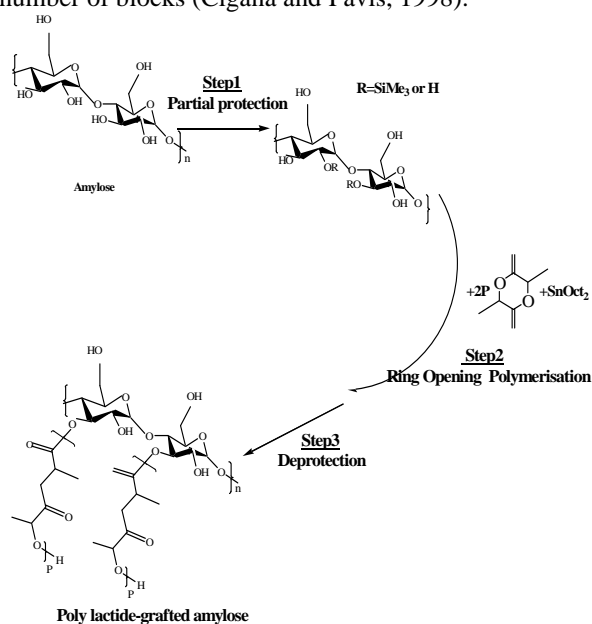


Figure 16. Schema of the three step polymerization of Amylose-g-PLA

In order to study the effect of number and chain length of the grafted PLA, three different structures have been synthesized (Table 3): 1.limited number but long chains of PLA grafts (run1); 2.higher numbers but shorter chains of PLA grafts (run2); 3.High grafting percentage of amylose and long chains of PLA (run3). The number and the length of the grafts in run1 and 2 are chosen in a way that the mass fraction of PLA in these copolymers is the same ($F_{PLA}=0.67\%$).

In Table 3, t (%) is the silylation yield of the amylose (the number of trimethylsilylether groups per 100 OH functions) and Y is the number of PLA grafts per 100 glucose units. DP_n is the average degree of polymerization of each PLA graft, expressed in lactyle unit (molecular weight 72 g/mol). F_{PLA} is the PLA weight fraction in the silylated copolymers.

Run	t(%)	DS	Y	DP _n	Mn _{graft}	F _{PLA}
1	90	2.7	30	15	1080	0.68
2	96	2.9	12	35	2520	0.66
3	83	2.95	51	74	5400	0.94

Table 3. Poly lactide-grafted silylated amylose parameters

Conclusions

The blends of thermoplastic starch and PLA are prepared. The efficiency of the plasticization procedure was observed by SEM images. All of the plasticizers (glycerol, Citric Acid and sorbitol) are able to destroy the granule structure of the starch. The blends of PLA and TPS plasticized by citric acid and sorbitol show the highest tensile strengths. Citric acid makes ester bonds with starch and improves its interaction with PLA and sorbitol makes hydrogen bonds with PLA. The study of morphology of these blends illustrates the co-continuity of starch and PLA for 40-60 % TPS. In this region the study of the improvement of the dispersion by addition of a compatibilizer can hardly be observed. The blends of 80/20 PLA/TPS are prepared. Finer dispersion of TPS in matrix is observed when sorbitol is used as plasticizer.

A three step procedure is used for the grafting reaction of PLA on amylose. This will enable us to study the role of the architecture of amylose-g-PLA on its compatibilizing efficiency in the starch/PLA blends.

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