Study of the Compatibilizer Effect in the Properties of Starch/Polyester Blends

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Abstract: The mechanical, viscoelastic and structural properties of starch/ poly (butylene adipate co-terephthalate) (PBAT) blown films produced by reactive extrusion were evaluated using citric acid (CA) and maleic anhydride (MA) as compatibilizers. Scanning electron microscopy images showed more homogeneous structure when CA and MA were included in the formulation. The tensile strength (MPa) was improved with the inclusion of the highest proportion of both compatibilizers (1.5 %wt). A larger elastic component with values between 0.42-0.45 for the degree of solidity $(1-c_1)$ was observed for the intermediate concentration of compatibilizers. A high level of glycerol (10 %wt) results in films with increased % elongation. Three partially miscible phases were observed in the blends. Biodegradable films of starch/PBAT with better properties could be produced by one-step reactive extrusion using CA and/or MA as compatibilizers.

Keywords: *Starch/PBAT blends, reactive extrusion, compatibilizers, biodegradable polymers.*

Introduction

The great environmental impact caused by the excessive quantity of non-biodegradable residues produced daily is worrying. Agricultural polymers, such as starch, could contribute to reduce these residues because they are biodegradable, obtained from renewable sources and with reduced costs[1,2].

Native starch is considered a non-plastic material, requiring thermal-mechanical processing, in the presence of plasticizers, with the aim to disrupt their semi-crystalline structure and result in an amorphous material, called thermoplastic starch (TPS)[3,4]. There are several current researches in order to use TPS as a biodegradable packaging material, however, this still have some disadvantages, as the elevated influence of the environmental conditions, defficient mechanical properties and difficulty in their stability and processability[5-7].

Among the proposals to improve the starch films properties, the production of blends of starch associated with syntetic polymers, as PBAT (poly (butylene adipate co-terephthalate)) have been broadly studied. However, these blends have poor interfacial adhesion in consequence of the hydrophilic characteristics of starch and hydrophobic properties of polyester. Using multifunctional molecules, as citric acid (CA) and maleic anhydride (MA), could be possible to improve their compatibility via esterification/transesterification reactions between the polymeric chains[8-10].

Reactive extrusion combines the steps of mixture by melting, grafting and fuctionalization in a single process, which is of great importance for the processing costs reduction in the production of the films[11,12]. On this basis, this work aim to produce, by one-step reactive extrusion, starch/PBAT blown films using fixed concentrations of PBAT (40 %wt), since this polyester is expensive and obtained by non-renewable sources. The main objective was evaluate the role of CA and MA as compatibilizers in starch/PBAT blown films by investigation of their structural, mechanical and viscoelastic properties.

Experimental

Materials

Native cassava starch was obtained from Indemil (Paranavaí, PR/Brazil). Glycerol was supplied by Dinâmica (Diadema, SP/Brazil), citric acid and maleic anhydride by Sigma-Aldrich (Steinheim, Germany) and PBAT by BASF (Ludwigshafen, Germany), with the commercial name Ecoflex®.

Methods

Films production

Samples were processed using a laboratory single-screw extruder (model EL-25, BGM, São Paulo, Brazil) with screw diameter D = 25 mm and screw length 28 D. All the components were manually mixed at the time of extrusion and pelletized with barrel temperatures of 100/120/120 °C for the three heating zones, and 120 °C for the die with six 2mm diameter holes and screw speed of 40 rpm. The feed rate was maintained so that the screw operated at full load. Then, the pellets were extruded to obtain the films with a barrel temperature profile of 100/120/120/130 °C and 130 °C for the 50 mm film-blowing die, maintaining screw speed of 40 rpm.

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The film thickness was controlled through the roll speed control and the air low rate and these parameters were adjusted for each formulation to maintain a thickness range of 100-150 mm.

Mechanical and viscoelastic properties

A texture analyzer model TA.XTplus (Stable Micro Systems, Surrey, England) fitted with a 50 kg load cell was used to determine the mechanical and viscoelastic properties of the films. Before the tests, the samples were conditioned at 23 ± 2 °C and 53 ± 2% of Relative Humidity (RH) for 48 hours.

The tensile test was based on American Society for Testing and Material Standard (ASTM) D882-91[13]. Ten samples of each formulation were cut, in longitudinal direction, with 50 mm in length and 20 mm in width and fit to the tensile grips. The crosshead speed was set at 0.8 mm/s and the initial distance between the grips was 30 mm. The tensile strength (MPa) and elongation at break (%) were determined.

For the stress relaxation test, the samples were cut with 100 mm in length and 20 mm in width and fit to the tensile grips, with initial distance between the grips of 80 mm. The crosshead speed was set at 0.8 mm/s and the samples were tensioned (stretching) until reach 1.0% of deformation (based in the results of elongation at break). The stress developed by the film under tension was recorded at 0.04 s intervals, for 60 s. These results were analyzed and normalized using the model proposed by Peleg[14]. Non-linear regression (Equation 1) was used to estimate the parameters c_1 and c_2, which provide information of the material viscoelastic characteristics using the STATISTICA 7.0 software (Statsoft, Oklahoma) as described by Müller, Laurindo and Yamashita[15].

$$\frac{F(t)}{F(0)} = 1 - \frac{c_1.t}{c_2 + t} \qquad (1)$$

where $F(t)$ is the force at time t, $F(0)$ is the initial force and c_1 and c_2 are the parameters estimated by non-linear regression. Using this model is possible obtain information on the viscoelastic characteristics of the films, in which (c_1 / c_2) represents the initial stress decay rate and (1-c_1) the degree of solidity.

Dynamical Mechanical Analysis (DMA)

A Dynamical Mechanical Analyzer (DMA TA model Q800) was used to determine the Storage Modulus (MPa) and loss factor (tan δ) for all the samples. The samples were scanned from –90 °C to 100 °C with heating rate of 3 °C/min and fixed frequency of 1 Hz. Glass transition temperatures (Tg) was obtained as the temperature of the tan δ peak.

Scanning Electron Microscopy (SEM) Analysis

A scanning electron microscope FEI Quanta 200 (FEI Company/Tokyo, Japan) was used to make observations of the fractured surface of the film samples. The samples were broken by cryogenic fracture. The coating was realized with a Sputter Coater (BAL-TEC SCD 050). Images were taken of the fractured surface, with 4000 × magnification. The samples were conditioned in a desiccator containing anhydrous calcium chloride ($CaCl_2$) for 48 hours before the analysis.

Experimental Design and Statistical Analysis

Aiming to compare the effect of maleic anhydride (MA), citric acid (CA) and glycerol in the properties of starch/PBAT blends, a *simplex-lattice* constraint mixture design was proposed (Table 1), in which the components CA, MA and glycerol represented 10%wt of total mixture weight and the other 90%wt were constituted by the mixture of starch and PBAT (55:45 w/w). Two replicates of the central point (A_7) were performed. A lower level of glycerol was fixed in 8.5%wt because was not possible to obtain films with good characteristics in lower concentrations. Also, the CA and MA upper level were fixed in 1.5%wt and the experiment evaluated the influence of the variations in the proportion of these components in the properties of the films. The results of

Table 1. Average responses obtained according to proposed mixture design and regression coefficients for the response variables.

Samples	Components (%)[a]			Tensile strength (MPa)	Elongation at break (%)	Degree of solidity (1-c_1)	Initial stress decay rate (c_1 / c_2) (s)
	GLY	CA	MA				
A_1	10.0	0.00	0.00	4.32 ± 0.31	264.47 ± 21.33	0.33 ± 0.03	0.70 ± 0.02
A_2	8.50	1.50	0.00	6.57 ± 0.11	16.39 ± 1.26	0.36 ± 0.06	0.81 ± 0.05
A_3	8.50	0.00	1.50	5.51 ± 0.49	10.31 ± 2.29	0.33 ± 0.02	0.73 ± 0.02
A_4	9.25	0.75	0.00	5.59 ± 0.11	383.35 ± 110.22	0.42 ± 0.02	0.84 ± 0.04
A_5	9.25	0.00	0.75	5.27 ± 0.34	13.87 ± 2.74	0.42 ± 0.03	0.54 ± 0.02
A_6	8.50	0.75	0.75	5.60 ± 0.52	17.55 ± 2.49	0.37 ± 0.02	0.63 ± 0.01
A_7	9.00	0.50	0.50	6.53 ± 0.38	5.85 ± 0.61	0.45 ± 0.02	0.52 ± 0.05
Coefficients		b_1		4.24*	278.83*	0.33*	0.72*
		b_2		6.50*	30.75*	0.35*	0.83*
		b_3		5.43*	24.67*	0.33*	0.74*
		b_{12}		2.15	684.46	0.36	--
		b_{13}		2.98	–781.40	0.39	–0.90
		b_{23}		–0.20	–270.40	0.14	–0.73
R^2				0.817	0.877	0.957	0.882

[a]In relation to the total weight of mixture. Values contained *significantly influenced the results ($p < 0.05$). b_1 – Gly; b_2 – CA; b_3 – MA; b_{12} – Interaction Gly/CA; b_{13} – Interaction Gly/MA; b_{12} – Interaction CA/MA.

the mechanical and viscoelastic properties were analyzed with STATISTICA 7.0 software (Statsoft, Tulsa-USA), using data modeling and analysis of surface contour for the mixture design.

Results and Discussion

Mechanical and viscoelastical properties

The results of tensile strength and relaxation tests were analyzed and quadratic polynomial equations were adjusted. Satisfactory correlation coefficients (R^2) were obtained, ranging from 0.817 to 0.957, showing a satisfactory adjustment of the experimental data. So, generated models allowed the adequate study of the influence of the proportions of plasticizer and compatibilizers in the properties of the films.

The tensile strength of the films was positively influenced by the components of the ternary mixture (glycerol, citric acid and maleic anhydride). The experimental zone with elevated values of resistance of the films was localized next to the point with maxim concentration (1.5 %wt) of citric acid (Figure 1). The increase of the tensile strength with increasing the proportion of the compatibilizers in the formulation could be resulted, mainly, of esterification/transesterification reactions between the polymeric chains, which produce more compatible films, with reduced interfacial tension, results in accordance with those observed by Wang et al.[12] in the study of TPS/PLA compatibilized blends and also in our previous works[16-18].

Greater elongation of the films was caused by increasing the proportion of glycerol (positive effect) (Figure 2). This property was also affected in important way by the Gly-CA interaction, which provides an increase of the % elongation. This fact evidenced the actuation of CA also as plasticizer, in addition to compatibilizing agent. Antagonistic effect for the MA-Gly interaction in the elongation of the films was observed, possibly due the facilitation of glycosylation reactions of the starch molecules with the presence of MA or also by the reaction between the compatibilizer and plasticizer, in accordance

with Raquéz et al.[19] and with this, the glycerol stayed less available to exerted their plasticizer effect and consequently reducing the films elongation. When the interaction between both compatibilizers (CA and MA) is analyzed, a negative influence was observed in the tensile strength properties and in the elongation of the films.

The viscoelastic properties of the films could be determined using a static test of relaxation, where a constant stress is imposed to the sample and a deformation is observed during the progress of time[15,20]. In relation to the relaxation properties, all the curves presented the characteristic shape of viscoelastic materials[14,21]. The compatibilizers and glycerol showed similar and positive effects on the degree of solidity, represented by ($1-c_1$) (Table 1).

When this value approaches zero, the viscous component determine the material comportment, and when results are closer to 1, the material tends to behave like an elastic solid. Thus, analyzing the components separately, the addition of higher proportions of the plasticizer and compatibilizers contributed to improve the elastic component of the samples (positive effects showed at Table 1), reaching values of 0.42-0.45. However, considering all the components, glycerol, CA and MA, their intermediate proportions results in more elastic films (Figure 3). These results were a consequence of the plasticizing effects of the glycerol, combined with the contribution of CA and MA also as plasticizers and/ or in the acid hydrolysis of the polymeric chains. Similar results were observed by Nobrega et al.[21] in the study of starch/PBAT films containing saturated fatty acids, as an effect of the higher water sorption by the materials, which increase the mobility and the rearrangement of the polymer matrix.

The stress decay rate at the beginning of the stress relaxation, calculated by the value of (c_1 / c_2) was positively influenced for all the components of the ternary mixture (Table 1). The CA showed an important effect for this property with higher concentration resulting in an increment of (c_1 / c_2) values (Figure 4).

When the initial stress decay rate (initial relaxation rate) tends to zero, the material shows lower relaxation
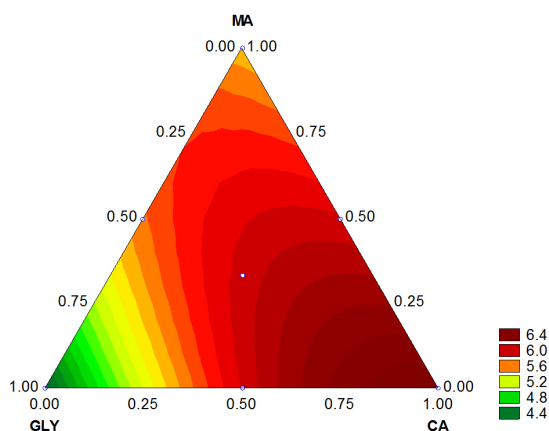

Figure 1. Surface contour showing the effect of the citric acid (CA), maleic anhydride (MA) and glycerol (GLY) in the tensile strength of the films.
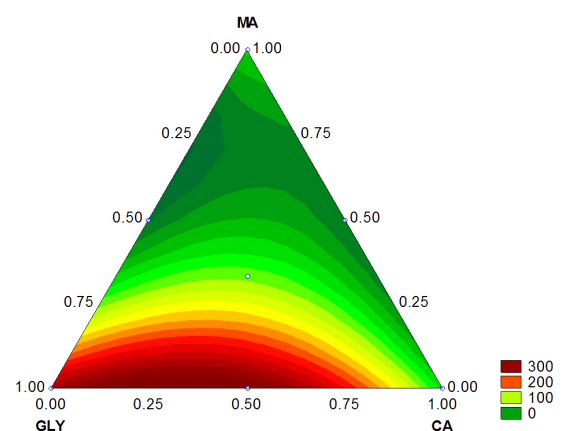

Figure 2. Surface contour showing the effect of the citric acid (CA), maleic anhydride (MA) and glycerol (GLY) in the elongation of the films.

and could better resist to the stress which is submitted. This comportment is observed in the obtained films when occurred interactions between gly-MA and CA-MA, which had a negative effect in this property, resulting in films with a more elastic comportment (Figure 4).

Dynamical Mechanical Analysis (DMA)

The application of dynamical mechanical analysis in the study of the relaxation of polymers is well established and consists of applying an oscillating force to a material and analyzing its response to this force. The storage modulus results are related to the ability of the material to store energy during shearing[22]. From the graphs in Figure 5, it can be seen that the formulation containing CA exhibits the highest storage modulus, which demonstrates that this material had a greater stiffness. As previously noted, this film has slightly lower glycerol content, which, together with esterification/transesterification promoted by CA explains this result. Wang et al.[23] in the study of for thermoplastic starch/PLA blends containing CA founded this same relation. Formulations containing maleic anhydride could not be evaluated because they were very fragile for testing.
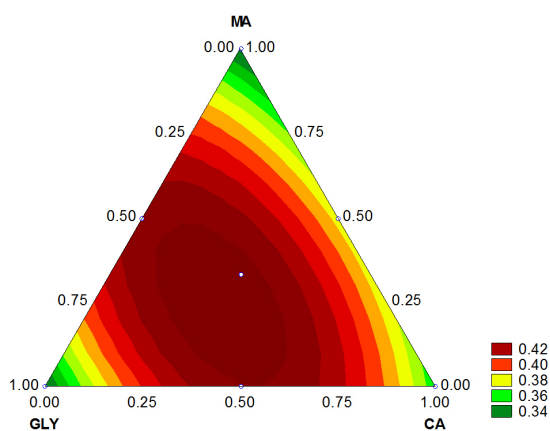
In the DMA analysis, the presence of a peak in the loss modulus or tan δ could represent the glass transition (Tg) of the material[4]. As can be seen from Figure 6, the samples show three Tg peaks, which indicates the presence of three partially miscible phases, as also reported by Jiang et al.[24] for blends of thermoplastic starch and poly(ethylene-vinyl alcohol). The relaxation at higher temperature results from the Tg of the phase rich in starch, being the peak observed at 56.8 °C for A_1 and is not possible to observe a peak for A_2. This shows that the presence of CA, aside from the slightly lower glycerol content, produces an increase in Tg, a fact also reported by Wang et al.[23] and Maliger et al.[25], which could be attributed to the improvement of the compatibility of the blends by CA. The relaxation peak values (–25.3 °C for A_1 and –27.6 °C for A_2) correspond to the Tg for the phase rich in PBAT and the peaks of –48 °C for A_1 and –48.6 °C for A_2 correspond to the Tg of glycerol mixed with a small quantity of polymeric material (phase rich in glycerol)[26].

Scanning Electron Microscopy (SEM) analysis

The SEM images (Figure 7) show that the inclusion of the both compatibilizers, citric acid and maleic anhydride (samples A_2 and A_3), changed the structural formation

Figure 3. Surface contour showing the effect of the citric acid (CA), maleic anhydride (MA) and glycerol (GLY) in the degree of solidity of the films.
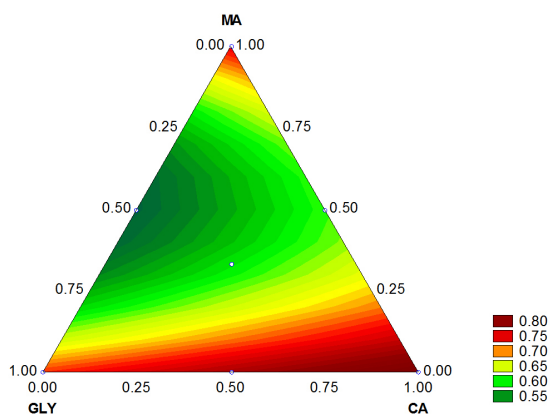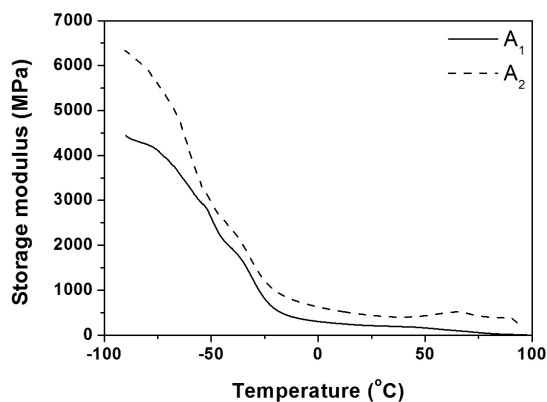
Figure 4. Surface contour showing the effect of the citric acid (CA), maleic anhydride (MA) and glycerol (GLY) in the initial stress decay rate of the films.

Figure 5. Storage modulus *vs* temperature of A_1 (10 %wt Gly) and A_2 (8.5 %wt Gly + 1.5 %wt CA) samples.
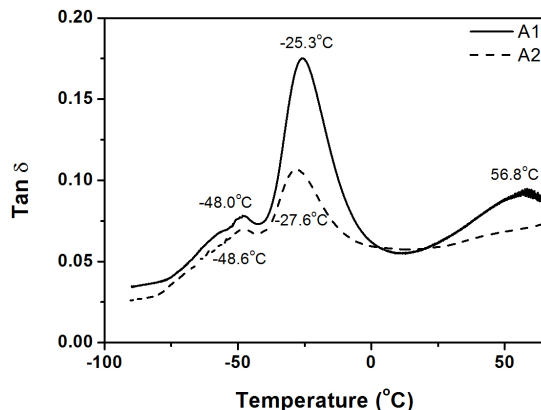
Figure 6. Phase angle (*tan* δ) *vs* temperature of A_1 (10 %wt Gly) and A_2 (8.5 %wt Gly + 1.5 %wt CA) samples.
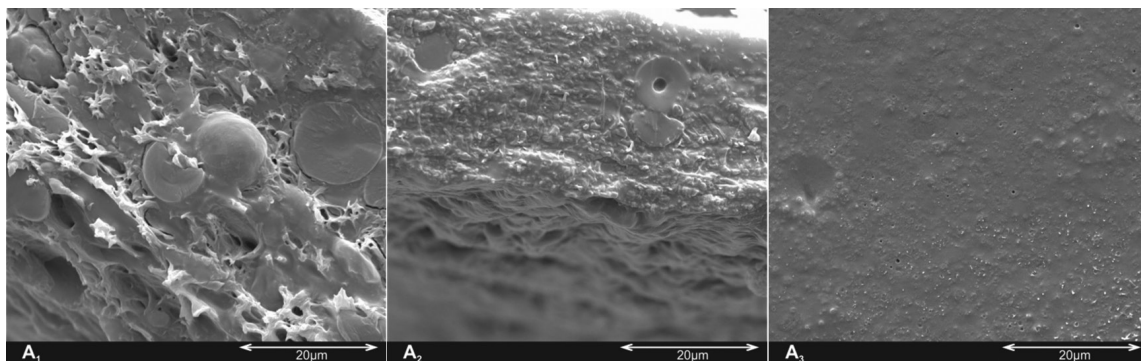
Figure 7. SEM images of cryofractured surface of starch/PBAT films prepared with A₁ (10 %wt Gly); A₂ (8.5 %wt Gly + 1.5 %wt CA) and A₃ (8.5 %wt Gly + 1.5 %wt MA) (Magnification 4000×).

of the matrix, making it more homogeneous, organized and compact when compared with the formulation containing only glycerol (A₁), which shows a better interfacial interaction between the starch (hydrophilic) and the polyester (hydrophobic) in the compatibilized formulations. The deficient interfacial adhesion of the non-compatibilized sample (A₁) is clear, observing the presence of non-disrupted starch granules and cavities caused by the removal of these granules of the superficies of this sample.

In the study of the maize starch/PBAT foams using maleic anhydride in the maleatation of the polyester, Nabar et al.[7] found that this process was efficient in promote a greater interfacial adhesion and no phases separation of the blends were observed. Raquéz et al.[19] evaluated the utilization of MA as compatibilizer in starch/PBAT blends and observed that the presence of MA improved the compatibility between the polymeric phases, provided by the grafting of anhydride in the starch and after promoting acid-catalyzed transesterification reactions.

In the sample containing 1.5% of citric acid (A₂), circular structures similar to washers were observed, which usually occur when CA is used in low concentrations (less than 1.5%) and are result of the starch citrate formed inside the starch granules, reinforcing the granular structure. When higher concentrations of CA are used (>2 %wt) this acts promoting acid hydrolysis of the starch, which could be the responsible by the disruption and dissolution of the granule[16,17]. Wang et al.[23] also observed that the disruption of starch granules is facilitated by the acidification promoted by using citric acid in TPS/PLA blends (4 %wt).

Conclusion

The mechanical and viscoelastic properties showed that the inclusion of CA and MA favored the compatibilization of the blends, which reinforced and stabilized the polymeric matrix. Stress relaxation tests showed that the combination of intermediate proportions of glycerol, CA and MA results in more elastic films and increasing the concentration of these components, the plasticizer effect of glycerol and the acidolysis promoted by compatibilizers, make the matrix behave like a viscous material. SEM images showed that the compatibilized

samples had a better interfacial adhesion and films more organized and compacts were obtained.

So, one-step reactive extrusion, using multifunctional molecules as compatibilizers, allied to using of reduced concentrations of polyester (PBAT), were adequate to produce biodegradable films with better properties and reduced costs, as an alternative to the syntetic packaging.

Acknowledgements

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