

# Effect of Modified *Eucalyptus nitens* Lignin on the Morphology and Thermo-mechanical Properties of Recycled Polystyrene

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The morphology and thermo-mechanical properties of recycled polystyrene-based materials (rPS) reinforced with 5 and 15% lignin from kraft pulping of *Eucalyptus nitens* were studied. The lignin was modified through two esterification processes using either acetic or maleic anhydride, and changes in the structure of the esterified lignin functional groups were analyzed by Fourier transform infrared spectroscopy. The lignin was then incorporated into rPS by melt mixing. Torque variation in the process was evaluated, and the values were compared to those of neat rPS and virgin PS. The results show a plasticizing effect of lignin with a reduction in the torque values. The morphology, studied through scanning electron microscopy, shows a particle size reduction of acetylated and maleated lignin and a more homogeneous dispersion at 5%. The thermal behavior of the composites, studied through differential scanning calorimetry, does not show significant changes in the glass-transition temperature of rPS with the presence of lignin. The dynamic mechanical analysis shows an increasing storage modulus with increasing lignin content. Thermal stability, studied through thermogravimetric analysis, improved for composites containing 5% esterified lignin. The flexural modulus also increased with lignin addition. These results suggest that the thermal and mechanical properties of post-consumer recycled polystyrene can be significantly improved with only 5% esterified lignin.

*Keywords:* Esterified lignin; Recycled polystyrene; Composites; Morphology; Thermal and mechanical properties

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## INTRODUCTION

During the past few years, the tendency to use natural organic compounds as additives or fillers in synthetic polyolefin mixtures has increased. Among these compounds, lignin is used to improve the properties of polymer matrices and blends, but differing results have been obtained (Stewart 2008). Lignin, along with cellulose, is one of the most abundant natural polymers and can be found to make up between 15% to 40% of various plants (Glasser 1990). Its structure is based on phenylpropane units forming amorphous, three-dimensional polymer macromolecules (Takayoshi 2006), through ether linkage in two thirds of the cases and C-C linkages in the rest (Chakar and Ragauskas 2004).

Lignin is obtained as a sub-product of kraft pulping from black liquor. The polar nature of lignin and its tendency to form hydrogen-bond type intramolecular linkages

increase immiscibility with non-polar polyolefins such as polyethylene (PE), polypropylene (PP), and polystyrene (PS). The reports from some authors are contradictory regarding the benefits of unmodified lignin in polymers. González and Espósito (1999) incorporated kraft lignin in PP, resulting in low interfacial adhesion and leading to a reduction of the physico-mechanical properties as the lignin content increased. The tensile strength dropped from 30.6 MPa to 16.4 MPa at a 55% lignin content.

Various processes have been developed to modify the chemical structure of lignin and improve compatibility with virgin polyolefins. Sailaja and Deepthi (2010) modified lignin with phthalic anhydride using pyridine as a catalyst and, through mixing with low-density polyethylene and maleic anhydride as compatibilizer, obtained a composite in which relative Young modulus increased from 1 MPa without lignin to 2.5 MPa with 25% lignin.

Liu *et al.* (2005) incorporated bamboo alkaline lignin in poly (4-vinyl pyridine) films at 0, 4, 8, 10, 15, and 20% through melt mixing. The glass-transition temperature ( $T_g$ ) of the blends was found to increase with the addition of lignin from 70 °C (0%) to 147 °C (20%) due to the formation of miscible phases, while thermal stability decreased from 354 °C to 316 °C. The tensile strength reached its maximum value at 15% lignin (33 MPa), and elongation at break was maximal (9%) at 10% lignin. Maldhure and Chaudhari (2011) mixed polypropylene and lignin modified with maleic anhydride through a microwave process and showed that thermal stability increased with lignin concentration. The degradation temperature shifted from 403 °C for neat polypropylene to 433 °C at 25% lignin. Kadla and Kubo (2004) produced blends of poly(ethylene oxide) (PEO) with acetylated lignin through a pyridine reaction with acetic anhydride that resulted in the formation of a miscible composite.

Most of the studies focused on mixing lignin with virgin polyolefins, whereas recycled polyolefins were seldom used. For example, Aradoaei *et al.* (2010) used lignin as a compatibilizer for recycled blends of poly(ethylene terephthalate) (PET) and low density polyethylene (LDPE) to obtain good compatibilization. Plastic recycling has increased during the past few years in an effort to reduce the amount of waste generated. However, recycling implies problems such as property loss due to polymer degradation (molecular structure and weight distribution), the presence of impurities, and higher cost of the end product (Parres *et al.* 2008; Vilaplana *et al.* 2006).

It is known that polystyrene is not very compatible with other polymers and composites. Therefore, the formation of polymeric mixtures with adequate miscibility is challenging (Escobar *et al.* 2008). Compatibilizers are used in some mixtures to improve the properties of the resulting composite (Parres *et al.* 2008).

The objective of this research was oriented towards modifying the chemical structure of lignin from *Eucalyptus nitens*. This was accomplished by the esterification of hydroxyl groups to reduce polarity, avoid build-up of molecules through the formation of hydrogen bonds, and increase miscibility with recycled PS. Lignin was subjected to two separate esterification processes, with either acetic anhydride or maleic anhydride. Melt mixing was used with post-consumer expanded polystyrene (rPS), at two different modified lignin contents (5% and 15%). The variation in  $T_g$  was studied through differential scanning calorimetry (DSC), the storage modulus was determined through dynamic mechanical analysis (DMA), and the thermal stability was studied through thermogravimetric analysis (TGA). The morphology was studied using a scanning electron microscope (SEM), and mechanical properties in flexion were determined.

## EXPERIMENTAL

### Methods

#### *Pulping and isolation of lignin*

The lignin used in this research was obtained through kraft pulping of *Eucalyptus nitens* wood. Four trials were conducted, with the processing of 2.5 kg of dry wood chips from *E. nitens* in a 25-L lab digester for each trial. Sodium hydroxide (NaOH) and sodium sulfide (Na<sub>2</sub>S) were used as reagents for white liquor pulping. White liquor and water were added at a 4:1 liquor:wood ratio, the equipment was closed and heated for 90 min to reach the cooking temperature, and the solution was cooked at 158 °C for 75 min.

Lignin extraction was performed with the following method. The black liquor (pH 12) was concentrated in a rotary evaporator to remove most of the aqueous liquid phase containing salts and NaOH. To this concentrate, 2 M sulfuric acid was gradually added under constant agitation to a pH of 3 to form a precipitant. The solution was filtered, under vacuum, with Advantec grade No. 5C paper and washed with distilled water and then with 2 M hydrochloric acid.

The resulting solid was diluted in sodium hydroxide, filtered again, and the liquid was precipitated with 2 M sulfuric acid. After a final filtering and washing with distilled water and 2 M hydrochloric acid, the solid was dried at 60 °C for 24 h.

#### *Esterification of lignin*

To acetylate the *E. nitens* lignin, 50 g was dissolved without catalyst in 1.5 L of acetic anhydride in a flat-bottom flask. This solution was heated at 120 °C in a heating mantle for 4 h with constant stirring and concentrated in a rotary evaporator before being filtered and washed with ethanol and acetone to remove excess acetic anhydride and acetic acid. The solid was then dried at 60 °C for 16 h and weighed to determine weight gain, which was 12%.

For the maleation process, 50 g of *E. nitens* lignin was dissolved in 2 L of a 10% maleic anhydride/acetone solution and heated at 50 °C for 1 h. The solution was allowed to stand for 24 h before being concentrated in a rotary evaporator. The maleated lignin was filtered and washed with toluene before being dried at 60 °C for 16 h. The weight gain of the lignin was 18.7%.

#### *Melt-blending process*

Expanded polystyrene (EPS) from packing materials (used by supermarkets) was washed with hot water and dried to constant weight for 8 h at 80 °C. The EPS was pressed at 4 bars and 120 °C to eliminate the high gas content found in EPS. The material was pre-ground in a knife mill to an average size of 1 to 2 mm and oven dried at 80 °C for 24 h.

Virgin polystyrene (PS STYRON 678 D, crystal) with a melt flow index value of 10 g per 10 min and a density of 1.05 g/cm<sup>3</sup> was supplied by The Dow Chemical Co. (Chile). Compounding was performed by adding EPS to a Thermo Haake Polydrive Rheomix 600 (Karlsruhe, Germany), supplied with a roller blade mixer at 180 °C for 4 min, followed by the addition of lignin, at a rotation speed of 60 rpm for 12 min. The compounds were then molded (190 mm x 170 mm) in a laboratory press for 15 min at 180 °C with a pressure of 120 bar to produce the test samples. Table 1 lists the composition of the composites.

**Table 1.** Composition of Lignin/rPS Composites

Sample	PS (%)	rPS (%)	<i>E. nitens</i> Lignin (%)	Acetylated <i>E. nitens</i> Lignin (%)	Maleated <i>E. nitens</i> Lignin (%)
PS	100	-	-	-	-
rPS	-	100	-	-	-
rPS/LN5	-	95	5	-	-
rPS/LN15	-	85	15	-	-
rPS/LNA5	-	95	-	5	-
rPS/LNA15	-	85	-	15	-
rPS/LNM5	-	95	-	-	5
rPS/LNM15	-	85	-	-	15

*FT-IR and SEM*

Modified and unmodified lignin were analyzed by Fourier transform infrared spectroscopy (FT-IR) on a Perkin Elmer FT-112 Spectrum Two instrument (Llantrisant, UK) to determine structural changes in terms of functional groups. A JEOL JSM 6610 LV (Peabody, MA) scanning electron microscope (SEM) operating at an accelerating voltage of 5 kV or 10 kV was used to determine the morphology of the particles.

*TGA, DSC, and DMA analysis*

To determine the thermal behavior of the composites, a dynamic test was carried out with a TGA Q50 (TA Instruments: New Castle, DE). The samples, with an average mass of 8 mg, were heated from 50 to 600 °C at a heating rate of 10 °C/min under a nitrogen atmosphere. The thermal stability of the composites was compared to neat rPS and virgin PS.

The  $T_g$  of the samples was determined by a DSC 822e (Mettler Toledo, (Greifensee, Switzerland) equipped with a STAR<sup>c</sup> v10.0 data analyzing software from Mettler Toledo. For this purpose, the ASTM D3418 standard (2012) was applied in a temperature range between 35 and 200 °C at a heating rate of 20 °C/min under a nitrogen atmosphere.

A Perkin Elmer DMA - 7e dynamic mechanical analyzer (Waltham, MA) was used to determine the storage modulus of the samples (dimensions 2 mm x 4 mm x 20 mm) as a function of temperature. The test was performed *via* three-point bending with a 15-mm support span, in a temperature range of 30 to 110 °C at a heating rate of 5 °C/min, with a static load of 1100 mN and dynamic load of 1000 mN at 1 Hz.

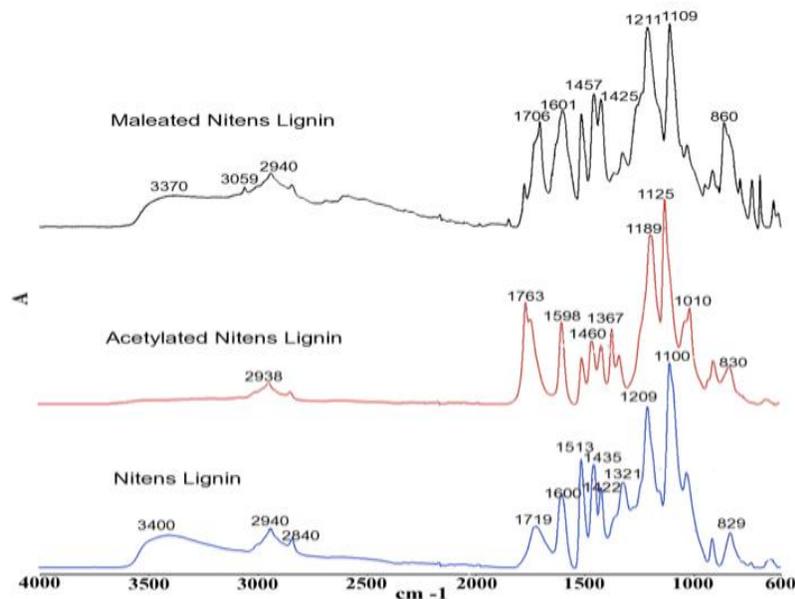
*Flexural tests*

The flexural properties of the composites were investigated on an Instron model 4468 testing machine (Norwood, MA) with a 5000-kg load cell. The test speed was 1.28 mm/min according to ASTM D790 (2010) and performed at room temperature (23 °C) and 60% relative humidity. The average and standard deviation (SD) were determined for 10 samples with a size of 80 mm (L) x 12.7 mm (W) x ~3 mm (T).

**RESULTS AND DISCUSSION****FT-IR**

As shown in Fig. 1, the presence of a wide band at 3400 cm<sup>-1</sup> in the unmodified lignin can be seen, which shows the presence of hydroxyl groups (-OH stretching vibration)

(Feldman and Banu 1997; Sun *et al.* 2002). The intensity of this band is reduced because of esterification, which is observed in the acetylated lignin. The reduction of this band is very important because it shows the reduction in lignin polarity, as hydroxyl groups (at  $3400\text{ cm}^{-1}$ ) are replaced by acetyl groups or carbonyl groups (at  $1763\text{ cm}^{-1}$ ).



**Fig. 1.** The infrared spectra of unmodified, acetylated, and maleated *E. nitens* lignin

In the case of maleated lignin, a lower reduction of the band corresponding to the aromatic and aliphatic -OH groups was observed. This was caused by partial esterification of -OH groups by reaction with maleic anhydride. A displacement towards low wavenumber direction at  $3370\text{ cm}^{-1}$  was also observed, which represents -OH vibrations associated to the carboxylic acid group (-COOH). This result is consistent with work reported in the literature that observed only the aliphatic hydroxyl groups reacted with maleic anhydride, generating a partial esterification and thus causing the intensity of this band to vary (Thielemans and Wool 2005). Also, some peaks were observed around  $2940\text{ cm}^{-1}$  (C-H stretching) and  $2840\text{ cm}^{-1}$  (C-H tensor), which is typical in lignin. Other important structures in lignin are aromatic rings, which were evidenced in the region from  $1400$  to  $1600\text{ cm}^{-1}$ .

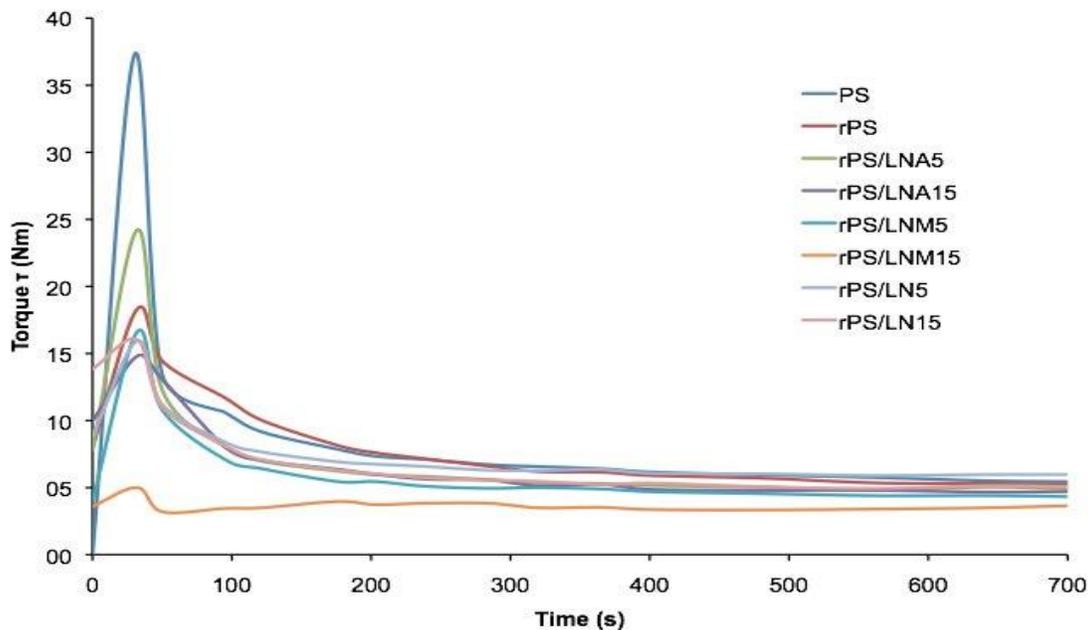
Finally, typical peaks of the monomers guayacil and syringyl were observed at  $1321\text{ cm}^{-1}$  with a slight intensity (Boeriu *et al.* 2004). Chemical modification also produced slight vibration shifts. This is observed, for example, in the band at  $1719\text{ cm}^{-1}$  (C=O) in *E. nitens* lignin; with acetylation, the band moved to  $1763\text{ cm}^{-1}$ , whereas with maleation, this band moved toward  $1706\text{ cm}^{-1}$ .

Acetylation of lignin has effects on specific bands, which were as follows:  $1763\text{ cm}^{-1}$  (C=O, ester);  $1367\text{ cm}^{-1}$  (-CH<sub>3</sub>);  $1189\text{ cm}^{-1}$  (C=O); and  $1125$  and  $1010\text{ cm}^{-1}$ , where the highest peak intensities were found at  $1125\text{ cm}^{-1}$  (C-O). The absence of a peak at  $1700\text{ cm}^{-1}$  indicates that lignin is free from acetic acid, and the absence of a peak in the range of  $1770$  to  $1840\text{ cm}^{-1}$  shows the lack of unreacted acetic anhydride in lignin (Gilarranz *et al.* 2001; Domínguez *et al.* 2008; Shukry *et al.* 2008).

In the case of maleation, the bands indicating a chemical modification were in the range between  $990$  -  $966\text{ cm}^{-1}$  corresponding to the bands C=C, bending (Faix 1991).

## Processing Results

The influence of modified and unmodified lignin in the ability to process rPS during melt mixing was studied by measuring the torque response. The blend values were compared to virgin PS and neat rPS. Figure 2 shows the torque behavior of neat polymers and the composites containing 5% and 15% of lignin.



**Fig. 2.** Torque response for neat polymers and composites

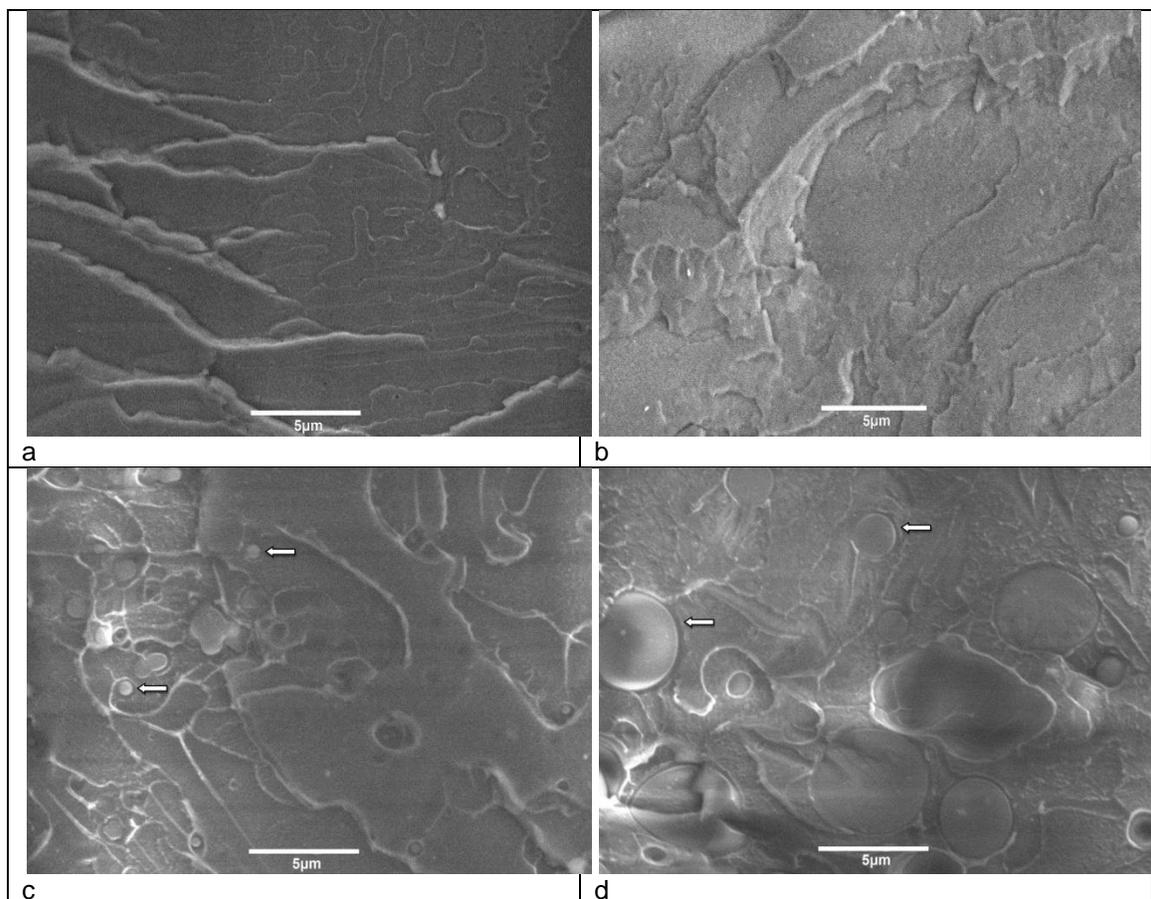
As shown in Fig. 2, the torque gradually increased as the material was fed in a solid and cold state. In a second stage, a progressive reduction of torque was observed until it stabilized after 5 min (300 s) of mixing. The presence of lignin reduced the torque, improving the ability to process the mixtures. As the amount of lignin was increased, the torque decreased from 5.67 Nm for rPS and PS to 3.51 Nm for rPS containing 15% maleated lignin (Table 2). These results show that the torque values were, in general, smaller for composites containing acetylated and maleated lignin. The esterification process seemed to increase lignin miscibility with the polymer matrix, producing a plasticizing effect, as reported by Aradoaei *et al.* (2010). Table 2 presents the final torque values after 12 min of mixing.

**Table 2.** Final Torque Values of the Samples

Sample	Torque (Nm)	SD (Nm)
PS	5.92	0.36
rPS	5.67	0.34
rPS/LN5	6.04	0.14
rPS/LN15	5.14	0.11
rPS/LNA5	5.13	0.16
rPS/LNA15	4.85	0.21
rPS/LNM5	4.56	0.20
rPS/LNM15	3.51	0.09

## SEM Results

Figures 3 and 4 show typical micrographs for all the compounds studied.

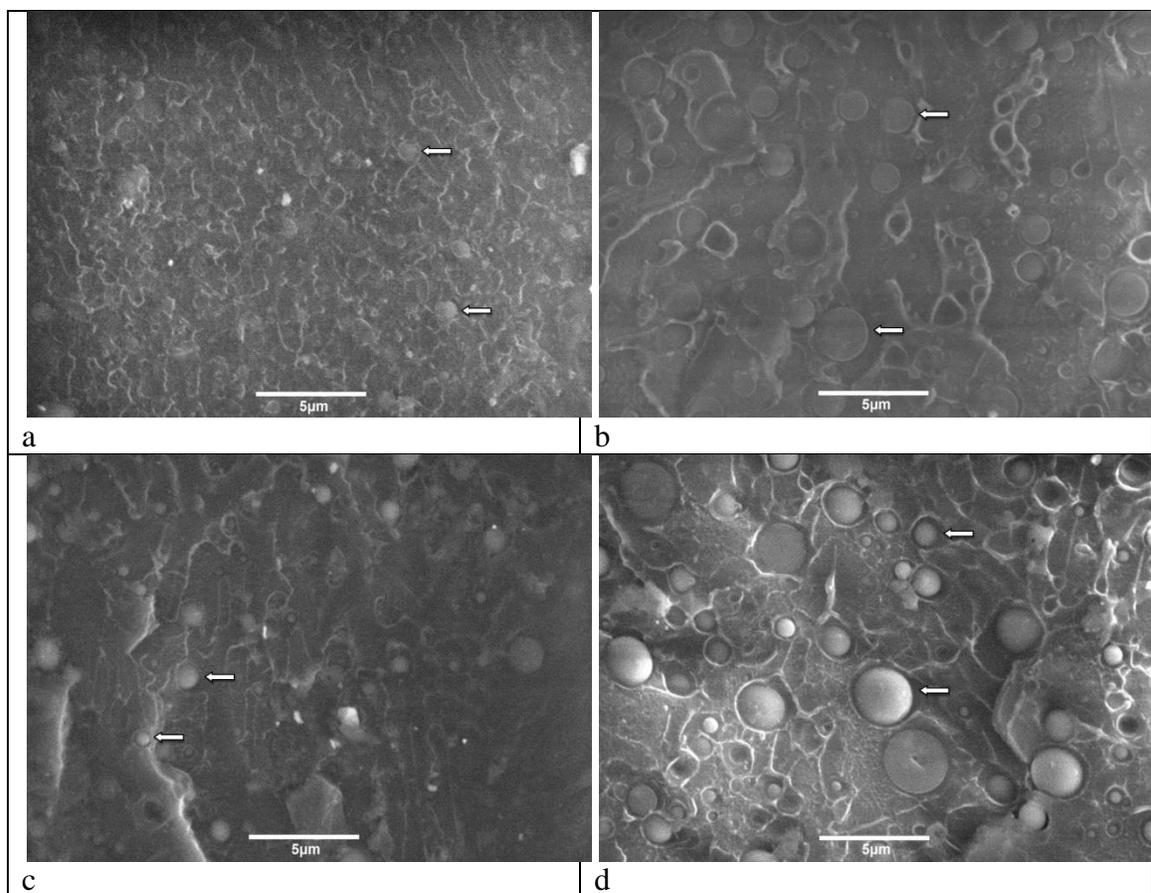


**Fig. 3.** SEM images of (a) PS, (b) rPS, (c) rPS/LN5, and (d) rPS/LN15 composites. Arrows denote particles

Virgin PS (Fig. 3a) and rPS (Fig. 3b) showed a homogeneous laminar morphology, which is characteristic of polystyrene. The incorporation of unmodified lignin at 5% (Fig. 3c) and 15% (Fig. 3d) presents agglomerated lignin, with particles reaching 6 to 8  $\mu\text{m}$  in size at 15% lignin, while in composites containing 5% lignin, the particles were not larger than 3  $\mu\text{m}$ . This morphological difference was probably due to higher intermolecular interaction between lignin particles at higher lignin contents.

When 5% and 15% esterified lignin were incorporated (Fig. 4), a clear reduction in lignin lump sizes was observed, with better lignin dispersion in rPS. Lignin acetylation and maleation were shown to reduce the amount of -OH groups of lignin (Fig. 1), which reduces molecular interaction through hydrogen bonding and polarity, leading to increased dispersion of lignin with the matrix of rPS.

The composites containing 5% acetylated or maleated lignin (Figs. 4a and 4c) show a more homogeneous lignin dispersion and smaller particle size. Also, no changes in the laminar morphology of rPS or any other plastic deformation of the matrix was observed, as reported in the literature when high-impact viscoelastic additives are incorporated to PS (Chang *et al.* 2006).



**Fig. 4.** SEM images of (a) rPS/LNA5, (b) rPS/LNA15, (c) rPS/LNM5, and (d) rPS/LNM15 composites. Arrows denote particles

### DSC Analysis

The study of the thermal behavior of rPS, by analyzing the change in  $T_g$  with lignin addition enables a determination of the compatibility of the mixtures. Because lignin has  $T_g$  values between 110 and 150 °C (Lisperguer *et al.* 2009), which are higher than those for rPS, an increase in the  $T_g$  value of the mixture and the presence of only one  $T_g$  implies a certain degree of compatibility among them. Table 3 shows the average values for each sample and the corresponding standard deviation.

**Table 3.**  $T_g$  Values of the Samples

Sample	$T_g$ (°C)	SD (°C)
Unmodified nitens lignin	131.0	0.6
Acetylated nitens lignin	134.7	0.5
Maleated nitens lignin	142.0	0.4
PS	92.1	0.2
rPS	102.8	0.3
rPS/LN5	102.7	0.6
rPS/LN15	102.7	0.5
rPS/LNA5	103.5	0.5
rPS/LNA15	100.8	0.5
rPS/LNM5	102.2	0.6
rPS/LNM15	101.8	0.4

Table 3 shows that rPS presented a  $T_g$  increase of approximately 10 °C compared to virgin PS, which is probably due to the additives used in the manufacturing of expanded PS (EPS). These additives have some degree of physical bonding with rPS, which causes restriction in chain mobility, thus increasing the  $T_g$  value. The incorporation of unmodified lignin, acetylated lignin, and maleated lignin at 5% and 15% does not affect the  $T_g$  values. The highest average value (103.5 °C) was obtained with 5% acetylated lignin (rPS/NA5), which suggest a higher lignin dispersion in the polymeric matrix in these composites. According to some authors (Liu *et al.* 2005), immiscible blends of unmodified lignin with other polymers cause a shift of  $T_g$  to higher values.

### DMA Analysis

The results of the DMA tests provide useful information regarding the viscoelastic behavior of materials, which is related to the structure and molecular movements. The storage moduli ( $E'$ ) for the samples are shown in Table 4.

**Table 4.** Storage and Flexural Modulus of the Samples

Sample	$E'$ (MPa)	SD (MPa)	Flexural Modulus (MPa)	SD (MPa)
PS	1525	47	3764	340
rPS	1629	33	2768	188
rPS/LN5	1626	27	3365	206
rPS/LN15	1818	10	3684	429
rPS/LNA5	1411	34	3454	428
rPS/LNA15	1759	14	3358	288
rPS/LNM5	1393	69	3385	218
rPS/LNM15	1802	67	3678	469

Table 4 shows that by adding 5% unmodified lignin, the  $E'$  value of rPS was not significantly affected. However, the incorporation of 15% unmodified, acetylated, and maleated lignin, as expected, increased the rigidity of the material by increasing the  $E'$  values from approximately 1600 to 1800 MPa. The incorporation of 5% acetylated and maleated lignin, however, decreased the  $E'$  values and caused a plasticizing effect in the material. This plasticizing effect also can be observed in Table 2, where the samples containing 5% of acetylated and maleated lignin had lower torque values than rPS.

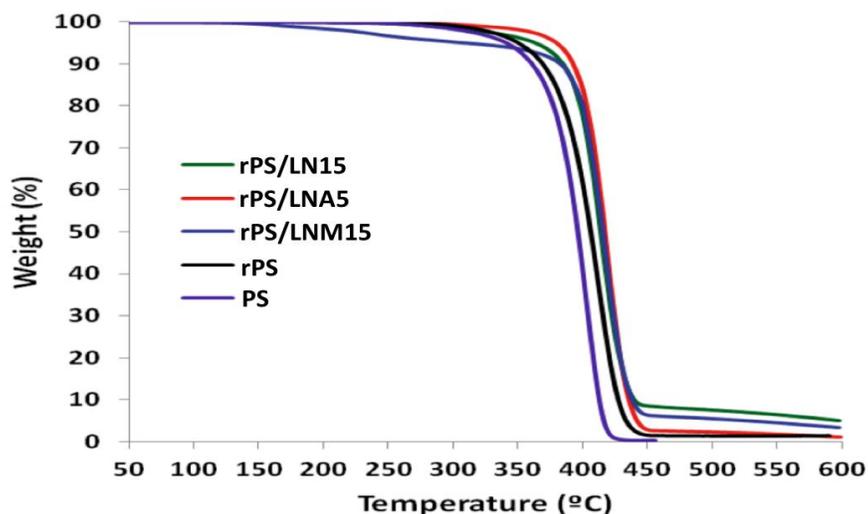
### Flexural Tests

Table 4 also shows the flexural modulus of the neat polymers and composites containing unmodified and esterified lignin. A general increase in flexural modulus was observed for rPS due to the incorporation of lignin, and this increment was higher with an increase in lignin content. The samples containing 15% unmodified and maleated lignin show a flexural modulus similar to virgin PS (around 3600 MPa). The presence of 15% lignin makes the matrix more rigid. The increase of flexural modulus values shown in Table 4 indicate that samples with a higher lignin content had higher storage modulus values than rPS.

Other polymers mixed with unmodified lignin, such as polylactic acid (PLA) and polyvinylpyridine (PVP), showed no variation in flexural modulus with lignin content up to 20%. With higher content, the flexural modulus and strength decreases by approximately 30% due to poor compatibility (Feldman and Banu 2003; Li *et al.* 2003; Liu *et al.* 2005).

## TGA Analysis

TGA curves of the polymers and the most representative rPS/LN composites are shown in Fig. 5.



**Fig. 5.** TGA curves of PS, rPS, and both unmodified and modified lignin/rPS composites

All the samples were degraded in just one stage. The virgin PS and rPS exhibited only a 5% mass loss up to around 340 °C, whereas samples containing maleated and acetylated lignin started degrading between 358 and 380 °C, with the exception of composites containing 15% maleated lignin (rPS/LNM15), which started degrading at 312 °C. The composites with the highest thermal stability were those containing 5% acetylated lignin (rPS/LNA5) and 5% maleated lignin (rPS/LNM5). At these concentrations, lignin has a stabilizing effect in the polymeric matrix and, as shown by the SEM micrographs in Fig. 4, there was a more homogeneous dispersion in the polymeric matrix. This behavior has also been detected in mixtures of lignin with other polymers; Maldhure and Chaudhari (2011) report that the degradation temperature of polypropylene (PP) shifted from 403 °C for pure PP to 433 °C for blends containing 25% lignin.

When the lignin content was increased to 15%, dispersion decreased and lignin particles formed larger lumps (Fig. 4). Adding 15% lignin reduced the thermal stability of the composites, which was more evident for samples containing 15% of maleated lignin. Table 5 shows the values of thermal stability tests for all the samples.

**Table 5.** Thermal Stability Parameters Obtained from TGA Curves

Sample	Thermal degradation at 5% (°C)	DTG peak (°C)	Final degradation temperature (°C)	Residues (%)
PS	332	409	438	0.4
rPS	349	412	442	0.7
rPS/LN5	360	410	450	2.9
rPS/LN15	356	406	444	7.6
rPS/LNA5	380	419	450	3.5
rPS/LNA15	358	410	443	6.9
rPS/LNM5	376	410	445	3.9
rPS/LNM15	312	409	443	6.7

As shown in Table 5, the incorporation of unmodified lignin caused an increase in the initial degradation temperature of rPS of between 10 and 15 °C, whereas acetylated and maleated lignin increased this initial degradation temperature between 20 and 30 °C, except for the composites containing 15% maleated lignin (rPS/LNM15). The derivative thermogravimetry (DTG) of the maximum weight loss rate did not show significant differences between the neat polymers and the composites containing lignin, nor between the final loss weight temperatures of the samples. As expected, the amount of residues was higher in composites containing higher amounts of lignin. The ash content of kraft lignin is about 8% of the material (Sameni *et al.* 2014).

## CONCLUSIONS

1. The results of this study show that in the process of mixing rPS and esterified lignin, the torque values decreased from 5.92 Nm for virgin PS to 3.51 Nm for rPS with 15% maleated lignin. A higher plasticizing effect was obtained using maleated lignin.
2. Scanning electron micrographs also show that the incorporation of 5% acetylated or maleated lignin produced a more homogeneous morphology in rPS.
3. The DSC tests showed that rPS (102.8 °C) had a higher  $T_g$  value than did virgin PS (92.1 °C), and the incorporation of modified lignin did not alter the  $T_g$  value of rPS.
4. The thermal stability of the samples (rPS, 349 °C) increased with the addition of 5% esterified lignin due to the stabilizing and antioxidant effect of lignin (rPS/LNA5, 380 °C), but the incorporation of 15% lignin reduced these values (rPS/LNM15, 312 °C). The flexural modulus of rPS (2768 MPa) also increased with lignin incorporation due to an increase in the rigidity of the polymeric matrix (rPS/LN15, 3684 MPa). This led to a higher storage modulus for the composites, as determined by DMA and flexural measurement.
5. With the results shown in the DMA, TGA, and flexion tests, the best performance was obtained on rPS compounds with 5% lignin, while using 15% resulted in a reduction of the properties. It was also observed that the acetylated lignin had better performance than the maleated lignin. It is for this reason that rPS/LNA5 blend was selected as having superior behavior.

## ACKNOWLEDGMENTS

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