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THERMAL AND MECHANICAL PROPERTIES EFFECTS OF THE INCORPORATION OF KRAFT LIGNIN ON POLYETHYLENE TEREPHTHALATE

Lívia De Martin Lazzari [1] – lilazzari@hotmail.com
Eloilson Domingos [1, 2] – eloilson.domingos@gmail.com
Joyce R Araujo[3] – jraraujo@inmetro.gov.br
Wanderson Romão [1, 2] – wandersonromao@gmail.com
[1] Federal Institute of Education, Science and Technology of Espírito Santo, ES, Brazil.
[2] Petroleomic and Forensic Laboratory, Chemistry Department, Federal University of Espírito Santo, 29075-910 Vitória, ES, Brazil.
[3] Materials Metrology Division, Inmetro, 25250-020, Duque de Caxias, RJ, Brazil

Abstract. *In this work, polyethylene terephthalate (PET_R), from soft drink bottles, kraft lignin (LF) and chemically modified lignin (LM) were used to form blends (PET/LF and PET/LM) with the aim to improve the mechanical properties of pure PET. PET/LF and PET/LM blends were produced in 0.5, 1, 3, and 5 wt% lignin. These polymers were processed by melt extrusion and injection molding. The characterization of the produced blends and of PET_R were performed by Fourier transform infrared spectroscopy (FTIR), thermogravimetry analysis (TGA), differential scanning calorimetry (DSC) and mechanical properties (elasticity modulus and tensile strength), where the results were evaluated and compared. FTIR spectra showed the chemical modifications in LM sample while TGA results showed that LF is thermally more stable than LM. DSC results showed that glass transition temperature of PET_R changes with the addition of the lignin. PET/LF blends have enough potential to be used as engineering material due to improving of their mechanical properties in relation to PET_R. PET/LF blends, containing 0.5 wt% and 1.0 wt% lignin, showed an increase in both, elasticity modulus and tensile strength, showing that the interaction between the polymeric matrix and lignin is more efficient when lignin is in small contents.*

Keywords: *polyethylene terephthalate; Kraft lignin; blends; mechanical properties*

1. INTRODUCTION

Synthetic or petroleum-based polymers have many practical uses but it can cause serious environmental problems because of their low biodegradability. Consequently, several strategies to replace or reduce the use of synthetic polymers have been developed (Aziz *et al.*, 2018; Gadioli *et al.*, 2014; Shah *et al.*, 2008; Vanini *et al.*, 2013). Sustainable development opens new

perspectives for products obtained from polymer recycling processes, as they have greater contribution in the total waste generated by the population (Karmakar; De; Goswami, 2018).

Polyethylene terephthalate (PET) is a semicrystalline and thermoplastic aromatic polyester, known for its mechanical properties and lightness, strength and high transparency being largely applied in food and cosmetic packages (Karagiannidis & Stergiou & Karayannidis, 2008; Romão *et al.*, 2009, 2010; Vanini *et al.*, 2013). Currently, recycled PET have been mixed with another polymers or fillers, producing a polymeric blend or a composite, which result in a material with different properties in relation to neat polymer and, in turns, adds value to the end material. Therefore, the compatibility between the components of the mixture is of great importance to achieve satisfactory thermal and mechanical properties for a specific application (Kiziltas & Gardner, 2011; Razak *et al.*, 2013; Torres-Huerta *et al.*, 2014).

Lignin is one of the three main constituents of a plant. It is the second most abundant polymer in the world, after cellulose. Generally, its structure depends on the species of wood and the processing condition. Kraft, sulfite and soda are the established processes from which lignin can be obtained (Chakar & Ragauskas, 2004; Laurichesse & Avérous, 2014).

Lignin from the Kraft process is produced by pulp and paper mills through the pulping process where the cellulose fibers and lignin are separated. Black liquor is a by-product of the wood pulping process, in which it has suspended particulate solids and organic compounds, that may have between 10 and 50 wt% Kraft lignin (Haddad *et al.*, 2016; Laurichesse & Avérous, 2014; Luiz *et al.*, 2018).

Nowadays, most of the lignin produced in the pulp and paper industry is burned for energy production. However, how the lignin is a complex polyfunctional macromolecule that is composed of a large number of polar functional groups, it has potential for several applications and can generate products with higher added value (Glasser *et al.*, 1983; Sahoo & Misra & Mohanty, 2011; Sameni *et al.*, 2018).

Polymer composites are a convenient method for developing products with desirable properties. The addition of lignin into PET has been used for the development of polymer composites and may undergo chemical modification before mixing with the polymer (Jeong *et al.*, 2012; Kadla & Kubo, 2004; Laurichesse & Avérous, 2014; Luiz *et al.*, 2018).

The objective of this work is to develop a new engineering material using PET reinforced with lignin obtained by Kraft process, with and without chemical modification, by melt extrusion and injection molding, comparing the thermal and mechanical properties of the composites with the PET_R matrix.

2. MATERIALS AND METHODS

2.1 Materials

Lignin from the Kraft process, referred here as LF, was supplied by FIBRIA CELULOSE S/A. Chemical modification of the lignin was done using ethylic alcohol 95% (v/v) (CAS 64-17-5), sodium hydroxide 97% (wt/wt) (CAS 1310- 73-2) and monochloroacetic acid 99% (wt/wt) (CAS 79-11-8), all supplied by Sigma Aldrich.

The process of obtaining the lignin was made by precipitation of the black liquor following the following steps: reduction of the pH of the liquor (start solution has pH>13) with CO2 injection, filtration of precipitated lignin, suspension of the filtered lignin in a H2SO4 solution, pH 2.5, filtration and washing of the lignin with acidic solution (pH 2.5 and 60 ° C).

PET was obtained by grinding colorless PET bottles in a Retsch mill, SM300 model with 2 mm sieve and 1500 rpm rotation, denominated in this work as PET_R. Bottle labels were removed and the area with glue impregnation was discarded.

2.2 Lignin Modification

The lignin modification was performed as described by Da Silva *et al.* (2011). In this method, 10.0 g of lignin was suspended in 270 mL of ethanol 95% (v/v) under continuous stirring with a mechanical stirrer (Ethik Technology, model 105), where 27 mL of a NaOH 30% aqueous solution (wt/v) was added at a rate of 1 mL min-1 using an electronic pipette (Transferpette S) at room temperature during 27 min. After addition of the NaOH solution, the final solution was stirred for further 60 min.

The next step was to add 12.0 g of monochloroacetic acid, gradually during 30 min, without further agitation. So, the mixture was stirred for additional 210 min, at 55 ° C. The residue was suspended in 670 mL of ethanol solution 95% (v/v), which was neutralized with glacial acetic acid and, subsequently, filtered. After filtration, the product was washed three times with approximately 50 mL of ethanol solution 95% (v/v) to remove the impurities and by-products, and dried at 60 °C in an oven until the mass of the product remained constant. The modified lignin was denominated in this work as LM (Da Silva *et al.*, 2011).

2.3 Specimens Preparation

Milled PET_R and LF and LM samples were dried in a vacuum oven at 60 °C for 24 h prior to melt extrusion and injection molding.

PET_R lignin blends were fabricated by extrusion using a Thermo Scientific Haake MiniLab II extruder. The reference specimens (pure PET, *i.e*. PET_R) and its blends were injected in a Thermo Scientific Haake MiniJet II injector. A temperature of 275 °C and a screw rotation speed of 100 rpm were used in the extrusion process. In the injection process, the injection temperature was 275 °C, the injection pressure was 450 bar, de injection time 4 seconds e the molding temperature was 25 °C. The formulations of the specimens are shown in Table 1.

Table 1. Composition of the formulations used to fabricate the tensile specimens.

Sample	PET_R (wt%)	LF (wt%)	LM (wt%)	Formulation name
1	100	0	0	PET_R
2	99.5	0.5	0	PET/LF 0.5wt%
3	99	1.0	0	PET/LF 1.0wt%
4	97	3.0	0	PET/LF 3.0wt%
5	95	5.0	0	PET/LF 5.0wt%
6	99.5	0	0.5	PET/LM 0.5wt%
7	99	0	1.0	PET/LM 1.0wt%
8	97	0	3.0	PET/LM 3.0wt%
9	95	0	5.0	PET/LM 5.0wt%

2.4 Fourier transform infrared spectroscopy – ATR-FTIR

The attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were obtained on a Frontier spectrometer from manufacturer Perkin Elmer. Each spectrum was recorded with a mean of 16 consecutive scans, with a resolution of 4 $cm^{-}1$ in the working range of 4000 to 630 cm^{-1}.

2.5 Thermogravimetry analysis (TGA)

Thermogravimetry analysis (TGA) was performed on a TA Instruments SDT Q600 instrument. Approximately 10 mg of sample was heated in alumina crucible (25 °C to 900 °C) at a heating rate of 10 °C min-1 under a nitrogen flow of 20 mL min-1.

2.6 Differential scanning calorimetry (DSC)

Differential Scanning Calorimetry (DSC) was done using TA Instruments Q200. Approximately 5 mg of sample (injected material was used) was heated in alumina crucible (25 °C to 400 °C) at a heating rate of 10 °C min-1 under a nitrogen flow of 50 mL min-1.

2.7 Tensile measurements

The tensile tests were performed using ISO 527-2-5A standard. The tests were conducted at the facilities of the Federal University of Espírito Santo (UFES)/LABPETRO, using a Lloyd Instruments LR5K Plus universal testing machine. The measurements conditions were: load cell of 5 kN, a 50 mm strain gauge with a measurable deformation of 25 mm and using a crosshead speed of 1 mm min-1.

3. RESULTS AND DISCUSSION

3.1 ATR-FTIR

The ATR-FTIR spectra of the LF and LM lignins are shown in Fig. 1a. One of the significant changes in the ATR-FTIR spectra, Fig. 1a, was the disappearance of the band in 1710 cm^{-1} of unmodified lignin, *i.e*. LF, which is attributed to the vibration of the carbonyl group conjugated to the aromatic ring. LM has two high intensity bands at 1598 and 1416 cm^{-1} attributed to the carboxylate. The appearance of these intense bands proves the efficiency of the carboxylation process in the modification reaction. The bands related to the stretching of the CH_2 group (≈ 2938 and 1453 cm^{-1}) are found in both the LF and LM samples, indicating that these groups did not participate in the chemical reaction (Da Silva *et al*., 2011).

FTIR spectrum shown in Fig. 1b corresponds to the PET_R sample and its respective blends with 1.0 wt% LF and LM content. The FTIR spectrum for PET_R shows bands of typical axial deformation in the regions of 2900 cm^{-1} corresponding to CH_2 group, 1714 cm^{-1} to C=O group, 1239 and 1117 cm^{-1} to the terephthalate group and 1092 and 1041 cm^{-1} to the methylene group and vibration of the C-O ester bond (Edge *et al.*, 1996; Pereira *et al.*, 2017; Silverstein & Webster & Kiemle, 2002).

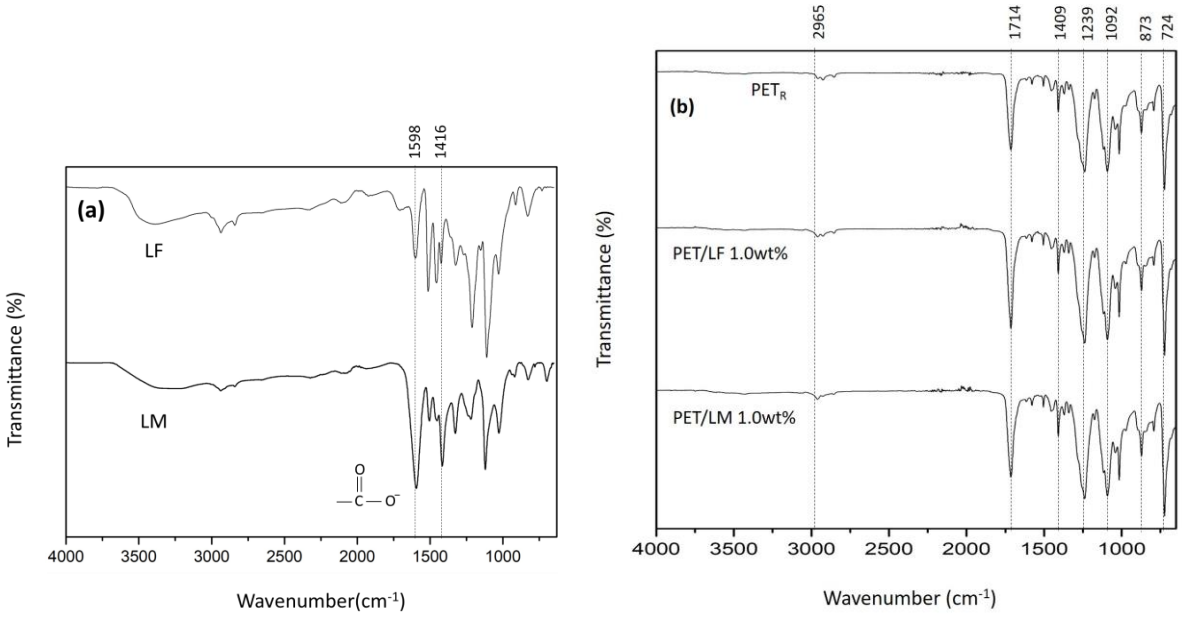

Figure 1 - ATR-FTIR spectra of (a) lignins obtained by Kraft process (LF) and modified (LM); (b) PET_R, and their respective blends (1.0 wt%) containing LF and LM.

Analyzing the data, it was observed that when comparing the FTIR spectrum of PET_R with the PET/LF and PET/LM, it was not possible to observe significant differences among them. This may be due to the low concentration of lignin used in the composite formulation. In addition, the most abundant bands of the LF and LM samples (1400 to 1000 cm^{-1}) overlap those observed for the PET_R polymer sample. A similar behavior was reported by literature (Luiz *et al.*, 2018), where the presence of LF lignin, in small amounts, in the composition of PET blends can not be detected by the ATR-FTIR technique. The author suggests that this may be due to the existence of a weak hydrogen bonding interaction between the two polymers, thus causing not shift or changes in the FTIR spectra related to the vibrational bands of chemical bonds.

3.2 TGA

TGA analysis of in LF and LM lignins is shown in Fig. 2. It is possible to observe, around 100 °C, the loss of ≈ 6 wt% for LF lignin and 22 wt% for LM lignin. This behavior is attributed to moisture loss. However, the chemical decomposition of the LF and LM lignins occurs in a wide temperature range, with a higher mass loss being observed between 200-700 ºC. LF loses about 81.02 wt% while the LM loses 34.01 wt% (Da Silva *et al.*, 2011; Grandmaison & Thibault & Kaliaguine, 1987; Jakab & Faix & Till, 1997).

Due to the complexity of lignin structure, the decomposition of this material involves several competing reactions. Lignin presents several chemical structures within its macromolecule, so that during the thermal degradation process, several bonds containing different binding energies are broken (Da Silva *et al.*, 2011; Grandmaison & Thibault & Kaliaguine, 1987; Jakab & Faix & Till, 1997). One of the mechanisms of degradation of lignin occurs through its dehydration, producing derivatives with unsaturated side chains. Carbon monoxide, carbon dioxide and methane are also formed (Hoareau *et al.*, 2004; Meier & Faix, 1999). The decomposition of aromatic rings occurs above 400 ºC (Rohella *et al.*, 1996). Prolonged heating leads to saturation of aromatic rings, disruption of C-C bonds and release of smaller molecules (such as water, CO_2, CO) that after may be rearranged (Hoareau *et al.*, 2004).

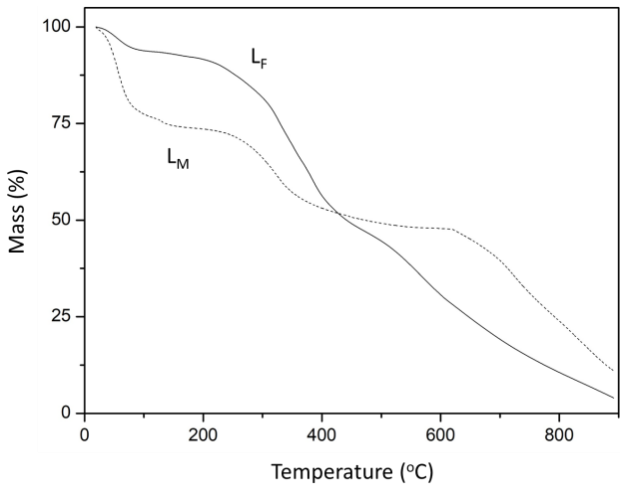

Figure 2 – TGA of the in natura lignin, LF, modified lignin, LM.

It is observed that LF lignin is more thermally stable compared to LM lignin, Fig. 2. In general, chemical modifications in the structure of lignin resulted in the incorporation of water molecules into its structure, making it more unstable. The total mass losses of LF and LM when heated to 900 °C were 96.02 and 88.93 wt%, respectively. It is further observed in Fig. 2 that the lignin continue to decompose at temperatures higher than 900 °C.

3.3 DSC

The DSC technique is the most accepted method to define the glass transition temperature (T_g) of the lignin samples. Normally, the T_g values of several non-derived lignins vary from 90 to 180 ºC. T_g of lignin is often difficult to detect due to the complex structure of this polymer. However, it is detected from interval where occurs a slope change in the heating curve (Awal & Sain, 2013; Cachet & Camy & Benjelloun-Mlayah, 2014; Gordobil *et al*., 2015). The T_g of LF and LM are 100 °C and 127 °C respectively, Table 2.

The variation in the values of T_g, T_c and T_m in relation to PET_R is a function of the processing and of the amount of lignin added. The PET_R presented values of T_g, T_c and T_m of 63.3, 119.5 and 253.8 ºC, respectively, Table 2. The DSC curves (Table 2) for the blends show well defined thermal events, such as the T_g slope, exothermic crystallization and endothermic melting peaks.

In general, PET/LF blends increases T_g and T_m values to ≈ 69-70 ºC and 257 ºC, respectively. This increase was higher in PET/LF blends than PET/LF blends (T_g ≈ 75 ºC and T_m = 258 ºC, except for PET/LM 5.0 wt% sample). The T_c has a maximum decrease in three units (119.5 → 116.4 ºC) of temperature for the PET/LF 1.0 wt% blend, being the most significant variation for PET/LM blends (T_c = 114 → 110 ° C), Table 2.

Lignin macromolecule has polar groups capable of producing "chemical" (dipole-dipole) interactions that tend to get closer to the PET_R chains. These secondary forces may have contributed to the increase of T_g and T_m for the studied blends. The PET/LM blends presented higher increases in these two properties in relation to PET/LF. Probably, the incorporation of carboxylate groups in the chemical modification favored the increase of polarity of the lignin, which may have taken more pronounced increase of T_g and T_m. (Canevarolo, 2006; Wellen & Canedo & Rabello, 2012).

The parameters obtained in the DSC measurements can be seen in Table 2, such as T_g, crystallization temperature (T_c), melting temperature (T_m), melting enthalpy (ΔH_m) and crystallinity degree (X_c).

Table 2 - DSC results for PET_R and PET/LF and PET/LM blends.

Sample	T_g (ºC)	T_c (ºC)	T_m (ºC)	ΔH_m (J/g)	X_c (%)
PET_R	63.30	119.50	253.79	-4.450	3.18%
PET/LF 0.5wt%	70.29	117.37	257.18	-4.901	3.52%
PET/LF 1.0wt%	69.70	116.42	256.59	-5.491	3.96%
PET/LF 3.0wt%	68.34	116.89	256.49	-5.889	4.34%
PET/LF 5.0wt%	68.80	117.99	253.09	-5.937	4.46%
PET/LM 0.5wt%	74.96	113.61	255.02	-5.715	4.10%
PET/LM 1.0wt%	74.76	113.05	258.26	-5.262	3.80%
PET/LM 3.0wt%	74.77	110.46	258.15	-5.659	4.17%
PET/LM 5.0wt%	74.98	109.45	256.34	-5.704	4.29%

Another point to be considered is that, when fillers are added in a polymer, the properties of the final material are expected to be intermediate between the properties of the two components (Rabello, 2000). This behavior can be observed in the T_g of the blends, where the its values are between those of the pure polymer, PET_R and the of LF and LM lignins.

The crystallinity degree percentages were obtained by comparing the enthalpy of each formulation with the theoretical enthalpy of the 100% crystalline PET (ΔH_m = 140 J g^{-1}) (Canevarolo, 2006) through Eq. (1) below:

$$X_c = \frac{\Delta H_m}{\Delta H_m^* * \varphi} * 100\% \quad (1)$$

When ΔH_m is the melting enthalpy of the PET in the analyzed blend, ΔH^*_m is the melting enthalpy of the 100% crystalline hypothetical PET and φ is the mass fraction of PET_R in the blend.

In general, in all cases, a low value of X_c was observed. This is due to the process of production of the specimens, performed by injection. The large differences between injection and mold temperatures ensured a material with predominantly amorphous characteristics, where the PET_R chains did not have enough time for organization. In addition, the presence of LK and LM lignins favor the crystallization of PET_R, increasing the X_c. It is possible that this material is acting with a nucleating agent (Luiz *et al.*, 2018; Wellen & Canedo & Rabello, 2012).

3.3 Tensile Tests

The results of the mechanical tensile tests for blends in terms of modulus of elasticity (*E*), maximum strength (σ) and strain at break (ε_{rup}) are listed in Table 3.

From the results of Table 3**,** we can see that the lignin modification process, *i.e.* LM lignin, did not produce an efficient molecular interaction in order to improve the mechanical properties of their blends. This is evidenced by the considerable reduction in values of σ, Table 3. This parameter correlates the tensile transfer capacity from the matrix to the filler, where it is well known that the higher interaction between the phases is an indicative of a higher the maximum tensile transfer from matrix to filler.

Table 3 – Results evaluated from tensile tests.

Sample	E (GPa)	ΔE (GPa)	σ (Mpa)	Δσ (Mpa)	ε_{rup} (%)	$\Delta\varepsilon_{rup}$ (%)
PET_R	1.33	±0.04	57.31	±0.60	NB	NB
PET/LF 0.5wt%	1.47	±0.06	60.20	±0.85	NB	NB
PET/LF 1.0wt%	1.55	±0.05	61.62	±0.67	NB	NB
PET/LF 3.0wt%	1.71	±0.05	39.56	±1.28	2.0	±0.54
PET/LF 5.0wt%	1.76	±0.12	37.77	±2.80	2.1	±0.29
PET/LM 0.5wt%	1.66	±0.29	20.59	±3.60	0.9	±0.16
PET/LM 1.0wt%	1.43	±0.22	20.41	±1.78	1.1	±0.40

*NB – Didn't break.

Formulations containing 3 wt% and 5 wt% LM were not tested because of difficulties in making these specimens. The addition of the LM matrix in the PET_R in these proportions weakened the material, thus, the specimens showed cracks even before the mold was withdrawn.

The elasticity modulus values correlate directly with the rigidity of the material (Canevarolo, 2006). An increase in this parameter indicates a higher resistance to deformation in the elastic regime. Despite the increase in this parameter of the blends with LM, we should look at these data carefully. We can see an increase in the standard deviation of this parameter. Again, it is shown that the fragility imposed to the material due to the addition of LM generates a high variability in the tensile tests results.

Table 3 shows an increase in *E* values when the LF lignin is added. This same behavior has been reported in the literature (Jeong *et al.*, 2012; Luiz *et al.*, 2018). PET/LF blends containing mainly 3% and 5% wt% of LF showed an increase of 29% and 32% in the tensile strength results measured in the elastic regime, respectively, in relation to PET_R. In relation to the values of σ, an increase was observed in formulations containing 0.5 and 1 wt% of LF. However, in formulations containing 3 and 5 wt% LF lignin, this parameter showed a considerable decrease (31 and 34% decay, respectively). In general, PET/LF blends containing 0.5 and 1.0 wt% LF had an increase in both mechanical properties, *E* and σ. This shows that the interaction of the matrix with LF lignin in small amounts is more satisfactory. It was observed that PET/LF, 0.5 wt% and 1.0 wt% blends, presented an increase of *E* and σ in the order of 11-17% and 5-8%, respectively. These results suggest that tensile transfer from the matrix to the filler occurs most efficiently when LF was added in small amounts (<1 wt%).

It is believed that the lignin particles may have acted as defect points in the matrix. This effect is best evidenced from the results of rupture strain. It is observed an increase in the fragility with the addition of lignin in the blends (JeonG *et al.*, 2012; Luiz *et al.*, 2018). Thus, it is clear that the formulations with less amount of LF lignin tend to deform much more than those with higher amount of filler, because in this case, the stresses are predominantly absorbed by the matrix and not by the filler.

PET/LF blends 0.5 and 1.0 wt% show an increase in the values of *E* and σ. In practice, recycled materials made from PET_R and some fibers are used in tissue production (Abipet, 2010; Rwei & Ni, 2004). Therefore, the increase of its mechanical properties can suggest an increase in the durability of these clothes.

4. CONCLUSION

In this study, LF and LM lignins were used to produce PET composites. The results of ATR-FTIR, TGA and DSC showed that chemical modifications occurred in LM sample. The results of TGA indicate that LF is thermally more stable than LM, so we concluded that the thermal stability of LF is one of the reasons for better mechanical properties of LF blends.

The blends showed no significant differences in the ATR-FTIR spectra. On other hand, the DSC curves showed a higher glass transition temperature for the PET_R/lignin blends when compared with pure PET_R.

PET/LF blends have shown promise for use as engineering material due to excellent molecular interaction with improvements in their mechanical properties, where the concentrations of 0.5 and 1.0 wt% of LF showed an increase in both the modulus of elasticity and the maximum tensile strength. This indicates that the interaction between the polymer matrix and lignin is satisfactory, when the filler is used in small amounts.

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