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Biaxial Orientation of Polylactide/Thermoplastic Starch Blends

The biaxial stretchability and film properties of polylactide/thermoplastic starch blends were investigated. Polylactide (PLA) and thermoplastic starch (TPS) were blended in various proportions. Blends containing 27, 42 and 60 wt.% TPS were prepared via a twin-screw extrusion process. Interfacial modification was performed by grafting the PLA with maleic anhydride. These blends were subsequently cast into sheets and biaxially drawn using a laboratory biaxial stretcher. The morphology of extruded strands and cast sheets was investigated using scanning electron microscopy. The compatibilized blends exhibited a much finer morphology as well as preferential minor phase size orientation along the machine direction. The addition of starch did not affect significantly the biaxial stretchability of the pure PLA. Even at high starch content (60 wt.%), the biaxial draw ratio at which the sample breaks is very similar to that of the pure PLA. At higher temperatures, all blends could be stretched at significantly much higher biaxial draw ratio and very thin films could be obtained. The starch content and processing variables affected the tensile properties.

1 Introduction

It is well known that the mechanical properties of polymers can be enhanced by uniaxial or biaxial orientation. In uniaxial processes, high stiffness can be obtained in the drawing direction. However, uniaxially oriented materials exhibit very large differences in the mechanical properties in the machine (MD) and transverse (TD) directions. In many applications, such as packaging, biaxial orientation is preferred. In this case, deformation of a sheet or film takes place in both machine and transverse directions. The use of a two-stage biaxial drawing process to manufacture the films can provide different values in the two directions as a function of the order and extent of drawing, or also can be used to provide equivalent properties in the two directions. In general, simultaneous biaxial drawing produces nearly equivalent mechanical properties in both MD and TD. The development of molecular orientation during the biaxial forming processes enables to produce materials that can be used in demanding structural applications or with en-

hanced optical or barrier properties. Typical processes include the double-bubble, thermoforming and tentering processes. Because the stretching takes place in the semi-solid state, high levels of orientation can be achieved depending on operating conditions. It is therefore critical to understand how the processing variables affect the film orientation and morphology, and how this microstructure correlates with the final film properties. Most of the studies on the biaxial orientation of polymers were done on polypropylene, poly(ethylene terephthalate) and polystyrene (Capt et al., 2001; Hegemann et al., 2002; Kanai et al., 2006; Orchard et al., 1990; Yuksekkalayci et al., 1999; Zhang and Ajji, 2003), which are widely used in the packaging industry.

Recently however, polylactide (PLA) has received a lot of attention. PLA is an aliphatic polyester obtained by ring-opening polymerization of lactide derived from the fermentation of sugar feed stocks such as corn. It possesses good mechanical properties, good clarity, is safe use in food-contacting articles as well as being compostable at the end of its life cycle. However, PLA is very brittle and is more expensive than conventional plastics. One route to reduce cost and increase its biodegradability is to add thermoplastic starch. Starch is a carbohydrate biopolymer derived from various natural sources. Starch granules, which consist of amylose and amylopectin, are semi-crystalline. When added to PLA in its dry native form, starch acts as a filler and the resulting composites exhibit high brittleness (Ke et al., 2000; Zhang et al., 2004). However if the starch is gelatinized to form thermoplastic starch (TPS), it can be blended into PLA to form a polymer blend. The so-called gelatinization is carried out in an extruder by applying shear and heat in presence of plasticizers such as water and glycerol. The TPS can be blended with other thermoplastic polymers using conventional processing equipment to form a two-phase system where the TPS can be the matrix or the dispersed phase. The melt blending of TPS has been studied with several biodegradable polyesters, especially with polycaprolactone (Avérous et al., 2000; Matzinos et al., 2002; Rosa et al., 2004; Shin et al., 2004), and with other biodegradable polyesters such as polyesteramide, poly(hydroxybutyrate-co-valerate) and poly(butylene succinate adipate) (Avérous and Fringant, 2001; Schwach and Avérous, 2004). In the case of PLA/TPS blends, many studies have reported enhanced processability and better-quality morphologies. Processes investigated include injection molding, multilayer films extrusion and foaming (Martin and Avérous, 2001; Martin et al., 2001; Park et al., 2000; Willett and Shogren, 2002). Although some improvements in the

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mechanical properties were observed, the brittleness of the resulting blends still remained relatively high, especially at high TPS content. This was attributed to the poor interfacial adhesion in the blends. Recently however Huneault and Li (2007) have shown that the PLA/TPS blend can be compatibilized by addition of maleic anhydride grafted PLA. Injection-molded compatibilized blends exhibited elongation at break in excess of 200 % compared to 3 to 10 % for PLA and unmodified blends. In this work, similar PLA/TPS blends were prepared in order to examine their behavior under biaxial stretching. A laboratory biaxial stretcher was used to perform simultaneous equibiaxial deformation tests and to address their processability. The influence of processing conditions on maximum drawability and mechanical properties was addressed. In addition, the effect of interfacial modification on processability and performance has been investigated by modifying the PLA.

2 Experimental

2.1 Materials

The polylactide, PLA 2002D from NatureWorks, was a semi-crystalline extrusion material. In the compatibilization study, the PLA was modified using 95 % pure maleic anhydride (MA) and a Luperox 101 (L101) peroxide initiator from Aldrich Chemical Company (2,5-dimethyl-2,5-di-(tert-butylperoxy)hexane). Wheat starch Supergel 1203 from ADM-Ogilvy was used. Water and glycerol were used as plasticizers.

2.2 Blend Compounding

The PLA and starch were blended using a twin-screw extrusion process as described by Rodriguez-Gonzalez et al. (2003). The blends were made on a Leistritz 34 mm co-rotating twin-screw extruder with an L/D ratio of 42. The first half of the extruder was used to prepare the thermoplastic starch (TPS). The extruder was fed with a starch suspension in a water/glycerol mixture. The initial starch content was 50 wt.% and the water/glycerol ratio adjusted to obtain the desired glycerol content in the final TPS. The starch was gelatinized under pressure in the first mixing zone at 130 °C. The water was then removed from the thermoplastic starch by vacuum just before mid-extruder to obtain a TPS with minimum residual water. The glycerol content in the TPS was 36 wt.% on a dry basis. The PLA (modified or not) was incorporated in the molten form at mid-extruder through a single-screw extruder side-feed. The PLA and TPS underwent mixing in a zone maintained at 180 °C. The resulting PLA/TPS blend was extruded through a strand die, water-cooled and pelletized. Blends containing 27, 42 and 60 wt.% TPS were studied. For interface modified samples, the PLA was grafted using 2 wt.% maleic anhydride and 0.25 wt.% peroxide initiator. These latter two components were introduced along with the PLA in the side-feed single-screw extruder. The details of this procedure are described elsewhere (Huneault and Li, 2007). It is believed that the maleic anhydride grafted onto the PLA is reacting with the hydroxyl group of the starch. Prior to any compounding or further pro-

cessing, the PLA and all blends were dried at 55 °C for 8 h in an air-circulating drier.

2.3 Sheet Casting and Biaxial Stretching

The pellets prepared as described above were extruded on a Randcastle cast film line, equipped with 20 cm wide flat die. The melt temperature was 175 °C and the sheets were calendered between water-cooled rolls maintained at 40 °C. The final thickness was 0.5 mm. These sheets were kept as is for morphological and mechanical characterization or cut into 10 cm × 10 cm specimens to be used in a Brückner laboratory biaxial stretcher. This apparatus was used to simulate operating conditions encountered in many industrial processes where biaxial orientation of a sheet or film takes place in the semi-solid state. A sample was placed on a carriage between clips (5 in each direction) and sent in an oven for a sufficient pre-heat period to insure thermal equilibrium. The temperature, speed and draw ratio in both machine and transverse directions can be set to reproduce typical processing conditions. In order to address the effect of the addition of starch on the processability of PLA, biaxial drawing tests were performed in equibiaxial simultaneous mode and at a constant speed of 1 m/min. The temperature was varied from 60 to 100 °C. For each test, the load and time were recorded and converted into stress vs. biaxial draw ratio curves. The stress and biaxial draw ratio at break were determined as a function of temperature to generate a processability map for all materials. The resulting biaxially stretched films were kept for further characterization.

2.4 Blends Characterization

The morphology of the pellets and cast sheets was investigated using scanning electron microscopy. The surfaces of the extruded strands and cast sheets were microtomed at room temperature. In order to enhance the contrast between the phases, selective removal of the plasticized starch phase was performed by treating the microtomed surfaces with hydrochloric acid (HCl, 1N).

The tensile mechanical properties were measured at room temperature at 50 mm/min according to ASTM D-638, in both machine and transverse directions. The tests were performed on rectangular 19 mm wide × 15 cm long strips cut out from the cast sheets and biaxially stretched films. The elastic modulus, the tensile strength and the elongation at break were evaluated. A video extensometer was used to determine the elastic modulus. All reported values are the average of five tests.

The crystalline structure of PLA was investigated by differential scanning calorimetry (DSC) and X-ray diffraction. The crystallinity of samples obtained at different draw ratios was determined from DSC measurements at a heating rate of 10 °C/min. The enthalpy of fully crystalline material for PLA was taken as 93 J/g (Fischer et al., 1973). Wide angle X-ray diffraction patterns were obtained by exposing the samples at 40 kV and 40 mA. The scanning was carried out at a rate of 1 step/s and a step size of 0.03° in the angular region (2θ) of 2 to 40°. The effect of orientation on crystallization was assessed by aligning the films with the X-ray beam along both machine and transverse directions.

3 Results and Discussion

3.1 Morphological Analysis

The morphology of the extruded strands and cast sheets, unmodified and compatibilized, was investigated by scanning electron microscopy after selective removal of the starch phase. All micrographs represent the cross section of the samples and the machine direction is indicated by the arrow. The micrographs for the blends with the lowest (27 wt.%) and highest (60 wt.%) thermoplastic starch contents are shown in Figs. 1 and 2, respectively. In both figures, micrographs A and B compare the morphology of the blends before and after the casting step. Micrographs C and D also compare the effect of further processing into sheets but in the case of blends compatibilized with maleic anhydride. In Fig. 1, it can be seen that the TPS/

PLA blends exhibited a two-phase system where the TPS is the minor phase. In the unmodified pellets, the morphology is quite coarse and the minor phase size ranges from 5 to 30 micrometers. After casting into sheets, there is no significant change in minor phase size and shape (Fig. 1B). In the compatibilized case, the TPS minor phase is nearly spherical, well dispersed and its size is significantly decreased down to around 3 micrometers. This is an indication that the grafting of PLA/TPS blends with maleic anhydride is efficient in reducing the interfacial tension and generating finer and more homogeneous morphologies. Stronger interfacial adhesion is also reflected during cast extrusion as shown in Fig. 1D, where domains slightly oriented in the machine direction can be observed. This is another indication that interfacial reactions are taking place by favoring the deformation along the flow. When the TPS content is increased to 60 wt.%, the TPS is still the minor phase but

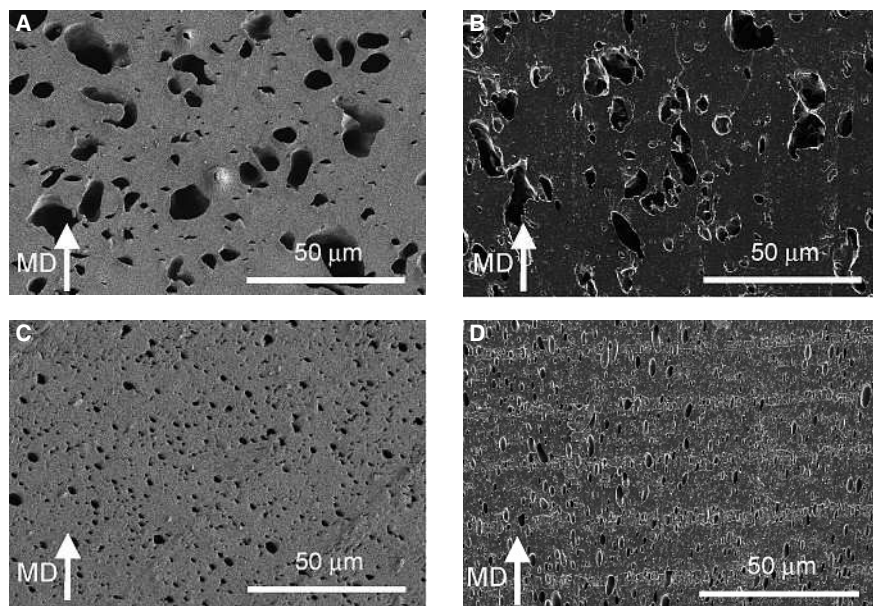


Fig. 1. Morphology of 27 wt.% TPS/PLA blend observed by SEM after selective removal of starch phase. Left column: extruded strands. A) unmodified. C) compatibilized. Right column: cast sheets. B) unmodified. D) compatibilized. Machine direction (MD) is indicated by arrow

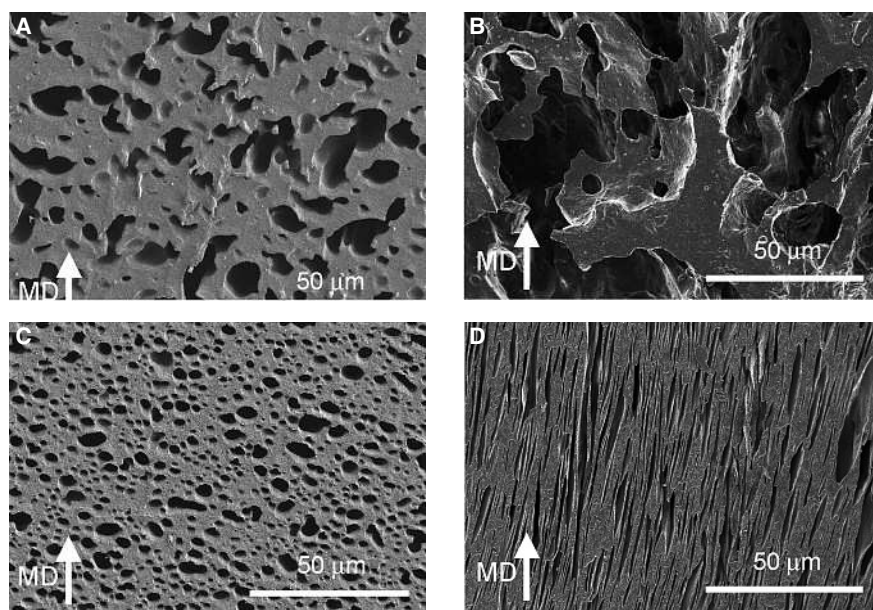


Fig. 2. Morphology of 60 wt.% TPS/PLA blend observed by SEM after selective removal of starch phase. Left column: extruded strands. A) unmodified. C) compatibilized. Right column: cast sheets. B) unmodified. D) compatibilized. Machine direction (MD) is indicated by arrow

the morphology of the unmodified pellets is very coarse and the shape of the particles is irregular (Fig. 2A). When this blend is cast into sheets, considerable coalescence occurs, as expected when compounding incompatible blends with high minor phase content. Large TPS phase and possibly co-continuity is observed. By contrast, the morphology of the compatibilized blends is much finer. Again, the efficiency of the compatibilization with maleic anhydride is shown, with a remarkable decrease of the TPS phase size (down to about 5 micrometers) and a more spherical shape (Fig. 1C). When further processed into sheets, substantial deformation in the machine direction is observed, as shown in Fig. 1D. The aspect ratio of the particles is noteworthy and much higher than in the 27 wt.% blend. This is to be expected since larger particles are more readily deformable along the flow direction. This is again an indication of the effectiveness of the compatibilizing strategy used in this study. All results described above were also observed for the intermediate blend containing 42 wt.% TPS i.e. a significant minor phase size reduction when compatibilizing and favored deformation of the particles in the machine direction after the cast process.

3.2 Properties of Cast Sheets

The compatibilization of polymer blends is expected to decrease the interfacial tension between the components in the molten state and enhance adhesion at the interface in the solid state. It was shown previously that interfacial modification during compounding yielded a more homogeneous smaller minor phase size and in order to investigate its effect on the mechanical performance, the tensile properties were evaluated. Typical tensile stress-strain curves are shown in Fig. 3 for neat PLA and the 27 wt.% and 60 wt.% blends, both unmodified and compatibilized. Data is reported for the machine direction only but the behavior was similar in the transverse direction. The elastic modulus, the tensile strength and the elongation at break were determined. Figs. 4, 5 and 6 report the results of the measured properties as a function of TPS content, for both unmodified and compatibilized blends, in both machine and transverse

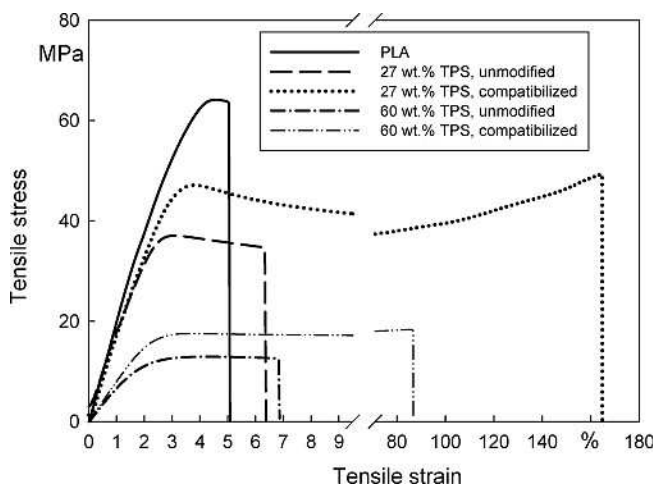


Fig. 3. Typical tensile stress-strain curves for cast sheets comparing neat PLA, 27 wt.% and 60 wt.% blends, both unmodified and compatibilized

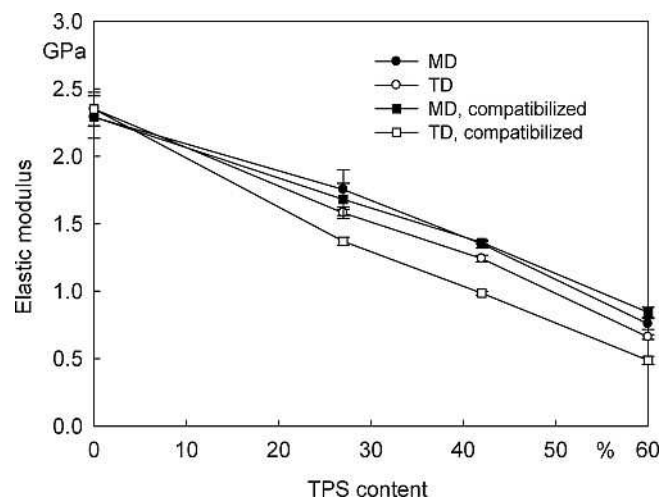


Fig. 4. Elastic modulus of cast sheets as a function of TPS content. Comparison between unmodified and compatibilized blends

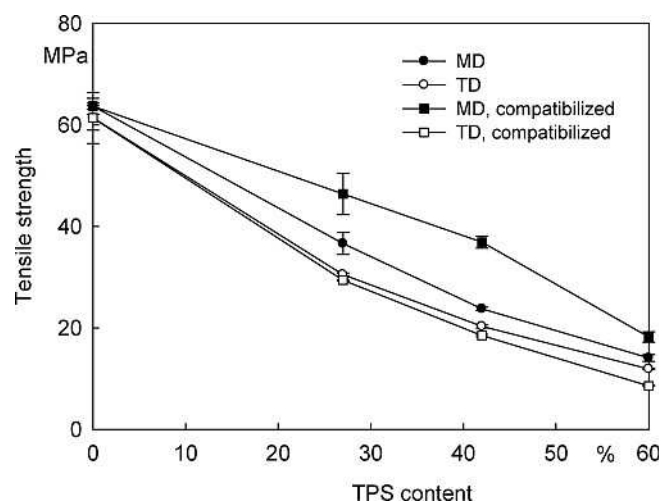


Fig. 5. Tensile strength of cast sheets as a function of TPS content. Comparison between unmodified and compatibilized blends

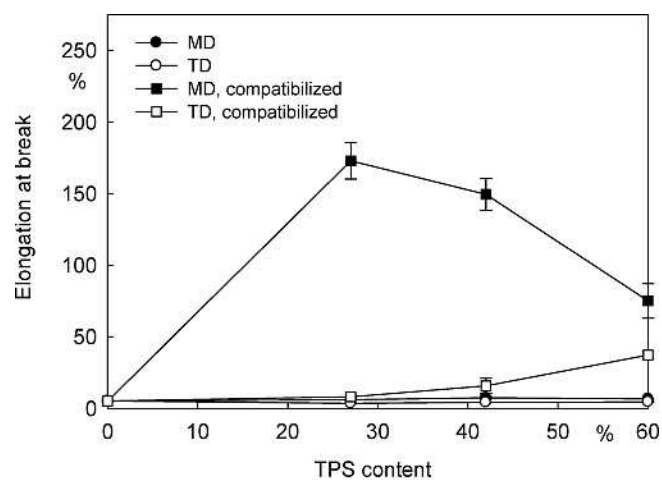


Fig. 6. Elongation at break of cast sheets as a function of TPS content. Comparison between unmodified and compatibilized blends

direction. In Fig. 4, it is shown that the elastic modulus decreases with the addition of TPS. Pure PLA is a quite rigid material with an elastic modulus of 2.3 GPa. When the TPS content is increased, the modulus decreases significantly. This is to be expected when a soft component such as thermoplastic starch is added. Similar properties were observed in both machine and transverse directions, indicative of the sheets isotropy. In the compatibilized case, the tensile modulus again decreased with TPS content, the values being slightly higher than the unmodified equivalent. This is not surprising considering the modulus is evaluated at the very early stages of tensile deformation, when interfacial debonding has not yet occurred. The differences between the values in the transverse and machine directions are however more pronounced than in the unmodified case. This anisotropy of properties is in accordance with the morphological observations mentioned above, where a preferential orientation in the machine direction and anisotropy of the blends were observed (Figs. 1D and 2D). Similar behavior was observed when measuring the tensile strength, as shown in Fig. 5. There is a significant reduction of the strength with TPS content and the values are lower in the transverse direction in the compatibilized case. The effect of compatibilization on the performance of the blends was more significant when measuring the elongation at break. It is when subjected to such higher tensile strain that strong interfacial adhesion would be revealed. Fig. 6 shows the elongation at break as a function of TPS content for both unmodified and compatibilized blends. The elongation at break did not vary significantly with starch content in the unmodified case. The values remained very low and similar to that of pure PLA (around 10 %). In the compatibilized case, a significant increase of the elongation at break was observed in the machine direction. Values increased up to 175 % for the 27 wt.% blend. When increasing the TPS content to 60 wt.%, the elongation at break drops off to 75 %, which is nevertheless still much higher than that of pure PLA. In the transverse direction, this impressive increase in elongation at break was not observed. Again, the enhanced deformation and orientation in the machine direction combined with strong interfacial compatibilization might be detrimental to the properties in the transverse direction. This is more noticeable in the case of ultimate properties such as elongation at break.

3.3 Properties of Biaxially Stretched Films

As mentioned in the introduction, PLA/TPS blends are good candidates for packaging applications. In this work, in addition to studying the cast process and properties of relatively thick sheets (0.5 mm), much thinner films were produced using a laboratory biaxial stretcher. At temperatures below 70 °C, the stiffness of the material was too high and the specimen was ejected from the clips. Above 90 °C, excessive sagging was observed during the preheating time. The stress vs. biaxial draw ratio curves for three temperatures i.e. 70, 80 and 90 °C are shown in Fig. 7. The stresses in both machine and transverse directions are given. Note that the biaxial draw ratio "1 × 1" represents the undrawn sample (initial cast sheet). The stresses in both machine and transverse directions are similar, which is representative of the initial isotropy of the cast sheets, as con-

firmed by their mechanical properties. PLA can be biaxially stretched significantly, reaching a maximum draw ratio before failure close to 6 × 6 at 90 °C. When the temperature is decreased to 70 °C, the maximum biaxial draw ratio attainable is significantly lowered to just above 3 × 3. However, the maximum stress developed is much higher and could generate better mechanical properties. Typical biaxial drawing curves for PLA/TPS blends are given in Fig. 8 for unmodified PLA/TPS blends drawn at 70 °C. These are representative of the behavior of all blends, compatibilized or not. All blends exhibited a stress-biaxial draw ratio curve shape similar to pure PLA. It was observed that the addition of thermoplastic starch does not affect significantly the stretchability of the pure PLA while lowering the maximum stress before break. Even at high starch content (60 wt.%), the biaxial draw ratio at which the sample breaks is very similar to that of pure PLA. At the highest temperature studied (90 °C), all blends could be stretched at draw ratios of at least 6 × 6 and even above 8 × 8 for the 27 wt.% compatibilized blend. This leads to very thin films having a thickness in the 5 to 15 micrometers range. From these tests, a

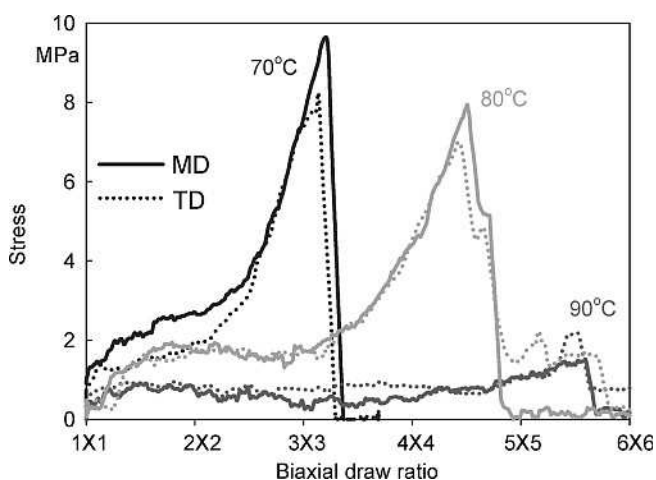


Fig. 7. Stress vs. biaxial draw ratio curves for neat PLA. Effect of temperature on maximum stress and biaxial drawability

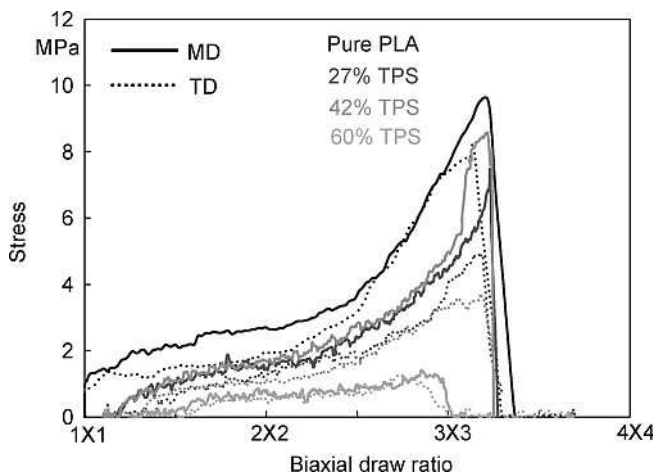


Fig. 8. Stress vs. biaxial draw ratio curves for unmodified TPS/PLA blends at 70 °C. Effect of the addition of thermoplastic starch on maximum stress and biaxial drawability

biaxial processability map can be drawn. Fig. 9A gives the maximum biaxial draw ratio attainable during stretching as a function of processing temperature. As the temperature was increased, the maximum biaxial draw ratio exceeded significantly that of pure PLA. At these higher temperatures however, it must be emphasized that the stress developed during drawing can be low, as shown in Fig. 9B, which gives the maximum stress developed during stretching as a function of processing temperature. This might hinder the final orientation in the film and be reflected in the mechanical properties.

The elastic modulus, the tensile strength and the elongation at break in both machine and transverse directions were evaluated for the biaxially stretched films. Since the values measured in both directions were similar, only the data for the machine direction will be shown in the graphs. Figs. 10A and B report the elastic modulus of unmodified PLA/TPS films stretched at the lowest and highest temperatures studied i.e. 70 °C and 90 °C, respectively. Again, the "1 × 1" draw ratio represents the unstretched cast films. Upon drawing at 70 °C, the modulus of pure PLA increases significantly, the maximum being at the highest attainable draw ratio at this temperature. When adding the TPS, the modulus is decreased, as in the case

of the cast films. The biaxial drawing enables to increase the modulus of the 27 and 42 wt.% TPS blends, while it has no effect on the 60 wt.% blend. This is in contrast with the results obtained when drawing at 90 °C, where the modulus of all blends remains more or less constant. This is in accordance with Fig. 9B, where it was shown that the stress developed during stretching at this temperature was extremely low for all blends. The mechanical properties therefore do not differ from the values measured for the cast sheets. At 90 °C, only the modulus of pure PLA is increased as a function of biaxial draw ratio, with a plateau at 4 × 4. Similar conclusions can be drawn for the tensile strength, as shown in Figs. 11A and B. Significant increases of the tensile strength are observed for pure PLA with maximums nearly reaching a value nearly twice of those for the cast films. At 90 °C, a maximum is again observed at 4 × 4. An analysis of the structure revealed a similar behavior when increasing the biaxial draw ratio. Fig. 12 shows the DSC thermograms of PLA cast sheets and films biaxially stretched at 90 °C. The cast sheets exhibit a small melting endothermic peak indicative of a very low crystalline ratio. When biaxially stretched to 2 × 2, the films remain essentially amorphous. Only at a biaxial draw ratio of 4 × 4 is the crystallinity

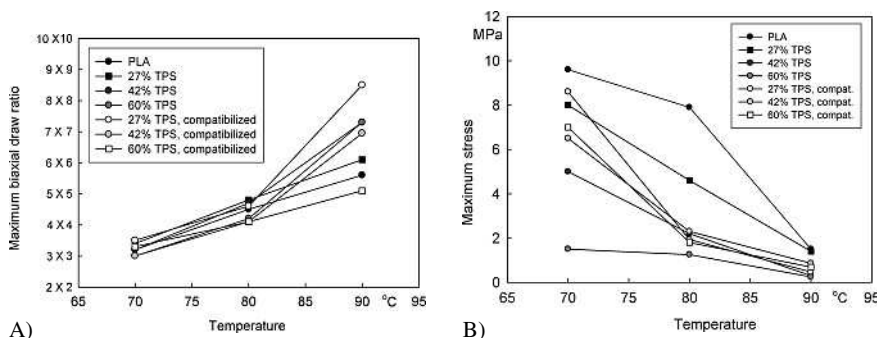


Fig. 9. Processability window for neat PLA and TPS/PLA blends as a function of temperature: A) maximum biaxial draw ratio. B) maximum stress

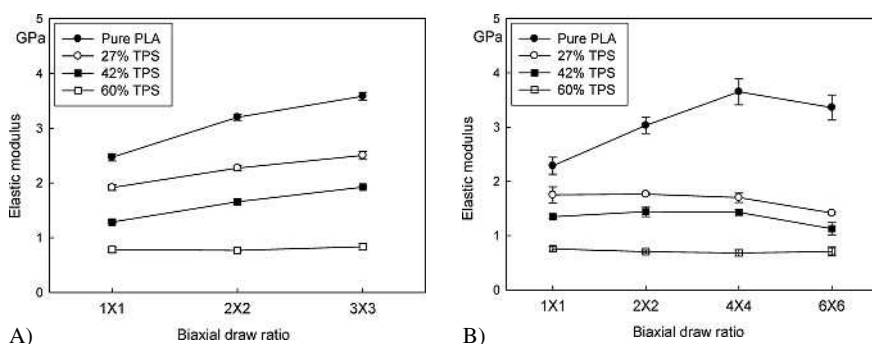


Fig. 10. Elastic modulus of biaxially oriented unmodified films as a function of biaxial draw ratio for films processed at A) 70 °C, B) 90 °C

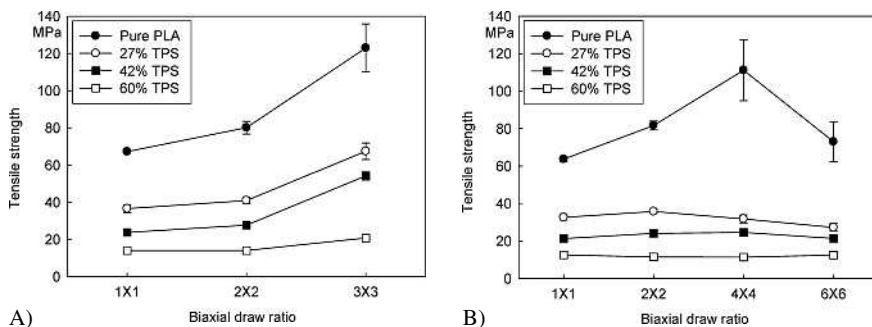


Fig. 11. Tensile strength of biaxially oriented unmodified films as a function of biaxial draw ratio for films processed at A) 70 °C, B) 90 °C

increased substantially to 20 %. This was confirmed by wide angle X-ray diffraction. The diffraction patterns for biaxial films stretched to 2×2 and 4×4 are shown in Fig. 13, for both machine (parallel) and transverse (perpendicular) directions. At a biaxial draw ratio of 2×2 , the characteristic crystallization peak of PLA (16.31°) peak is not visible. At 4×4 however, a strong crystallization peak is observed. No obvious differences of the intensity of the peaks between the machine and transverse directions. These results are indicative of orientation and strain induced crystallization. As observed for the case of the cast sheets, increasing the TPS content was found to decrease the tensile strength of the blends. As in the case of

the modulus, increasing the draw ratio yields higher tensile strength at 70°C for the low TPS content blends (27 and 42 wt.%) and values remain equal to those of the cast sheets when stretched at 90°C . The elongation at break of the cast sheets was not improved by the addition of TPS without interfacial modification. In the case of biaxially stretched films, the elongation at break for the unmodified blends increased with biaxial draw ratio and sometimes exceeded that of pure PLA, depending on the drawing temperature. Figs. 14A and B show the results for the unmodified blends biaxially stretched at 70 and 90°C , respectively. For pure PLA, important improvements are noted, with values reaching 80 and 100 % strain when drawn at 70 and 90°C , respectively. For the 27 and 42 wt.% blends stretched at 70°C , the elongation at break increases up to 40 %. The value for the 60 wt.% blend is more modest at 20 %. It must be stressed that the initial morphology (cast sheet) of this particular blend is very coarse and inhomogeneous (Fig. 2B), which could result in poor ultimate properties. When stretched at a higher temperature, a similar behavior is observed except for the lowest TPS content blend (27 wt.%), which behaves more like pure PLA. Similar results were obtained for compatibilized case: again, the best properties were obtained for the low starch content blend (27 wt.%). Although adding the TPS did not always favor an increase in the tensile properties, one of the positive outcomes is that adequate processing conditions can be selected to obtain films with desired thicknesses and satisfactory mechanical performance depending on the application. In most cases, the absolute values of the modulus, tensile strength and elongation at break were found to be quite adequate and, more importantly, these properties are equal in the transverse and machine directions.

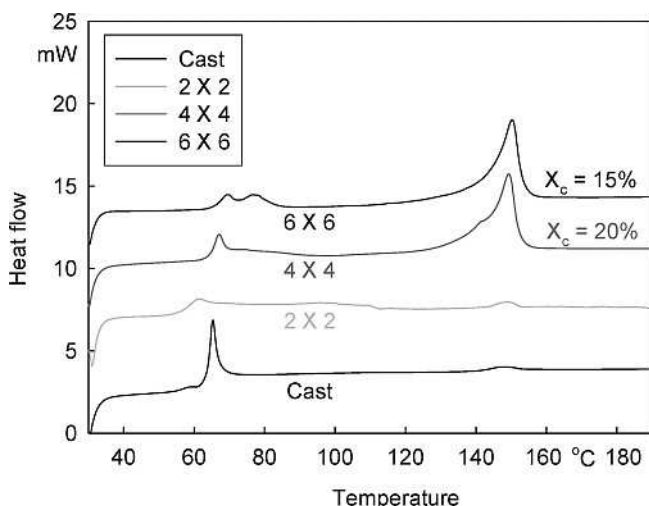


Fig. 12. Crystallinity (X_c) of PLA cast sheets and films biaxially stretched at 90°C . Thermograms obtained from DSC measurements

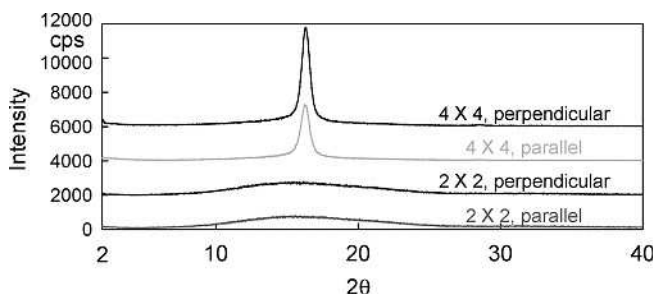


Fig. 13. X-ray diffraction patterns for biaxial films stretched to 2×2 and 4×4 at 90°C for both machine (parallel) and transverse (perpendicular) directions

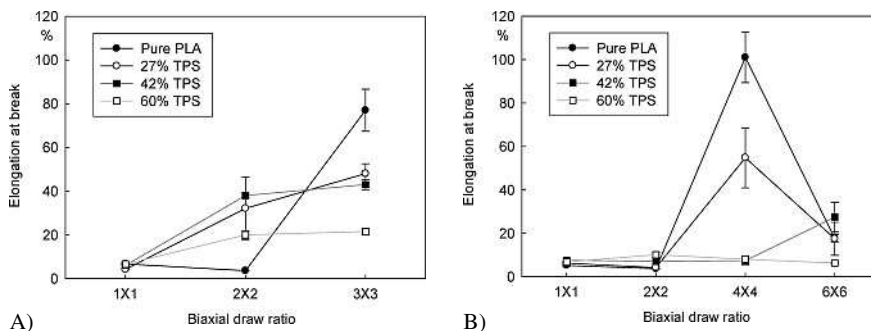


Fig. 14. Elongation at break of biaxially oriented unmodified films as a function of biaxial draw ratio for films processed at A) 70°C , B) 90°C

polymer film processing, where deformation of a sheet takes place in both machine (MD) and transverse (TD) directions. A significant effect of drawing temperature was observed. Very high biaxial draw ratios at break could be reached and adding TPS did not significantly reduce PLA drawability. Even at high TPS content (60 wt.%), the biaxial draw ratio at which the sample breaks is very similar to that of the pure PLA. At higher temperatures (above 90 °C), all blends could be stretched at biaxial draw ratios as high as 6 × 6 and very thin films were obtained (final thickness below 20 micrometers).

At the lowest temperature of the processability range (70 °C), the tensile modulus and tensile strength increased as a function of biaxial draw ratio and the elongation at break only increased significantly for the blends having low TPS contents. At higher temperature (90 °C), the addition of TPS to PLA did not improve its mechanical properties which essentially remained constant.

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