ORIGINAL ARTICLE

Synthesis of bis(pyrrolidone-4-carboxylic acid)-based polyamides derived from renewable itaconic acid—application as a compatibilizer in biopolymer blends

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The properties and morphologies of blends of poly(butylene succinate) (PBS) and glycerol-plasticized thermoplastic starch (TPS) were investigated. Bis-pyrrolidone-type monomers (obtained from itaconic acid) with various sizes of alkylidene spacers were synthesized and polycondensed with various diamines. The resultant polycondensates were used as compatibilizers to improve interfacial adhesion in PBS/starch blends. The presence of long hydrophobic $-\text{CH}_2-$ sequences in the compatibilizers improved the elongation-at-break during tensile tests. The enhanced compatibilization induced by these copolymers is presumably because of the hydrophobic interaction with PBS and the hydrophilic hydrogen bonding with starch. The uncompatibilized TPS/PBS exhibited a dispersed morphology with blends of low- and high-starch content, whereas the compatibilized blends presented a co-continuous phase.

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INTRODUCTION

The widespread use of synthetic nondegradable polymers has had a severe environmental impact, and one solution to this problem is to use biodegradable polymers. Thermoplastic starch (TPS) is one of the most studied materials because of its renewable origin, biodegradability and low cost. However, plasticized starch cannot be used to replace conventional plastics because of its poor mechanical properties and water sensitivity.^{1,2}

To overcome these shortcomings, inexpensive TPS has been blended with biodegradable polyester to retain most of the physical properties of the polyesters. A considerable amount of research has been conducted on the development of starch blends with polyester polymers,³ such as polylactide (PLA)-starch,^{4–7} polycaprolactone (PCL)-starch^{8–10} and poly(butylene succinate) (PBS)-starch.^{11–13} These blends present several advantages.¹⁴ The composition of the blends can be adjusted to obtain properties that meet the needs of the application, and the blending process is inexpensive compared with the cost of developing new synthetic materials.

Unfortunately, the mechanical properties of these blends tend to diminish considerably as the plasticized starch fraction increases. The properties of plasticized starch/polymer blends can be greatly improved by using a compatibilizer.^{15,16}

Studies of starch blends with aliphatic polyesters (PCL, PBS, PHBV) showed, in all cases, that a polymer with acceptable properties could be produced with only a moderate amount of starch. The compatibility between the starch and the aliphatic polyester is commonly improved by incorporating anhydride functionalized compatibilizers into the polyester backbone. Only a small amount of the compatibilizer is required to produce a blend that has tensile strength similar to that of synthetic polyester.¹⁷

Itaconic acid (IA), which is produced by fermentation from hexoses, is an interesting renewable building block for diverse applications.¹⁸ This acid has also been recognized as one of the ‘Top Value Added Chemicals’ from carbohydrate biomass.¹⁹ The primary interest in IA stems from the diacid character of its acrylic functionality. Thus, itaconic acid reacts with primary amines in a Michael addition-cyclocondensation sequence to produce carboxylic acid-functionalized pyrrolidones.²⁰ Polyamides with various sizes of alkylidene spacers can be synthesized by the polycondensation of these diacids with different diamines. The resulting amphiphilic polycondensates should exhibit an adjustable hydrophilic–hydrophobic balance.

In this paper, we report on the improved interfacial adhesion between PBS and plasticized starch obtained using polycondensate compatibilizers synthesized from itaconic acid.

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MATERIAL AND METHODS

Preparation and properties of bis(pyrrolidone)-based compatibilizers

General methods and reagents. NMR spectra were recorded in D₂O or DMSO with a Bruker AC 250 (Wissembourg, France) at frequencies of 250 and 62.9 MHz for ¹H and ¹³C NMR, respectively. The chemical shifts (δ) are reported in p.p.m. relative to TMS.

The molecular weight distribution of the polycondensates was determined by size-exclusion chromatography on a customized Waters HPLC system that was equipped with a Waters 600 HPLC pump, a Waters (Milford, MA, USA) 710plus automated injector, a Jasco (Jasco International Co., Ltd., Tokyo, Japan) CO-965 column oven and a Waters 410 Refractive Index detector. The analyses were performed on a system of three columns in series (SB 805 HQ, SB 803 HQ and SB 802.5 HQ) (Shodex, Germany). DMSO was used as the mobile phase at a flow rate of 1 ml min⁻¹. The temperature of the column oven was set at 35 °C. Processing of all of the chromatographic data was performed using version 2.0 of the Empower software package (Waters) customized with a GPC license. Analyses were performed on samples dissolved in DMSO at ~1 g l⁻¹. An injection volume of 50 μl was eluted at a rate of 1 ml min⁻¹ during an acquisition period of 45 min. The column porosity allowed good separation of molecules ranging from 8500–4 000 000 g mol⁻¹. The instrument was calibrated using monodisperse pullulan standards to calculate the Mw and Mn.

Differential scanning calorimetry experiments were conducted using a TA 2920 DSC instrument (TA Instruments Ltd., New Castle, DE, USA). Sealed pans were used to encapsulate typically 20 mg of the compatibilizer. For accurate heat capacity measurements, the sample and reference pans were matched. The DSC instrument was calibrated from the melting temperature and enthalpy of the standard material indium. The samples were accurately weighed in an aluminum pan and hermetically sealed. An empty pan was used as the reference.

Itaconic acid and p-toluenesulfonic acid were supplied by Sigma Aldrich (Lyon, France), ethylenediamine (extra pure) was purchased from Acros (Geel, Belgium) and 1,6-diaminoethane (98%) was supplied by Alfa Aesar (Schiltigheim, France).

Synthesis and polycondensation of bis(pyrrolidones). The starting bis-(pyrrolidones) were prepared by heating a solution of itaconic acid (60 g, 0.51 mol) and the corresponding diamine (0.5 equiv.) in water (500 ml) to reflux for 16 h. The water was removed using a Dean Stark apparatus (University of Reims, Gaffer-service, Reims, France) to yield an oil, which was then triturated with methanol to yield the product as a white solid. Several successive trituration–filtration sequences may be necessary to recover the product with a high yield. However, the addition of a trace amount of AcOEt may favor the crystallization of the product.

Bis-1,2-(4-carboxypyrrolidin-2-on-1-yl)ethane. Yield: 115.9 g, 89%. *F* = 239–243 °C. ¹H NMR (D₂O): δ (p.p.m.) 2.95 (m, 4 H), 3.63 (m, 2 H), 3.78 (m, 4 H), 4.01 (m, 4 H). ¹³C NMR (D₂O): δ (p.p.m.) 34.2 (2 CH₂), 36.1 (2 CH), 39.9 (2 CH₂), 49.9 (2 CH₂), 176.5 (2 CO), 177.3 (2 CO).

Bis-1,6-(4-carboxypyrrolidin-2-on-1-yl)hexane. Yield: 132.1 g, 83%. *F* = 245–247 °C. ¹H NMR (DMSO): δ (p.p.m.) 1.06 (m, 4 H), 1.28 (m, 4 H), 2.31 (m, 4 H), 3.03 (m, 6 H), 3.39 (m, 4 H). ¹³C NMR (DMSO): δ (p.p.m.) 26.0

(2 CH₂), 26.8 (2 CH₂), 34.1 (2 CH₂), 35.9 (2 CH), 41.6 (2 C CH₂), 48.8 (2 CH₂), 172.3 (2 CO), 175.1 (2 CO).

The polycondensates were prepared by heating bis(pyrrolidone) and the diamine (1 equiv.) in the presence of a p-toluenesulfonic acid as a catalyst (PTSA) (0.03 equiv.) in a small amount of water for 1 h at 100 °C under argon. The mixture was then heated to 170 °C for 3 days under a continuous vacuum to remove the water. The reaction schemes and simplified nomenclature of the products are depicted in Figure 1.

The compatibilizers were stored for 5 days in glass hygrometers at 20 °C at different relative humidities (0, 13, 33 or 50% RH) before being placed in pressure-tight cells. The glass transition temperatures of these compatibilizers were determined using DSC. In fact, after an initial scan from –50 to 200 °C at a heating rate of 5 °C min⁻¹ to delete any thermal events that occur in the compatibilizer, the samples were rapidly cooled to –50 °C (25 °C min⁻¹). The measurements were performed during a second scan at a rate of 10 °C min⁻¹ from –50 to 200 °C. The glass transition temperature, *T*_g^{1/2}, which corresponds to a half variation in calorific capacity during the transition, was determined graphically.²¹ The procedure was similar for all samples, regardless of their compositions.

Blends preparation and processing conditions

Native corn starch, which contained ~74% amylopectin, 26% amylose and 0.2% proteins, and had a moisture content of 12% w/w, was purchased from Sigma Aldrich (Germany). Glycerol (<0.5% H₂O) was obtained from Carlo Erba reactif (Italy).

Polybutylene succinate (PBS) was supplied by the Mitsubishi Chemical Corporation (Tokyo, Japan) (GSPLA as a reference). The water content of the starch was considered in all of the experiments.

All of the products were used without any further purification.

The processing began with the preparation of the blend (starch with 25% of glycerol). Corn starch (containing 12% of moisture) was weighed and introduced into a turbo-mixer. After the addition of glycerol, the two compounds were mixed at a high speed (2000 r.p.m.).

The starch–glycerol blend was extruded on a single screw extruder (SCAMIA S 2032, France) equipped with a conical-shaped element (see description and figures in Onteniente *et al.*²²). This design is suitable for high shearing. The extruder had two heating zones situated around the head (115 °C) and at the die (95 °C). The extruded blends were granulated.

These different plastic granules were premixed with PBS at ratios of 30:70 (starch-to-PBS) (SPB30), 40:60 (SPB40), 60:40 (SPB60) and 70:30 (SPB70) at room conditions. The compatibilizer (1%) was added to each of the resulting TPS–PBS pellets. Each mixture was manually fed into the extruder. The resulting blends were granulated then extruded again to improve the dispersion of the compatibilizer within the matrix. The last extrusion was performed at 65 r.p.m. in a three-zone single-screw extruder (Scamex, France), which was heated to 120 °C in all zones. The screw was 220-mm long, and the L/D ratio was equal to 11. A flat die (heated to 110 °C) was used to obtain the materials in a ribbon form.

Specimen preparation and mechanical tests. The pellets obtained by extrusion were transformed into tensile test samples (ISO 527-1 BA), which were ~1-mm thick, using a cookie cutter and press. The samples were hydrated in

Figure 1 Reaction scheme and nomenclature of the synthesized compatibilizers.

50% RH in chambers that were maintained at 20 °C. The tensile measurements were performed using a tensile test machine (GT-TEST 108, Strasbourg, France) equipped with a load cell of 2 kN. The strength, modulus and elongation-at-break were measured using a crosshead speed of 10 mm min⁻¹ under constant conditions (50% RH, 20 °C) in an environmentally controlled room. Averages were obtained for ten samples.

Glass transition detection. Mechanical relaxation measurements were performed on a Dynamic Mechanical Analyzer (DMTA MK IV, TA Instruments Ltd.). Molded materials were obtained using an injection molding machine (DSM Xplore, Geleen, The Netherlands), (pellets obtained by extrusion processing were transformed into strip samples (ISO 527-2 5 A) (strips, 22 · 10 · 1 mm³)) and were hydrated for at least 10 days at 50% RH (relative humidity) in chambers controlled at 20 °C. The samples were measured in the dual cantilever mode with a vibration frequency of 1 Hz, a strain of 0.1% and a heating rate of 2 °C min⁻¹.

The temperature of the α relaxation was determined at the maximum of $\tan \delta = E''/E'$, which corresponds to the molecular mobility associated with the calorimetric glass transition of the material.

Blend morphology

Investigation of SEM pictures. Scanning electron microscopy micrographs of the different blends were obtained using a scanning electron microscope (model SEM XL 30 from PHILIPS, Eindhoven, The Netherlands). Cross-sections of the extruded samples were obtained after fracturing in liquid nitrogen, and then they were treated with methylene chloride (DCM) for 15 min to highlight the dispersion of starch in the PBS. These samples were fixed on carbon-adhesive bearings and coated with gold-palladium, using a plasma sputtering apparatus (model SCD 040 from BALZERS, Weisbaden, Germany) before the SEM investigation.

Investigation by confocal microscopy. The morphology of each TPS–PBS–compatibilizer blend was examined using a Leica TCS SP2 confocal microscope with a $\times 63$ magnifying oil objective (numerical aperture 1.4). The samples in film form were placed on the microscope stage, and the acquired picture was magnified twice. When the fluorescent compatibilizer was detected, the appropriate software was used to select the region of interest. A 20 mW–Helium–Neon laser was used at full intensity, and fluorescence recovery was monitored at the lowest possible intensity.

RESULTS AND DISCUSSION

Synthesis and analysis of compatibilizers

Different conditions were tested to optimize the synthesis of polyamides with the highest possible molecular weight. The different polymers were synthesized, according to the previously described procedure, and the product was directly isolated as a transparent, yellow, brittle solid, which was then analyzed using ¹H NMR and size-exclusion chromatography.

The suspension of bis(pyrrolidone) in water dissolved immediately after the amine was added to the solution. The aqueous solvent, which helps the formation of a polyamide salt during the first step of the reaction, was removed when the reaction was placed under vacuum. Although no important differences were observed between the different acid catalysts tested (PTSA, H₃BO₃ and H₂SO₄), a slightly higher conversion was obtained using PTSA.

Various reaction temperatures (100, 150, 170 and 200 °C) were studied. As expected, the molecular weight increased with the reaction temperature, but some degradation was observed at 200 °C. A kinetic study of the synthesis of the C₂C₂ polyamide was therefore conducted to determine the reaction time that would lead to a polymer with sufficient molecular weight but without degradation of the compounds. In this work, the minimum molecular weight for an optimum interpenetration of the two phases was arbitrarily targeted as 20 000 g mol⁻¹. However, the molecular weight continuously increased with the reaction time, from ~ 2000 g mol⁻¹ after 3 h,

and reached a plateau at approximately 30 000 g mol⁻¹ after 72 h at 170 °C. A further increase of the reaction time led to coloring of the product, which was most likely owing to degradation. Four different polyamides were prepared by condensing a combination of 1,2-bis(4-carboxypyrrolidin-2-on-1-yl)ethane or 1,2-bis(4-carboxypyrrolidin-2-on-1-yl)hexane with ethylene diamine or hexylene diamine at 170 °C for 72 h in the presence of a catalytic amount of PTSA (Figure 1).

¹H NMR analysis of the polycondensates is exemplified with the C₂C₂ compound: a signal at 3.21 p.p.m. corresponding to the methylene group CH₂–NH–CO and a signal at 8.21 p.p.m. corresponding to the NH group indicated the formation of the amide. The NMR result also confirms the complete consumption of the starting diamine. Similar spectra were observed for all of the compounds.

Regarding the polymer size, the best result was obtained for C₂ C₂ (Mw = 31 000, Ip = 1.8, DPn = 96). As expected, similar results were obtained for the C₂ C₆ (Mw = 24 100, Ip = 1.96, DPn = 64) and C₆C₂ (Mw = 25 200, Ip = 2.12, DPn = 67) polyamides. The lowest molecular weight was obtained for C₆C₆ (Mw = 23 200, Ip = 2.06, DPn = 59). As expected, the molecular weights of the polyamides decreased as the monomer size increased.

Thermal properties of the synthesized compatibilizers

The glass transition temperatures of the synthesized polymers decreased as the water content increased (Table 1). The samples exhibited hydrophilic behavior. This result could be explained by the presence of amide groups, which are strong hydrogen-bonding groups and preferentially form hydrogen bonds with water.²³ Indeed, among the four hydrophilic polymers studied, C₂C₂ exhibited considerable sensitivity to water because its T_g varied from –15 °C at 50% RH to 124 °C at 0% RH. This behavior was attributed to its smaller hydrophobic CH₂ sequences compared with the other synthesized polymers.

Not surprisingly, the polycondensate C₆C₆ was less sensitive to water and had T_g values ranging from 29 to 48 °C. We have thus, according to these DSC analyses, synthesized a variety of polycondensates with different sensitivities to water. This property of adjustable hydrophilicity in a compatibilizer is of great interest.

Mechanical and thermal properties of the TPS/PBS blends

Mechanical properties. Figure 2 presents the elongation-at-break, tensile strength and modulus for PBS as a function of TPS concentration. All of the systems were systematically characterized at 50% RH and 20 °C. In all cases, the TPS contained 25% glycerol.

The strain-at-break of the PBS composites increased with increasing TPS content (Figure 2a). The low strain-at-break of PBS is explained by the chosen characterization procedure: the tensile test specimens were prepared using a cookie cutter to facilitate the characterization of defaults in the material. Indeed, samples obtained

Table 1 Glass transition values of the synthesized polycondensates obtained at different relative humidities

Polycondensate	Glass transition temperature (°C)			
	0% RH	13% RH	33% RH	50% RH
C2C2	124	98	38	–15
C2C6	103	85	69	64
C6C2	98	70	51	45
C6C6	48	37	34	29

Figure 2 Effect of starch content on (a) the strain, (b) modulus and (c) stress of the starch-poly(butylene succinate) (PBS) blends.

using cutting procedures are sensitive to fracture propagation. As PBS is known to be fragile to fracture propagation, low strain-at-break values were obtained for the pure material. In contrast, the plasticized starch containing 25% glycerol exhibited plastic behavior, and it was characterized by a higher strain-at-break.

The strain of the PBS/TPS mixtures varied very slightly, increasing from 32% for SPB30 to 36% for SPB70, whereas the values for the pure component were 22 and 92% for PBS and starch, respectively. This behavior suggests that the mechanical properties were related to interfacial defaults between PBS and starch, which has already been reported for TPS/polyester blends.^{24–27}

Figure 3 Glass transition values measured with a dynamic mechanical analyzer (DMA) of starch and poly(butylene succinate) (PBS) blends with starch/PBS ratios of 0:100, 30:70, 40:60, 60:40, 70:30 and 100:0.

The tensile modulus progressively decreased with the addition of TPS, which had a much lower intrinsic modulus at the glycerol concentration used here (25%) (Figure 2b). Furthermore, as the starch content increased to 70%, the modulus of the blends decreased because of the increased content of the discontinuous PBS phase. The strength-at-break (that is, stress) of TPS–PBS was shown to decrease with the increasing amount of starch (Figure 2c), as already observed by other investigators.^{12,13,28}

The mechanical properties of the PBS–TPS blends exhibited three different zones: (i) below 30% starch content, the starch acted as filler in the continuous PBS matrix. As the blends were subjected to an external tensile load, the PBS matrix was the primary load-bearing phase. (ii) When the starch content in the TPS–PBS blends was between 30 and 70%, the mechanical properties varied only slightly. (iii) Above 70% starch content, the PBS matrix became discontinuous, and the effective cross-section area of the continuous phase was reduced, which resulted in decreased stress.

Dynamic mechanical properties. The most commonly used method to measure the miscibility in polymer–polymer blends or partial-phase mixing in such blends is by comparing the α relaxation of the blend with that of the unblended constituents.^{29–31}

Figure 3 shows the $\tan \delta$ peaks for 100% PBS, 100% starch and starch–PBS composites. The following salient features are apparent:

- Presence of two α -transitions in the TPS–PBS composites, which correspond to a starch-rich phase and a PBS-rich phase and suggests that the compatibility between the two components is limited.
- Presence of a β -transition in all samples, except pure PBS. Such β -transitions were also observed in starch–glycerol–water systems within a similar range of temperatures.^{24,32,33}
- Decrease in the $(\tan \delta)_{\max}$ of PBS and an increase in the $(\tan \delta)_{\max}$ of the starch peaks.
- Changes in the α -transition temperature of the PBS and starch fractions.

In fact, the α -transition of PBS slightly increased with increasing starch content and was observed to range from -13.83 to -9.40 °C for PBS and SPB70, respectively. In contrast, the α -transition of TPS considerably decreased from 28.92 °C for pure TPS to 8.77 °C for

Figure 4 Scanning electron microscope (SEM) pictures of the extruded thermoplastic starch (TPS)/poly(butylene succinate) PBS blend: (a) SPB30 and (b) SPB70.

SPB70 then decreased slightly for all TPS–PBS composites as the PBS content increased.

The β -transition exhibited a very slight shift to lower temperatures as the amount of PBS increased. This shift could be because of some solubilization of glycerol in PBS. As the β -transition of the plasticized starch increases with the glycerol content, this negative shift of the peak shows that a part of the glycerol migrates in the PBS phase.

Morphology. The mechanical properties and the morphologies of polymer blends are known to be strongly inter-related. The morphology is of paramount importance; however, in the case of polymer incompatibility, which leads to the development of a two-phase material. Most starch-based plastics have been unable to replace conventional petrochemical polymers because of phase inversion at high-starch contents and the appearance of a continuous TPS phase with poor mechanical properties.^{24,26,30,34}

Figure 5 Effect of synthesized compatibilizers on (a) the strain, (b) modulus and (c) stress of SPB30.

Figure 6 Effect of synthesized compatibilizers on the glass transition values of SPB30 measured with a dynamic mechanical analyzer (DMA).

The morphology of the fractured TPS–PBS blends is shown in Figure 4. The PBS phase was extracted with dichloromethane for 15 min to improve the contrast in the micrographs of the blends.

The morphology of a blend with relatively high-starch content (SPB70) was compared with that of a blend with low-starch content (SPB30). As shown in Figure 4a (SPB30), a clear edge and cavity can be observed between the starch granules and the PBS matrix. The starch granules exhibited a broad-size distribution, and some of them were detached from the PBS matrix. The morphology of the high-starch content blend (Figure 4b) still exhibits small cavities but no starch nodule because of the lower PBS content. These results indicate the presence of a dispersed nodular morphology in blends with low- or high-starch contents.

This morphology is typical of incompatible blends and results in poor mechanical properties.

Characterization of the TPS/PBS/compatibilizer blends

As noted above, the starch α -transition in the TPS–PBS blend exhibited a considerable shift at lower temperatures, which indicates some interfacial interaction between the two polymers. This interaction might be because of hydrogen bonding between the starch hydroxyl groups and the polyester. Furthermore, the compatibility of TPS and PBS could be improved by adding the previously synthesized compatibilizer.

Mechanical and thermal properties. All of the synthesized compatibilizers were tested with the SPB30 blend.

Figure 5 shows the tensile properties of SPB30 with different compatibilizers. The addition of 1% C_2C_2 resulted in little increase of the elongation-at-break and stress, and a slight increase of the

Figure 7 Effect of synthesized compatibilizers on the morphologies of the TPS/PBS blends using confocal microscopy: (a) SPB70- C_2C_2 , (b) SPB30- C_2C_2 , (c) SPB30- C_2C_6 , (d) SPB30- C_6C_2 and (e) SPB30- C_6C_6 . A full color version of this figure is available at *Polymer Journal* online.

modulus. Only a 16% improvement of strain compared with that of a pure blend was observed with the C_2C_2 compatibilizer.

A 45% improvement of the elongation-at-break and a 30% improvement of the Young's modulus were observed when C_2C_6 and C_6C_2 were used as compatibilizers, whereas the addition of C_6C_6 resulted in a considerable decrease of strain. In fact, the presence of insoluble components in the SPB30- C_6C_6 composite, which act as flaws in the matrix and result in poor mechanical properties, were apparent from simple visual observation. The mechanical properties of these blends appeared to depend not only on the mechanical properties of each component but also on the interfacial properties and were therefore directly related to the compatibilization.

The DMA traces of $\tan \delta$ for the SPB30-compatibilizer blends (Figure 6) show three transitions. The lowest transition at ~ -53.42 – -43.11 °C corresponds to the β -transition of starch, and the α -transition is between 5.53 and 6.14 °C. The second transition corresponds to the α -transition of PBS, which is generally between -13.06 and -7.44 °C.

After adding the compatibilizer, the peak for the α -transition of the PBS in the compatibilized blends was observed to shift toward higher temperatures, whereas the α -transition of starch remained constant.

The addition of 1% C_2C_2 had no effect on glass transition, whereas C_2C_6 , C_6C_2 and C_6C_6 increased the β -transition of starch and the α -transition of PBS. This behavior would indicate an enhancement of the interfacial adhesion between the PBS and starch.

The enhanced compatibilization induced by these amphiphilic polycondensates was presumably owing to hydrophobic interactions with PBS and hydrogen bonding with starch.

Morphology. The interest of combining SEM and confocal microscopy is to first obtain information about the distribution of

the compatibilizers in the complete material structure; second, the use of SEM allows access to the morphology of the material. The comparison of both measurements allows conclusions about the distribution and effects of compatibilizers in/on the material morphology.

Confocal microscopy. In this study, the morphology of the TPS-PBS blends compatibilized with poly(bis-pyrrolidone) was examined. Neither starch nor PBS exhibit fluorescent properties.

Although pyrrolidone does not belong to the organic molecules that present typical fluorescent groups, this compatibilizer nevertheless exhibits fluorescent behavior.

Different examples of fluorescent PAMAM dendrimers (poly(amido-amine)) containing amine or hydroxyl groups have been described.^{35,36} The fluorescence of our synthesized compounds could be explained by the presence of the same groups as in these PAMAM dendrimers.

Figure 7 shows the morphology of the blends compatibilized with C_2C_2 (SPB30 and SPB70).

As expected, C_2C_2 did not improve the compatibilization adhesion between the starch and the PBS. In fact, less fluorescence was obtained for SPB30 than for SPB70. The black and red areas depict the PBS and starch phases, respectively. This result implies that the C_2C_2 compatibilizer adhered only to the starch. However, this interaction is because of an interaction between the hydroxyl group in the starch molecule and the amide groups of the compatibilizer. This morphology suggests that the hydrophobic $-CH_2-$ sequences in C_2C_2 are too small to allow an affinity with PBS. The fluorescence behavior of the other compatibilizers was characterized by a smaller black area than with C_2C_2 . However, longer hydrophobic sequences in compatibilizers should lead to good interactions with PBS.

Figure 8 Effect of synthesized compatibilizers on the morphology of SPB30 using scanning electron microscopy (SEM): (a) SPB30- C_2C_2 , (b) SPB30- C_2C_6 , (c) SPB30- C_6C_2 and (d) SPB30- C_6C_6 .

Figure 7e shows the C_6C_6 insolubles in the SPB30- C_6C_6 blend, and confirms the visual observation: the C_6C_6 structure is also too hydrophobic to obtain an interaction with the binary system, even with the hydrophobic polyester phase.

As expected, a more homogeneous distribution is observed in Figures 7c and d, which reveals that the C_6C_2 and C_2C_6 structures have a good hydrophobic-hydrophilic balance for an optimum interaction with the PBS-starch system

SEM observations. Figure 8 presents the SEM micrographs of the SPB30-compatible blends. Compatibilization with C_2C_2 resulted in a further reduction of the cavities in TPS, which indicated a slight enhancement of the compatibility between the PBS and starch. Improved compatibilization morphology was also observed in the case of C_6C_2 and C_2C_6 . In addition, the micrographs (Figures 8b and c) revealed a homogeneous distribution of the starch phase at the investigated scale, which suggests the formation of a co-continuous phase with the polyester.

DISCUSSION

The mechanical properties of the blends of starch with PBS, as determined using extrusion processes, are poor as a result of incompatibility. Increasing the starch content decreased the modulus and tensile strength (Figure 2).

Control over the morphology of these materials is a key point of the polymer blend system but also depends on the polymer volume ratio (Figure 4). At a low-starch content, starch particles are dispersed in the PBS. When the concentration of starch increases, the dispersed starch particles form a larger continuous phase in the entire sample. In this study, the SPB30 system was chosen to be compatibilized for the following reasons: (i) SPB30 is a typical ratio for industrial polyester/starch blends; and (ii) SPB30 shows a dispersed morphology, and this work sought to convert the SPB30 system to a co-continuous morphology, using amphiphilic compatibilizers synthesized from itaconic acid.

The transformation from a co-continuous to a dispersed phase was achieved by the use of C_2C_6 or C_6C_2 as compatibilizers. The change in morphology was observed by SEM, which revealed a better dispersion in PBS in the presence of compatibilizer (Figure 8). The increase in the interfacial surface affected the macromolecular movements, as shown in Figure 6 (a slight effect on the β - and α -transition temperatures). This result can be explained by hydrogen interactions between, on the one hand, amide and ester functional groups and on the other hand, amide and hydroxyl groups.

Therefore, we improved the mechanical properties of the SPB30 blend by compatibilization with an amphiphilic copolymer (C_2C_6 and C_6C_2). That both molecules had the same affect reveals that the compatibilization effect is simply controlled by the hydrophilic-hydrophobic balance, regardless of the position of the functional groups. A good distribution of the compatibilizer in the polymer matrix was revealed using confocal microscopy (Figure 7).

CONCLUSIONS

Plasticized starch can be successfully blended with PBS by compatibilization with an amphiphilic copolymer. The mechanical properties of the polymer blend studied here were improved through the addition of an amphiphilic polycondensate, C_2C_6 or C_6C_2 , which most likely interacts with the TPS and PBS by hydrogen bonding to the amide groups. The good distribution of the compatibilizer in the polymer matrix was demonstrated using confocal microscopy. The

C_2C_6 and C_6C_2 compatibilizers expanded the co-continuous morphology of the SPB30 samples. The change in morphology was confirmed using SEM, which revealed greater dispersion in PBS in the presence of the compatibilizer.

Amphiphilic compatibilizers could provide an interesting alternative to the frequently used reactive compatibilizers, such as maleic anhydride, which are more difficult to manipulate.

The use of itaconic acid, which is a renewable chemical identified as one of the top 12 value-added chemicals that can be obtained from biomass as one of the main components of these new compatibilizers, is another interesting feature of this study.

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