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Lignin as additive in polypropylene/coir composites: Thermal, mechanical and morphological properties

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ABSTRACT

PP/CF composites were prepared and the effect of lignin incorporation in the presence and absence of compatibilizer (maleic anhydride grafted polypropylene, PP-g-MA) was investigated by means of mechanical, thermal and morphological properties. Lignin added to the composite was obtained by the Acetosolv process. The composites were prepared in a Haake torque rheometer and assessed by means of tensile testing, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and scanning electron microscopy (SEM). The results showed that in the absence of PP-g-MA, incorporation of lignin did not affect tensile strength and in its presence this property was reduced. Thermal analysis revealed that incorporation of lignin in the composites resulted in increase in both the initial thermal decomposition temperatures and oxidation induction times.

1. Introduction

Incorporation of fibers from lignocellulosic materials – natural composites in which the cellulose fibers are bound together by lignin and hemicellulose – to reinforce polymeric materials for the production of synthetic composites has been intensively investigated in recent decades. Advantages of these fibers compared to synthetic fibers are related to their lower cost, low abrasion in processing equipment, low density and because they are obtained from renewable sources (Jawaid & Abdul Khalil, 2011; Silva, Souza, Machado, & Hourston, 2000; Tomczak, Sydenstricker, & Satyanarayana, 2007).

Composite properties may originate from several factors such as characteristics of the polymer matrix, fiber type and adhesion between the phases.

Polymers used as matrices for natural fiber composites should be processed at temperatures below the degradation temperature of lignocellulosic fibers (around 200 °C). These polymers include polypropylene (PP) which has a processing window between 180 °C and 240 °C.

Several types of fibers have been studied as reinforcement, including coir, curaua, sisal, bamboo, and sawdust (Bettini, Uliana, & Holzschuh, 2008; Bonse et al., 2010; Brígida, Calado, Gonçalves, & Coelho, 2010; Rozman et al., 2000; Spinacé, Fermoseli, & De Paoli, 2009). These fibers may differ in the composition of their main constituents (lignin, cellulose and hemicellulose), structure and microfibrillar angle. In addition, climate, soil conditions and plant age will influence chemical and structural composition of same kind fibers (John & Thomas, 2008).

Coir fibers (CF) have low cellulose content and high microfibrillar angle, yielding lower tensile strength and high elongation compared to other types of lignocellulosic fibers. Coir fiber is among the fibers with high lignin content, which may vary by region and growth conditions (Satyanarayana, Sukumaran, Mukherjee, & Pillai, 1986).

Lignin has a complex and non-uniform structure with aliphatic and aromatic constituents. It consists of phenylpropanoid units having various substituent functional groups (Fig. 1). Depending on the plant species the structure of lignin may vary by botanical origin, growing conditions of the original plant, extraction conditions, etc. The main precursors are three aromatic alcohols, namely p-coumaryl, coniferyl and sinapyl alcohols, which undergo crosslinking and give rise to the complex structure of lignin (Buranov & Mazza, 2008; Pouteau, Dole, Cathala, Averous, & Boquillon, 2003; Pouteau, Baumberger, Cathala, & Dole, 2004).

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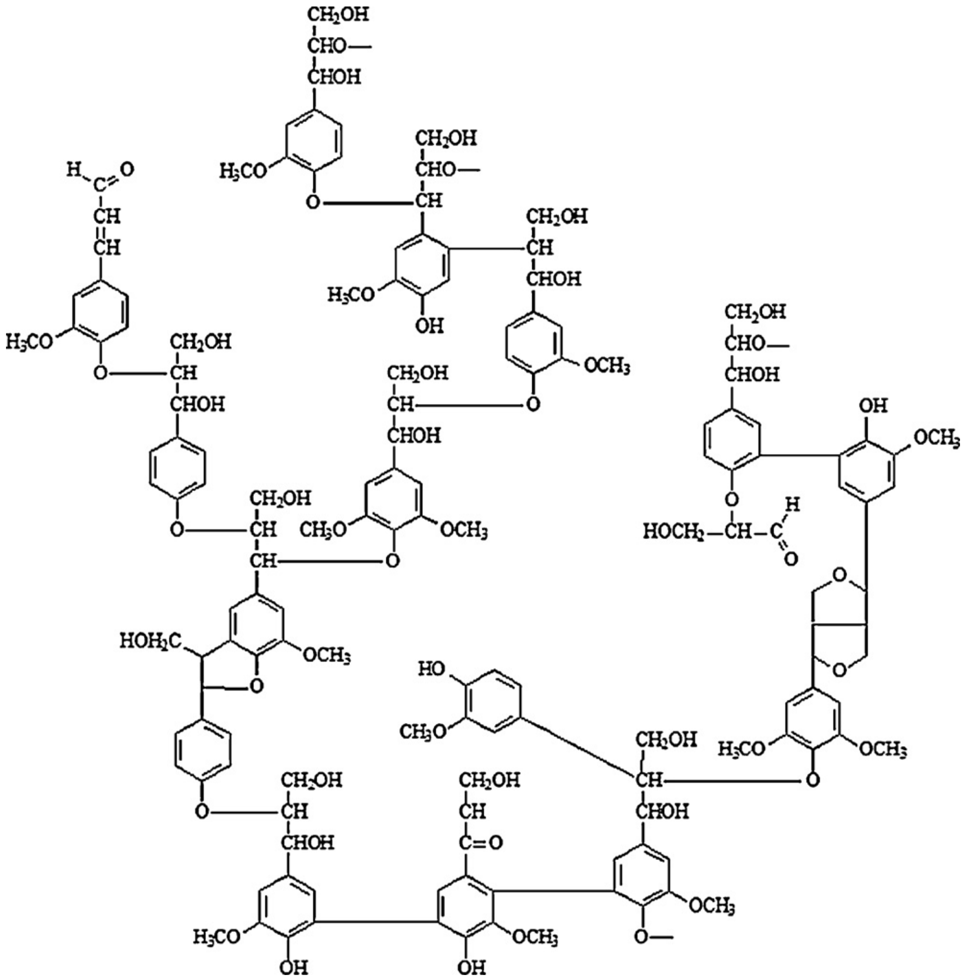

Fig. 1. Representation of the structure of lignin.

This polymer can be isolated and, currently, there are several methods for extracting lignin from lignocellulosic materials. However, the structure of natural lignin is not preserved in any of these techniques, because delignification involves the breaking of covalent bonds in natural lignin.

These procedures include acetosolv, which involves extraction by solubilization in acetic acid, acetylating some phenylpropanoid hydroxyls present in the structure and then precipitation of acetylated lignin by increasing pH (Benar, Gonçalves, Mandelli, & Schuchardt, 1999).

Due to its structure, lignin has been investigated as compatibilizer and as antioxidant. Utilization as compatibilizer is justified by the presence of both aliphatic and polar groups, which may provide compatibility between nonpolar polymers and lignocellulosic fibers. The antioxidant function arises from its structure similar to hindered phenols used as primary antioxidants in polymers (Gregorová, Cibulková, Kosiková, & Simon, 2005; Pouteau et al., 2003; Rozman et al., 2000)

Antioxidants, commonly used in polymers, continue to act even after disposal in landfills, which is not desirable because this slows down the decomposition process of the generated polymer waste. The use of lignin as an antioxidant would overcome this disadvantage since it acts as an antioxidant during the product's lifetime and is more susceptible to biodegradation in disposal environments.

Lignins are polar, thus exhibiting low solubility in nonpolar media such as polyolefins, which may limit reaction with the polymer radicals produced during processing and service life of the product (Pouteau et al., 2003).

Studies by Gregorová, Cibulková, Kosiková, and Simon (2005), however, showed increased antioxidant efficiency when lignin was added along with commercial antioxidants such as Irganox 1010 in virgin and recycled polypropylene.

In this context, the aim of this study was to assess the effect of lignin incorporation on the mechanical, thermal and morphological properties of polypropylene/coir composites in the presence and absence of compatibilizer.

2. Experimental

2.1. Materials

PP powder was supplied by Quattor (Mauá, Brazil), under code HP550K, with melt flow rate (MFR) of 4.0 g/10 min. Antioxidant and lubricant incorporated to the formulations were Irganox B215 and calcium stearate, respectively. Irganox B215 is a mixture of a phenolic antioxidant (Irganox 1010) and a phosphite (Irgafos 168) supplied by Ciba Especialidades Químicas (São Paulo, Brazil).

The compatibilizer used was PP grafted with maleic anhydride (PP-g-MA), under code Polybond 3200 (MFR = 110 g/10 min at 190 °C and 2.16 kg), supplied by Crompton-Uniroyal Chemical (São Paulo, Brazil).

Green coir fiber with length of 12–14 cm was supplied by Projeto Coco Verde (Rio de Janeiro/RJ).

Lignin was obtained in the laboratory by the acetosolv process from coir.

Table 1
Compositions of prepared composites.

Sample	C_{PP} (%)	C_{CF} (%)	C_L (%)	C_{MA} (phr)
CL0	70	30	–	–
CL5	70	25	5	–
CL10	70	20	10	–
CL0MA	66	30	–	4
CL5MA	66	25	5	4
CL10MA	66	20	10	4

C_{PP}: polypropylene concentration; C_{CF}: coir fiber concentration; C_L: lignin concentration; C_{MA}: PP-g-MA (compatibilizer) concentration.

2.2. Methods

The coir fibers were dried at 70 ± 3 °C for 72 h and ground in a Wiley type cutting mill (TE-6500 Tecnal), using a 1 mm screen. After the milling process the concentrations of constituent holocellulose (Wise, Murphy, & D' Addieco, 1946) and lignin (ASTM D-1106) were determined.

Lignin extraction: 100 g of coir fibers were subjected to extraction with a solvent mixture composed of 93% glacial acetic acid and 0.3% hydrochloric acid p.a. (in relation to the mass of solvent) and refluxing for 3 h at 110 °C. The solvent/fiber ratio was 10/1 wt/wt. After extraction the mixture was filtered and rinsed with 85% acetic acid at 80 °C and subsequently with distilled water at 80 °C. Next, the material was concentrated in a rotary evaporator by reducing the volume in 90%. The concentrated extract was added dropwise to water at 80 °C under stirring until precipitation of the lignin. After precipitation, lignin was filtered, washed with water at 60 °C until neutral pH and dried in an oven at 60 °C (Benar et al., 1999).

The final material was added to the composite at different concentrations to verify the influence of lignin on compatibilization.

The polypropylene/coir composites (PP/CF) were prepared in a Haake torque rheometer, equipped with a Rheomix 600p mixing chamber at the following conditions: temperature 180 °C, rotor frequency 50 rpm and total mixing time of 10 min. The compositions presented in Table 1 were obtained in duplicate. The content of lignocellulosic material was kept at 30%, based on previous study (Bettini et al., 2010). When lignin was incorporated the amount of coir was reduced to maintain the total content of lignocellulosic material at 30%.

Prior to mixing fiber and lignin were dried in an oven for 24 h at 80 °C.

Type IV tensile test specimens were obtained by compression molding at 180 °C. Tensile tests were performed in an Instron 5567 computerized universal testing machine, according to ASTM 638 at test speed of 5 mm/min and temperature of 23 °C.

Thermogravimetric analyses (TGA) were conducted in a Q-50 TA Instrument apparatus. Samples with masses between 10 and 15 mg were heated in nitrogen atmosphere at a rate of 20 °C/min from room temperature to 700 °C.

Oxidation induction time (OIT) measurements were performed by differential scanning calorimetry (DSC) in a Q100 TA Instruments calorimeter. Samples of 7–10 mg were heated at a rate of 20 °C/min up to 180 °C in nitrogen atmosphere. After 3 min at 180 °C the atmosphere was changed to oxygen and oxidation induction time was measured.

The fractured surfaces obtained in tensile tests were coated with a gold–palladium alloy and examined in a CamScan CS 3200LV scanning electron microscope (Cambridge) under high vacuum (10–5 mbar).

3. Results and discussion

3.1. Determination of lignin and holocellulose content from coir fiber

Lignin and holocellulose contents were determined for proper interpretation of the results obtained from the composites. The lignin and holocellulose contents obtained were 30.1 ± 2.9% and 72.5 ± 2.4%, respectively.

The values of insoluble lignin content obtained in our experiments are lower than those found in the literature, which range from 36 to 47%. These differences can be attributed to the nature of the fiber, which is a consequence of the cultivation region, climatic conditions, plant age and species (Bilba, Arsene, & Ouensanga, 2007; Espert, Vilaplana, & Karlsson, 2004).

Regarding the content of holocellulose, which represents the sum of cellulose and hemicellulose contents, the results indicate that this amount makes up the major part, as expected.

3.2. Mechanical properties

Table 2 contains the tensile test results. Analysis of the first set of results, which assesses the incorporation of lignin in the PP/CF composites, shows that lignin incorporation does not affect composite tensile strength. In addition, large variability in % elongation was observed.

Addition of compatibilizer (PP-g-MA) resulted in an increase in tensile strength and reduction in % elongation. Standard

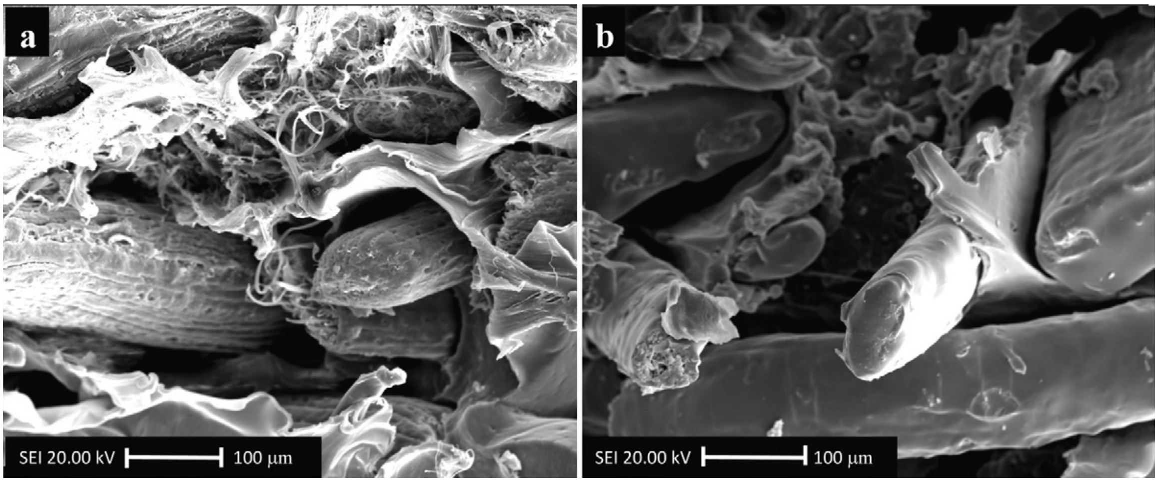

Fig. 2. Micrographs of tensile fractured surfaces of the following composite samples: (a) PP/CF (70/30) and (b) PP/CF/lignin (70/20/10).

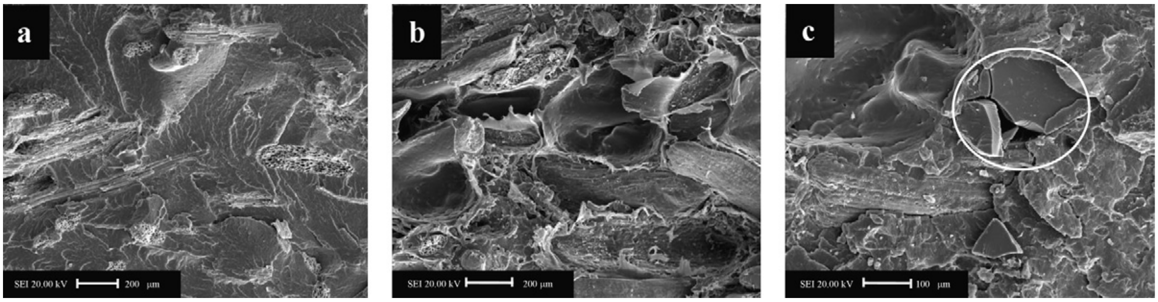

Fig. 3. Micrographs of tensile fractured surfaces of the following composite samples: (a) PP/CF/PP-g-MA (70/30/4), (b) and (c) PP/CF/lignin/PP-g-MA (70/20/10/4).

Table 2
Lignin and holocellulose contents in the coir fibers.

Composition		
(PP/CF/lignin)/PP-g-MA	Tensile strength (MPa)	Elongation at break (%)
(70/30/0)/0	11.6 ± 3.6	3.3 ± 3.2
(70/25/5)/0	11.3 ± 1.4	13.8 ± 9.6
(70/20/10)/0	10.8 ± 0.8	14.9 ± 7.5
(70/30/0)/4	22.7 ± 3.8	1.3 ± 0.9
(70/25/5)/4	20.6 ± 2.1	2.7 ± 1.3
(70/20/10)/4	18.7 ± 2.0	2.5 ± 1.2

deviations were lower for all samples, whether containing lignin or not, confirming the effectiveness of the compatibilizer in improving adhesion and hence providing stress transfer from the matrix to the fibers. However, when lignin content was increased in samples compatibilized with PP-g-MA, tensile strength decreased and % elongation at break increased. Albeit small, these differences indicate reduced adhesion efficiency between the PP matrix and fibers.

For a better understanding of the results obtained in tensile tests, fractured samples were investigated in scanning electron microscopy. Fig. 2 contains micrographs of the fractured surfaces of PP/CF composites, with and without lignin, and Fig. 3, micrographs of the fractured surfaces of PP/CF/PP-MA composites, with and without lignin.

Fig. 2 shows fibers with a rough surface (a) and with a very smooth coating (b). These micrographs indicate that the coir fibers were coated with lignin, reducing physical anchoring between fibers and matrix provided by surface irregularities. It is interesting to note that the values of tensile strength did not change, despite the lower cellulose content in the composites containing lignin, since the sum of fiber and lignin was maintained at 30%. Cellulose is the constituent that accounts for the strength of cellulosic fibers; hence this result indicates that the increase in total lignin content might have contributed to increased adhesion because lignin is the least polar constituent of lignocellulosic fibers.

In examining Fig. 3, it appears that incorporation of lignin reduced composite compatibility. Moreover, no coating is seen on the fibers, likely indicating the formation of a third phase consisting of lignin, which is highlighted in the circle in Fig. 3c. PP-g-MA consists of a PP backbone, just like the composite matrix, and maleic anhydride branches, which may react or interact with the hydroxyl groups from the lignocellulosic fibers. So, when PP-g-MA is incorporated into the composite it will likely migrate to the composite interface. Lignin, however has a complex structure and is quite bulky, so despite having polar and nonpolar groups in its structure, positioning at the interface is impaired due to steric hindrance when the compatibilizer is present. Hence, a separated lignin phase is formed.

3.3. Thermal properties

Thermal properties of PP/CF composites were assessed to verify the possible antioxidant and protective properties of lignin, since

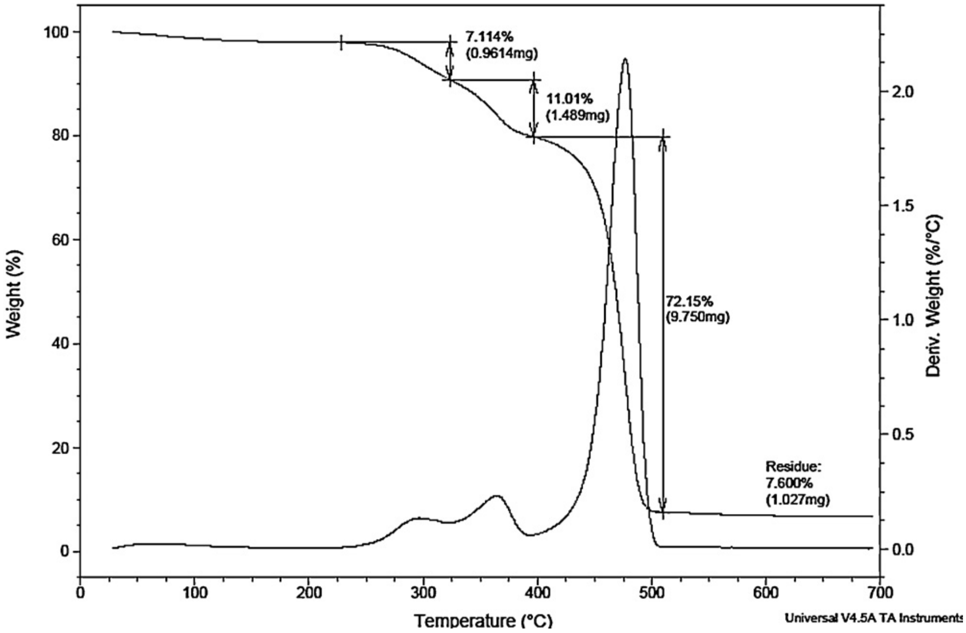

Fig. 4. TGA thermogram of the PP/CF composite containing no lignin.

Table 3
Initial degradation temperature, obtained by TGA, and oxidation induction times, obtained by DSC, of the PP/CF composites, in the presence and absence of lignin, and in the presence and absence of compatibilizer (PP-g-MA).

Sample	Compositions (PP/CF/Lignin)/PP-g-MA	T_1 (°C)	T_2 (°C)	T_3 (°C)	OIT (min)
CL0	(70/30/0)/0	211.2	325.4	396.9	9.41
CL5	(70/25/5)/0	219.2	322.2	396.1	45.7
CL10	(70/20/10)/0	238.2	320.1	393.1	66.7
CL0MA	(70/30/0)/4	191.8	319.8	397.8	11.3
CL5MA	(70/25/5)/4	201.0	320.4	392.5	17.9
CL10MA	(70/20/10)/4	230.7	320.4	391.6	26.3

its degradation temperature is much higher than that of the other fiber constituents.

Thermogravimetric analysis was conducted in nitrogen atmosphere. A typical mass loss curve is shown in Fig. 4. The initial mass loss at temperatures between room temperature and 150 °C is attributed to loss of inter- and intramolecular water. The initial decomposition temperatures of PP/CF composites, with and with no compatibilizer, are presented in Table 3. The PP/CF composite containing neither compatibilizer nor lignin shows initial decomposition temperature at 211.2 °C, which is higher than the initial decomposition temperature of coir at 190.18 °C, obtained under the same conditions (Fig. 5). The higher initial decomposition temperature of the composite is likely due to the protection of the fibers provided by polypropylene as long as they are coated with this polymer.

The addition of compatibilizer PP-g-MA reduced the initial decomposition temperature. This fact may be attributed to the presence of unreacted maleic anhydride in PP-g-MA, which can lead to side reactions during cellulose decomposition.

When lignin was added to the composite the initial decomposition temperature increased for both the compatibilized and non-compatibilized composites.

According to Tomczak et al. (2007) hemicellulose degrades between 200 and 260 °C, cellulose between 240 and 350 °C and lignin between 280 and 500 °C. In our analysis (Fig. 4) two overlapping peaks are observed, as well as mass losses of 23.95% and 43.89% for the decomposition ranges of 190.2–316.9 °C and 316.9–475 °C, respectively, which are very close to those observed by other authors.

From the micrographs presented in Fig. 2b, it can be seen that incorporation of lignin in the PP/CF composite results in fibers with a very smooth surface. These micrographs indicate that the coir fibers became coated with lignin, which acts as a protective barrier against thermal degradation, since lignin has a superior degradation temperature in relation to cellulose and hemicellulose. In the case of the PP/CF composite (Fig. 3b and c) compatibilized with PP-g-MA lignin did not coat the fibers, but became a dispersed phase in PP and hence did not act as a protective barrier for the fibers. However, even so, the initial degradation temperatures of these composites were shifted to higher values in relation to the PP/CF/PP-g-MA composites, without lignin.

The high thermal stability of lignin is due to the presence of complex phenylpropanoid units, which consist of aromatic phenyl groups. These aromatic structures are very stable mainly due to the overlapping of p-orbitals which allows complete delocalization of the π electrons. Moreover, the presence of several hydroxyl groups also contributes to stability since the unpaired electrons also come into resonance, increasing the stability of the aromatic structure and impeding its break, which occurs only at high temperatures (Morrison & Boyd, 1992; Wise et al., 1946).

Since lignin may act as a primary antioxidant oxidation induction time (OIT) analyses were performed. Table 3 presents OIT values of the investigated composites.

The results presented in Table 3 show a sharp increase in OIT when lignin is incorporated into the PP/CF composite. In the absence of compatibilizer this increase is more prominent, which is an indication that lignin may act both as antioxidant and thermal protective barrier for fibers. In the case of the compatibilized

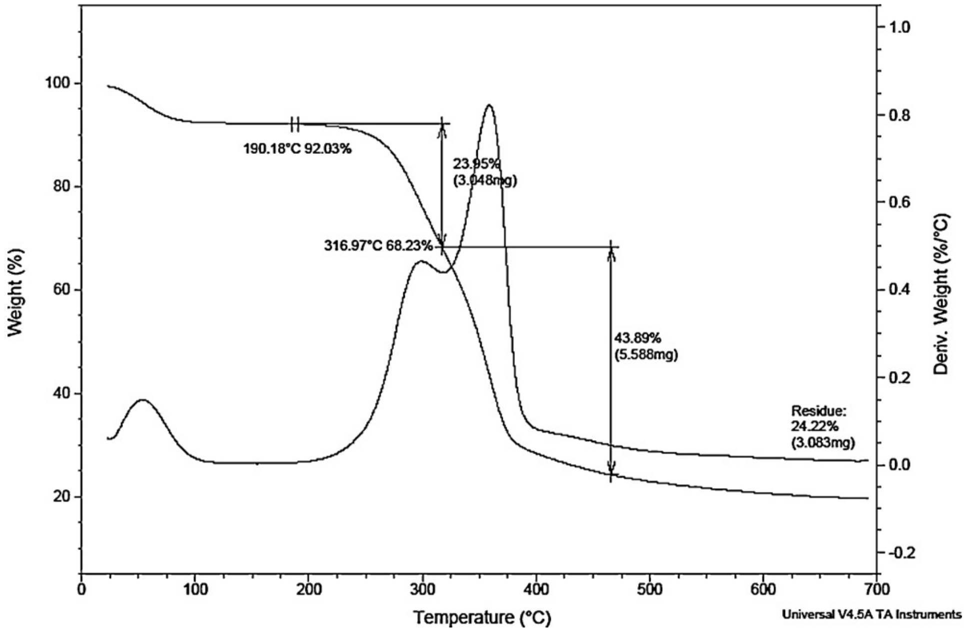

Fig. 5. TGA thermogram of coir, obtained in nitrogen atmosphere.

composites, there is no evidence by SEM that the fibers are coated with lignin, thus its role in increasing OIT would originate only from its antioxidant action. This would explain the smaller variation in oxidation induction times when PP-g-MA is present.

4. Conclusions

Addition of lignin to PP/CF composites did not alter composite tensile strength when total content of lignocellulosic material (lignin and coir) was maintained at 30%. Analysis of SEM micrographs indicated that coir fibers were coated with lignin, making them less rough. Thus, opposite effects can be observed with respect to the adhesion between PP and the fibers: reduction in polarity at the interphase, which results in increased adhesion towards PP, and reduction in roughness which may lead to reduction in contact area between PP and fiber.

With respect to thermal analysis, addition of lignin to the PP/CF composite resulted in a marked increase in both their initial decomposition temperatures and oxidation induction times. Two probable protection mechanisms have been proposed: the role of lignin as a primary antioxidant and its action as barrier against thermal degradation by coating the coir fibers.

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