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Citric acid and maleic anhydride as compatibilizers in starch/poly(butylene adipate-co-terephthalate) blends by one-step reactive extrusion

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ABSTRACT

Starch/poly(butylene adipate-co-terephthalate) films were obtained by one-step reactive extrusion using maleic anhydride (MA) and citric acid (CA) as compatibilizers. The mechanical, structural, optical and barrier properties of the films were analyzed when glycerol (GLY), CA and MA were added to the starch/PBAT (55:45, w/w) according to mixture design. FTIR analysis showed that CA and MA were able to promote esterification/transesterification reactions and that CA induced them more efficiently. When a greater proportion of compatibilizer (1.5 wt%) was used, the resulting films were more opaque and had a greater tensile strength. A greater proportion of GLY (10.0%, w/w) improved the elongation at the break of the films. The barrier properties to water vapor of the films were improved by high levels of CA (1.5 wt%) and intermediate levels of GLY (9.25 wt%). The inclusion of compatibilizers resulted in blends with improved properties, representing a potential replacement for non-biodegradable films.

1. Introduction

The market needs biodegradable packaging materials that can be effectively and safely deposited in the soil, and showing the same mechanical performance of the petroleum-derived plastics. This requirement has stimulated new research into starch/polyesters blends, which represent a new class of materials in development (Nabar, Raquéz, Dubois, & Narayan, 2005; Yu, Dean, Yuan, Chen, & Zhang, 2007).

Starch, an abundant and renewable polymer, has been widely used as a component of polymeric plastic blends in the form of thermoplastic starch (TPS). TPS is obtained from the disruption of the granules when these are submitted to mechanical/thermal treatment in the presence of a plasticizer, resulting in a homogeneous and amorphous matrix (Raquéz, Nabar, Narayan, & Dubois, 2008; Zullo & Iannace, 2009). TPS has several favorable attributes that make it suitable for utilization in biodegradable film production; however, its applicability is limited by deficient mechanical properties and a high sensitivity to moisture (Avérous & Fringant, 2001; Yoon, Chough, & Park, 2006). Poly(butylene adipate co-terephthalate) (PBAT) is a biodegradable aliphatic–aromatic copolyester with mechanical and barrier properties that is capable of overcoming the limitations of TPS. Biodegradable polyesters, such as PBAT, have a higher cost than the polymers they are being developed to replace. The addition of starch into the formulation may enable the reduction of the cost of the final product (Mani & Bhattacharya, 2001; Ren, Fu, Ren, & Yuan, 2009).

The greater difficulty in making starch/PBAT blends is the deficient interfacial adhesion between the hydrophilic starch and the hydrophobic polyester. To address this issue, multifunctional substances, such as maleic anhydride (MA) and citric acid (CA), are added to promote esterification/transesterification reactions (crosslinking) at the interface between polymeric chains to improve their compatibility. This fact, according to Zhang and Sun (2004) has been effective for the morphology control in several polymeric systems.

Using reactive extrusion for the preparation of starch/polyester blends has the advantage of combining several chemical processes into the extruder without using solvents (Wang, Yu, & Ma, 2007). In previous studies, researchers functionalized the starch or polyester by grafting reactive groups, such as CA and MA, onto the backbone. These graft-copolymers were then used as compatibilizers in a second step (Kalambur & Rizvi, 2006; Raquéz, Nabar, Srinivasan, et al., 2008; Shi et al., 2008). To make the process faster and more efficient, this work aimed to evaluate the influence of CA and MA, added directly to the starch/PBAT mixtures, on the mechanical, optical and barrier properties of blown films produced by one-step reactive extrusion. An additional objective was to reduce the PBAT ratio as much as possible, while still obtaining films with acceptable properties, to increase the content of starch, a renewable polymer.

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2. Materials and methods

2.1. Materials

Native cassava starch (amylose 20.8 ± 0.6 wt%) was obtained from Indemil (Paranavaí, PR, Brazil). Glycerol was supplied by Dinâmica (Diadema, SP, Brazil), citric acid and maleic anhydride was supplied by Sigma–Aldrich (Steinheim, Germany), and PBAT (poly(butylene adipate-co-terephthalate)) was supplied by BASF (Ludwigshafen, Germany), under the commercial name Ecoflex®.

2.2. Methods

2.2.1. Film production

Pellets were processed using a laboratory single-screw extruder (model EL-25, BGM, São Paulo, Brazil) with a screw diameter (*D*) of 25 mm and a screw length of 28*D*. The components were manually mixed at the time of extrusion and were extruded with a barrel temperature profile of 100/120/120/120 °C from the feeding zone (zone 1) to the die zone (zone 4), screw speed of 40 rpm and die with six 2 mm diameter holes. Then, the pellets were extruded to obtain the films with a barrel temperature profile of 100/120/120/130 °C for the four zones and 130 °C for the 50 mm film-blowing die with internal air for the formation of the film "bubble" and screw speed of 40 rpm. The feed rate was maintained to ensure that the screw operated at full load, and the film thickness was controlled via the roll speed control and the air flow rate. These parameters were adjusted for each formulation to maintain a thickness of 100–150 μm.

2.2.2. Opacity

Opacity was determined by means of a colorimeter (BYK Gardner-USA) at a 10° angle and using illuminant D_{65} (day light) according to the Hunterlab methods (Hunter Associates Laboratory, 1997). Sample opacity (*Y*) was calculated as the ratio between the opacity of the sample placed under a black pattern (Y_b) and the opacity of the sample placed under a white pattern (Y_w) according to Eq. (1).

$$Y = \left(\frac{Y_b}{Y_w}\right) \times 100 \quad (1)$$

The opacity results (*Y*) were divided by the sample thickness and expressed on an arbitrary scale (0–1% μm^{-1}). The measurements were completed in triplicate.

2.2.3. Water vapor permeability (WVP)

The tests were conducted using the ASTM method E-96-95 (1996) with some modifications. Before the analysis, the samples were stored at 25 °C and 53% RH for 48 h. Each film sample was fixed in the circular opening of a permeation cell with a 60 mm internal diameter with silicone grease to ensure that humidity migration occurred only through the film. The interior of the cell was filled with a magnesium chloride solution ($MgCl_2$/32.8% RH) and the device was stored at 25 °C in a desiccator to maintain a 42% RH gradient across the film. A saturated sodium chloride solution was used in the desiccator to provide 75% RH.

The samples were weighed every 3 h during the 72 h of testing time. Changes in the weight of the cell or mass gain (*m*) were plotted as a function of time (*t*). The slope of the line was calculated by linear regression ($R^2 > 0.97$), and the water vapor permeation ratio (WVPR) was obtained with Eq. (2):

$$\mathrm{WVPR} = \left(\frac{m}{t}\right) \cdot \left(\frac{1}{A}\right) \quad (2)$$

where *m*/*t* is the angular coefficient of the curve and *A* is the sample permeation area. The WVP ($\mathrm{g\,Pa\,s^{-1}\,m^{-1}}$) was calculated as:

$$\mathrm{WVP} = \frac{\mathrm{WVPR} \cdot \mathrm{st}}{\mathrm{sp}(\mathrm{RH}_1 - \mathrm{RH}_2)} \quad (3)$$

where st is the mean sample thickness (m), sp is the water vapor saturation pressure at the assay temperature (Pa), RH_1 is the relative humidity of the desiccator and RH_2 is the relative humidity in the interior of the permeation cell. The tests were conducted in duplicate.

Table 1
Plasticizer and compatibilizer concentrations. *Simplex-lattice* mixture design.

Samples	Pseudocomponents			Components (%)[a]		
	x_1	x_2	x_3	GLY	CA	MA
A_1	1.00	0.00	0.00	10.0	0.00	0.00
A_2	0.00	1.00	0.00	8.50	1.50	0.00
A_3	0.00	0.00	1.00	8.50	0.00	1.50
A_4	0.50	0.50	0.00	9.25	0.75	0.00
A_5	0.50	0.00	0.50	9.25	0.00	0.75
A_6	0.00	0.50	0.50	8.50	0.75	0.75
$A_{7.1}$	0.33	0.33	0.33	9.00	0.50	0.50
$A_{7.2}$	0.33	0.33	0.33	9.00	0.50	0.50

GLY (x_1), glycerol; CA (x_2), citric acid and MA (x_3), maleic anhydride.
The pseudocomponents were calculated based on the concentration restrictions of the components presented in Section 2.2.6.
[a] In relation to the total weight of mixture.

2.2.4. Mechanical properties

A texture analyzer model TA.XT2i (Stable Micro Systems, Surrey-England) fitted with a 50 kg load cell was used to determine the tensile properties of the films. Tensile tests were based on the American Society for Testing and Material (ASTM) standard D882-91 (1996). Ten samples of each formulation were cut in the 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. Before the tests, the samples were conditioned at 23 ± 2 °C and 53 ± 2% RH for 48 h. The tensile strength (MPa) and elongation at break (%) were determined.

2.2.5. Fourier transform infrared spectroscopy (FTIR)

FTIR analyses were conducted on blown films from 4000 to 500 cm^{-1} with a spectral resolution of 4 cm^{-1}. A Perkin-Elmer Spectrum 2000 FTIR with a Universal Attenuated Total Reflectance (UATR) Pike Miracle module was used. The samples were conditioned in a desiccator containing anhydrous $CaCl_2$ (0% RH) at 23 ± 2 °C for 10 days before the analysis.

2.2.6. Experimental design and statistical analysis

Formulations were tested with varying amounts of CA, MA and GLY, according to a mixture design *simplex-lattice* (Table 1). These three components represented 10% of total mixture weight, while the other 90% consisted of the mixture of starch and PBAT (55:45, w/w). The lower limit of GLY was set at 8.5 (wt%) because it was not possible to obtain films with good characteristics at lower concentrations. The CA and MA upper limits were also fixed at 1.5 (wt%), and the experiment evaluated the influence of these components on the properties of the films. The results were analyzed with STATISTICA 7.0 software (Statsoft, Tulsa, USA) using data modeling and analyzing the surface contours of the mixture design. Quadratic models (Eq. (4)) had better adjusted to the results.

$$y = \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_1 x_3 \quad (4)$$

Table 2
Average values obtained for apparent opacity, water vapor permeability (WVP), tensile strength and elongation at break of the films. Regression coefficients for the response variables and model adjustment.

Samples	WVP ($\times 10^{-10}$ g s^{-1} m^{-1} Pa^{-1})	Opacity (% μm^{-1})	Tensile strength (MPa)	Elongation at break (%)
Results				
A_1	3.600 ± 0.026	0.452 ± 0.006	4.321 ± 0.317	264.466 ± 21.332
A_2	1.966 ± 0.017	0.656 ± 0.006	6.575 ± 0.115	16.386 ± 1.259
A_3	3.847 ± 0.815	0.203 ± 0.005	5.512 ± 0.487	10.306 ± 2.293
A_4	1.789 ± 0.030	0.419 ± 0.009	5.592 ± 0.109	383.351 ± 11.218
A_5	3.548 ± 0.207	0.301 ± 0.003	5.268 ± 0.339	13.868 ± 2.737
A_6	4.650 ± 0.355	0.256 ± 0.012	5.599 ± 0.523	17.549 ± 2.494
$A_{7.1}$	2.147 ± 0.136	0.363 ± 0.006	6.534 ± 0.384	5.855 ± 0.604
$A_{7.2}$	2.011 ± 0.227	0.381 ± 0.008	6.054 ± 0.774	6.093 ± 0.525
Coefficients				
β_1	3.72*	0.44*	4.24*	278.83
β_2	2.09	0.65*	6.50*	30.75
β_3	3.97*	0.20*	5.43*	24.67
β_{12}	−6.42	−0.37	2.15	684.46
β_{13}	−3.15	–	2.98	−781.40
β_{23}	4.52	−0.53	−0.20	−270.40
R^2	0.826	0.952	0.817	0.877
Lack of fit (p)	0.104	0.102	0.269	0.332

β_1, glycerol (GLY); β_2, citric acid (CA); β_3, maleic anhydride (MA); β_{12}, GLY/CA interaction; β_{13}, GLY/MA interaction; β_{12}, CA/MA interaction.

* Significantly influenced the results ($p < 0.05$).

where y is dependent variable, β is the regression coefficient for each component, x_1 is glycerol, x_2 is citric acid and x_3 is maleic anhydride.

3. Results and discussion

3.1. Data modeling

Quadratic models adjusted for all of the properties evaluated were significant and lack of fit was not observed. The component interactions for the analyzed variables did not significantly influence but contributed to the model adjustment. The correlation coefficients (R^2) were satisfactory, ranging from 0.817 to 0.952, and indicated a good fit for the experimental data. These generated models make it possible to study the influence of the plasticizer and compatibilizers proportions on the film properties.

3.2. Water vapor permeability and opacity

Water vapor permeability (WVP) should be as low as possible when the objective of the packing is to reduce moisture transfer between the packaged material and the atmosphere (Gontard, Guilbert, & Cuq, 1992). The WVP values of the films ranged from 1.789 to 4.650 × 10^{-10} g s^{-1} m^{-1} Pa^{-1} (Table 2). Wang, Zhang, Han, and Shihe (2009) evaluated the use of citric acid as an additive in the plastification of TPS/montmorilonite blends and observed that the WVP results were from 2.0 × 10^{-10} g s^{-1} m^{-1} Pa^{-1}.

GLY contributed to the increase in WVP because, in higher concentrations, it causes structural modifications in the polymeric network and increases the molecular mobility, which facilitates the diffusivity of water. However, when glycerol is used in lower proportions, more fragile and brittle films are formed, and the resulting pores and cracks allowing greater movement of water through the matrix. The effect of the plasticizers and, particularly, glycerol on the films was also evaluated by other researchers (Alves, Mali, Beléia, & Grossmann, 2007; Galdeano, Grossmann, et al., 2009; Galdeano, Mali, Grossmann, Yamashita, & García, 2009; Parra, Tadini, Ponce, & Lugão, 2004) and showed similar results.

Antagonistic effects (negative signals) were observed for the interactions between each compatibilizer and glycerol, which resulted in decreased WVP values (Fig. 1). Possible reactions between the compatibilizers and glycerol could be responsible for the observed results. This phenomenon has already been reported by Raquéz, Nabar, Srinivasan, et al. (2008) and by Holser (2008) for MA and for CA, respectively. In these cases, the quantity of glycerol available to act as a plasticizer will be reduced leading to lower WVP values.

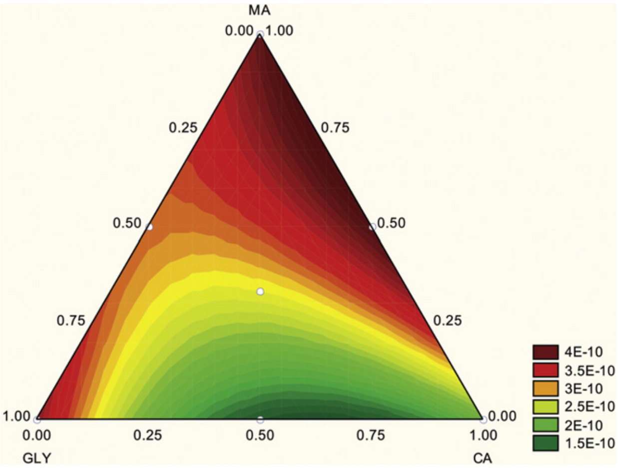

Fig. 1. Surface contours showing the effects of the mixture variables on the water vapor permeability (WVP) of the films.

All of the components contributed positively and significantly to the opacity values (Table 2), but the effect of CA was most significant (Fig. 2). This result is due, in large part, to the crosslinking reactions achieved by both compatibilizers. Crosslinking increases the polymeric chain compaction, which makes it more difficult for light to pass through the matrix and results in more opaque films. Alternatively, a negative effect was observed for the interactions between GLY-CA and CA-MA in which the more opaque films were those that contained a greater amount of MA (Fig. 2).

3.3. Mechanical properties

Increased proportions of CA had a positive effect on the tensile strength and resulted in stronger films (Fig. 3). The same result was observed for MA, but with a smaller effect (Table 2). The increase in tensile strength with the inclusion of compatibilizers was a result of crosslinking reactions (transesterification) between the polymeric molecules (Olivato et al., 2011).

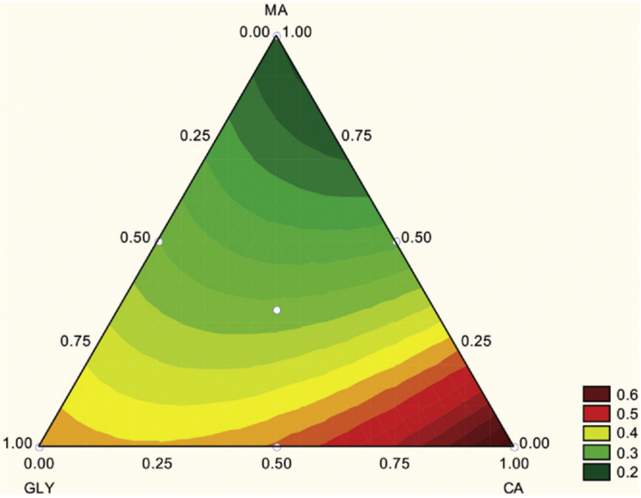

Fig. 2. Surface contours showing the effects of the mixture variables on the opacity of the films.

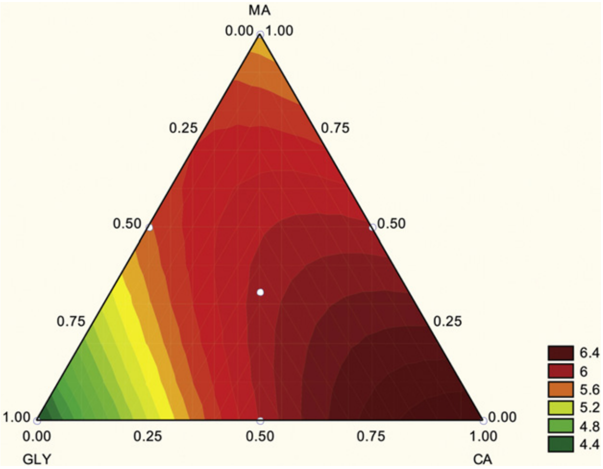

Fig. 3. Surface contours showing the effects of the mixture variables on the tensile strengths of the films.

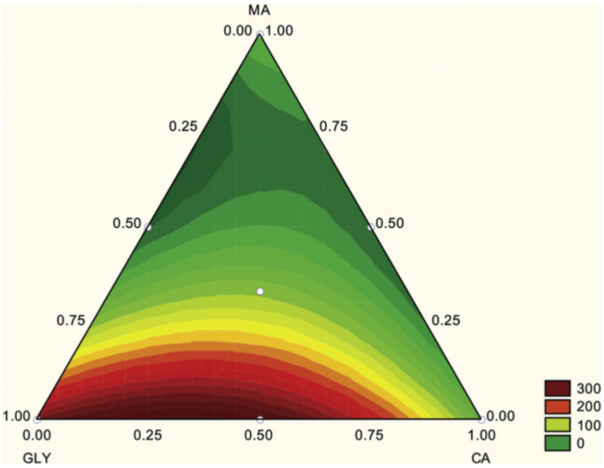

Fig. 4. Surface contours showing the effects of the mixture variables on the elongation at the break of the films.

Elevated amounts of glycerol resulted in films with a high elongation at the break (Fig. 4), which can be explained by its action as plasticizer, allowing higher molecular displacement and a less rigid structure. Similar results were observed by other authors (Alves et al., 2007; Cuq, Gontard, Cuq, & Guilbert, 1997). This property was also influenced positively by the interaction between GLY and CA, which indicated that CA could act as a plasticizer and a crosslinking agent, but in low concentrations the plasticizer effect is more pronounced. Shi et al. (2007) studied citric acid/glycerol co-plasticized thermoplastic starch and observed the same action of citric acid as plasticizer.

An antagonistic effect was also observed for the interaction between GLY and MA, which results in a decrease of the elongation of the films. This finding is in keeping with the WVP results and suggests a possible reaction between these two components that reduces the plasticizing effect. Shi et al. (2008) evaluated the influence of CA in films based on starch and polyvinyl alcohol (PVA) and observed that increasing the crosslinking reactions results in an increase in tensile strength and a decrease in the elongation at the break. These effects are similar to those observed in this work. Zhang and Sun (2004) also found a similar tendency in the mechanical properties of composites compatibilized with MA.

Although a greater reactivity would be expected for the MA, which has twice the molar concentration compared with CA for a given weight fraction, the efficiency of MA as a crosslinking agent was reduced and a lower tensile strength was observed. The increase in the hydrolysis of the polymer chains promoted by maleic acid (from MA) could explain this result. Raquéz, Nabar, Narayan, et al. (2008) observed that, during the grafting reactions of

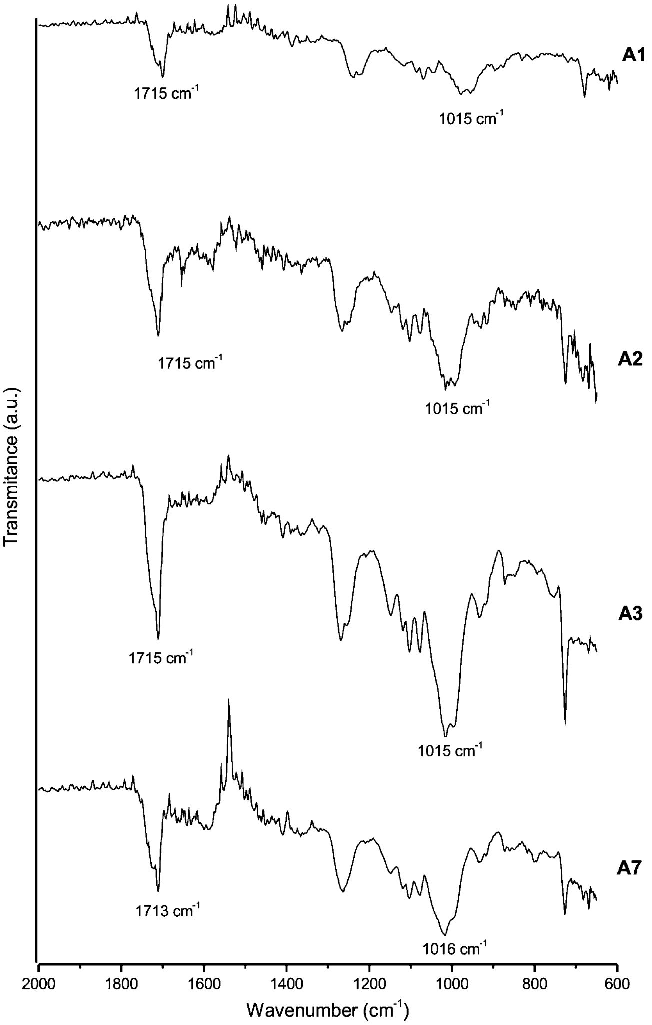

Fig. 5. FTIR spectrum of the blown films: A$_1$ (10% GLY); A$_2$ (8.5% GLY + 1.5% CA); A$_3$ (8.5% GLY + 1.5% MA) and A$_7$ (9.0% GLY + 0.5% CA + 0.5% MA).

MA in starch for starch/PBAT blend production there was a reduction in the molecular weight of the thermoplastic starch, due to the glucosidation and hydrolysis reactions favored by this compatibilizer, which is in keeping with the observations in this work.

In summary, it is possible to obtain blown films more resistant and with good processability when greater proportion of the compatibilizers, reduced concentrations of non-biodegradable polyesters (PBAT) and elevated proportions of starch are used. So, fully biodegradable films with reduced cost and acceptable properties could be produced by one-step reactive extrusion.

3.4. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra were obtained for the samples A_1, A_2, A_3 and A_7 (Fig. 5). The presence of starch was indicated by the C–O–C stretching present in the anhydroglucose ring between 1020 and 1000 cm^{-1} as can be seen in all spectra. The absence of peaks around 1785 cm^{-1} (C=O ring anhydride carbonyl) at the A_3 and A_7 spectra shows that the ring of MA was opened and was converted into maleic acid. It is possible that a reaction between maleic acid and the hydroxyl groups of starch occurred (grafting), and the one remaining carboxylic group was available to promote interesterification reactions with the polyester molecule (PBAT) or another starch molecule.

Peaks of around 1715 cm^{-1} characterize the presence of ester carbonyl stretch (C=O) that was originally present in the PBAT structure. These peaks were also a result of the esterification or interesterification reactions promoted by both compatibilizers. The greater intensity of these peaks in the compatibilized films (spectra A_2, A_3 and A_7 in Fig. 5) is clear, when compared with those in the formulations containing only the plasticizer (spectrum A_1 in Fig. 5). Shi et al. (2007) evaluated the use of CA in corn starch-based films and observed that esterification reactions between starch and CA occurred during the reactive extrusion process.

4. Conclusion

With the inclusion of the compatibilizers in the formulations, films with better mechanical, optical and barrier properties were obtained. Both CA and MA allowed the formulations to overcome the deficiencies associated with the incompatibility observed when TPS is used with PBAT. The compatibilizing effect is due to the incorporation of these molecules in the polymer chains, which promotes the esterification/transesterification reactions that were seen to occur through the FTIR spectra. Although MA is a more reactive compound, in similar conditions of concentrations, the efficiency of MA as a crosslinking agent was lower (lower tensile strength) when compared with CA. The additional vantage to use the one-step reactive extrusion, combined with the costs reduction due to the inclusion of a high concentration of starch and still, the lower utilization of non-renewable resources, allows obtaining a product with the physical, chemical and economic characteristics that could represent an environmentally friendly alternative to the utilization of the non-biodegradable synthetic polymers.

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