

Compatibilizers for biodegradable starch and poly (lactic acid) materials produced by thermoplastic injection

Compatibilizantes para materiais biodegradáveis de amido e poli (ácido láctico) produzidos por extrusão e injeção termoplástica

Compatibilizantes para materiales biodegradables de almidón y poli (ácido láctico) producidos por extrusión e inyección de termoplásticos

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Abstract

Studies using starch to produce biodegradable materials have proved attractive due to its availability and low cost in relation to commercial biodegradable polymers, such as poly (lactic acid) and others. Starch-based materials do not have adequate mechanical properties for production and use on a commercial scale, requiring mixtures (blends) with other biodegradable polymers to improve these properties. However, these blends need compatibilizers due to the immiscibility between the starch and the polymer. The present work aimed to study the effect of different compatibilizers (3-(trimethoxysilyl) propyl methacrylate, citric acid, and maleic anhydride) on the functional properties of biodegradable starch and poly (lactic acid) (PLA) materials produced by extrusion and thermoplastic injection. Citric acid was considered the best compatibilizer for these materials because it improved the processability, and the materials presented properties suitable for applications where good mechanical resistance is required. In addition, the materials containing citric acid and maleic anhydride were more uniform from the morphological point of view.

Keywords: Biodegradable polymers; Citric acid; Maleic anhydride, 3-(trimethoxysilyl) propyl methacrylate, Mechanical properties.

Resumo

Estudos utilizando amido para a produção de materiais biodegradáveis têm se mostrado atrativos devido à sua disponibilidade e baixo custo em relação aos polímeros biodegradáveis comerciais, como o poli (ácido láctico) e outros. Os materiais à base de amido não apresentam propriedades mecânicas adequadas para produção e uso em escala comercial, necessitando de misturas (blendas) com outros polímeros biodegradáveis para melhorar essas propriedades. No entanto, essas blendas necessitam de compatibilizantes devido à imiscibilidade entre o amido e o polímero. O presente trabalho teve como objetivo estudar o efeito de diferentes compatibilizantes (3-metacriloxipropiltrimetoxissilano, ácido cítrico e anidrido maleico) sobre as propriedades funcionais de materiais biodegradáveis de amido e poli (ácido láctico) (PLA) produzidos por extrusão e injeção termoplástica. O ácido cítrico foi considerado o melhor compatibilizante para esses materiais, pois melhorou a processabilidade, e os materiais apresentaram propriedades adequadas para aplicações onde se exige boa resistência mecânica. Além disso, os materiais contendo ácido cítrico e anidrido maleico foram mais uniformes do ponto de vista morfológico.

Palavras-chave: Polímeros biodegradáveis; Ácido cítrico; Anidrido maleico; 3-metacriloxipropiltrimetoxissilano; Propriedades mecânicas.

Resumen

Los estudios que utilizan amida para la producción de materiales biodegradables también han demostrado su atractivo debido a su disponibilidad y bajo costo en comparación con los polímeros biodegradables comerciales como el poli(ácido láctico) y otros. Los materiales a base de almidón no tienen propiedades mecánicas adecuadas para la producción y el uso a escala comercial, lo que requiere mezclas con otros polímeros biodegradables para mejorar estas propiedades. Estas mezclas necesitan compatibilizadores debido a la inmiscibilidad entre la amida y el polímero. El objetivo de este trabajo es estudiar el efecto de diferentes compatibilizantes (metacrilato de 3-(trimetoxisilil)propilo, ácido cítrico y anhídrido maleico) sobre las propiedades funcionales del almidón y poli(ácido láctico) (PLA) materiales biodegradables producidos por extrusión e inyección de termoplásticos. El ácido cítrico fue considerado el mejor compatibilizador para estos materiales, debido a su mejor procesabilidad, y los materiales tienen propiedades adecuadas para aplicaciones donde se requiere buena resistencia mecánica. Además, los materiales que contienen ácido cítrico y anhídrido maleico son más uniformes desde el punto de vista morfológico.

Palabras clave: Polímeros biodegradables; Acido cítrico; Anhídrido maleico; 3-metacriloxipropiltrimetoxisilano; Propiedades mecánicas.

1. Introduction

Conventional plastics from fossil sources have an environmental impact as they are not biodegradable. Because of this, many studies have been done for the production of biodegradable materials using starch, since it can be degraded by the action of microorganisms, reducing the environmental impact, in addition to its low cost and its wide availability in various plant components, becoming a promising alternative to replace these fossil plastics.

Starch-based materials are generally fragile and hydrophilic, which is detrimental for commercial applications, requiring blends with other biopolymers, such as poly (lactic acid) (PLA), to improve mechanical and barrier properties. PLA is one of the most used biopolymers by the industry lately, being an open-chain aliphatic polyester thermoplastic with good mechanical properties. However, the materials produced with starch-PLA blends are rigid and brittle due to the difference in polarity between them, requiring plasticizers to increase starch chains' mobility and reduce intermolecular interactions.

Compatibilizers can be incorporated into the blend to enhance the compatibility and stability between the components. These agents improve interfacial adhesion, and the compatibilization mechanism varies according to each blend and compatibilizer.

This study aimed to evaluate the effect of three different compatibilizers (maleic anhydride, citric acid, and 3-(trimethoxysilyl) propyl methacrylate) in starch-PLA biodegradable materials produced by extrusion and thermoplastic injection, on a pilot scale, with potential application in industrial production (Müller, et al., 2011; Olivato et al., 2012; Shirai et al., 2018)

2. Methodology

2.1 Materials

For the production of the blends, corn starch (14% moisture) was purchased from Aпти (Brazil); citric acid, maleic anhydride, and 3-(trimethoxysilyl) propyl methacrylate (KH-570) were acquired from Sigma-Aldrich (Germany). Glycerol (Dinâmica, Brazil) as a plasticizer and PLA Ingeo 4043D (Natureworks LLC, Cargill, USA) also were used. Silica and ethyl alcohol were from Synth (Brazil).

2.1.1 Preparation of KH-570 solution (Hydration Reaction)

The solution contained 20% KH-570, 72% absolute ethyl alcohol and 8% distilled water (w/w). KH-570 was dissolved in absolute ethanol at room temperature for 10 min under gentle agitation. Then, distilled water was placed in the mixture at a speed of 0.2 mL/min until the process was completed (Chen et al., 2014).

2.1.2 Production of biodegradable materials by thermoplastic injection

According to previous tests (data not shown), the formulations of materials containing poly (lactic acid) (PLA), starch, glycerol, and compatibilizer (maleic anhydride - MA, citric acid - CA, or 3-(trimethoxysilyl) propyl methacrylate - KH) are described in Table 1.

Table 1 –Formulation of the biodegradable materials with different compatibilizers.

Formulation	Component (% - w/w)			
	PLA	Starch	Glycerol	Compatibilizer
Control	40.00	38.40	21.60	0
MA 0.75	40.00	37.92	21.33	0.75
CA 0.75	40.00	37.92	21.33	0.75
KH 0.75	40.00	37.92	21.33	0.75

MA - maleic anhydride, CA - citric acid, and 3-(trimethoxysilyl) propyl methacrylate (20% solution w/w). Source: Authors.

All components (PLA, starch, glycerol, and compatibilizer) were manually mixed and extruded in a single-screw extruder (model EL-75, BGM, Brazil), 25 mm in diameter and 700 mm in length, with temperatures of 90/155 /155/120 °C in the respective four heating zones, with a screw speed of 40 rpm to produce pellets. The pellets were injected in a laboratory-scale injector (AX-Plasticos, Brazil), with a temperature profile of 130/150/150 °C from the feeder to the nozzle, molded in the shape of a bone dog (type IV specimen) (ASTM 648-14, 2014).

2.2 Mechanical Properties

Mechanical tensile tests (Young's modulus, tensile strength, and elongation at break) were performed using a Universal Testing Machine (EMIC, model DL 2000, Brazil) according to ASTM 638-14 (2014). The specimens were conditioned at room temperature under $53 \pm 2\%$ relative humidity for one week before the analysis according to ASTM 618-13 (2013).

2.3 Scan Electronic Microscopy (SEM)

The microstructure analyzes of the samples were performed using a scanning electron microscope (Philips, model FEI Quanta 200, USA), where the samples were broken after immersion in liquid nitrogen (cryogenic fracture) and metalized with a thin layer of gold using a metallizer (Bal-Tec, model SCD-050, Germany). All samples analyzed used a 20kV voltage accelerator and 2000x magnification.

2.4 Mass Loss in Water (MLW)

The specimens of each formulation were first dried in desiccators at 0% relative humidity for one week at room temperature, then the initial masses (M_i) were weighed, and then the samples were immersed in distilled water, maintaining a 30:1 (m:m) ratio of water and sample respectively, for 48 h at room temperature. Then the samples were dried at 105°C for 4 h to determine the final mass (M_f). Each analysis was performed in triplicate. To calculate the mass loss in water, Equation 1:

$$\text{Mass Loss in Water (MLW) (\%)} = \frac{(M_i - M_f)}{M_i} \times 100 \quad (1)$$

2.5 Moisture Sorption Isotherms

The sorption isotherms of the biodegradable materials were determined in an Aquasorp isotherm generator (Decagon Devices, USA), using the dynamic method. The Guggenheim-Anderson-de-Boer (GAB) model (Equation 2) was fitted to the moisture content as a function of water activity (a_w) by nonlinear regression (Statistica Software 7.0, Statsoft, USA).

$$X_w = \frac{C \cdot k \cdot m_0 \cdot a_w}{(1 - k \cdot a_w)(1 - k \cdot a_w + C \cdot k \cdot a_w)} \quad (2)$$

X_w is the moisture content (g of water/g of dry mass), m_0 is the water content in the monolayer, k is the heat of sorption in the multilayer and C , is the Guggenheim constant, representative of the heat of sorption in the first layer in the sample.

2.6 X-Ray Diffraction (XRD)

The relative crystallinity index (RCI) of biodegradable materials was determined using the X'Pert PRO equipment (Panalytical, Philips, Netherlands), using copper Ka radiation ($\alpha = 1.5418 \text{ \AA}$), and operating at room temperature at 40kV. The RCI was estimated from the ratio between the area of the crystalline region and the sum of crystalline and amorphous regions, the total area (Equation 3) (Köksel et al., 1993; Müller et al., 2011).

$$IC = \frac{A_c}{A_t} = \frac{A_c}{A_c + A_a} \quad (3)$$

2.7 Statistical Analysis

All data obtained were evaluated by analysis of variance (ANOVA) and Tukey's test at a 5% significance level ($p < 0.05$) using the Statistica software, version 7.0 (StatSoft, USA).

3. Results and Discussion

3.1 Mechanical Properties

The tensile strength (Table 2) of the control (7.51 MPa), CA 0.75 (7.23 MPa), and MA 0,75 (5.57 MPa) materials were statistically similar. The KH 0.75 (12.39 MPa) was significantly higher than others and almost 2 times more resistant than MA 0.75 (5.57 MPa). Material containing KH-570 had higher tensile probably because of the silane agent that reinforced the blend favoring covalent bonds in PLA (unsaturated polyester) and esterification reactions in starch (Chen et al., 2016; Cehavir, 2017). Generally, a silane agent is used to increase the interaction between components, remove moisture and improve the distribution of charges in a polymer matrix, resulting in better dimensional stability (Taib & Julkapli, 2019).

Table 2 – Mechanical properties of PLA/TPS blend materials with different compatibilizers

Formulations	Tensile Strength (MPa)	Elongation at Break (%)	Young Modulus (MPa)
Control	7.51 ± 2.4 ^b	2.63 ± 1.3 ^b	702 ± 90 ^a
CA 0.75	7.23 ± 4.5 ^b	6.38 ± 3.7 ^a	393 ± 287 ^b
MA 0.75	5.57 ± 2.7 ^b	6.08 ± 2.1 ^a	312 ± 217 ^b
KH 0.75	12.39 ± 4.2 ^a	2.76 ± 0.7 ^b	762 ± 70 ^a

Formulations containing MA - maleic anhydride, CA - citric acid, and 3-methacryloxypropyltrimethoxysilane (20% solution m/m). Different letters represent a significant difference ($p \leq 0.05$) between formulations by Tukey's test. Source: Authors.

In a study with compatibilizers in blends of polypropylene (PP) and TPS, samples containing KH-570 had better mechanical properties due to esterification reactions in TPS, modifying the polymer surface and improving the polysaccharide dispersion (Chen et al., 2016). Films produced with PLA and starch modified by 3-chloropropyltrimethoxysilane had higher YM ($2,270 \pm 0.2$ MPa) and tensile strength (39.40 ± 2.3 MPa) than the control ($1,910 \pm 0.1$ MPa and 23.94 ± 4.0 , YM and tensile strength, respectively) (Jariyasakoolroj & Chirachanchai, 2014). The authors justify the performance of the compatibilizer due to covalent bonds that 3-chloropropyltrimethoxysilane made with PLA.

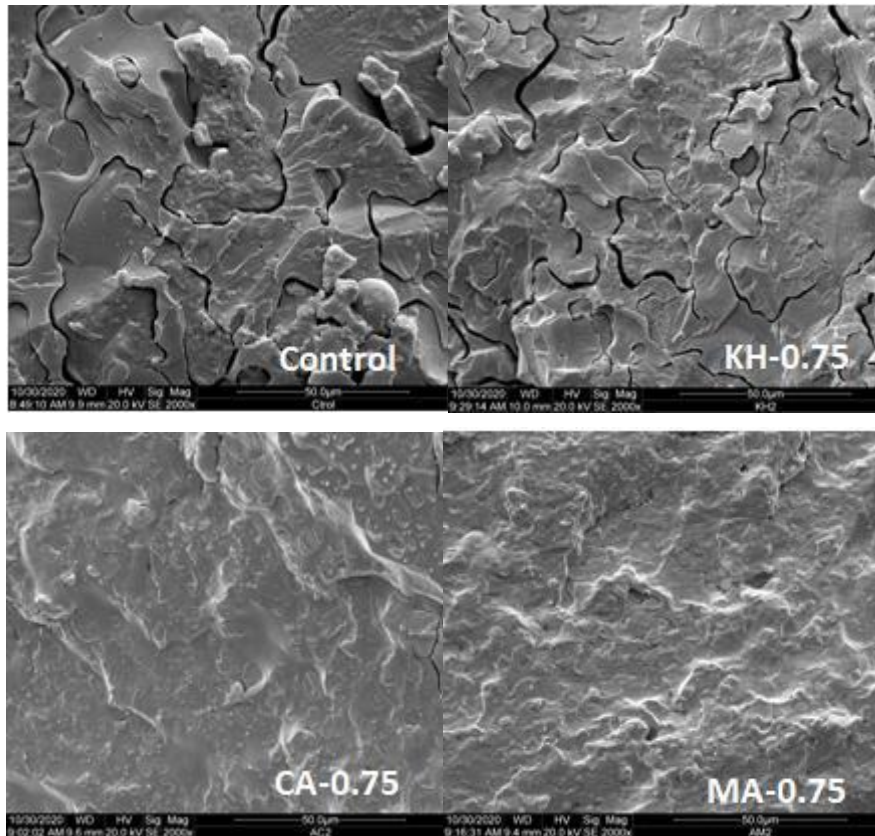
Elongation at break (Table 2) of the injected material CA 0.75 (6.38%) was almost three times more flexible than KH 0.75 (2.76%) and control (2.63%) ones. The CA 0.75 material had the highest elongation, possibly due to the plasticizing effect of the citric acid and the new crosslinking between the polymers, improving the compatibility. The CA can partially hydrolyze the thermoplastic starch structure, increasing flexibility and accelerating the starch granule fragmentation (Shirai et al., 2018). Therefore, high concentrations of CA and larger amounts of starch in blends can considerably increase elongation and decrease tensile strength, YM, and water vapor barrier (Ibrahim et al., 2017; Wang et al., 2007). The elongation at break of the injected materials containing maleic anhydride was similar to those reported for PLA/starch materials (2.5 ~ 4.5 %) (Hwang et al., 2013; Zhang & Sun, 2004) and did not differ from the control material.

Regarding the Young's Modulus (Table 2), which is related to the material stiffness, the control (702 MPa) and KH 0.75 (762 MPa) materials presented the highest values, with no significant difference between them. KH-570 reinforced the bonds, making the material stronger and more rigid (higher values of tensile strength and YM), reducing the flexibility by result. CA 0.75 (393 MPa), and MA 0.75 (312 MPa) materials presented lower values, an average difference of 50~55%. This behavior can be explained by the plasticizing effect of compatibilizing agents such as CA (Ning et al., 2010) and MA (Clansen et al., 2015), decreasing the stiffness of the materials due to the lower interaction between the polymers chains (KOH et al., 2018). In blends of starch/PLA with MA and polyethylene glycol was reported (Akrami et al., 2016) a reduction in YM using compatibilizers due to starch gelatinization and the absence of starch granules in the structure. Other authors reported this behavior (Huneault & Li, 2007; Martin & Avérous, 2001) in studies involving these blends. The high YM and rigidity are intrinsic of PLA materials due to its chemical structure, where the regular distributions of polar bonds in ester groups affect the physicochemical interactions of polymer chains, reducing the bending during deformation and the high PLA glass transition temperature ($T_g \sim 60^\circ\text{C}$), which at room temperature is in a glassy state (Perego & Cella, 2010). For the mechanical properties, factors such as the proportion of the blend components, type of polymer, method of materials production, screw speed, material moisture, among others, can directly influence the properties and characteristics of the material (Ning et al., 2010; Duan et al., 2019; Olivato et al., 2012).

3.2 Scanning Electronic Microscopy (SEM)

The control and KH-0.75 materials presented voids and fractures, according to the micrographs obtained by SEM (Figure 1), probably due to the immiscibility between starch and PLA, due to the hydrophilic character of starch and the hydrophobic of PLA (Akrami et al., 2016; Zaaba & Ismail, 2019).

Figure 1 - Scanning electron microscopy of PLA/Starch blends with compatibilizers.



Source: Authors

The materials produced with the formulations CA and MA showed greater uniformity, with a smoother surface, absence of fractures and cracks, indicating better interfacial adhesion and compatibility between components. In starch/PLA blends containing CA, it was observed that the starch granules became less visible compared to the control, possibly due to better dispersion and fusion of these granules in the PLA matrix, resulting in a continuous phase (Ibrahim et al., 2017). CA can accelerate the starch granule fragmentation during the extrusion due to glycerol input into the polysaccharide molecular structure, achieving greater plasticization and slightly depolymerization of PLA and starch (Wang et al., 2007). MA not grafted onto PLA can also act as a plasticizer in PLA/starch blends, reducing film stiffness compared to the formulation containing only MA grafted (Clansen et al., 2015). In the presence of MA, the size of starch granules is drastically reduced, benefiting his dispersion in PLA (Wang et al., 2007). Although the initiator was not used, the starch dispersion occurred because no granules were observed, with a continuous phase without cracks, different from Zhang & Sun (2004), where only free-radical initiators could promote adhesion between PLA and starch.

3.3 Mass Loss in Water (MLW)

The mass loss in water (MLW) of the biodegradable PLA/starch materials produced by thermoplastic injection are shown in Table 3. The control, CA 0.75, and KH 0.75 materials presented MLW around 22%, differing statistically from MA 0.75, losses close to 40%.

Table 3 – Mass loss in water for PLA/starch blends.

Sample	Mass Loss in Water (%)
Control	24.0 ± 1.5 ^b
CA 0.75	23.4 ± 4.2 ^b
KH 0.75	21.3 ± 0.6 ^b
MA 0.75	38.2 ± 0.8 ^a

Different letters represent a significant difference ($p \leq 0.05$) between formulations by Tukey's test. Source: Authors.

The high MLW of the MA 0.75 material was probably due to partial PLA degradation, as the material showed a darker color, tending to brown (a sign of secondary reactions) (González-López et al., 2018) making the material more hydrophilic due to PLA depolymerization, characteristic of blends containing MA with PLA (Clansen et al., 2015). The KH 0.75 material did not increase MLW compared to control because, as previously discussed, the silane agent (KH) had no plasticizing effect, being morphologically similar to the Control material.

3.4 Moisture Sorption Isotherms

The moisture sorption isotherms of PLA/starch materials with different compatibilizers were modeled using the Guggenheim-Anderson-de-Boer (GAB) model, and the parameters and coefficients of determination are shown in Table 4.

Table 4- GAB model parameters.

Material	GAB Parameter			
	m_0 (g.100 g ⁻¹)	k	C	R ²
Control	4.05	0.89	16.045	0.94
CA 0.75	4.61	0.86	1.921	0.97
KH 0.75	3.72	0.83	6.678	0.98
MA 0.75	5.15	0.83	5.693	0.98

Different letters represent a significant difference ($p \leq 0.05$) between formulations by Tukey's test. Source: Authors.

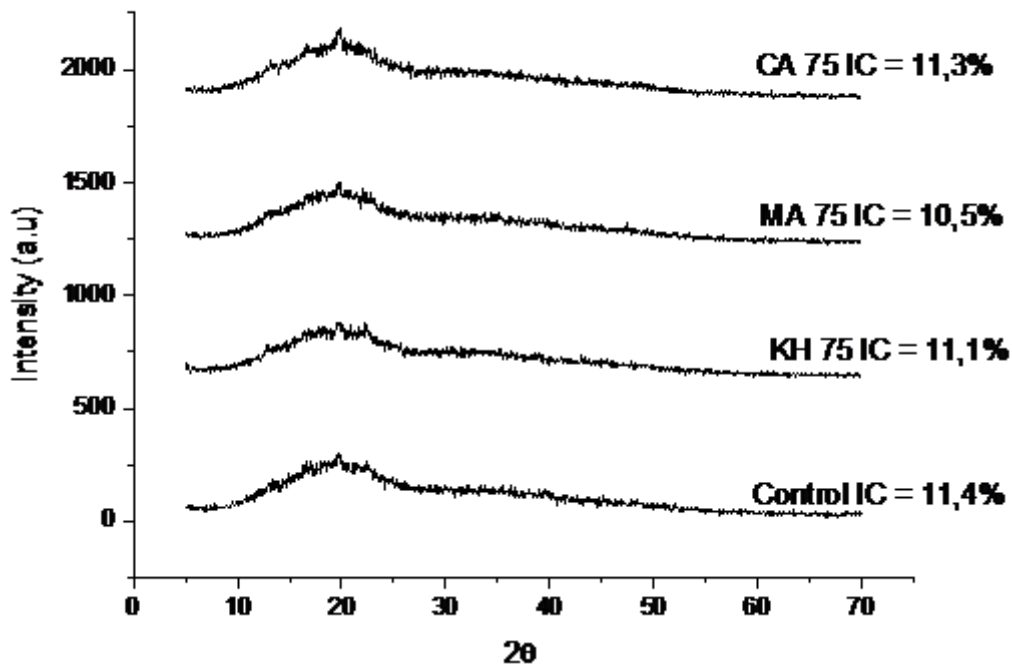
The m_0 is related to the water content in the monolayer of polymeric materials, and they were higher for the MA 0.75 (5.15 g.100 g⁻¹) materials. These values are in accordance with the MLW (Table 3), demonstrating that materials containing maleic anhydride were more hydrophilic than the control, probably due to PLA depolymerization (reactions caused by MA) or by MA interaction with glycerol (reducing plasticizer available), contributing to higher hydrophilicity (Olivato et al., 2012; Rigolin et al., 2019). The formulation containing maleic anhydride had the highest m_0 and water vapor permeability, despite the better compatibility between the polymers. Hydrophilic materials have limited applications as food packaging because of their high water vapor permeability (Ning et al., 2010; Mali et al., 2010; Moghaddam et al., 2018).

The KH 0.75 (3.72 g.100g⁻¹) material had the lowest m_0 , although its morphology presented phase separation and voids (Figure 1), a greater hydrophobicity was achieved, and the MLW (Table 3) was similar to the control and citric acid. Several authors (Chen et al., 2016; Jariyasakoolroj & Chirachanchai, 2014; Chen et al., 2017) report that silane agents, such as KH-570, can influence the materials' morphology, improving adhesion between components and ensuring high hydrophobicity in blends containing starch due to covalent bonds by the silanol group. Other factors such as the polarity and concentration of the polymers adopted in the blend can directly influence the blend's affinity with water, promoting changes in the m_0 .

3.5 X-Ray Diffraction (XRD)

The diffractograms of the biodegradable materials are shown in Figure 2, and all had a peak at $2\theta = 19^\circ$, i.e., the compatibilizers did not influence the materials' crystallinity. In films produced with PLA/Poly(butylene adipate-Co-terephthalate) (PBAT) (Palsikowski et al., 2018), a peak at $2\theta = 19^\circ$ were also identified, which are characteristic of the PLA crystalline phase, and the low crystallinity was due to the rapid cooling of the polymer after extrusion (Ke & Sun, 2011; Tábi et al., 2010; Carrasco et al., 2010).

Figure 2 - Diffractogram and crystallinity index (CI) of PLA/starch blends with different compatibilizers.



Source: Authors.

Large fractions of amorphous regions were identified in the diffractograms, where the peaks (crystalline area) are not easily identified. Starch may present four relevant peaks (close to $2\theta = 15.0^\circ$, 17.3° , 20.0° , and 23.0°), however, in the present study, they are absent, possibly due to the formation of these amorphous zones by addition of PLA (blend) and glycerol (plasticizer), in addition to other factors such as processing, temperature, and addition of other components (Palsikowski et al., 2018; Hu et al., 2013).

The low crystallinity was probably due to the destruction of the semi-crystalline granular structure of starch during the thermoplastic extrusion, where glycerol as a plasticizer breaks the hydrogen bonds and increases the mobility of the chains, resulting in the formation of amorphous zones in the structures (Akrami et al., 2016; Mali et al., 2010; Phetwarotai et al., 2012). Materials containing PLA produced by thermoplastic injection also tend to have low crystallinity due to molecular orientation, and to reverse this effect, an annealing step would be necessary to increase the degree of crystallinity; however, this process would be economically unfeasible (Nanthananon et al., 2015). Crystallinity can directly influence the mechanical, optical, water vapor barrier properties, and the stability of materials over long periods, either with thermoplastic starch (molecular rearrangement of amylose and amylopectin leads to increased crystallinity) or with PLA, according to its isomeric structure (Mali et al., 2010; Kale et al., 2007; Zhang et al., 2008).

The crystallinity index (CI) for the samples had slight variation between the control (11.4%) and the other formulations with compatibilizers. Authors (Raj et al., 2020) produced specimens by thermoplastic injection from a blend between PLA/Polyamide 12 (PA12) with maleic anhydride as a compatibilizer and observed that formulations containing this agent did not show significant changes in thermal properties and crystallinity since there was no change in the crystallization temperature (97°C), improving only the mechanical properties and the compatibilization of the structures. This fact also occurred in blends of PLA/Polypropylene (PP) with maleic anhydride (Pivsa-Art et al., 2016), where the crystallization temperature was also not changed with the addition of the compatibilizer.

4. Conclusion

The effect of different compatibilizers (3-methacryloxypropyltrimethoxysilane, citric acid, and maleic anhydride) on the functional properties of biodegradable materials of starch and poly (lactic acid) (PLA) produced by extrusion and thermoplastic injection were investigated. Citric acid is the best compatibilizer for these materials, as it improves processability, and the materials have adequate mechanical properties for industrial use. Furthermore, materials containing citric acid and maleic anhydride are more uniform from a morphological point of view. For future work, citric acid can be optimized at different concentrations with starch and PLA to evaluate better mechanical and barrier properties, as well to investigate the potential for producing films or other composites.

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