Recycled Polystyrene Composites Reinforced With Esterified and Non-Esterified Kraft Lignins

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Abstract

Recycled polystyrene and Kraft lignins represent waste materials/by-products, generated in huge quantities worldwide, which remain inadequately valorized. In this study, unmodified and maleated Kraft lignins were used as fillers in recycled polystyrene (RPS) to produce composites at different concentrations (0, 10, 20 and 30%) via melt blending. Also, RPS composites with 20% of maleated Kraft lignins were prepared by applying a previous surface treatment to the maleated Kraft lignins with RPS in solution. A complete mechanical, thermal and morphological characterization was performed on the RPS based composites containing Kraft lignins.

The morphological study revealed better compatibility with RPS for unmodified Kraft lignins than maleated Kraft lignins except for the composite where maleated lignins surface treatment was applied. In this case, the RPS was well incorporated in the porous structure of maleated Kraft lignins. The results also showed that addition of unmodified Kraft lignins led to better mechanical and thermal properties of the composites than when maleated Kraft lignins were added. For the composite formulated with 20% maleated Kraft lignins with a previous surface treatment, the properties were improved to become comparable to those of composites with unmodified Kraft lignins. The poor mechanical and thermal properties of RPS composites with maleated Kraft lignins could be related to the porous structure of the maleated Kraft lignins.

Keywords: Kraft lignins, recycled polystyrene, composites, thermal and mechanical properties, morphology

1. Introduction

Kraft lignins represent underestimated macromolecules issued from Kraft pulping industries. They are considered as a by-product and their main application is as fuel, to produce energy for the Kraft process. New applications for lignins have been studied in different fields such as energy, chemicals and composite materials (Doherty, Mousavioun, & Fellows, 2011; Stewart, 2008; Lora & Glasser, 2002). Lignins could be good candidates for composite materials, because of their antioxidant (Gregorovà, Cibulkovà, Kosikovà, & Simon, 2005; Maldhure, Ekhe, & Deenadayalan, 2012), thermal (Barzegari, Alemdar, Zhang, & Rodrigue, 2013) and biodegradable (Mikulàsovà, Kosikovà, Alexy, Kacik, & Urgelovà, 2001) properties. Kraft lignins have also been used as coupling agents (Mariotti, Wang, Rodrigue, & Stevanovic, 2014), lubricants in plastic processing (Nadji et al., 2009) or fillers in different composites based on low density polyethylene (LDPE), and high density polyethylene (HDPE), or on polypropylene (PP) (Kharade & Kale, 1999), and polystyrene (PS). In order to improve the interfacial adhesion, the modification of industrial lignins was studied to decrease their hydrophilicity and increase interactions with the matrix, thus improving compatibility with hydrophobic matrices such as HDPE and PP (Sobczak, Brüggeman, & Putz, 2013; Kumar, Tyagi, & Sinha, 2011). Polystyrene is an interesting matrix for lignins incorporation because of similarities in aromatic structures between the two polymers. Polystyrene based composites have been studied using wood pulp and various fibers (Maldas, Kokta, Raj, & Daneault, 1988; Singha & Rana, 2013; Vilaseca, López, Llauró, PèLach, & Mutjé, 2004). Some studies have also been done on lignins filled PS (Barzegari, Alemdar, Zhang, & Rodrigue, 2012). A wide range of Kraft Indulin AT lignins (0 - 80%) in

polystyrene was used and the effect of coupling agent addition (SEBS) on mechanical properties was studied. Polystyrene composites were also reinforced with Soda lignins of rice straw modified with transition metal cations like Fe (III), Ni (II) and Co (II) (El-Zawawy, Ibrahim, Belgacem, & Dufresne, 2011). However, few studies have been done on recycled polystyrene (RPS) composites (Perez-Guerrero, Lisperguer, Navarrete, & Rodrigue, 2014). The main fillers tried so far were lignocellulosic fibers such as wood and Curaua fibers (Simonsen and Rials, 1996; Borsoi, Scienza, & Zattera, 2013). Comparisons have also been made between virgin and RPS composites. Sugar bagasse fibers have been modified by vinylsilanization and composite formulations with those fibers showed better thermal stability and mechanical properties than untreated fibers (Zizumbo et al., 2011). This was confirmed by morphological analyses (SEM) revealing better interfacial adhesion. Lisperguer, Nunez, and Perez (2013) modified hardwood Kraft lignins with maleic anhydride and used them as fillers in RPS. Only thermal and morphological properties of the RPS composites with 2, 5 and 10% of maleated lignins were studied. Thermal stability improvement for composites containing 2 and 5% of maleated Kraft lignins was observed.

In our previous study (Schorr, Diouf, & Stevanovic, 2014a), three Kraft lignins were esterified by maleic anhydride. It was shown by SEM that maleated Kraft lignins particles presented important porosity that was not observed for non-esterified Kraft lignins. Our hypothesis was that the maleated Kraft lignins with this new morphology could represent interesting substrates for incorporation in RPS.

To the best of our knowledge, very few studies were done on RPS composites containing unmodified or maleated Kraft lignins. In this study, RPS composites containing different concentrations of unmodified and maleated Kraft lignins were produced to determine their effect on mechanical and thermal properties of the composites, therefore establishing the possibility to revalorize these materials. Softwood Kraft lignins could be interesting fillers for RPS composites because of the presence of aromatic rings in their structure and their higher molecular mass compared to hardwood Kraft lignins. Maleated softwood Kraft lignins were supposed to be good fillers because of their porous structure which may promote their incorporation in polystyrene matrix through physical anchoring between two polymers.

2. Methods

2.1 Materials

The polymer matrix was recycled polystyrene (RPS) from packaging materials. It was grounded to an average size of 2 mm. Kraft lignins were used as fillers. Softwood Kraft lignins were precipitated from black liquor of a Quebec Kraft pulp and paper industry (Kruger Wayagamack) with carbon dioxide, as described in our previous study (Schorr, Diouf, & Stevanovic, 2014b). For esterification, maleic anhydride (99%), 1,4-dioxane (99.9%), 1-methylimidazole (99%) and ethyl ether (99.9%) were used as received from Sigma Aldrich. To dissolve RPS and maleated lignins, toluene and acetone were also used as received from Sigma Aldrich.

2.2 Synthesis of Maleated Kraft Lignin

To improve their compatibility with polystyrene, Kraft lignins were esterified with maleic anhydride. At ratio of 1/5 w/w, lignins/anhydride were mixed with 1,4-dioxane (20 mL/g lignins) and to 1 mL/g lignins mixture a solution containing 0.5 g of 1-methylimidazole in 10 mL of 1,4-dioxane was added to catalyze the reaction. The mixture was stirred under nitrogen for 4 h at 75°C. After the solution was cooled down, ethyl ether was added to precipitate the maleated Kraft lignins (60 mL/g lignins). The solution was left at 4°C overnight to allow settling of the particles. The lignins were then filtered and washed three times with water for 10 minutes (60 mL/g lignins). The maleated Kraft lignins were finally dried overnight at room temperature and then again overnight in a vacuum oven at 60°C. The obtained maleated Kraft lignins were characterized as described elsewhere (Schorr et al., 2014a).

2.3 Composites Fabrication

An internal batch mixer (Haake Büchler Rheomix) was used to blend the RPS with lignins. The temperature was fixed at 175°C with a rotor speed of 60 rpm. The procedure used was to introduce first 2/3 of the RPS in the mixer for 6 min and then the lignins were incorporated. Finally, the rest of RPS (1/3) was added after 3 min and the compounds were mixed for 3 more minutes. Unmodified and maleated Kraft lignins were used at different concentrations as presented in Table 1. The composites were finally produced by compression molding in a laboratory scale press (Carver Laboratory Press Model C) to obtain plates with dimensions of 100 x 100 x 2.5 mm^3. Molding was performed at 195°C with a force of 3 metric tons for 5 min. From the resulting plates, samples were cut to perform all the characterizations.

To improve interactions between lignins and RPS, a surface treatment of lignins particles was performed in solution. First, RPS was solubilized in toluene (at 6.7% concentration) during 30 min at room temperature, while maleated Kraft lignins were partially solubilized in acetone (at 6.7% concentration) during the same time at room

temperature. These two solutions were then mixed together for one hour at room temperature. The mixture was dried at room temperature during 3 days and one night at 103°C to remove the remaining solvents.

Table 1. Composition of Maleated Kraft lignins or unmodified Kraft lignins/RPS composites

Coding	Sample name	Filler	Content (wt.%)
a	RPS	none	0
b	RPS+KL 10%	Unmodified Kraft lignins	10
c	RPS+KL 20%	Unmodified Kraft lignins	20
d	RPS+KL 30%	Unmodified Kraft lignins	30
e	RPS+MKL 10%	Maleated Kraft lignins	10
f	RPS+MKL 20%	Maleated Kraft lignins	20
g	RPS+MKL 30%	Maleated Kraft lignins	30
h	RPS+MKL 20%-solubilized	Surface treated maleated Kraft lignins	20

2.4 Morphological Analysis

Morphology of the composites was studied with a scanning electron microscope. First, the samples were fractured in liquid nitrogen and their surfaces were coated with a gold/palladium alloy. Micrographs were taken using a JEOL model JSM-840A scanning electron microscope at 15 kV.

2.5 Density Determination

A gas (nitrogen) pycnometer ULTRAPYC 1200e (Quantachrome Instruments) was used to determine the density of the composites. For each composite, three replicates were made and the average density was calculated with a standard deviation of less than 1%.

2.6 Mechanical Analysis

The samples for impact and flexion tests were cut with a saw as rectangular pieces (100 x 12 x 2.5 mm^3). Charpy impact test was performed on a Tinius Olsen model Impact 104. A 1 J hammer was used for the tests. Six replicates were done to get an average and standard deviations, which were determined to be less than 14%. Three point bending flexural tests were performed using an Intron model 5565 with a 50 N load cell at room temperature with a support span of 60 mm and a crosshead speed of 5 mm/min. The test was carried out according to (ASTM D 790, 2010). For each composite, six replicates were tested to get an average for the flexural modulus. Standard deviations were less than 8% in each case.

2.7 Thermal Analysis

Differential scanning calorimetry (DSC) analyses were performed on a Mettler Toledo DSC 822e to determine glass transition temperature. Around 7 mg of each sample was placed in a sealed aluminum cell. First, the temperature was increased from 30 to 100°C followed by cooling back to 30°C, both at rate of 5°C/min. In the second step, the temperature was increased from 30 to 200°C at 10°C/min. In all cases, the tests were performed under nitrogen (at flow of 35 mL/min) and three replicates were made. The thermogravimetry (TGA) was also used to characterize the thermal stability of the samples. The measurements were performed on a Mettler Toledo TGA/DTA 851e. Around 7 mg of the sample were used for each analysis performed three times. The temperature was increased from 30 to 700°C at a heating rate of 10°C/min. One series of experiments was performed under nitrogen (50 mL/min) and the other under air (50 mL/min).

2.8 Statistical Analyses

The experiments were conducted according to a D-Optimal design (Table 1). The factors studied included three Kraft lignins modifications (unmodified, maleated, and maleated with a surface treatment) and four different contents (0, 10, 20, and 30%). Thus, 9 combinations with six replicates were produced. *Statistical Analysis System (SAS) 9.3* was used for the statistical analysis. An analysis of variance (ANOVA) was performed on this experimental plan (two factors).

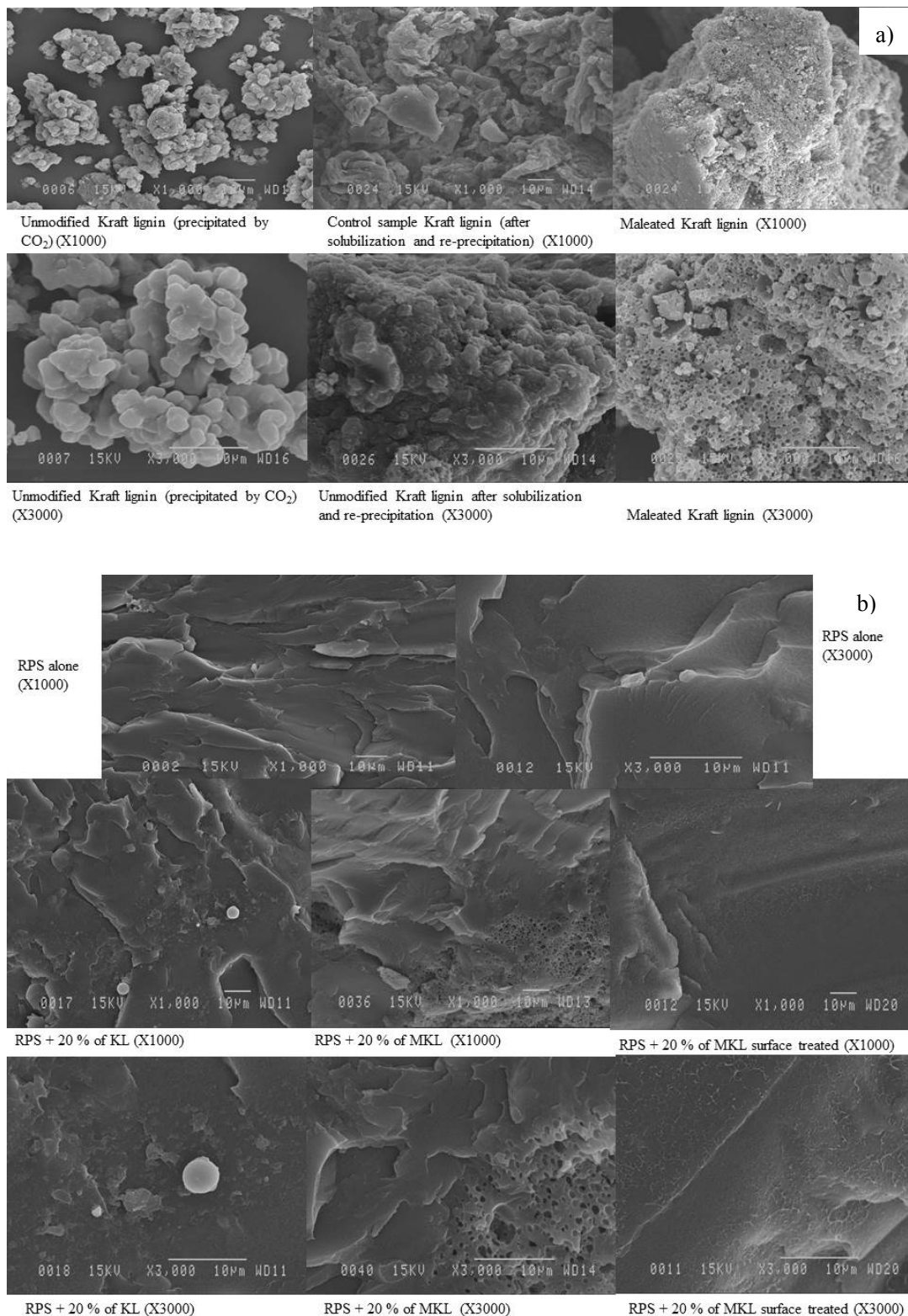## 3. Results and Discussion

3.1 Morphology

Figure 1. Micrographs at different magnifications (1000X and 3000X): a) for unmodified Kraft lignin, control sample Kraft lignin and maleated Kraft lignins and b) for RPS, as well as composites with 20% unmodified Kraft lignins compared to composites with maleated Kraft lignins with a surface treatment

Figure 1 presents typical micrographs of different Kraft lignins and different RPS composites at 20% lignin content. Unmodified Kraft lignins alone are composed of non-porous small spherical particles which have the possibility to agglomerate together. Maleated Kraft lignins are shown to have a porous structure compared to unmodified Kraft lignins, which seems to be due to the esterification process (Schorr et al., 2014a). Indeed, the SEM micrograph (Figure 1a) clearly demonstrated the difference between the unmodified lignin, the Kraft lignin as the control sample (observed after solubilisation in solvent used for esterification, precipitated by the same protocol that was used to recover esterified lignin) and the maleated Kraft lignin. Only one sample was determined to have porous structure and it was the maleated Kraft lignin which leads us to the conclusion that the porosity was related to the effect of esterification and not to the experimental protocol used. The RPS alone exhibits a smooth surface with some impurities due to its recycled origin. RPS composites with unmodified Kraft lignins (RPS+KL) have a rough surface due to the presence of unmodified Kraft lignins inside the matrix. This roughness can be related to poor adhesion between the phases which exposes the lignin particles following the cryogenic fracture. RPS composites with maleated Kraft lignins (RPS+MKL) have a smoother texture probably because they have better compatibility with the RPS matrix. Nevertheless, the porous structure can still be seen which indicates that RPS had not penetrated these small pores, probably due to the high RPS viscosity in the melt state. However, for composites based on surface treated maleated Kraft lignins, smooth surfaces were obtained without any porosity. This indicated that RPS was able to penetrate better the porous lignins structure when treated in solution (lower concentration of molecules and lower viscosity of the system). In this case, homogeneous samples were produced; i.e. good distribution of lignin particles. This may be ascribed to van der Waals intermolecular interactions between Kraft lignins and RPS and by π-π interactions due to the presence of aromatic rings in both phases.

3.2 Density

Figure 2 presents the density of the composites produced. For composites based on unmodified or maleated Kraft lignins, density increases linearly with concentration of added lignins, with RPS+MKL giving lower values than RPS+KL. This is ascribed to the porosity created inside maleated Kraft lignins which is still present in the composites as reported in Figure 1. However, the composite with the surface treated maleated Kraft lignins was determined a much higher density than the others. Actually, its density is 3% and 5% higher than that of composites with unmodified Kraft and maleated Kraft lignins, respectively. This could be related to the presence of RPS filling the porous structures inside esterified lignin particles.
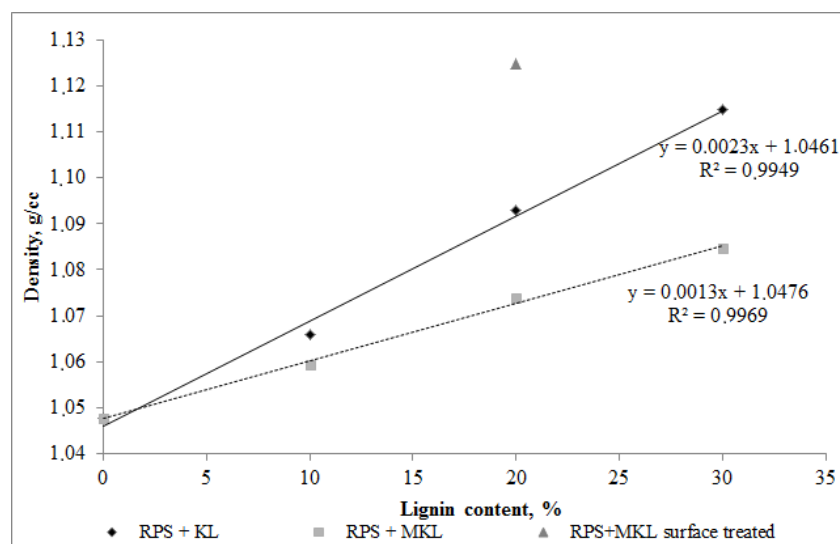

Figure 1. Density of the different composites as a function lignins concentration

3.3 Mechanical Properties of the Composites

Table 2 reports on the mechanical properties of all the samples produced. It can be seen that the addition of 10 and 20% of unmodified Kraft lignins increased the impact strength of RPS. For composite at 20% of unmodified Kraft lignins, the impact strength increased by 63% compared to RPS alone. Borsoi et al. (2013), who studied recycled and virgin polystyrene with Curaua fibers, also observed an increase but only 11% for recycled PS compared to 30%

for virgin PS. On the other hand, adding 30% of unmodified Kraft lignins caused the impact strength to decrease below the neat matrix value. This result can be associated with particle agglomerations creating defects inside the composites at higher filler content. For composites made with maleated Kraft lignins, the impact strength is slightly decreasing with increasing lignins content, but the differences are not statistically significant. This trend can be associated with the difficulty to disperse the particles in the matrix and also to low adhesion to the RPS matrix because of the porous structure limiting stress transfer. Actually, voids can act as stress concentrators and crack initiators. There is also reduced contact area between both phases when interfacial voids are present. Finally, maleated Kraft lignins with surface treatment were shown to have the highest impact strength of all the samples produced. This can be the result of good physical adhesion (RPS molecules filling the surface voids from the solution treatment) as well as good compatibility between RPS from the solution treatment and RPS molecules from the bulk polymer (matrix). The sample at 20% content of maleated Kraft lignin with surface treatment had a 74% higher impact strength than neat RPS.

Table 2 also shows the results of flexural modulus. In this case, composites with all studied lignins, except for the composite containing 10% of unmodified Kraft lignin, were determined to have slightly increased value of flexural modulus compared to the RPS matrix, by 6 to 13%. At 20% of unmodified Kraft lignins, the flexural modulus increased by 10% compared to RPS. This result is consistent with a study on polystyrene and Indulin AT Kraft lignins for which a 23% improvement of flexural modulus at 20% lignin content has been reported (Barzegari et al., 2012). With respect to the type of lignins used, no significant changes can be observed indicating that the type of mechanical testing highly influences the behavior of the materials produced.

Table 2. Mechanical properties (impact strength and flexural modulus) of the samples produced.

Coding	Sample	Impact strength (kJ/m^2)	Flexural modulus (GPa)
a	RPS	1.9 [A]	3.1 [A]
		(0.2)	(0.1)
b	RPS+KL 10%	2.2 [B]	3.1 [AB]
		(0.2)	(0.1)
c	RPS+KL 20%	3.1 [C]	3.4 [CD]
		(0.3)	(0.2)
d	RPS+KL 30%	1.7 [AD]	3.5 [D]
		(0.2)	(0.2)
e	RPS+MKL 10%	1.7 [D]	3.4 [CD]
		(0.2)	(0.2)
f	RPS+MKL 20%	1.6 [D]	3.3 [BC]
		(0.1)	(0.2)
g	RPS+MKL 30%	1.5 [D]	3.4 [CD]
		(0.1)	(0.3)
h	RPS+MKL 20% surface treated	3.3 [C]	3.3 [BC]
		(0.5)	(0.1)

*For each composite, values in parenthesis are standard deviations. Values followed by the same letter are not significantly different, while values followed by different letters are significantly different at 0.05 probability.

3.4 Thermal Properties

3.4.1 Differential Scanning Calorimetry (DSC)

The glass transition temperature (Tg) of the different sample produced is presented in Figure 3.
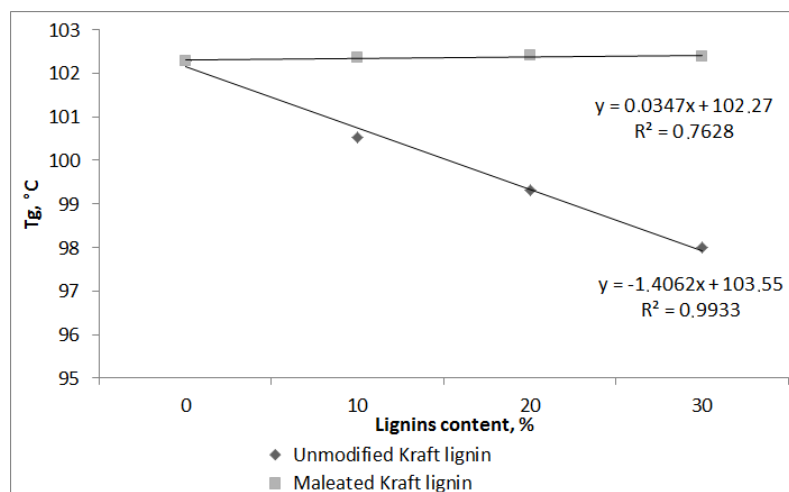
Figure 3. Glass transition temperature as determined by DSC. Lines are linear regressions

RPS alone was determined to have the highest Tg, while Tg was found to decrease linearly (slope of -1.4) with increasing unmodified Kraft lignins content, especially for unmodified and surface treated lignins. This observation could confirm that partial mixing between unmodified Kraft lignins and RPS occurred, while this was not the case for maleated Kraft lignins for which Tg was almost independent of lignins content (slope of 0.03). This result seems to confirm that unmodified Kraft lignins are better mixed with the matrix than their maleated counterparts. However, RPS composites based on surface treated maleated Kraft lignins have similar Tg as unmodified Kraft lignins. This indicates again that the treatment step is necessary to allow better compatibility of maleated Kraft lignins with RPS.

3.4.2 Thermogravimetric Analysis (TGA)

TGA results under nitrogen are presented in Figure 4 and show the thermal stability of the samples produced. To compare the results, the temperature for 5% mass loss was determined to be 251°C for unmodified Kraft lignins and 199°C for maleated Kraft lignins. Thus, the degradation of maleated Kraft lignins occurred at a lower temperature than that of unmodified Kraft lignins. Their thermal degradation occurred up to 700°C where 44% of unmodified Kraft lignins and 37% of maleated Kraft lignins remained as a cross-linked complex. RPS had the highest temperature for 5% mass loss (378°C) and its degradation occurred up to 458°C with 3% of RPS remaining at 700°C. This value can be associated with contamination and/or additives inside the RPS matrix. The behavior of the composites can be described as a combination of the behavior of RPS and lignins. For RPS containing unmodified Kraft lignins, it can be seen that the 5% mass loss temperature slightly decreased to 372-380°C depending on the amount of lignins inside the composite, whereas for RPS with maleated Kraft lignins, this temperature was even lower between 293-373°C. This could be explained by the less thermally stable unmodified Kraft lignins and especially, maleated Kraft lignins. Lisperguer et al. (2013) reported higher degradation temperatures for 2 and 5% of maleated Kraft lignins compared to the value at 10%. A decrease of the first degradation temperature of the RPS based composites was also observed. As shown in Table 3, for 50% mass loss, the temperature was slightly higher for the composite containing unmodified or maleated Kraft lignins (419-421°C) than for RPS alone (415°C), especially for composites based on surface treated maleated Kraft lignins (428°C). Finally, for all the composites, the degradation ended around 450°C and the residues increased with lignins content: from 5% for RPS alone to 13% at 30% of unmodified Kraft lignin content. The thermal degradation of the composites with unmodified Kraft lignins left higher residues than that of composites with maleated Kraft lignins. This could be related to a higher thermal resistance of unmodified Kraft lignins under nitrogen compared to maleated Kraft lignins which contain more oxygen-containing functional groups.
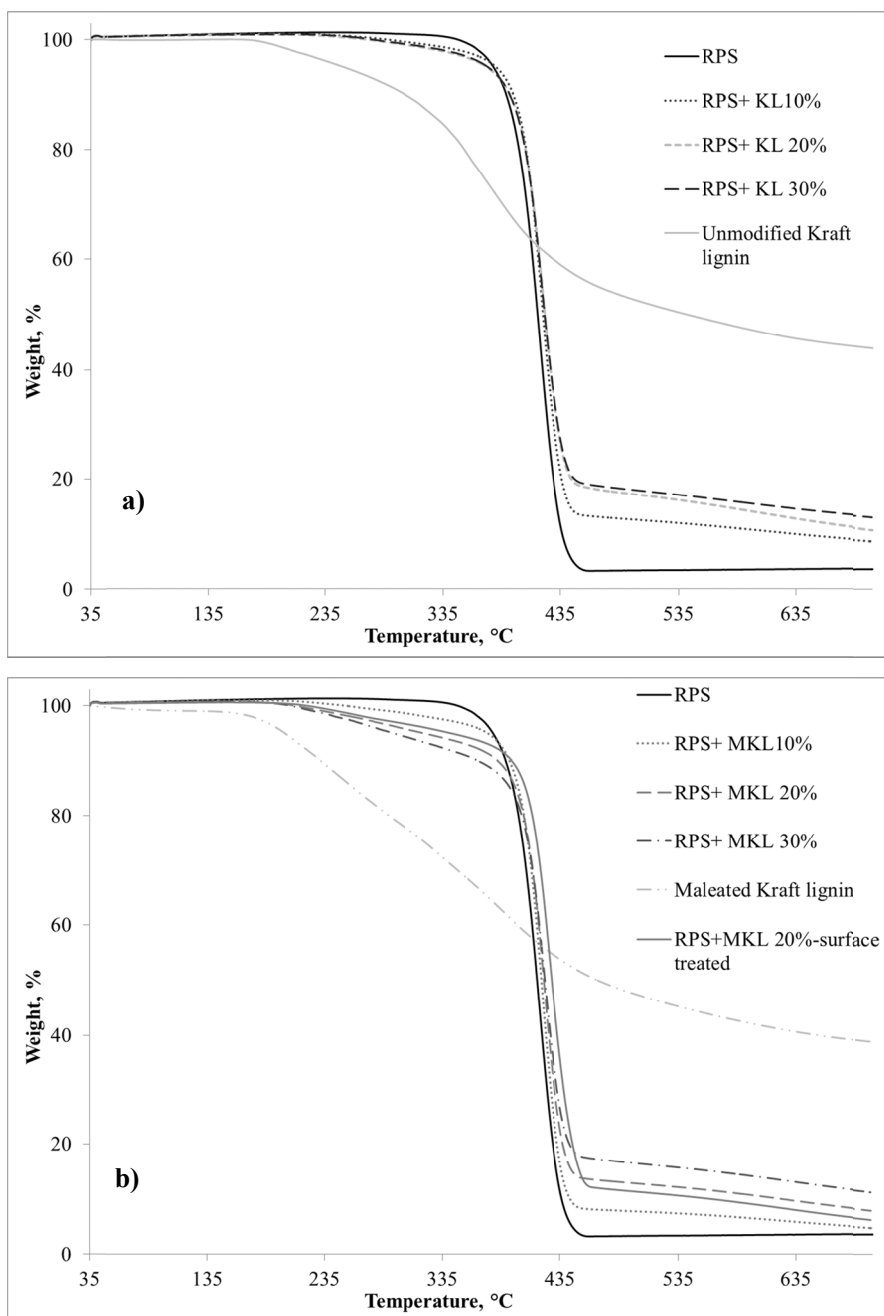
Figure 4. TGA curves under nitrogen for: a) unmodified Kraft lignin, RPS and composites with unmodified Kraft lignins, and b) maleated Kraft lignin, RPS and composites with maleated Kraft lignins

The maximum rate degradation temperature from DTG (Table 3) of the composite with maleated and unmodified Kraft lignins was a few degrees higher than for RPS alone (416°C). The highest temperature (428°C) was determined for the composite containing surface treated maleated Kraft lignin (Table 3).
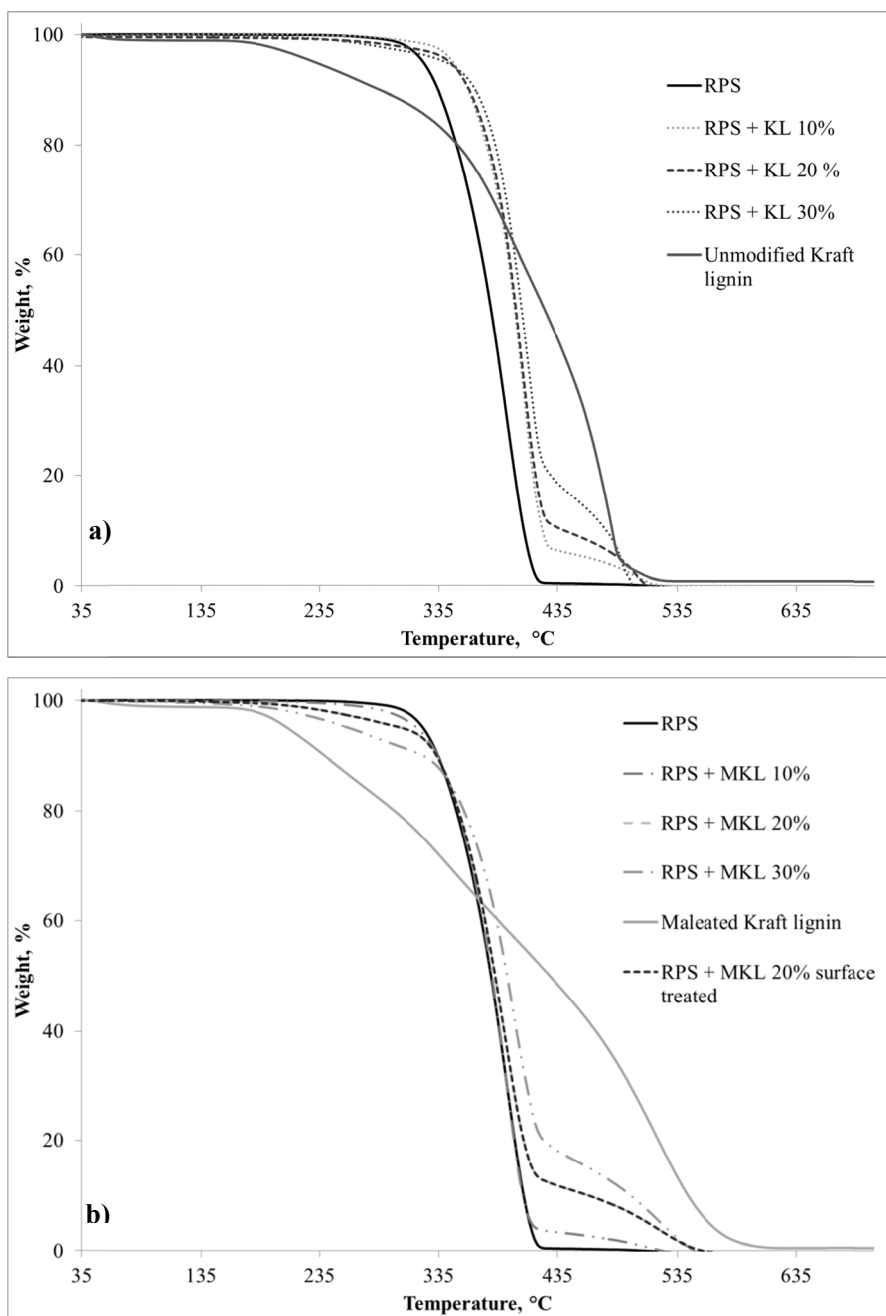
Figure 5. TGA curves under air TGA: a) unmodified Kraft lignin, RPS and composites with unmodified Kraft lignins, and b) maleated Kraft lignin, RPS and composites with maleated Kraft lignins

TGA results under air are presented in Figure 5. Under air, more differences between the samples were observed. While the temperature of 5% mass loss was determined to be 322°C for neat RPS, it decreased to 231 and 208°C for unmodified and maleated Kraft lignins, respectively. Maleation decreased the thermal stability probably due to the increase of ester and carboxylic functions in lignins. As shown in Table 3, this temperature increased for RPS composites with unmodified Kraft lignins content (341-347°C). For composites with maleated Kraft lignins, this temperature decreased with increasing content (260-317°C), except for the composite based on surface treated maleated Kraft lignins (325°C). For 50% mass loss, the temperatures were few degrees higher for all the composites containing unmodified Kraft lignins compared to those containing 30% of maleated Kraft lignins or the composite based on surface treated maleated Kraft lignins. As seen in Table 3, the final degradation temperatures under air of composites with unmodified or maleated Kraft lignins was higher than for RPS alone. This difference could be explained for the unmodified Kraft lignins by the condensation reactions taking place

during melt mixing step leading to formation of C-C bonds, which rendered structure more thermally stable, as reported elsewhere (Bridson, Van de Paz, & Fernyhough, 2013). These condensed structures could be more difficult to degrade in the composite. As a result, degradation occurs at higher temperature. For composites with maleated Kraft lignins, the performance of the composites could be explained by the Kraft lignin structure modification during esterification, as discussed previously.

Table 3. Thermal properties obtained from TGA and DTG (under nitrogen and air)

	RPS	RPS+ KL 10%	RPS+ KL 20%	RPS+ KL 30%	RPS+ MKL 10%	RPS+ MKL 20%	RPS+ MKL 30%	RPS+ MKL 20% surface treated
Under N$_2$								
T$_{5\%}$ (°C)	378	380	372	373	373	319	293	342
T$_{50\%}$ (°C)	415	420	421	421	419	421	422	428
Residues (%)	4	9	11	13	5	8	11	6
T$_{max}$ DTG (°C)	416	419	419	419	419	421	421	428
Under air								
T$_{5\%}$ (°C)	322	347	344	341	317	304	260	325
T$_{50\%}$ (°C)	379	399	400	405	379	382	392	401
T$_f$ (°C)	435	513	508	496	515	549	546	535
T$_{max}$ DTG (°C)	389	402	401	401	387	387	395	404

T$_{5\%}$: Temperature of 5% mass loss; T$_{50\%}$: Temperature of 50% mass loss; T$_f$: Final degradation temperature; T$_{max}$ DTG: Temperature for maximum degradation rate (DTG).

For the DTG under air, the temperature for maximum degradation rate is 389°C for RPS alone, which slightly increased to 402°C for RPS containing unmodified Kraft lignins, but remained unchanged for RPS containing maleated lignins. Therefore, as indicated by the thermal properties under air, unmodified Kraft lignins could be used as antioxidants in RPS based composites as such an activity had been already demonstrated for Indulin AT lignins in virgin polystyrene (Barzegari et al., 2013). Maleated Kraft lignins may also be used as an antioxidant, but only with a solubilization step prior to formulation of RPS based composite.

4. Conclusion

The main goal of this investigation was to determine if Kraft lignins can be used as functional fillers in thermoplastic resins. For this purpose, different concentrations of unmodified and maleated Kraft lignins (10-30%) were introduced in RPS. The composites were produced by melt blending and the compression molded composites were characterized in terms of mechanical, thermal and morphological properties. To study the effect of lignins compatibility with the matrix, a trial was also performed with surface treated maleated Kraft lignins in a RPS solution. From the results obtained, several conclusions can be drawn:

1) The incorporation of unmodified Kraft lignins in RPS showed by SEM a rough surface on the composite compared to maleated Kraft lignins which showed a smoother texture due to better compatibility between two compounds, but a porous structure was still present. However, for the composite based on surface treated maleated Kraft lignins, smooth surfaces were obtained without any porosity showing better incorporation of maleated Kraft lignins with the solubilization step. This was also confirmed via density measurements.

2) The linearly decreasing glass transition temperature for composites with unmodified Kraft lignins indicates that partial mixing of the unmodified Kraft lignins with the RPS matrix occurred in the composites compared to composites with maleated Kraft lignins which showed a Tg decrease only for the composite based on surface treated maleated Kraft lignins.

3) The mechanical properties (flexion and impact) were improved, especially the impact strength, for the composite with 20% of unmodified Kraft lignins and for the composite based on surface treated maleated Kraft lignins.

4) Unmodified Kraft lignins acted as antioxidants in the composite as observed by the better thermal stability (TGA) under air.

5) The condensation created in unmodified Kraft lignins during the melt mixing step could create alone a stronger composite than possible with the maleation of Kraft lignins even with surface treated maleated Kraft lignins.

6) Finally, the composites based on RPS were shown to have good properties while being easily processed. In this case, 20% of a petroleum-based polymer has been replaced by renewable materials: unmodified Kraft lignins.

Acknowledgments

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