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Compatible blends of thermoplastic starch and hydrolyzed ethylene-vinyl acetate copolymers

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ABSTRACT

Ethylene-vinyl acetate copolymer (EVA) with 19% of vinyl acetate and its derivatives modified by hydrolysis of 50 and 100% of the initial vinyl acetate groups were used to produce blends with thermoplastic starch (TPS) plasticized with 30 wt% glycerol. The blends were characterized by Fourier transform infrared spectroscopy, scanning electron microscopy, X-ray diffraction, water absorption, stress–strain mechanical tests, dynamic mechanical analysis and thermogravimetric analysis. In contrast to the blends with unmodified EVA, those made with hydrolyzed EVA were compatible, as demonstrated by the brittle fracture surface analysis and the results of thermal and mechanical tests. The mechanical characteristics and water absorption of the TPS were improved even with a small addition (2.5 wt%) of hydrolyzed EVA. The glass transition temperature rose with the degree of hydrolysis of EVA by 40 and 50°, for the EVA with 50 and 100% hydrolysis, respectively. The addition of hydrolyzed EVA proved to be an interesting approach to improving TPS properties, even when very small quantities were used, such as 2.5 wt%.

1. Introduction

Thermoplastic starch (TPS) is a natural biodegradable polymer prepared by destructuring of starch. Among the biodegradable polymers, TPS is a promising material because of its low cost and inherent biodegradability since its basic components are all biodegradable materials, such as starch and glycerol. Starch is one of the most interesting raw materials for biodegradable plastics because it is not just renewable but overwhelmingly abundant, being produced in any climate and agricultural conditions.

TPS is already used in several commercial products, but intense research continues to improve its properties and widen the possible range of its applications. Research is now focused on modifying the structure of starch, usually by chemical modification during extrusion (Kalambur & Rizvi, 2005, 2006; Moad, 2011; Raquez, Narayan, & Dubois, 2008; Xie, Yu, Liu, & Chen, 2006), and improving its blending with other polymers (Carvalho, 2008; Chang, Jian, Zheng, Yu, & Ma, 2010; Da Roz, Carvalho, Gandini, & Curvelo, 2006; Gandini, 2008; Sankri et al., 2010; Scaffaro, Morreale, Lo Re, & La Mantia, 2009; Taguet, Huneault & Favis, 2009; Yu, Dean, & Li, 2006). Both of these strategies are aimed at reducing its hydrophilicity and improving mechanical properties. Generally, blends of TPS are produced with nonpolar polymers whose function is to increase its hydrophobicity and improve its water resistance. The main drawback of this approach is the poor compatibility between hydrophilic starch and hydrophobic polymers. In this context, the development of new low cost and effective modifiers and compatibilizers is of great importance and e-caprolactone, methylenediphenyl diisocyanate, dioctyl maleate, poly(vinyl alcohol), cellulose fibrils and mineral fillers have all been tested to improve the interfacial interactions of these blends (Averous & Halley, 2009; Curvelo, de Carvalho, & Agnelli, 2001; Prinos, Bikiaris, Theologidis, & Panayiotou, 1998; Schwach, Six, & Averous, 2008; Yin, Zhang, & Yao, 2006; Yu et al., 2006).

Ethylene-vinyl acetate copolymer (EVA) is a commercial polymer used in several applications, including the compatibilization of polymers and as a medium for dispersion of fillers in low-surface-energy polymers (Nordqvist, Sanchez-Garcia, Hedenqvist, & Lagaron, 2010). One interesting aspect of EVA is that it can easily be modified to give more polar copolymers. The main modification can be obtained by hydrolyzing the acetate group. The partial hydrolysis of acetate groups can result in tunable copolymers of hydrophilic vinyl alcohol and hydrophobic ethylene and vinyl acetate groups (Hirata, Marais, Nguyen, Cabot, & Sauvage, 2005; Kim, Yoon, Mun, Rhee, & Lee, 2006; Tambe, Singh, Patri, & Kumar, 2008). The hydroxyl group can improve compatibility with TPS, so that EVA can be used itself as a polymer counterpart or as a compatibilizer between TPS and other low polarity polymers. One other advantage of EVA is its low cost, compared to compatibilizers such as poly(ethylene-g-maleic anhydride) (PE-g-MA) (Bikiaris & Panayiotou, 1998; Karayannidis, Sideridou, Zamboulis, Bikiaris, & Sakalis, 2000; Sailaja, 2005; Sailaja & Chanda, 2000,

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2002), poly(ethylene-*co*-vinyl alcohol) (EVOH) (Sailaja & Chanda, 2002), poly(ethylene-*co*-acrylic acid) (EAA) and poly(ethylene-*co*-glycidyl methacrylate) (PEGMA) (Sailaja, 2005; Taguet et al., 2009). Furthermore hydrolyzed EVA is also harmless and has good environmental affinity (Hirata et al., 2005; Kim et al., 2006; Tambe et al., 2008).

The objective of this study was to produce new low-cost modified EVA copolymer for the production of compatible polymer blends with glycerol-plasticized-TPS. To this end EVA with 19% vinyl acetate content was partially (50%) and completely hydrolyzed and blended with TPS. The materials were characterized by Fourier transform infrared (FTIR) spectroscopy, water uptake, tensile tests, X-ray diffraction, scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and dynamical mechanical analysis (DMA). The influence of the degree of hydrolysis of modified EVA on the mechanical properties of modified-EVA/TPS blends was studied.

2. Experimental

2.1. *Materials*

Regular native cornstarch (28% amylose) with 11% moisture, reagent grade glycerol and stearic acid were used as received. Commercial EVA copolymer 19% vinyl acetate content with melt flow index (MFI) 2.5 g × 10 min^{-1} was used as received.

2.2. *EVA modification by hydrolysis*

EVA was hydrolyzed by the method reported by Hirata et al. (2005) and Tambe et al. (2008), briefly described here: EVA was dissolved in tetrahydrofuran, and 3.0 M alcoholic NaOH was added to the solution causing the precipitation of the polymer. The mixture was heated at 50 °C and maintained under agitation for 6 h. After completion of the reaction the resulting mixture was neutralized with 3.0 M aqueous HCl solution. The hydrolyzed EVA was washed on a Buchner funnel repeatedly with distilled water to remove solvents and inorganic salt and dried to a powder.

2.3. *Characterization of modified EVA*

2.3.1. *Degree of hydrolysis*

The hydroxyl content was determined by back-titration of the excess acetic anhydride used in the presence of pyridine. For this procedure, 1 g hydrolyzed EVA was dissolved in 25 mL toluene and 5 mL of a mixture of acetic anhydride/distilled pyridine (70:30, w/w) was added and the mixture was refluxed for 24 h. Unreacted acetic anhydride was determined by titrating against standard 0.5 N alcoholic KOH solution, with phenolphthalein as indicator (Tambe et al., 2008).

2.3.2. *Fourier transform infrared spectroscopy*

Hydrolyzed EVA copolymer powder was converted into a thin film by hot pressing at 150 °C. FTIR spectra of this film were recorded with Thermo Scientific NICOLET-IR200 spectrophotometer.

2.4. *Thermoplastic starch preparation*

To prepare TPS, the starch, glycerol (30 wt%), EVA and stearic acid (0.5 wt%), as demolding agent, were mixed in polyethylene bags until a homogeneous material was obtained (see Table 1 for compositions). The mixtures were processed in a single-screw extruder (AX Plasticos Ltda, Brazil) with an 16 mm screw ($L/D = 40$) operating at 30 rpm with the following zone temperatures from

Table 1
Composition of the TPS/EVA blends, crystallinity (B-type and VH-type) index determined by XRD, and loss tangent (tan δ) determined by DMA, water uptake at equilibrium and tensile-stress data of Young's modulus (E), elongation at rupture (ε_m) and tensile strength (σ_m) for TPS and its blends with EVA and hydrolyzed EVA with 50% hydrolysis (EVA50H) and 100% hydrolysis (EVA100H).

Material identification	EVA content in the EVA-TPS blend (wt%)	Percent hydrolysis of EVA vinyl acetate groups (%)	$X_{c\,\text{B-type}}$ ($2\theta = 16.8°$)	$X_{c\,\text{VH-type}}$ ($2\theta = 19.7°$)	tan δ peak (°C)	Water uptake at equilibrium (%)			Mechanical analysis		
						43 RH	53 RH	75 RH	σ_m (MPa)	ε_m (%)	E (MPa)
TPS	–	–	0.17	0.46	42.2	7.3	9.4	22.0	3.5 ± 0.2	28.8 ± 5.9	45.2 ± 7.8
EVA	–	0	–	–	–15.0	–	–	–	22 ± 1.0	272 ± 10	175 ± 30
EVA50H	–	50	–	–	–5.0	–	–	–	26 ± 1.0	75 ± 10	391 ± 30
EVA100H	–	100	–	–	80.0	–	–	–	40 ± 1.0	23 ± 10	1050 ± 100
TPS2.5EVA	2.5	0	0.08	0.44	60.3	3.0	5.8	13.8	6.7 ± 0.8	40.9 ± 12.6	67.0 ± 28.6
TPS5.0EVA	5.0	0	0.07	0.44	59.0	3.0	5.7	13.7	6.7 ± 0.5	38.5 ± 9.1	69.6 ± 25.5
TPS7.5EVA	7.5	0	0.04	0.45	67.8	2.9	5.7	13.7	6.2 ± 0.5	35.5 ± 12.3	65.7 ± 6.1
TPS10.0EVA	10.0	0	0.05	0.46	73.4	2.8	5.3	13.6	6.4 ± 0.3	46.8 ± 10.4	46.5 ± 4.3
TPS2.5EVA50H	2.5	50	0.07	0.44	78.5	4.4	7.5	16.1	5.3 ± 0.8	20.7 ± 4.2	94.9 ± 29.3
TPS5.0EVA50H	5.0	50	0.05	0.46	77.7	3.4	6.3	14.3	6.1 ± 0.4	59.0 ± 4.4	51.5 ± 5.4
TPS7.5EVA50H	7.5	50	0.04	0.45	104.0	3.2	6.2	14.0	6.2 ± 0.4	37.6 ± 7.9	59.4 ± 13.7
TPS10.0EVA50H	10.0	50	0.10	0.47	82.4	3.1	6.1	14.0	5.7 ± 0.7	44.0 ± 10.2	54.2 ± 9.1
TPS2.5EVA100H	2.5	100	0.08	0.45	93.8	3.4	6.1	14.5	8.2 ± 0.9	50.6 ± 13.2	76.1 ± 10.4
TPS5.0EVA100H	5.0	100	0.08	0.43	99.1	3.4	6.3	14.3	9.9 ± 1.1	42.2 ± 7.9	70.3 ± 8.7
TPS7.5EVA100H	7.5	100	0.06	0.42	80.4	3.3	6.3	14.5	9.1 ± 0.3	37.3 ± 7.6	76.4 ± 16.9
TPS10.0EVA100H	10.0	100	0.06	0.42	88.4	3.4	6.5	14.1	8.7 ± 0.5	50.5 ± 5.9	59.6 ± 11.1

feed to die: 85, 110, 105 and 100 °C. The extruded samples were hot pressed at 150 °C into 2 mm thick plates.

2.5. *Thermoplastic starch characterization*

2.5.1. *Fourier transform infrared (FTIR) spectroscopy*

Spectra of the TPS blends were recorded in the Thermo Scientific NICOLET-IR200 FTIR spectrophotometer, in the attenuated total reflectance mode (ATR).

2.5.2. *Water uptake*

Water absorption experiments were conducted on circular specimens, 11 mm in diameter, cut from 2 mm thick hot-pressed plates of TPS. Before the tests, the specimens were dried at 70 °C to constant weight. They were then conditioned in sealed containers at 25 ± 2 °C, in 43, 53 and 75% relative humidity (RH) atmospheres in equilibrium with saturated aqueous solutions of K_2CO_3, $Mg(NO_3)_2{\cdot}6H_2O$ and NaCl, respectively, as stipulated in ASTM E104. The water uptake at equilibrium was computed from the gain in weight. The % water uptake (W) was given by the relation

$$W\ (\%) = \left[\frac{M_f - M_0}{M_0}\right] 100 \qquad (1)$$

where M_f is the mass at equilibrium and M_0 is the initial mass.

2.5.3. *Tensile tests*

The tensile tests were performed in a Universal Testing instrument, equipped with a load cell of 200 kg. The samples, previously conditioned at 53% of RH and 25 ± 1 °C for 30 days, were tested as stipulated in the ASTM D638M type II procedure, with crosshead speed of 50 mm/min. At least 8 samples of each composition were tested and the average values were taken.

2.5.4. *Dynamic mechanical analysis (DMA)*

These tests were conducted with a Netzsch DMTA 242C dynamic mechanical analyzer working in the dual cantilever mode, with maximum deformation corresponding to amplitudes in the range of 7.5–11 μm. Measurements were performed under flowing air, with an applied force oscillating at a frequency of 1 Hz and with a maximum dynamic force of 6 N, over a temperature range of −150 to 200 °C rising at 3 K/min. The specimens (35 mm × 5 mm × 2 mm) were cut from the hot-pressed molded plates. Owing to the high flexibility of EVA and the modified EVA, these materials were analyzed in the tensile mode, with a 10 μm amplitude and 6 N dynamic force.

2.5.5. *X-ray diffraction*

Diffractograms were recorded on a Rigaku diffractometer. Scattered radiation was detected in the Bragg-angle (2θ) range of 3–40°, scanned at 28°/min. The degree of crystallinity was estimated from the ratio of the heights of the V-type and B-type diffraction peaks at $2\theta = 19.7°$ and 16.8° respectively, above the baseline of the diffractogram read at $2\theta = 6.7°$ (Hulleman, Kalisvaart, Janssen, Feil, & Vliegenthart, 1999).

2.5.6. *Scanning electron microscopy (SEM)*

The morphological characterization was performed on the cryogenically fractured (liquid nitrogen) surfaces of the blends, using a Leo 440 scanning electron microscope. Samples were sputter-coated with gold after drying in a Balzers SCD050 Sputter Coater.

2.5.7. *Thermogravimetric analysis (TGA)*

Thermogravimetric analyses were measured with a Shimadzu TGA-50 instrument. About 5 mg of sample was poured in platinum pans. The samples were heated from ambient temperature to 750 °C at a heating rate of 10 °C/min under nitrogen flow (25 mL/min).

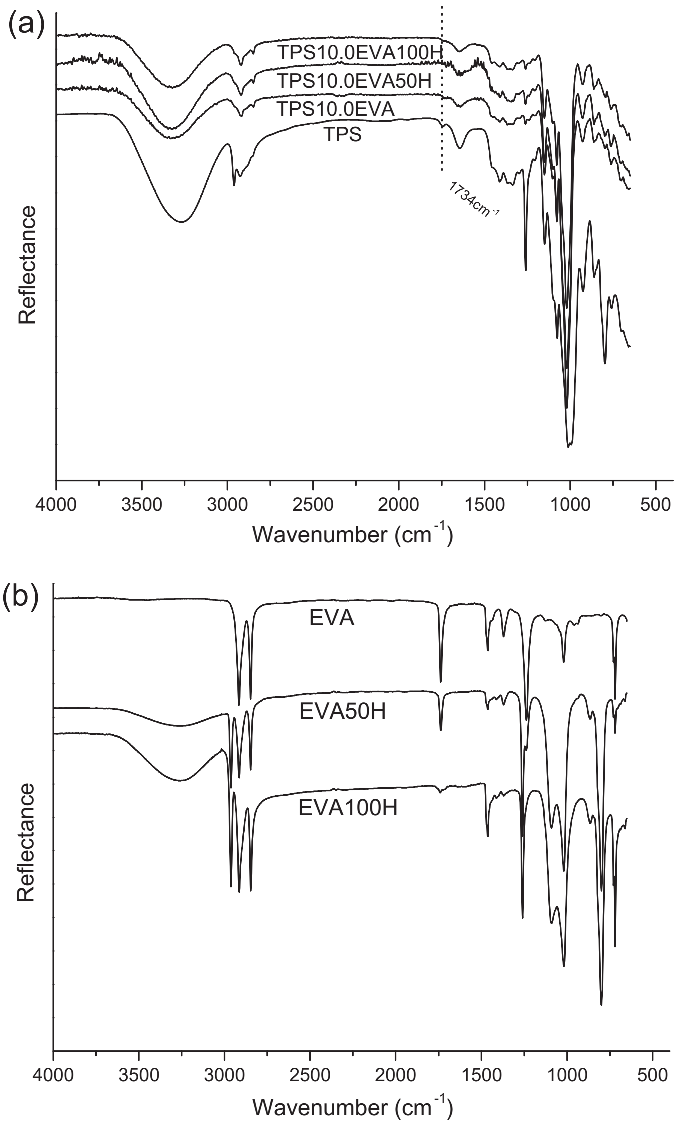

Fig. 1. FTIR spectra of (a) TPS and its blends with 10 wt% of EVA and the 50 and 100% hydrolyzed products and (b) pristine EVA, EVA50H, EVA100H.

3. Results and discussion

3.1. *EVA hydrolysis*

The EVA materials were named EVA, EVA50H and EVA100H, for the unmodified EVA, 50% hydrolyzed EVA and 100% hydrolyzed EVAs, respectively. The EVA, EVA50H and EVA100H were characterized by FTIR spectroscopy, as shown in Fig. 1b. As expected and reported elsewhere (Yin et al., 2006), the intensity of the peak due to the acetate group, at 1735 cm^{-1}, decreased and a peak due to —OH stretching appeared at 3200–3400 cm^{-1}, confirming the modification of EVA by hydrolysis. The OH contents of hydrolyzed polymers were determined by reaction with excess acetic anhydride and subsequent titration, by the method described by Tambe et al. (2008). The values obtained were 49.3 and 99.8%, for the samples for which the theoretical expected degrees of hydrolysis were 50 and 100%, respectively. This result shows a very good agreement between the experimental and theoretical values.

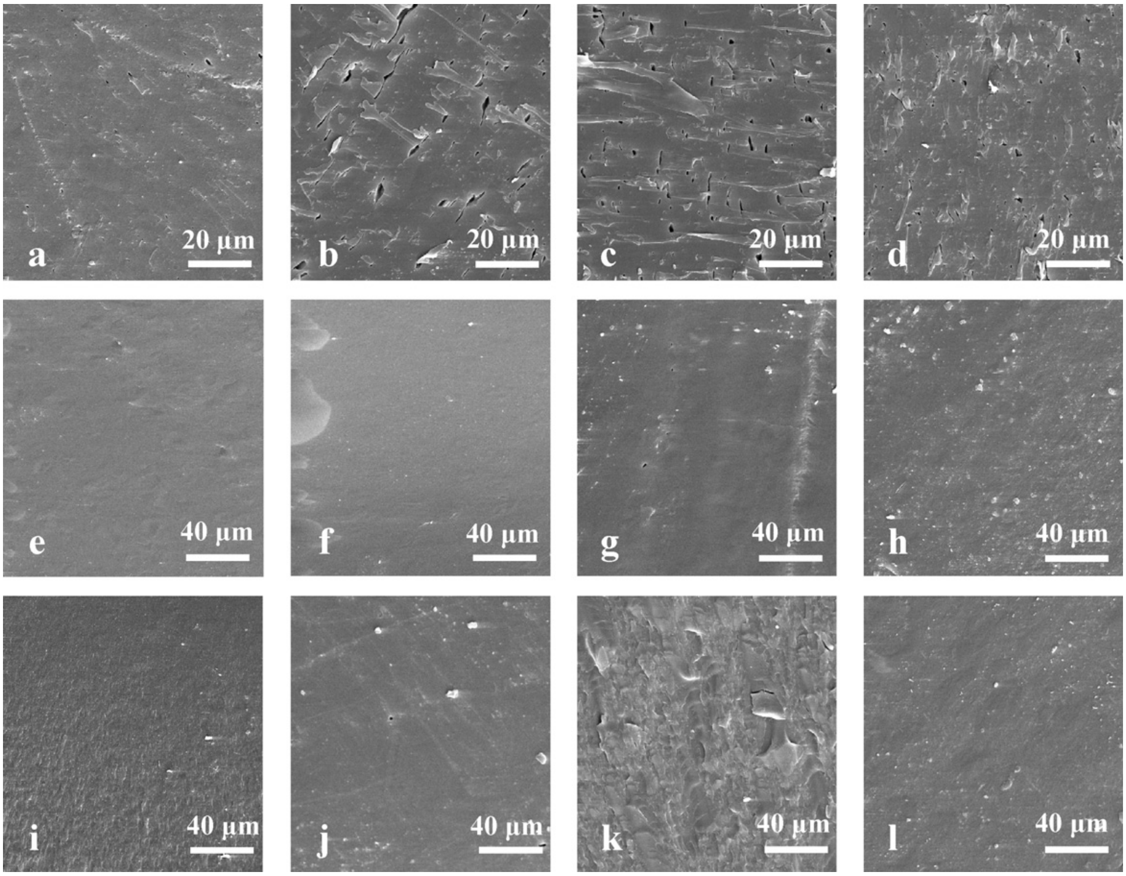

Fig. 2. SEM images of brittle fractures surface of the blends: (a) TPS2.5EVA, (b) TPS5.0EVA, (c) TPS7.5EVA, (d) TPS10.0EVA, (e) TPS2.5EVA50H, (f) TPS5.0EVA50H, (g) TPS7.5EVA50H, (h) TPS10.0EVA50H, (i) TPS2.5EVA100H, (j) TPS5.0EVA100H, (k) TPS7.5EVA100H and (l) TPS10.0EVA100H.

3.2. *Preparation and characterization of thermoplastic starch blends*

The compositions of thermoplastic starch mixtures with EVA are given in Table 1. The glycerol content is based on dry starch (TPS = starch + glycerol) and the proportion of EVA and its modified products based on the sum of TPS and EVA, all on a dry basis.

FTIR spectra of the blends (Fig. 1a) show mainly the typical absorption of TPS (Sankri et al., 2010), since the concentration of EVA/hydrolyzed EVA is quite low in the blends. In general, the EVA, EVA50H and EVA100H peaks are masked by the TPS peaks. The main peaks observed and attributed to TPS were: (i) 3000–3600 cm^{-1}: stretching vibration mode of the hydrogen-bonded O—H groups of starch, (ii) 950–1200 cm^{-1}: C—C and C—O stretching vibration modes and C—O—H bending modes, and (iii) 700–950 cm^{-1}: C—O—C α(1–4) and the C—O—C ring stretching modes. FTIR did not show any specific modification due to molecular interaction of TPS and EVA and EVA50H or EVA100H.

The morphology of the TPS/EVA blends was investigated by scanning electron microscopy. Fig. 2 shows the brittle fracture surfaces obtained in liquid nitrogen. Despite the degree of hydrolysis of EVA, the blends were immiscible as expected, however they showed increasing compatibility with the hydrolysis of the EVA. The presence of holes in TPS/EVA blends due to phase debonding indicated poor adhesion between the EVA and TPS phases. In contrast, images of the brittle fracture surfaces of the blends with EVA50H and EVA100H showed no holes. In all cases, the surface is very smooth, with no sign of debonding, indicating a very good interfacial adhesion between TPS and both EVA50H and EVA100H. This result shows that the low compatible blend of TPS–EVA can be converted to a compatible blend by hydrolyzing the EVA component of the blend.

The stress–strain data for Young's modulus, tensile strength and elongation at break are presented in Table 1. The addition of EVA, EVA50OH or EVA100OH to TPS caused an increase in all these properties, which was more pronounced with the addition of EVA50H and EVA100H that with the raw EVA. This result indicates that the chemical modification of EVA increases the compatibility between the EVA phase and TPS.

The stress–strain curves of the TPS–EVA and TPS–modified EVA blends show a linear profile at low strain. With the addition of EVA, EVA50H or EVA100H, the Young's modulus, ultimate tensile strength and elongation at break rise. The data for these properties are presented in Table 1. It is clear that, even with a small amount of EVA, EVA50H or EVA100H, an appreciable increase in each variable was observed. It is interesting to note that these mechanical properties are almost independent of the proportion of EVA, EVA50H or EVA100H added. EVA50H and EVA100H cause a higher increase in these properties than EVA, indicating the compatibilization of the components.

DMA plots of storage modulus (E') and tan δ against temperature, for EVA polymers and for the blends, are presented in Figs. 3 and 4, respectively. In Fig. 3, it is possible to observe that the glass transition temperature increases with EVA hydrolysis. Taking the glass transition as the peak in tan δ, T_g increases from −15 °C for EVA to −5 and 80 °C for EVA50H and EVA100H, respectively. This increase in T_g was due to the increase in intermolecular interaction caused by the strong hydrogen bonding of the —OH groups present in EVA50H and EVA100H.

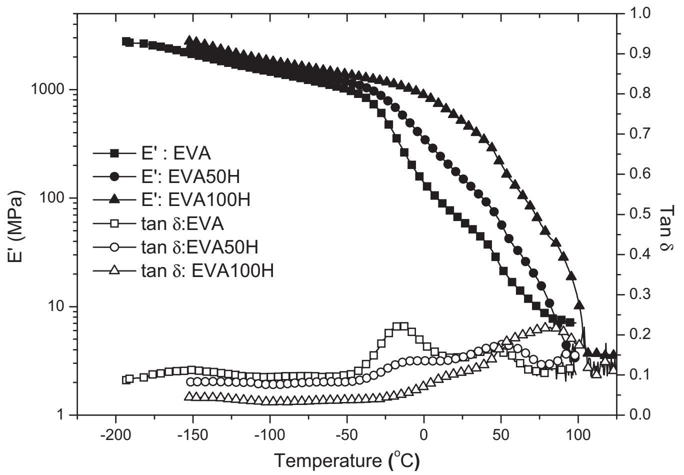

Fig. 3. Dynamic mechanical analysis curves for the storage modulus (E') and tan δ for EVA, EVA50H and EVA100H.

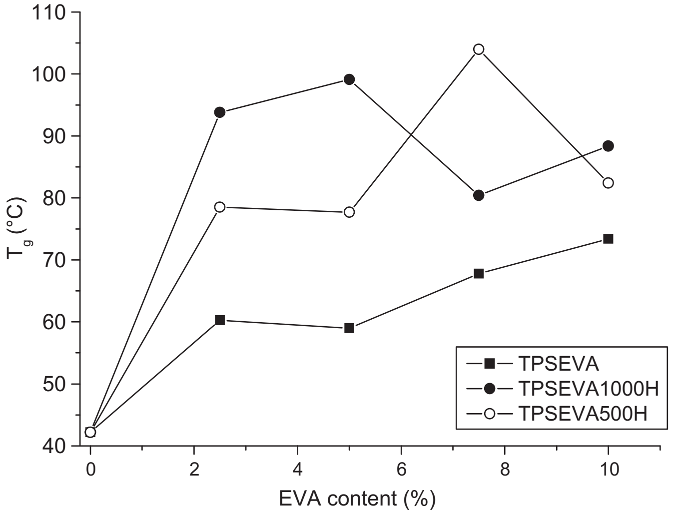

Fig. 5. Glass transition temperature (determined from tan δ peak) plotted against EVA, EVA50H and EVA100H content in the blends with TPS.

Fig. 4 shows the DMA results for the tan δ and storage modulus of the blends. The data for the peak in tan δ, which can be taken as the T_g for the blends are presented in Table 1. Two important findings were observed: (i) the storage modulus increases with the addition of EVA50H or EVA100H and with the increase in its content in the blends and (ii) the storage modulus plateau in the rubbery region after the glass transition rises with the addition of EVA and is more pronounced with 2.5 wt% EVA50H or EVA100H in the blends, changing little when more is added. This is a very interesting finding, since even this small addition of EVA50H or EVA100H improves the thermal and mechanical properties of TPS blends.

Fig. 5 shows the variation of the tan δ peak (data in Table 1) with EVA, EVA50H and EVA100H content. For the blends with EVA the peak in tan δ (or T_g) increased almost linearly with the amount of EVA added. For the blends with EVA50H and EVA100H, the T_g increased with the degree of hydrolysis at low contents ($\leq$5 wt%), but it did not show a clear relation with the proportion of EVA50H and EVA100H in the blend. It is noteworthy that a small addition (2.5 wt%) of EVA50H and EVA100H was sufficient to increase the T_g from 43 °C for pure TPS to ~80 and 90 °C for the blends with EVA50H and EVA100H, respectively. The increase in the T_g values of the blends was not expected since the values of T_g for EVA and modified EVA are below that of TPS. This effect can be attributed to the strong interaction between the components of the blend. Despite the fact that the system is immiscible, a certain degree of miscibility could exist and the cohesive energy of the blend can be higher than that of the separated components. The behavior of highly polar polymer mixtures capable of forming hydrogen bondings is very complex and further investigation of this system should be done.

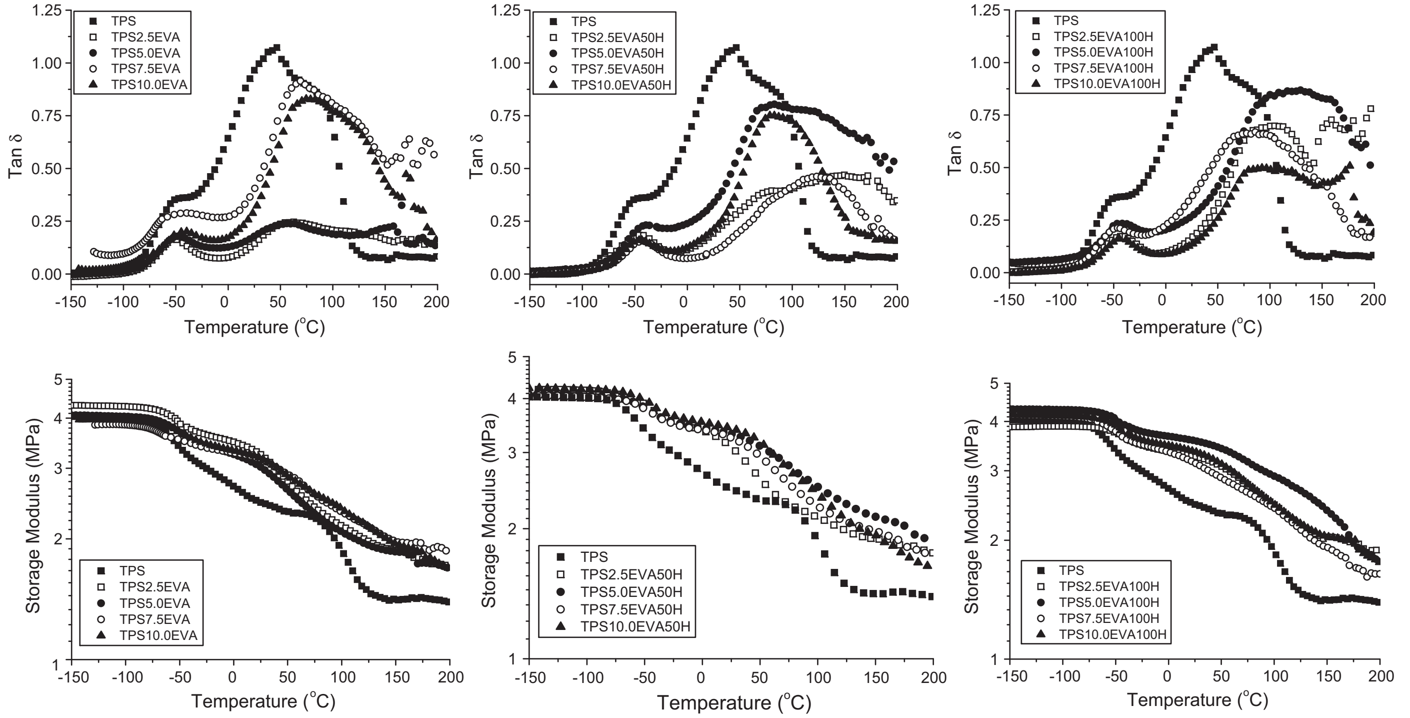

Fig. 4. Dynamic mechanical analysis data for blends plotted against temperature: (top) tan δ and (bottom) storage modulus of TPS blend with (left) EVA, (middle) EVA50H and EVA 100H (right).

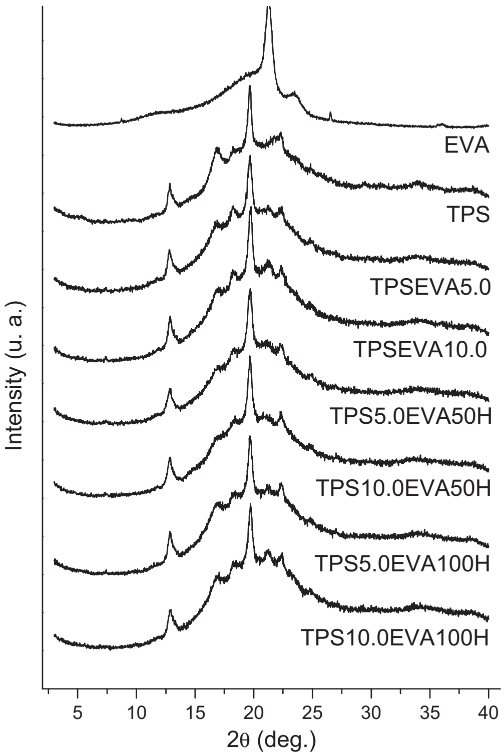

Fig. 6. X-ray diffraction patterns of EVA, TPS and TPS/EVA and TPS/modified EVA.

The water uptake, measured at 43, 53 and 75% RH, resulted in a sharp weight increase with time until equilibrium was reached, which took from 5 to 7 days. The data for the equilibrium water uptake are given in Table 1. As expected, these values increased with increasing atmospheric moisture content. Water uptake shows an important decrease when EVA, EVA50H or EVA100H was added to the TPS blends, but, as for T_g, storage modulus and elongation, it was almost independent of the EVA, EVA50H or EVA100H contents. In a general way, the decrease in water uptake at 43, 53 and 75% RH decreased respectively from 7.3 to ~3%, from 9.4 to ~6% and values from 22.0 to ~14%. The fall observed was greater than 50% in all cases, increasing the stability of the material to environmental changes.

X-ray diffractograms of all blends showed similar curves. In Fig. 6 only some of the spectra were included for the sake of clarity. The original A-type crystallinity of corn starch was replaced by a B-type diffraction pattern (vanSoest & Hulleman, 1996) in the TPS, due to the formation of amorphous starch during extrusion, which recrystallizes into the B-pattern (Bastioli, 1998; vanSoest & Essers, 1997; vanSoest & Vliegenthart, 1997). EVA film exhibited the characteristic orthorhombic diffraction peaks of polyethylene at $2\theta = 21.4°$, $23.5°$ and $35.2°$ (Jin, Chen, & Zhang, 2010). The B and V peaks were used to estimate the crystallinity index (X_c) of the corresponding structures, given in Table 1 (VH-type at $2\theta = 19.7°$ and $22.4°$ and B-type at $2\theta = 16.8°$). The presence of EVA, EVA50H or EVA100H did not cause important changes, either in the diffraction patterns or in the intensity of the peaks.

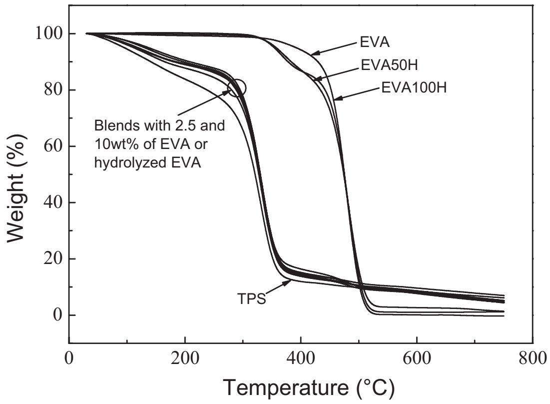

Fig. 7. Thermogravimetric curves of TPS, EVA, hydrolyzed EVAs and the blends containing 2.5 and 10% EVA and it is hydrolyzed derivatives.

Fig. 7 shows the TGA curves of TPS, EVA, hydrolyzed EVAs and the blends containing 2.5 and 10% EVA and its hydrolyzed derivatives. The blends with intermediate proportions of EVA showed intermediate behavior and are not shown in Fig. 7 for the sake of clarity. The thermal stability of hydrolyzed EVA is very similar between them and somewhat inferior to that of EVA. However the onset of degradation for these materials is all around 330 °C. TPS shows a progressive loss of mass before the onset of thermal degradation due to the loss of water and plasticizer. The onset of thermal degradation is around 280 °C. The profile of the TGA analysis for the blends is very similar to that of TPS since it is the main component of the blend (at least 90 wt%). A decrease of mass loss before the onset of thermal degradation was observed for the blends, making these materials more stable.

The results of ultimate tensile-stress mechanical tests, DMA, thermal analysis and water absorption are consistent in showing that important improvements in TPS properties can be produced by the addition of small quantities (2.5 wt%) of EVA50H or EVA100H. Further studies are under course to determine the influence of the EVA50H or EVA100H on the compatibility of TPS with other important polymers such as LLDPE and PLA.

4. Conclusions

Two samples of a commercial EVA copolymer (19% vinyl acetate), modified by hydrolysis of 50 and 100% of the vinyl acetate groups, were produced and used in blends with thermoplastic starch. The blends with EVA50H and EVA100H were compatible, showing a smooth brittle fracture surface without signs of decoupling between the EVA and TPS phases. The glass transition temperature determined by dynamic mechanical tests increased by 40 and 50 °C for the blends prepared with EVA50H and EVA100H, respectively. Mechanical properties measured by stress–strain tests (Young's modulus, tensile strength and elongation at break) increased with the addition of EVA, EVA50H and EVA100H. Water absorption showed a decrease of more than 50% for all blends. In general, the improvement in the properties was observed even when 2.5 wt% of EVA50H or EVA100H was added. X-ray diffraction pattern of TPS apparently was not affected by the inclusion of EVA, EVA50H or EVA100H. This study shows that the addition of only 2.5 wt% of EVA50H and EVA100H was able to improve the mechanical, thermal and water absorption characteristics of TPS, which could thus be an interesting way to expand the use of this kind of material without interfering appreciably in its cost or biodegradable character.

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References

Averous, L., & Halley, P. J. (2009). Biocomposites based on plasticized starch. *Biofuels, Bioproducts & Biorefining-Biofpr*, *3*(3), 329–343.

Bastioli, C. (1998). Properties and applications of Mater-Bi starch-based materials. *Polymer Degradation and Stability*, *59*(1–3), 263–272.

Bikiaris, D., & Panayiotou, C. (1998). LDPE/starch blends compatibilized with PE-g-MA copolymers. *Journal of Applied Polymer Science*, *70*(8), 1503–1521.

Carvalho, A. J. F. (2008). Starch: Major sources, properties and applications as thermoplastic materials. In M. Belgacem, & A. Gandini (Eds.), *Monomers, polymers and composites from renewable resources* (pp. 1–512). Elsevier.

Chang, P. R., Jian, R. J., Zheng, P. W., Yu, J. G., & Ma, X. F. (2010). Preparation and properties of glycerol plasticized-starch (GPS)/cellulose nanoparticle (CN) composites. *Carbohydrate Polymers*, *79*(2), 301–305.

Curvelo, A. A. S., de Carvalho, A. J. F., & Agnelli, J. A. M. (2001). Thermoplastic starch-cellulosic fibers composites: Preliminary results. *Carbohydrate Polymers*, *45*(2), 183–188.

Da Roz, A. L., Carvalho, A. J. F., Gandini, A., & Curvelo, A. A. S. (2006). The effect of plasticizers on thermoplastic starch compositions obtained by melt processing. *Carbohydrate Polymers*, *63*(3), 417–424.

Gandini, A. (2008). Polymers from renewable resources: A challenge for the future of macromolecular materials. *Macromolecules*, *41*(24), 9491–9504.

Hirata, Y., Marais, S., Nguyen, Q., Cabot, C., & Sauvage, J. (2005). Relationship between the gas and liquid water permeabilities and membrane structure in homogeneous and pseudo-bilayer membranes based on partially hydrolyzed poly(ethylene-co-vinyl acetate). *Journal of Membrane Science*, 7–17.

Hulleman, S. H. D., Kalisvaart, M. G., Janssen, F. H. P., Feil, H., & Vliegenthart, J. F. G. (1999). Origins of B-type crystallinity in glycerol-plasticised, compression-moulded potato starches. *Carbohydrate Polymers*, *39*(4), 351–360.

Jin, J., Chen, S. J., & Zhang, J. (2010). Investigation of UV aging influences on the crystallization of ethylene-vinyl acetate copolymer via successive self-nucleation and annealing treatment. *Journal of Polymer Research*, *17*(6), 827–836.

Kalambur, S., & Rizvi, S. S. H. (2005). Biodegradable and functionally superior starch–polyester nanocomposites from reactive extrusion. *Journal of Applied Polymer Science*, *96*(4), 1072–1082.

Kalambur, S., & Rizvi, S. S. H. (2006). An overview of starch-based plastic blends from reactive extrusion. *Journal of Plastic Film & Sheeting*, *22*(1), 39–58.

Karayannidis, G. P., Sideridou, I. D., Zamboulis, D. N., Bikiaris, D. N., & Sakalis, A. J. (2000). Thermal behavior and tensile properties of poly(ethylene terephthalate-co-ethylene isophthalate). *Journal of Applied Polymer Science*, *78*(1), 200–207.

Kim, J., Yoon, T., Mun, S., Rhee, J., & Lee, J. (2006). Wood–polyethylene composites using ethylene-vinyl alcohol copolymer as adhesion promoter. *Bioresource Technology*, 494–499.

Moad, G. (2011). Chemical modification of starch by reactive extrusion. *Progress in Polymer Science*, *36*(2), 218–237.

Nordqvist, D., Sanchez-Garcia, M. D., Hedenqvist, M. S., & Lagaron, J. M. (2010). Incorporating amylopectin in poly(lactic acid) by melt blending using poly(ethylene-co-vinyl alcohol) as a thermoplastic carrier. (I) Morphological characterization. *Journal of Applied Polymer Science*, *115*(3), 1315–1324.

Prinos, J., Bikiaris, D., Theologidis, S., & Panayiotou, C. (1998). Preparation and characterization of LDPE/starch blends containing ethylene/vinyl acetate copolymer as compatibilizer. *Polymer Engineering and Science*, *38*(6), 954–964.

Raquez, J. M., Narayan, R., & Dubois, P. (2008). Recent advances in reactive extrusion processing of biodegradable polymer-based compositions. *Macromolecular Materials and Engineering*, *293*(6), 447–470.

Sailaja, R. R. N. (2005). Mechanical properties of esterified tapioca starch–LDPE blends using LDPE-co-glycidyl methacrylate as compatibilizer. *Polymer International*, *54*(2), 286–296.

Sailaja, R. R. N., & Chanda, M. (2000). Use of maleic anhydride-grafted polyethylene as compatibilizer for polyethylene–starch blends: Effects on mechanical properties. *Journal of Polymer Materials*, *17*(2), 165–176.

Sailaja, R. R. N., & Chanda, M. (2002). Use of poly(ethylene-co-vinyl alcohol) as compatibilizer in LDPE/thermoplastic tapioca starch blends. *Journal of Applied Polymer Science*, *86*(12), 3126–3134.

Sankri, A., Arhaliass, A., Dez, I., Gaumont, A. C., Grohens, Y., Lourdin, D., et al. (2010). Thermoplastic starch plasticized by an ionic liquid. *Carbohydrate Polymers*, *82*(2), 256–263.

Scaffaro, R., Morreale, M., Lo Re, G., & La Mantia, F. (2009). Degradation of Mater-Bi (R)/wood flour biocomposites in active sewage sludge. *Polymer Degradation and Stability*, 1220–1229.

Schwach, E., Six, J. L., & Averous, L. (2008). Biodegradable blends based on starch and poly(lactic acid): Comparison of different strategies and estimate of compatibilization. *Journal of Polymers and the Environment*, *16*(4), 286–297.

Taguet, A., Huneault, M. A., & Favis, B. D. (2009). Interface/morphology relationships in polymer blends with thermoplastic starch. *Polymer*, *50*(24), 5733–5743.

Tambe, S., Singh, S., Patri, M., & Kumar, D. (2008). Ethylene vinyl acetate and ethylene vinyl alcohol copolymer for thermal spray coating application. *Progress in Organic Coatings*, 382–386.

vanSoest, J. J. G., & Essers, P. (1997). Influence of amylose–amylopectin ratio on properties of extruded starch plastic sheets. *Journal of Macromolecular Science-Pure and Applied Chemistry*, *A34*(9), 1665–1689.

vanSoest, J. J. G., Hulleman, S. H. D., deWit, D., & Vliegenthart, J. F. G. (1996). Crystallinity in starch bioplastics. *Industrial Crops and Products*, *5*(1), 11–22.

vanSoest, J. J. G., & Vliegenthart, J. F. G. (1997). Crystallinity in starch plastics: Consequences for material properties. *Trends in Biotechnology*, *15*(6), 208–213.

Xie, F. W., Yu, L., Liu, H. S., & Chen, L. (2006). Starch modification using reactive extrusion. *Starch-Starke*, *58*(3–4), 131–139.

Yin, J., Zhang, J., & Yao, Y. (2006). Melt grafting of poly(ethylene-vinyl acetate) copolymer with maleic anhydride. *Journal of Applied Polymer Science*, 841–846.

Yu, L., Dean, K., & Li, L. (2006). Polymer blends and composites from renewable resources. *Progress in Polymer Science*, 576–602.