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Crosslinking starch/oat hull mixtures for use in composites with PLA

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Abstract

Modification of composite components has been proposed as a tool to improve their functional properties. The present work studied crosslinking of a starch/oat hull mixture by reactive extrusion with sodium trimetaphosphate (STMP), for application in composites with polylactic acid (PLA). The treated mixture was characterized regarding degree of substitution, FT-IR, and thermal properties. The native and modified mixtures were processed by injection molding, together with PLA and glycerol. The microstructure, mechanical properties, shrinkage, density, and thermal properties of the composites were determined. The FT-IR results, increase in phosphorus content and thermal stability after starch/fiber mixture treatment with STMP suggested the occurrence of crosslinking. Better interfacial adhesion between oat hulls and the polymeric matrix was observed in electron micrographs of the composites containing the modified components. Slight decreases in tensile strength and modulus were observed in the modified composites, suggesting that extrusion and subsequent milling may have broken some structures/linkages.

Keywords: biocomposites, reactive extrusion, lignocellulosic fibers, injection molding, reticulation.

1. Introduction

Several studies have been performed aiming to improve the mechanical and barrier properties of biodegradable packaging materials based on starch. Among them, the blend of starch with other biodegradable polymers is one of the most commonly used options[1]. The commercial availability of some blends, especially starch/PLA, demonstrates the impact of this solution in the substitution of non-degradable and/or non-renewable polymers[2-4]. Another strategy used with the same objective is to reinforce the structure of the polymeric matrix by adding lignocellulosic fibers, which can be used in the native, purified, or modified form[5-7]. Native fibers from coconut[8], sisal[9], jute[10,11], sugarcane[12], and oat hulls[13-15] were added to composites containing different biodegradable polymeric blends.

The advantages of lignocellulosic fibers, when compared with traditional fibers such as, for example, glass fibers, are mainly their low cost, availability, diversity of morphologies, and biodegradability. This last feature is of vital importance when looking at the end-of-life scenario of composite materials[16]. However, due to their hydrophilic structure, natural fibers may not demonstrate good interaction with the polymeric matrices[11,13,17]. Furthermore, this hydrophilic character may contribute to the increase in water absorption

of the composites, negatively affecting their mechanical properties and dimension stability[2].

Chemical modification of fibers and/or matrices is one of the tools used to improve compatibility with most of biodegradable polyesters and their blends. These modifications allow better interfacial adhesion between the fiber and matrix, providing efficient stress transfer so that the reinforcing effect of the material is achieved.

There are several types of chemical treatments (mercerization, oxidation, crosslinking, grafting, etc.) applied to the fibers, as well as studies on their influence on the properties of the composites prepared with the treated fiber[18-24].

In the same manner, chemically modified starch, mainly in the form of crosslinked starch, has been used with the aim of improving the functional properties of biodegradable polymeric blends[25-28]and fiber composites[29,30].

A new approach was used by Kumar et al.[31] and Wang et al.[17], which promoted crosslinking directly in composites of starch/cellulosic fibers, through UV irradiation and reactive extrusion with sodium trimetaphosphate, respectively. The process in these systems can form homogeneous or heterogeneous crosslinking (starch-starch, starch-cellulose, and cellulose-cellulose), which will reinforce the structure of the composites. Similar results were observed by Niu et al.[32]

using a mechanochemical approach to crosslink cellulose fibers and poly(vinyl alcohol) (PVA) through pan-milling with succinic anhydride as a crosslinking agent.

Among the long list of fiber sources, oats hulls, which are a rich fiber by-product from oat processing, are a promising option as fillers in composites, and have been used in both natural[13-15] and modified form[23]. According to Cardoso et al.[23], although superficial fiber modification using alkaline hydrogen peroxide solution[24] has improved interfacial adhesion between oat fibers and the matrix (starch/poly(butylene adipate co-terephtalate)(PBAT), the improvement was not enough to promote a significant effect on composite reinforcement.

Based on the above, the objective of this investigation was to evaluate the impact of crosslinking starch and fiber on the properties of starch/oat hull/PLA composites.

2. Materials and Methods

2.1 Material

Cassava starch (Indemil Ltda., Guaíra, Brazil), PLA - REVODE201, (Hisun,Taizhou, China), micronized oat hulls (4.6% ash, 3.9% protein, 2.1% lipid, 23.1% cellulose, 26.2% hemicellulose, and 3.8% lignin- w/w, db) provided by SL Alimentos Ltda. (Mauá da Serra, Brazil), and glycerol (Dinâmica, Diadema, Brazil) were used for composite production. Sodium trimetaphosphate and sodium sulfate from Sigma-Aldrich (St. Louis, USA), and sodium hydroxide (Synth, Diadema, Brazil) were used for starch/fiber modification.

2.2 Starch/fiber modification

A mixture of oat hulls and cassava starch containing 35.7wt% (db) of hulls was modified by reactive extrusion, based on the methodologies of Wurtzburg[33] and Wang et al.[17] After homogenization, sodium trimetaphosphate, and sodium sulfate, both in the proportion of 3 wt% (starch/hull mass basis) were added. The material was conditioned to 32% moisture and pH 10.5 by adding the required amount of NaOH dissolved in the conditioning water. Furthermore, prior to extrusion, the sample was maintained under refrigeration (7-10 °C) for 12 h to achieve moisture balance and allowed to stand for 1 h to reach ambient temperature. Reactive extrusion was performed in a single-screw extruder (AX Plasticos, Diadema, Brazil) with D =1.6 cm, L/D=40, four heating zones, and a 0.8 mm die diameter. The temperature profile was 90/110/110/110°C and the screw speed was 100 rpm. These conditions were established in preliminary tests. The extruded material was cut into pieces of approximately 1 cm, dried at 60 °C for 3 h, and ground (particle size < 0.250 mm) in a Marconi MA090 mill (Marconi, Piracicaba, Brazil).

2.3 Characterization of the modified starch/hull mixture.

The phosphorus content, substitution degree, and Fourier Transform Infrared (FT-IR) spectra of the modified starch/hull mixture were determined. Aiming to remove the remaining free reagents, a portion of 50 g was washed with ethanol/water (1:1), followed by three washes with distilled water, until neutral pH. Furthermore, the material was dried

at 60 °C for 12 h and ground in a laboratory IKA-A 11 Basic Mill (Ika, São Paulo, Brazil).

2.3.1 Phosphorus content and Degree of Substitution (DS)

The degree of substitution (DS) was calculated by means of Equation 1.

$$SD = 162\,P / \left(3100 - 102\,P\right)$$

Eq. 1

where P is the phosphorus content (%); 162 is the molecular weight of the monomeric starch unit; 3100 refers to the atomic weight of the phosphorus multiplied by 100; and 102 is the mass of the phosphate substituent group[34]. The phosphorus content was determined by colorimetry at 660 nm (AJX 1600 spectrophotometer, Micronal, São Paulo, Brazil) following the method described by Walinga et al.[35] The phosphorus content of the native mixture (NM) of starch/hulls was also determined.

2.3.2 Fourier Transform Infrared Spectroscopy (FT-IR)

The sample was dried in a desiccator containing $CaCl_2$ (~ 0% RH) for one week and analyzed in a Fourier transform infrared spectrophotometer (Bruker, model Vertex 70, Germany) using an attenuated total reflection (ATR) module operating over the spectral range of 4000 cm^{-1} - 400 cm^{-1}, with a 4 cm^{-1} resolution and 10 scans per sample. For comparison, this analysis was also performed for the native mixture of starch/hulls (NM) and in the crosslinked mixture without washing (CM).

2.3.3 Thermogravimetric Analysis (TGA)

The analysis was conducted using TGA – 4000 equipment (PerkinElmer, Cleveland, USA). The samples were scanned from 30 to 800 °C, with a heating rate of 10 °Cmin^{-1} under a nitrogen atmosphere (flow rate 20 mL min^{-1}). The native mixture (NM) and the washed crosslinked mixture (WCM) were analyzed.

2.4 Composites production by injection molding

The components of the formulations (starch, oats hulls, glycerol, PLA) were manually mixed and the mixtures dried at 60 °C for 3 h. The compounding was performed using a single-screw extruder model EL-25 (BGM, Taboão da Serra, Brazil) with a screw diameter of 25 mm and barrel length of 700 mm (L/D = 28). The temperature profile was set at 90/150/150/140 °C from feeder to die zone, the screw speed was set at 35 rpm, and a two-hole cylindrical die (2 mm) was used. The obtained materials were further pelletized and stored in sealed bags. Before injection molding, the pellets were dried (50 °C/1 h), to avoid problems with moisture during processing, performed in a lab-scale injection molding machine AX16 II (AX-Plasticos, Diadema, Brazil). The processing parameters, defined in preliminary tests, were: temperature profile 150/175/175 °C; mold temperature 20 ºC; injection time 9.5 s; cooling time 30 s; and mold opening time 1 s. Specimens in a dog bone shape were obtained. The performance of two different formulations of composites was compared, both containing 20% oat hulls, 36% starch, 12% glycerol, and 32% PLA (w/w), one being formulated with the raw mixture of starch/hulls and the other containing the mixture modified as explained in 2.2.

The proportion of oat hull was selected in preliminary tests as the highest level that can be added in composites with PLA/starch with adequate dispersion and without failures in the injected specimens.

2.5 Composites characterization

2.5.1 Scanning Electron Microscopy (SEM)

The microstructure of the composites was recorded using a FEI Quanta 200 scanning electron microscope (FEI Company, Tokyo, Japan). The specimens were dried in a desiccator containing $CaCl_2$ for ten days, fractured in liquid nitrogen, and coated with gold using a BAL-TEC SCD 050 (Leica Microsystems, Germany) sputter coater. Images of the surface and fracture were obtained.

2.5.2 Longitudinal shrinkage

The linear shrinkage measured along the flow direction was calculated as the difference between the dimension of the mold cavity and the molded specimen using Equation 2, according to the method ASTM D955-00[36].

$$Shrinkage\left(\%\right)=\left(\frac{Lm-Ls}{Lm}\right)\times 100 \qquad \text{Eq. 2}$$

where: Lm = mold length and Ls = specimen length.

The analysis was performed 48 h after injection and ten replicates were evaluated.

2.5.3 Density

The density was determined as the relation of weight and volume of samples previously kept in a desiccator with anhydrous CaCl2 (~ 0% RH) for 2 weeks. The volume was calculated by measuring the length, width, and thickness of the sample. Three replications were used.

2.5.4 Mechanical properties

Tensile tests were realized using a universal testing machine model DL2000 (EMIC, São Jose dos Pinhais, Brazil) according to the ASTM D 638-03 method[37], with some modifications. Ten test specimens of each composite were previously conditioned in a desiccator at 53±2% RU ($Mg(NO_3)_2$ saturated solution) and 25 °C for ten days. Each specimen was fitted in the tensile grips, which had an initial distance of 60 mm. The crosshead speed of the test was 50 mm min^{-1}.

2.5.5 Thermogravimetric Analysis (TGA)

The thermal stability was determined as explained in 2.3.3, comparing composites containing the native starch/hull mixture (NMC) with those containing crosslinked mixture (CMC).

2.6 Statistical analyses

Results are expressed as means ± standard deviation. Differences among samples were tested by analysis of variance (ANOVA) followed by the Tukey's test (p <0.05). Analyses were performed using the software STATISTICA® 7.0 (Statsoft Inc., Oklahoma, USA).

3. Results and Discussions

3.1 Characterization of crosslinked mixture of starch/hulls

3.1.1 Phosphorus content and Degree of Substitution (DS)

The phosphorus content of the native mixture (NM) of starch/oat hulls was $0.34 \pm 0.05\%$ (w/w), which essentially came from the hulls. The crosslinked mixture (CM) presented $1.57 \pm 0.12\%$ phosphorus and the increase in this parameter represents the level of phosphorus linked to the starch and/or cellulose chains, since the sample was washed to eliminate the non-reacted STMP.

The degree of substitution (DS) represents the average number of substituent groups attached per monomeric unit. Thus, in the case of starch and cellulose, this represents the average of substituent groups per anhydroglucose unit. The DS calculated for the crosslinked mixture (CM) was 6.1×10^{-2}. Although this is a low value, studies have proven that when modifications of similar DS were promoted in starch, a large impact on its properties was observed[38,39]. At the same time, Wang et al.,[17] using a similar process to crosslink a mixture of starch/purified sisal fiber, reported similar DS (6×10^{-2}, transforming their data to percent of substituents per monomeric unit). Observing that the DS increased steadily with increasing fiber content from 2.5 to 25%, the authors suggested the fiber could have participated in the crosslinking reaction together with the starch. The results of our work can be considered good, since in the purified fiber the cellulose is more exposed, while in the oat hulls it is covered by other components such as hemicellulose and lignin.

3.1.2 Fourier Transform Infrared Spectroscopy (FT-IR)

The FT-IR analysis was performed aiming to detect chemical alterations in the structure of the blend components promoted by the modification process. The spectra of the native (NM) and modified mixtures, with (WCM) and without washing (CM), were similar (Figure 1). The band around 3500-3200 cm^{-1} (with peak at 3288 cm^{-1}) is due to stretching of the O-H groups. A band around 2900 cm^{-1} (peak at 2926 cm^{-1}), attributed to C-H stretching of aliphatic groups, is also observed[40]. Related to the band at 3288 cm^{-1}, the decreased intensity observed in the spectra
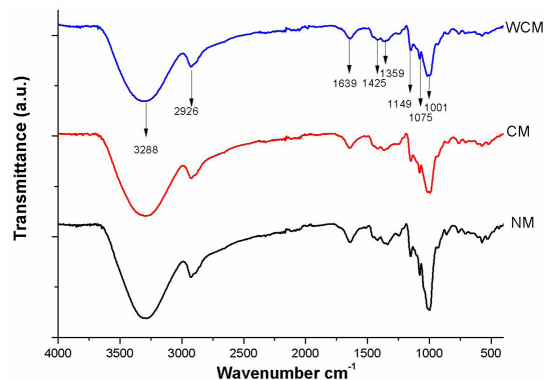

Figure 1. FT-IR spectra of native (NM) and crosslinked mixtures, without (CM) and with washing (WCM).

of CM and WCM compared with NM could indicate a decrease in the number of hydrogen bonds. The same effect was observed by Shalviri et al.[41] in starch/xanthan gum mixtures crosslinked by STMP.

In the region of 1640 cm^{-1} (1639 cm^{-1}) another band is observed, which is firstly attributed to the presence of water in the samples. In addition, in this region comprising bands from 1640 – 1424 cm^{-1}, other nearby bands may be superimposed, such as those originated from carboxyl-conjugated carbonyl stretches from fiber components.[17]

The absorption bands at 1149 cm^{-1} and 1075 cm^{-1} are attributable to C-O-C and C-OH stretching, respectively[40].

However, specific bands involving phosphate groups (as 1298 and 997 cm^{-1} ascribed to P=O and P-O, respectively) were not detected in the WCM and CM samples, even when, in the latter case, all the added phosphorus was present. This is probably due to the low level of phosphorus added, as already reported by Sechi and Marques[34]. Another possible reason is that these bands may be being covered up by others, nearby, with an overlap occurring. Therefore, the only evidence of crosslinking via phosphate groups in the FTIR spectra would be a decrease in the intensity of the band corresponding to the hydrogen bonds in the CM and WCM samples.

3.1.3 Thermogravimetric Analysis (TGA)

When comparing thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of the untreated mixture (NM) with that of the crosslinked mixture (CM), conformational similarities were observed (Figure 2).

In the two samples, the loss mass was initiated at approximately 100 °C, being due to the loss of water and volatiles[13]. A more expressive loss mass was also observed, showing peaks of maximum degradation rates in the DTG curves of NM and CM at 333 and 340 °C, respectively. These temperatures, which are included in the range from 300 to 400 °C, correspond to the degradation of starch, cellulose, hemicellulose, and lignin[19]. The fact that the peak has moved to a higher temperature in the case of CM may be attributed to the formation of crosslinks, giving higher thermal stability to the material. Yoon et al.[28] and Niu et al.[32] observed

similar behavior promoted by crosslinking in a starch/PVA blend and cellulose/PVA composites, respectively.

3.2 Composites characterization

3.2.1 Morphology- Scanning Electron Microscopy (SEM)

Some differences can be observed when comparing the micrographs of composites elaborated with the native mixture of starch/hulls, coded NMC, with those elaborated with the crosslinked mixture (CMC) (Figure 3).

The surface of NMC (left side) is rough, making it appear that the components were only compacted. The fibers are poorly inserted in the polymeric matrix and there seems to be little interaction between them. On the other hand, CMC presented a smoother surface (left side), with the fiber better wrapped by polymers.

In the fracture images (Figure 3, right side), gaps and fissures were observed in the two composites, but with lower dimensions in the case of CMC. This fact, associated with the coating of oat hulls observed in CMC indicate the better adhesion between fiber and matrix in the sample containing the modified mixture. It is possible that crosslinking via covalent or non-covalent bonds may have occurred, resulting in better interaction. Other authors reported the enhancement of fiber/matrix adhesion when the fiber was modified by different treatments[19-23].

Wang et al.[23] observed poor adhesion between sisal fiber and starch in composites in which STMP was used as the crosslinking agent. The authors presented only the micrographs of the reticulated samples and reported the presence of holes and smooth grooves, indicating the modification was not sufficient to impart the desired compatibilization.

Another point to highlight is the presence of remnant non-gelatinized starch granules, in both samples, indicating that the operational conditions were not sufficient to promote the complete disruption of granular structure. Even though the CMC underwent additional extrusion processing pre-treatment, to crosslink the starch/hull mixture, several starch granules retained their shape. This result is closely related to the higher thermal stability of CM (item 3.1.3). Kaewtatip and Thongme[26] also observed remnant starch granules in fractured surfaces of crosslinked starch/thermoplastic
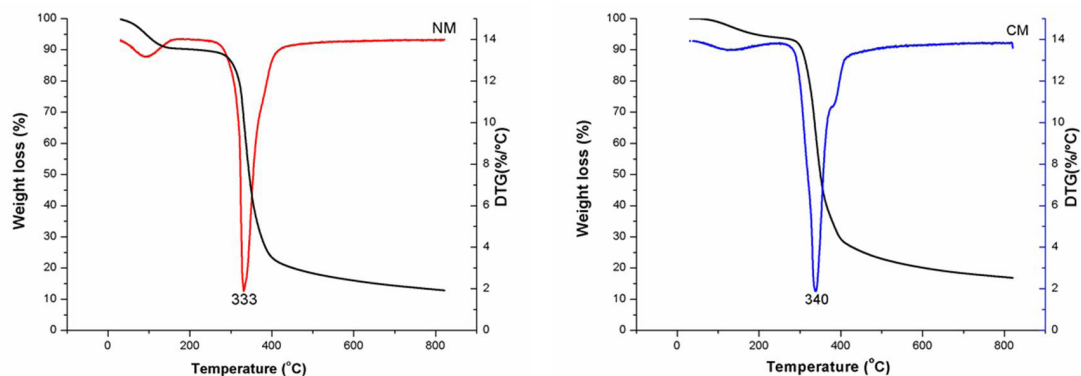

Figure 2. Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of the untreated (NM) and crosslinked (CM) oat hull/starch mixtures.
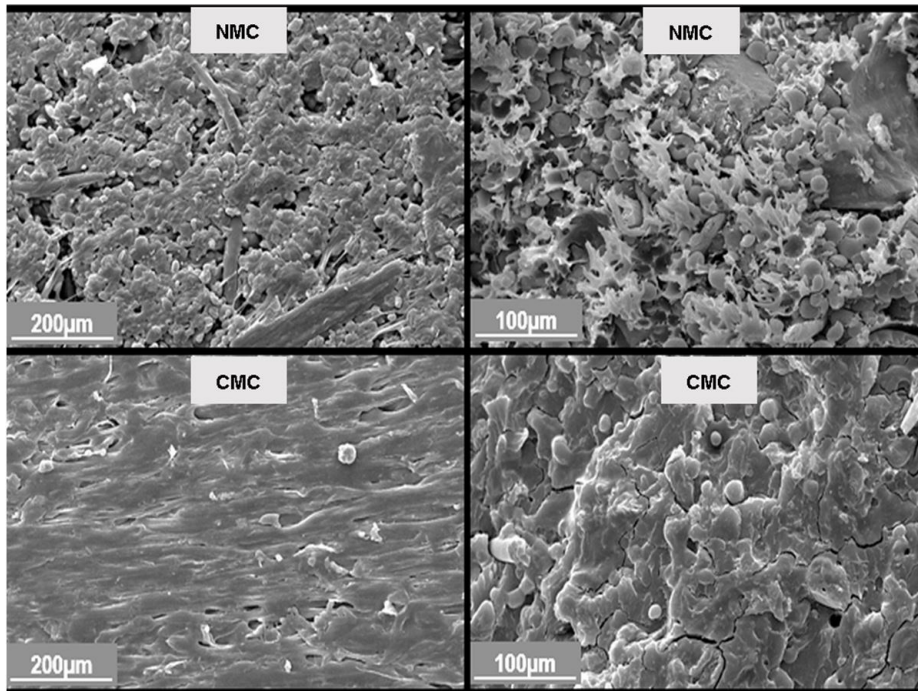
Figure 3. SEM micrographs of composites containing the native (NMC) and the crosslinked (CMC) starch/hull mixtures.

starch (TPS) materials, attributing this result to the higher resistance conferred by crosslinking.

3.2.2 Longitudinal shrinkage

Shrinkage is an undesirable phenomenon in the injection molding process, as it causes dimensional changes and, consequently, low quality specimens[42]. There was no significant difference between the linear shrinkage of composites containing raw or modified mixtures of starch/hulls. The median value was 0.39%, which is considered low, indicating good dimensional stability.

While crystalline and semi-crystalline materials normally present high shrinkage, ranging from 1.0 to 4.0% in traditional polymers, such as LDPE and HDPE, less shrinkage is observed in amorphous materials[43]. Müller et al.[18] reported that TPS injected specimens present high shrinkage that increases with storage time. The addition of wood fibers up to 15 wt% promoted a fast decrease in shrinkage, which was almost negligible. This behavior of fibers as fillers in composites is a general rule, in different polymer matrices[43]. In the present study, both fibers and PLA must have helped to preserve the original dimension of the molded pieces. Although only the primary shrinkage was evaluated (the measurement was performed 48 h after processing), it not being possible to predict the behavior during storage, based on the literature data[18,43] it is possible to wait for the protective action of oat hulls, ensuring dimensional stability over time.

3.2.3 Density

There was a significant difference between the densities of the samples (Table 1), with those of NMC being lower. This can be justified by the microstructure of the sample

Table 1. Density and mechanical properties of the composites.

Sample	Density	σ (MPa)	ε (%)	YM (MPa)
NMC	1.29 ± 0.015^b	4.65 ± 0.18^a	5.75 ± 0.40^b	144.75 ± 4.91^a
CMC	1.33 ± 0.016^a	4.31 ± 0.17^b	6.16 ± 0.17^a	133.55 ± 7.30^b

σ: tensile strength, ε: elongation, YM: Young modulus. Results expressed as mean ± standard deviation. Means followed by same letters in a column do not differ significantly (Tukey's test p≤0.05).

(Figure 3), in which low compaction and a higher incidence of free spaces were observed, contributing to the low density.

The higher compaction in the case of CMC, which contributed to its high density, may have been caused by several factors, such as: the physical effects of extrusion and milling which the mixture of starch/oat hulls was subjected to in the pre-processing; the reticulation promoted by STMP during pre-processing; the better compatibility between PLA and the other components promoted by these physical and chemical modifications.

Ayoub and Rizvi[44] explained that the occurrence of crosslinking in starch, during extrusion, increases the viscosity of melted material, resulting in denser extrudates.

3.2.4 Mechanical properties

The composite containing the crosslinked mixture of starch/oat hulls (CMC) presented slightly lower tensile strength and Young's modulus and higher elongation than those of NMC (Table 1). Although the crosslinking process was used to increase the strength and stiffness of the composites, the opposite result obtained was not totally unexpected. Depending on the composition of the polymer matrix, the degree of crosslinking, and the crosslinking agent
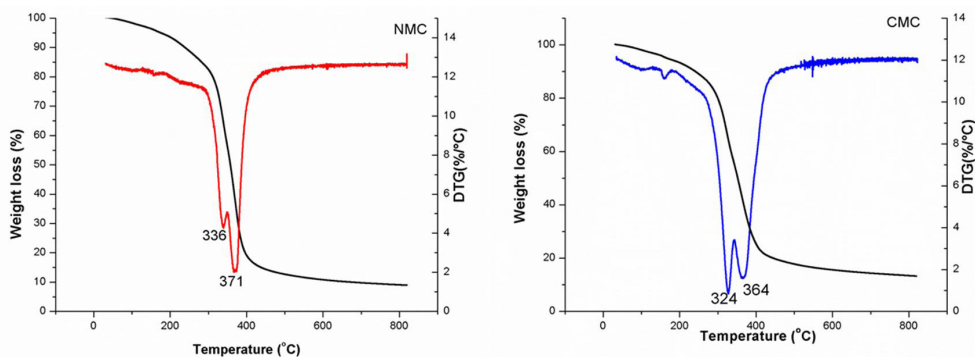
Figure 4. TG and DTG curves of composites.

employed, contrary results can be observed. Das et al.[25], using borax, formaldehyde, and epichlorohydrin as cross-linkers in starch/poly(vinyl alcohol) films, observed that only borax promoted increases in strength and modulus, while epichlorohydrin increased the strain and formaldehyde did not affect the mechanical properties.

Thus, it is possible that the level of crosslinking achieved by the reaction with STMP (item 3.1.1) was not sufficient to promote the expected effect on the mechanical properties of the composite, despite the improvements promoted in its morphology (Figure 3). In addition to the degree of substitution being low, it is necessary to remember that not all the phosphate groups attached to the chains of starch or cellulose form crosslinks.

Wang et al.[17] did not obtain improvements in mechanical properties from the reticulation of TPS/sisal fiber composites, although they used the purified fiber, which could have facilitated its interaction with the starch. The authors justified the results considering that the extent of crosslinking (similar to that obtained in our work) was low to structurally reinforce the polymeric matrix. On the other hand, Niu et al.[32] obtained a remarkable improvement in the strength of PVA/cellulose composites after crosslinking with succinic anhydride, applying a pan-milling process. In this case, the better fiber dispersion and chemical modification promoted could have compensated the possible effects of milling (reduction in aspect ratio of fibers and/or polymer chain scission) that harm the strengthening.

3.2.5 Thermogravimetric Analysis (TGA)

The TG and DTG curves of the composites are shown in Figure 4. Both samples presented three degradation peaks. The first occurred at temperatures around 100 °C and is related to vaporization of water and other volatiles[13]. The other two peaks occurred at 336 and 371 °C for NMC and at 324 and 364 °C for CMC.

As previously discussed (item 3.1.3), the degradation curves observed in the DTG figures represent the overlap of curves corresponding to the degradation of the fiber components (cellulose, hemicellulose, lignin) and starch. Similar results were observed by Cardoso et al.[23] and Rosa et al.[19], in composites containing oat and coconut fibers, respectively. Although in the case of CMC the peaks of maximum degradation have occurred at slightly lower

temperatures, the higher residual weight indicated relatively high thermal stability.

TGA analysis of the mixture of starch/PLA, without oat hulls, was also performed (figure not shown), with two degradation peaks being observed at 339 and 398 °C. While the first peak is attributed to the starch degradation, the second corresponds to the degradation of PLA[45]. In the case of DTG curves of composites (Figure 4), the peak related to PLA degradation was shifted to lower temperatures, being overlapped with the curves of the other components. The lower level of PLA in the composites, together with the lower degradation temperatures of the other components explains the decrease in PLA thermal stability. Other authors observed similar results in other fiber composites[19,45].

4. Conclusions

Reactive extrusion using STMP as a crosslinking agent was an efficient process to modify starch/oat hull mixtures. The higher thermal stability of the treated mixture was an indication of the occurrence of reticulation. When the crosslinked mixture was processed together with PLA, denser composites with a smooth surface were obtained, due to the better interfacial adhesion between fibers and matrix. The resistance of the composites containing the modified mixture were slightly lower than that of the control sample. It is possible that the additional processing applied to promote the crosslinking, consisting of extrusion and grinding, ruptured structures in the fiber and/or starch, which weakened the performance of the final material.

5. Acknowledgements

6. References

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