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Biodegradable Starch-Based Films Containing Saturated Fatty Acids: Thermal, Infrared And Raman Spectroscopic Characterization

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Abstract: Biodegradable films of thermoplastic starch and poly (butylene adipate co-terephthalate) (PBAT) containing fatty acids were characterized thermally and with infrared and Raman spectroscopies. The symmetrical character of the benzene ring in PBAT provided a means to illustrate the difference between these spectroscopic techniques, because a band appeared in the Raman spectrum but not in the infrared. The thermal analysis showed three degradation stages related to fatty acids, starch and PBAT. The incorporation of saturated fatty acids with different molecular mass (caproic, lauric and stearic) did not change the nature of the chemical bonds among the components in the blends of starch, PBAT and glycerol, according to the thermal analysis, infrared and Raman spectroscopies.

Keywords: *Fatty acids, PBAT-starch blends, blown extrusion, thermal analysis.*

Introduction

The non-biodegradable and non-renewable nature of the plastic packaging material has increased the interest in materials based on biopolymers from renewable resources with the intention of reducing the environmental impact. The biopolymers include those that occur naturally as proteins, cellulose, starch and others, and the chemically synthesized from monomers that occur naturally, e.g., lactic acid^[1-4].

Starch is not a real thermoplastic, but in the presence of a plasticizer, temperature range of 90-180 °C and shear; it melts and flows, allowing its use in injection and blown extrusion equipments, similar to those for synthetic plastics. Films produced with thermoplastic starch have high water vapor permeability (WVP) and poor mechanical properties^[5-7]. To solve these limitations and due to the high cost of synthetic biodegradable polymers currently available, some researchers developed biodegradable films using blends of starch and synthetic polymers^[8-10]. Fatty acids are promising components, which can create effective barriers to water vapor and provide structural support, thus limiting the oxygen and carbon dioxide transfer through the film^[11,12].

Extrusion is faster, requires less space and demands fewer production stages compared to casting process, often cited in the literature for biodegradable film manufacturing^[11-3,7,13]. In addition, most of commercial polymer films are manufactured by extrusion.

Vibrational spectroscopy is an important tool to obtain information on chemical, conformational, crystal and morphological of a polymer, besides of this, it is also important in understanding dynamical behavior of polymer chains^[4].

Physically, the two processes, infrared (IR) and Raman, are different. The infrared absorption occurs when the frequency of the incident radiation has the same value as the difference of energy between two vibrational states, i.e., the process involves a resonance between the difference in energy levels of molecules and electromagnetic radiation. A vibrational mode in a molecule is "IR active" if occurs a variation in the intrinsic dipole moment of the molecule during the vibration^[14].

In Raman scattering, a visible or ultraviolet radiation interacts with the molecule and it is scattered with a slightly changed frequency. This difference in frequency corresponds to the difference of energy between two vibrational states. In Raman activity the dipole moment is that induced by electromagnetic radiation, i.e., there must be a change in molecule polarizability during the vibration^[14].

Thermogravimetric analysis is another important tool for biodegradable film characterization. Polymers, in general, when subjected to heat treatment show structural changes characterized by chemical bonds ruptures in their molecular chains. These changes evidenced by the decrease in molar mass, with evolution of volatile products. Thus, the initial temperature of thermal decomposition is important as they indicate the maximum processing temperature.

The aim of this work was to study the changes in thermal stability due to the incorporation of fatty acids in biodegradable films produced by blown extrusion from blends of thermoplastic starch and poly(butylene adipate-co-terephthalate), and also to characterize the films through combination of FT-IR and FT-Raman spectroscopic analysis, and thermal analysis.

Material e Methods

Materials

Native starch from cassava (Indemil, Brazil) and commercial glycerol (Dinâmica, Brazil) used to produce thermoplastic starch. The biodegradable polymer used was poly (butylene adipate-co-terephthalate) (PBAT), manufactured by Basf (Germany) under the commercial name of Ecoflex® 7011. The fatty acids used were caproic acid (99%, Vetec, Brazil), lauric acid (98%, Vetec, Brazil) and stearic acid (PA, Synth, Brazil).

Preparation of blends of thermoplastic starch and PBAT by blown extrusion

The films were produced by blown extrusion using a pilot extruder BGM (model EL-25, Brazil) with a blowing system made up of a 250-mm diameter screw, four heating zones and an external cooling air ring with a 300-350-mm diameter for film formation. The screw speed was maintained at 35 rpm. The three barrel zones were operated at 120 °C and the balloon circular die at 130 °C.

Films were produced according to the formulations shown in Table 1.

FT-IR spectroscopy

The infrared spectroscopic analysis were performed on a spectrometer FT-IR Thermo Scientific Smart Omni-Sampler

Table 1. Formulations used in the production of the films.

| Film | Fatty acid | Starch (%) | Glycerol (%) | PBAT (%) | Fatty acid (%) |
|------|------------|------------|--------------|----------|----------------|
| C20 | - | 56.0 | 14.0 | 30 | - |
| C25 | - | 52.5 | 17.5 | 30 | - |
| Ca20 | Caproic | 54.8 | 13.7 | 30 | 1.5 |
| Ca25 | Caproic | 51.4 | 17.1 | 30 | 1.5 |
| La20 | Lauric | 54.8 | 13.7 | 30 | 1.5 |
| La25 | Lauric | 51.4 | 17.1 | 30 | 1.5 |
| E20 | Stearic | 54.8 | 13.7 | 30 | 1.5 |
| E25 | Stearic | 51.4 | 17.1 | 30 | 1.5 |

(model Nicolet iS10, USA) equipped with Attenuated Total Reflectance module with germanium base. The samples were conditioned for 7 days in a desiccators containing calcium chloride. Analyses were performed on mid-infrared in the range of 4000 cm^{-1} to 675 cm^{-1} , with spectral resolution of 4 cm^{-1} . 100 scan were taken from each sample and 120 scans from the background.

FT-Raman spectroscopy

FT-Raman spectra were obtained using a FT-Raman spectrometer Bruker (model FRS-100/S, USA), exciting radiation of 1064 nm (NIR) from an Nd:YAG Coherent Compass 1064-500N, laser power at 100 mW, with Ge detector cooled with liquid nitrogen and coupled with an optical microscope Nikon (model Eclipse E-400, Japan). Analyses were performed in the region of 4000 cm^{-1} a 0 cm^{-1} , with spectral resolution of 1 cm^{-1} , and 512 scans. Analyses were performed at the Laboratory of Molecular Spectroscopy of the Institute of Chemistry of Universidade de São Paulo (USP, Brazil).

Thermal analysis (TGA)

Analyses were obtained in a thermogravimetric analyzer Shimadzu (model TGA50, Japan), under nitrogen flow with a rate of 50 mL/min. Samples were heated from 25 °C to 450 °C with a rate of 10 °C/min. Analyses were performed at POLIMAT Laboratory at Universidade Federal de Santa Catarina (UFSC, Brazil).

Results and Discussion

Infrared spectroscopy

Figure 1a shows the FTIR spectra of samples C20, Ca20, La20 and E20 and in Figure 1b FTIR spectra of samples C25, Ca25, La25 and E25.

There were no differences in the profile shape of transmittance in the FT-IR spectra of the samples. However, there were differences in the peaks intensity. The most relevant difference could be observed in the spectra of samples E20 and E25, where there are two bands in the region of 2915 cm^{-1} and 2850 cm^{-1} , attributed to asymmetric and symmetric stretching of C-H bond of aliphatic^[15,16]. These bands are present in the spectrum of stearic acid (not shown), characterizing the presence of this component in the blend.

Fatty acids have infrared spectra with characteristic bands in the region of 3400-2400 cm^{-1} due to their strong hydrogen bonds, intra-and inter-molecular, a strong band between 1700-1730 cm^{-1} which is attributed to C=O group. But when in a conjugated system type, C=C or a phenyl group, the absorption occurs at lower frequencies, the C-O stretch in the region between 1210-1320 cm^{-1} and the bands that represents the deformations of the CH_2 group in 1410 and 1460 cm^{-1} , approximately.

Some bands are present in the spectrum, while others suffered some kind of displacement or are absent, as is the case of broadband in the region of 3400-2400 cm^{-1} , indicating that the acids are

compounding the polymer matrix. Thus the band characteristic of free fatty acids, which allow strong interactions of hydrogen, did not appear in the spectrum.

The bands can identify the PBAT and fatty acids: 1717 cm^{-1} (stretching of C=O); 1454 and 1410 cm^{-1} (angular deformation of C-H₂ bond) and, specifically for PBAT, the band at 1270 cm^{-1} (stretching of C-O bond in esters)^[16,17]. The band at 732 cm^{-1} , according to Solomons and Fryhle^[16], assigned to the out of plane deformation of benzene ring, which is present in PBAT.

According to Ning et al.^[18], the band at 1018 cm^{-1} is a characteristic peak of the deformation in C-O bond in the glucose ring and the bands in the region of 1080 and 1101 cm^{-1} assigned to C-O bond of the C-O-H group in the starch. In the region of 1160 and 930 cm^{-1} there are characteristics bands of stretching in C-O of ether, which are presents in the polymer and the starch.

Comparing the FT-IR spectra of the films containing fatty acids with the control, is observed that, apparently, there was no formation of new bonds among the components, since no new peaks or bands were observed, only those characteristics of the pure components in the blend. That does not mean an incompatibility among the components, because the scanning electronic microscopy and mechanical properties of the films containing fatty acids showed properties similar or superior to the control film^[19]. Probably there was an increase in existing bonds, interactions not detected by infrared spectroscopy or even overlapping bands.

Raman spectroscopy

Figure 2a shows the Raman spectra of samples containing 20% glycerol, C20, Ca20, La20 and E20, and Figure 2b the Raman spectra of samples with 25% glycerol, C25, Ca25, La25 and E25.

The Raman spectra were similar for all samples as occurred in the infrared analysis. The region between 1200-1500 cm^{-1} is rich in structural information, the vibrational Raman spectra of carbohydrates showed characteristic vibrations in this region. The majority of the bands are due to coupled vibrations involving hydrogen atoms. The band at 480 cm^{-1} describes the degree of polymerization in polysaccharides and is one of the dominating and important skeletal vibration modes of the pyranose ring^[20,21]. The Raman band at 1260 cm^{-1} attributed to CH_2OH , which indicates the V-form amylase deformation^[22,23]. The vibrations from the glycosidic linkage observed in the region of 920-960 cm^{-1} , in our study the band at 940 cm^{-1} ^[21,24].

The band near 1715 cm^{-1} assigned to the stretching of carbonyl group (C=O), present both in fatty acids and in the polymer. The bands observed at approximately 1460 cm^{-1} and 2920 cm^{-1} assigned to angular vibrations (H-C-H) in the plane and the stretching (C-H) of the alkyl groups present in the films^[25,26].

The "shoulder" seen in the region of 1380 cm^{-1} (Figure 3 – sample E25) is probably due to angular deformations of C-H bond^[22,27], the latter is more clearly defined in samples containing stearic acid due to the size of the chain of this fatty acid.

The polymer PBAT presents benzene ring in his structure (Figure 4) and in Raman spectra the bands corresponding to this group are at 630, 1041 and 1605 cm^{-1} , assigned to the vibrations of the aromatic ring^[26] and at 3080 cm^{-1} attributed to carbon-hydrogen stretching of aromatic rings. The band characteristic of aromatic ring near 1600 cm^{-1} does not appear in the FTIR spectra (Figure 1), this kind of vibration is not detected by this technique probably due to the symmetrical character of the benzene ring present in the PBAT structure (Figure 4).

Thermal analysis (TGA)

Figure 5a shows the thermogravimetric degradation curves of the samples C20, Ca20, La20 and E20, and in 5b the samples C25, Ca25, La25 and E25 and Table 2 the temperatures at the maximum rate of degradation of each stage present in the thermograms and the residue content.

Figure 5a and Table 2 shows that the samples C20 and Ca20 presents three degradation stages, the first is related to the

water loss of the blend, the second related to the degradation of fatty acids and thermoplastic starch and the third is related to PBAT degradation.

The samples La20 and E20 presented a thermogravimetric curve with four degradation stages, the first stage related to water loss, the third stage related to TPS degradation and the fourth to PBAT degradation. The second stage of the sample La20 related to the degradation of a fraction of glycerol and lauric acid, which has a degradation temperature (T_d) around 180 °C, the stage begins with a temperature of 140 °C and its end is around 280 °C. The same occurs with the sample E20 and the loss of stearic acid, T_d around 220 °C, where the degradation begins at 160 °C and ends at 285 °C. This change of behavior of the samples may be due to an incompatibility between the more hydrophobic fatty acids and the components of the blend.

From Figure 5b and Table 2 can be seen that there are three stages of thermal degradation of the films containing 25% glycerol

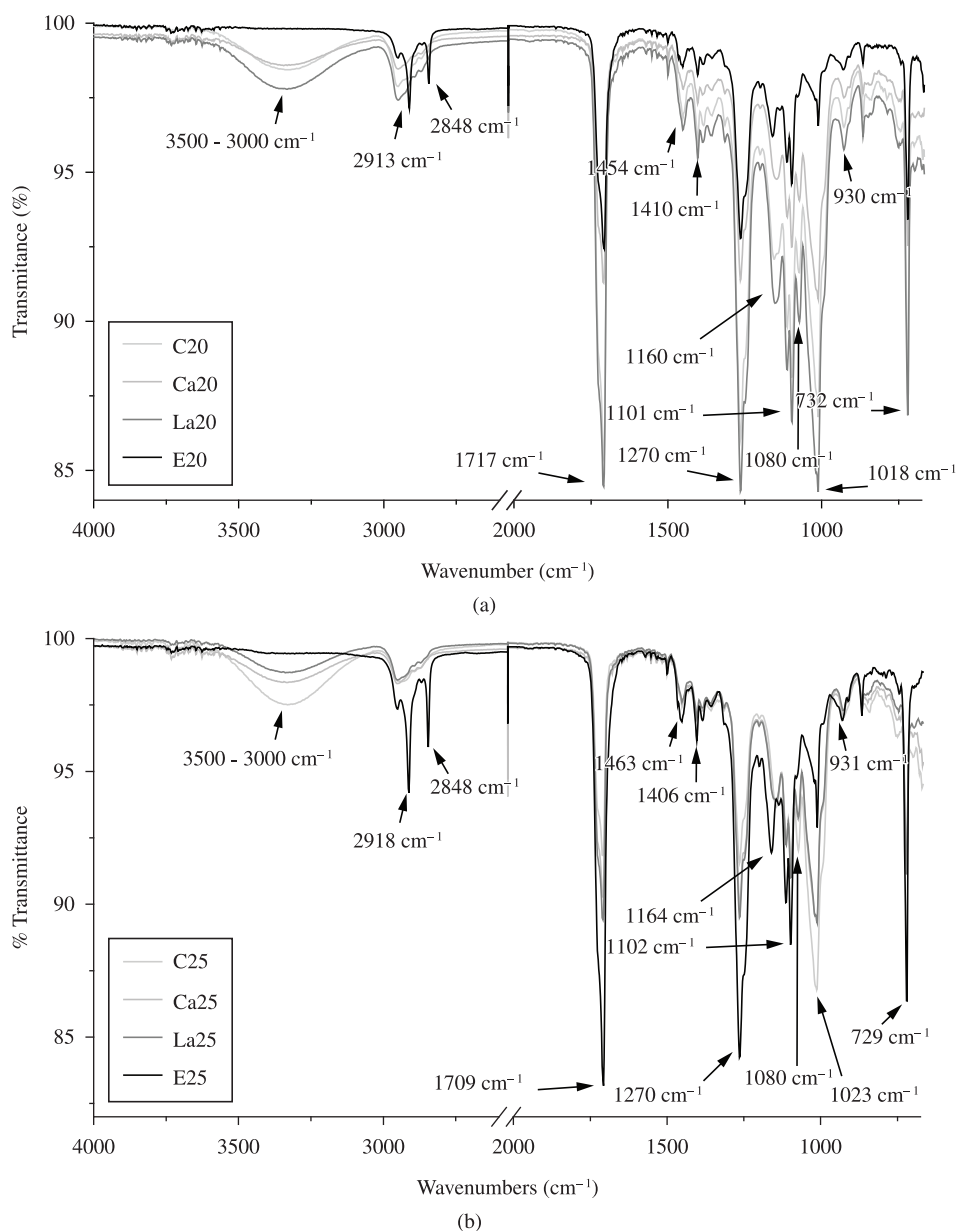


Figure 1. FTIR spectra of the samples containing 20% glycerol in TPS (a) and 25% glycerol in TPS (b).

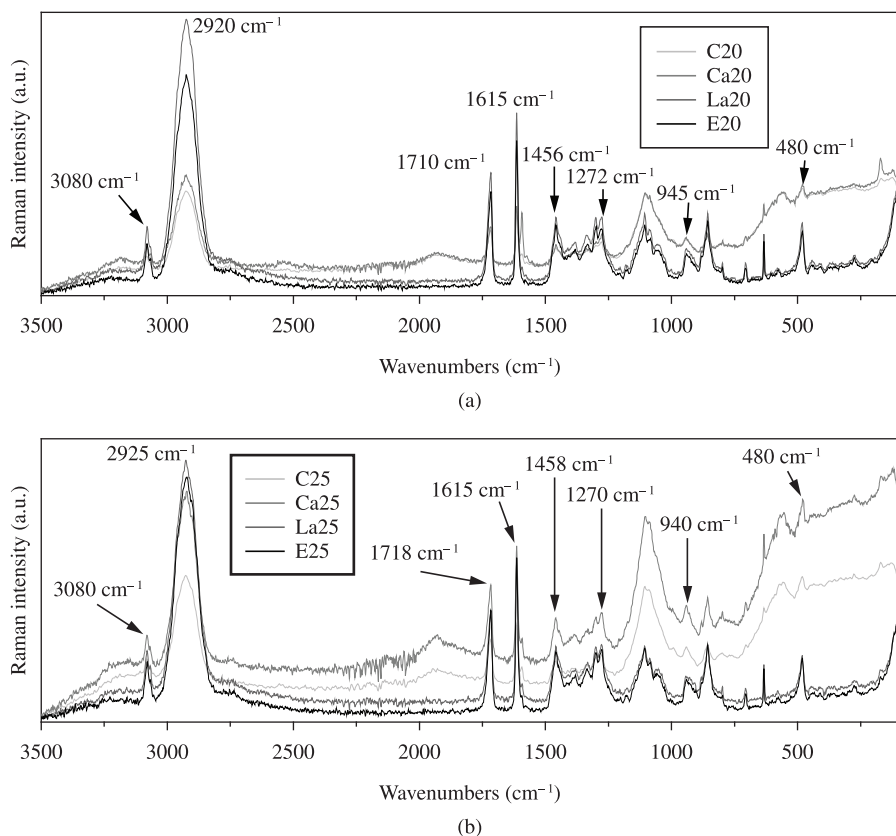


Figure 2. Raman spectra of the samples containing 20% glycerol in TPS (a) and 25% glycerol in TPS (b).

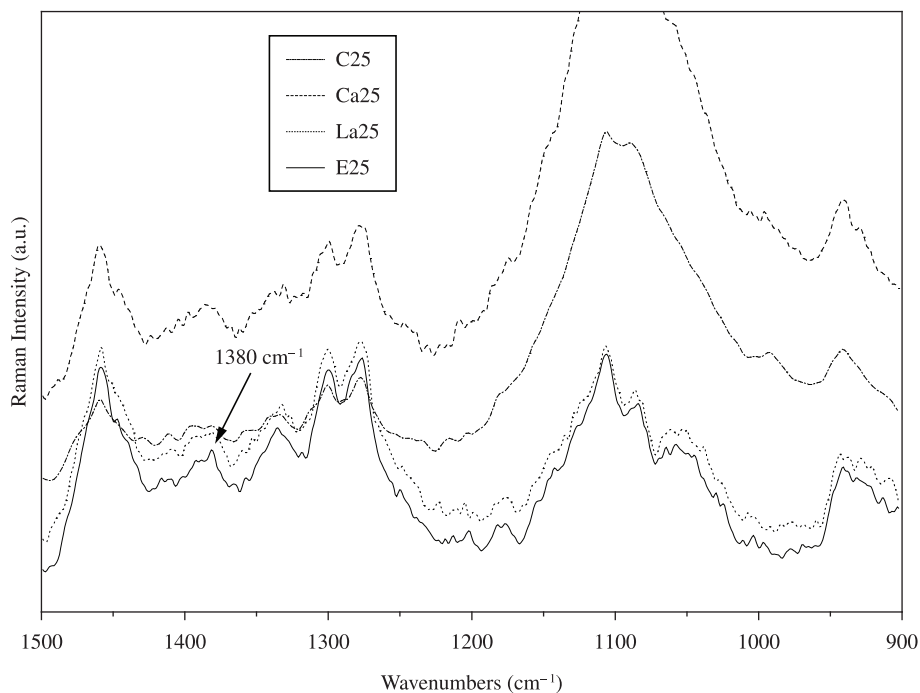


Figure 3. Raman spectra of samples containing 25% glycerol in TPS (partial of 1000 to 1500 cm⁻¹).

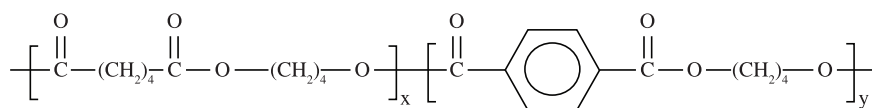


Figure 4. Chemical structure of poly (butylene adipate-co-terephthalate) (PBAT).

in the temperature range from 20 to 450 °C. The temperature range for the first stage of thermal degradation was around 75 °C and is associated to the loss of water present in the formulation.

The second stage, which the maximum degradation temperature was in the range of 335-343 °C, is associated to the degradation of TPS and fatty acids. Scapim^[28], studying PBAT/TPS blend films,

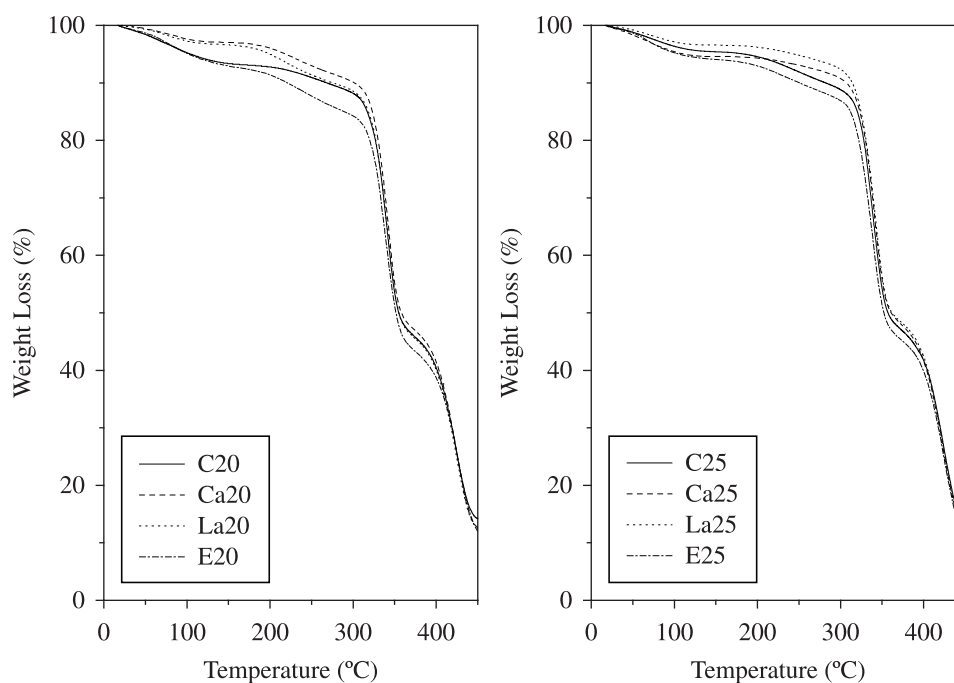


Figure 5. TGA curves of the films containing starch, glycerol, PBAT and fatty acids.

Table 2. Temperature at the maximum rate of degradation of each stage (Tmax) and residues content, obtained by TGA analysis of the samples from films of starch, glycerol, PBAT and saturated fatty acids.

| Film | Glycerol (%) | Stage | Tmax (°C) | Residue content (%) |
|------|--------------|-------|-----------|---------------------|
| C | 20 | I | 86.9 | 14.4 |
| | | II | 340.6 | |
| | | III | 423.3 | |
| | 25 | I | 72.0 | 13.5 |
| | | II | 340.7 | |
| | | III | 424.1 | |
| Ca | 20 | I | 85.7 | 12.8 |
| | | II | 342.2 | |
| | | III | 424.4 | |
| | 25 | I | 68.0 | 9.6 |
| | | II | 340.5 | |
| | | III | 423.4 | |
| La | 20 | I | 76.2 | 16.5 |
| | | II | 216.8 | |
| | | III | 341.0 | |
| | | IV | 424.7 | |
| | 25 | I | 74.0 | 10.3 |
| | | II | 342.5 | |
| E | 20 | III | 423.9 | 16.4 |
| | | I | 74.0 | |
| | | II | 236.8 | |
| | | III | 341.1 | |
| | 25 | IV | 426.4 | 8.9 |
| | | I | 65.4 | |
| | 25 | II | 336.5 | |
| | | III | 424.7 | |

C – films with 30% of PBAT, 20 and 25% of glycerol compared to TPS. Ca, La, E – films with 30% of PBAT, 20 and 25% of glycerol compared to TPS and 1.5% of caproic, lauric and stearic acid, respectively.

obtained a value of 317 °C for maximum temperature of thermal degradation of the films consisting only of starch and glycerol.

The third stage corresponds to the PBAT degradation and showed a Td around 424 °C. Scapim^[28] observed the temperature at the maximum rate of PBAT degradation of 397 °C, and Alves^[29], studying films of natural fibers and PBAT, obtained a Td of 375 °C.

For the films with higher glycerol content containing lauric or stearic acid, La25 and E25, did not present a stage only related to the thermal degradation of fatty acids, as observed for the samples with 20% glycerol. This may due to the glycerol in the blend that might have increased the interaction between the components, preventing the degradation of pure components.

Temperatures at maximum rate of degradation stages attributed to the degradation of starch and PBAT were close for all samples, indicating that the components of the blends do not affect the decomposition mechanism of starch and PBAT.

Conclusions

The incorporation of saturated fatty acids with different molecular mass (caproic, lauric and stearic) did not change the nature of the chemical bonds among components in the blends of starch, PBAT and glycerol, according to the thermal analysis, infrared and Raman spectroscopic techniques.

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