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LIGNIN-ESTER DERIVATIVES AS NOVEL THERMOPLASTIC MATERIAL

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Abstract

Spruce and eucalyptus lignins isolated by an organosolv process and lauroyl chloride were used as raw material for the synthesis of lignin-ester derivatives. The obtained products presented new and interesting properties suitable for use as thermoplastic materials. Esterification of the lignins was confirmed by FTIR, GPC, DSC and contact angle measurements. The modification of lignin –OH groups increased the molecular weight properties, changed its thermal behavior (reducing greatly Tg), and improved the hydrophobicity of the material. For composite elaboration, commercial cellulose acetate was used as reinforcement in different percentages (5%, 10%, 25% and 50%) to manufacture composites by press moulding. Thermal and mechanical tests as well as wetting behavior of the composites surface against water analysis were carried out. Surface morphology was analyzed by SEM. The mechanical test revealed tensile strength and Young modulus values of 130–900 kPa and 2–50 MPa respectively, with high elongation at break (5–130%) for eucalyptus lignin composites, while spruce lignin composites showed more a rigid (40–60 MPa) and tough (300–1400 kPa) behavior, but with the ability to deform only up to 6%.

1. INTRODUCTION

The huge environmental concern about damaging effects of commercial synthetic polymers on the environment due to their non-renewable nature and ultimate disposal is rapidly increasing, creating a big demand of eco-friendly biomass based products. For this purpose, lignin, one of the main structural components of lignocellulosic biomass and the second most abundant macromolecule in nature, can offer a large amount of organic material that could be used in the production of biopolymers. Moreover, this natural source is cost effective and biodegradable.

Numerous studies can be found about lignin applications in the polymer field. Some recent advances which involved the use of lignin in the development of new polymer composite materials have been summarized; relevant studies about addition and the influence of lignin in thermoplastics (PS, PET, PP, etc.), thermosets (PF-phenol formaldehyde) and foam-based materials (PU-polyurethane) have been done¹. Moreover, the use of monomers from lignin such as vanillin and its chemical modification can offer a new vanillin-based homopolymers with comparable thermal properties than PS².

However, although its abundance and chemical nature make it as one of the best options to be used as polymer precursor in the polymer industry, lignin by itself presents some disadvantages for plastics production, even when is added to hydrophobic polymers (synthetic or biopolymers) since the presence of hydroxyl groups in lignin often generate a poor compatibility between both components^{1,3-5}. Moreover, it is a rigid and brittle polymer and presents poor film forming ability as well as difficulty during processing due to its high softening point (T_g)⁶⁻⁷. These characteristics are caused by its natural condensed structure and strong intermolecular hydrogen bonding interactions which

restrict the thermal mobility of lignin providing high T_g value⁸. However, due to its complex structure based on various phenylpropane units with various functional groups including aromatic and aliphatic hydroxyl (-OH), methoxyl (-OCH₃), carbonyl (-C=O) groups principally; lignin has high potential for chemical modifications, which can lead to value-added polymeric materials with specific and desirable properties⁷. Hence, chemical modification of hydroxyl groups present in lignin is the best alternative to increase its range of applications in the polymer industry area¹⁰⁻¹².

The esterification, one of the easiest chemical reactions to perform considering the reaction parameters and used reactants⁸, allows the change of some of the original properties of lignin, such as increasing its hydrophobicity as well as its solubility in organic solvents¹³. In addition, when lignin is modified by esterification, hydroxyl groups are functionalized by ester substituents¹⁴, thus reducing the number of hydrogen bonding and leading to an increase of the free volume in the molecule, providing greater mobility of the chains¹⁵. Therefore, esterification is a potential route to lower the glass transition point of lignin and increase its thermoplasticity^{11,14,15}, highly desirable for current industrial polymeric processing technology. In addition, it is well-known that the reduction of T_g is higher when increasing the length of the attached chain. Lewis et al., 1943¹⁶ was the first author who published a study about the modification of lignin with fatty acids and showed that esterified lignin gained new and very interesting properties like changes in solubility and thermal behavior. Later, Glasser and Jain, 1993¹⁷ also revealed a consistent decline in T_g with increasing ester substituent size.

Although there are some studies about chemical modification of lignins with fatty acids, state of the art review reveals none of them has been used for composites elaboration using functionalized lignins as matrix.

On the other hand, cellulose acetate is a well known material in the film forming industry, it has proved to provide stiffness as bulk load in different matrices as its crystalline structure generates stiffness networks within the matrix; on the other hand, acetyl groups attached to the OH-groups characteristic of cellulose enhances the particle interaction between cellulose and the modified lignins¹⁸⁻²⁰. Moreover, triethylcitrate (TEC) is a natural ester obtained from citric acid and widely used as plasticizer or as stabilizer in different composite materials, its natural origin and its biocompatibility makes it a good plasticizer for biobased composite materials²¹.

Therefore, this study was focused on the synthesis of lignin-ester derivatives using a long aliphatic chain (12 carbons) to obtain a reduction of its softening point and make it a thermoplastic product, capable of being processed by press moulding; the use of cellulose acetate as reinforcement was aimed to provide better consistency to the final material. The main objective was to produce a fully environmental-friendly material by using fully biobased functionalized polymers (cellulose and lignin). The new physicochemical properties of lignin after chemical modification like molecular weight, hydrophobicity and thermal properties were evaluated and compared to other studies. Thermal, mechanical and morphological behaviors of elaborated composites were analyzed.

2. MATERIALS AND METHODS

2.1. Materials. Lignin samples were isolated from Eucalyptus and Spruce woods as described by Gordobil et al., 2016²². Commercial cellulose acetate with 39.8 wt.% acetyl content (average Mn~30000 determined by GPC) was supplied by Sigma Aldrich. N,N-dimethylformamide (99%), pyridine (99%) and hydrochloric acid (37%) was provided by

Fisher. Triethyl amine ($\geq 99\%$) (Sigma Aldrich), ethanol absolute (99.9%) (Sharlab), and lauroyl chloride (98%) (Across organic) were also used.

2.2. Synthesis of lignin-ester derivatives. 5 g of lignin was dissolved into 150 mL of DMF in a two-necked flask with a magnetic stirrer. Triethylamine (7.5 mL) was added and pyridine (27.5 mL) was used as a catalyst. The reaction was conducted at 20 °C for 2 h. After that, the solution was poured into 5 L of 2% ice-cold hydrochloric acid. The precipitate was filtered and washed with excess distilled water and ethanol to remove unreacted fatty acids. The samples were then dried in vacuum at 35 °C overnight. Modified lignin from spruce (OS_{12C}) and eucalyptus (OE_{12C}) were kept inside Petri dishes at room temperature.

2.3. Composites processing. Synthesized lignin-ester derivatives were manually blended with commercial cellulose acetate at different concentrations (5, 10, 25, 50%) with a stainless rod, using a silicone mould in a water bath at 50 °C for composites with OE_{12C} and at 80 °C for composites with OS_{12C}. For OS_{12C} composites elaboration a plasticizer was needed to allow its processing, triethyl citrate (TEC) was used for this purpose at 5% and 10% of the total weight of components as it is a good biobased plasticizer. Compression moulding was used for composites processing. Blends were placed between stainless plates coated by Teflon and then placed in the press which was preheated to 40 °C. Blends were hot-pressed readily at 5-7 bar for 3 minutes after which they were cooled to room temperature.

2.4. Characterization.

The FT-IR analysis of unmodified and esterified lignins was performed on a PerkinElmer UATR Two FT-IR spectrophotometer. A total of 8 scans were accumulated

in transmission mode with a resolution of 4 cm^{-1} . The spectra were obtained from a range of 4000 to 650 cm^{-1} .

Size exclusion chromatography analysis was used to evaluate the average molecular weight (Mw) and polydispersity (Mw/Mn) of the obtained lignin samples. N, N Dimethylformamide (DMF) eluent was used as GPC mobile phase, at a flow rate of 0.7 mL/min and $35\text{ }^{\circ}\text{C}$, using a Jasco Inc. chromatograph provided with an LC-NetII/ACD interface, a column oven CO-2065Plus and a RI-2031Plus intelligent refractive index. A guard column and two columns PolarGel-M (Varian Inc.) were employed. Calibration was made using polystyrene standards provided by Fluka, ranging from 250 to 70.000 g/mol.

The glass transition temperature of isolated and esterified lignins was determined by METTLER TOLEDO DSC 822 differential scanning calorimetry. Samples about 5-10 mg were tested under nitrogen atmosphere at a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$. The isolated lignins were heated from $25\text{ }^{\circ}\text{C}$ to $200\text{ }^{\circ}\text{C}$. Each sample was first run from 25 to $110\text{ }^{\circ}\text{C}$ (10 min) and cooled down to $25\text{ }^{\circ}\text{C}$ to eliminate any interference of water. On the other hand, chemical modified lignins and composites were analyzed from $-50\text{ }^{\circ}\text{C}$ to $200\text{ }^{\circ}\text{C}$. In this case also the samples were heated until $110\text{ }^{\circ}\text{C}$, then was cooled down to $-50\text{ }^{\circ}\text{C}$ and reheated to $200\text{ }^{\circ}\text{C}$. The obtained results are from the second heating thermogram.

Thermogravimetric analyses were carried out with TGA/SDTA 851 METTLER TOLEDO. Isolated and esterified lignins were analyzed to determine their thermal stability. Samples about 5-10 mg were tested under nitrogen atmosphere at a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$ from $25\text{ }^{\circ}\text{C}$ to $800\text{ }^{\circ}\text{C}$. Composites were also analyzed at the same conditions to know if the addition of cellulose has an influence on thermal stability.

Dynamic contact angle measurements were carried out with water using a Dataphysics Contact angle system OCA 20, in order to determine the changes in the hydrophilic character of lignin before and after chemical modification. Uniform strips have been used for this propose. To examine water repellence of composites, water (WCA) was used by the placement of a droplet (5 μ l) and at different times (1, 10, 20, 30, 40, 50, 60, 90, 120 s). The average value of five measurements per sample was calculated.

The morphology of composites surfaces was observed with a Scanning electron microscope JEOL JSM-6400F with field-emission cathode, at room temperature. The samples were gold sputtered up to a thickness of 20 nm. An accelerating voltage of 20 kV was used to collect the micrographs with a lateral resolution of 10-11 Å at 20 kV.

Mechanical test of composites was performed by MTS Insight 10 equipment provided with pneumatic clamps (Advantage Pneumatic Grips) and with a loading cell of 250 N with a speed of 5 mm/min. Thicknesses of samples ranged between 0.4-0.7 mm. The starting distance between the clamps was set at 22.5 mm. Samples with 5 cm length and 5 mm width were prepared. The values quoted are the average of eight measurements.

3. RESULTS AND DISCUSSION

3.1. Verification of the esterification reaction. The chemical modification was confirmed by different techniques such as FTIR, GPC, contact angle and DSC. FTIR spectra (Fig. 1) of lignin-ester derivatives confirmed that the esterification process was successful at studied conditions. This modification is highlighted for its short period of time at room temperature. Chemically modified lignins showed that the signal around 3400 cm^{-1} which corresponds to O-H stretching vibrations in aromatic and aliphatic

hydroxyl groups was reduced and the appearance of two new peaks around 1740 cm^{-1} and 1760 cm^{-1} are clearly seen. They are assigned to aliphatic and aromatic ester bonds, respectively. The intense increase of peaks at 2930 cm^{-1} and 2840 cm^{-1} are assigned to long chain alkyl groups (aliphatic carbon) which are present in fatty acid chloride^{16,23}.

Moreover, chemically modified lignins presented some different properties compared to isolated ones such as molecular weight properties, thermal behavior, hydrophobicity as well as its physical appearance. After esterification of lignins with lauroyl chloride, a significant increase in M_w can be observed as it was expected (Table 1). This demonstrated that fatty acid has been successfully grafted to lignin samples. It is well known that the weight average should increase when lignin is modified with ester groups; also the molecular weight increase as the length of the ester substituent is increased^{12,17,24}.

Table 1. Weight average (M_w), number average (M_n) and polydispersity index (M_w/M_n).

	M_n	M_w	PDI
OE	1498	9490	6.3
OE_{12C}	3364	21569	6.4
OS	896	3124	3.5
OS_{12C}	5363	24601	4.6

DSC is one of the most accepted methods to define the glass transition temperature (T_g) of lignin molecule. This thermal parameter of polymers provides important information to use lignin in polymer applications and to process it by current industrial processing techniques like hot pressing. T_g of lignins is often very difficult to determine due to the heterogeneity of the lignin chemistry, as well as the broad molecular weight distributions. Thus, the temperature range in which this phenomenon occurs is usually quite wide²⁵. Some previous studies discussed about thermoplasticity of lignin^{7,17} considering that lignin molecule presented a thermal softening point²⁶. That transition generally occurs at

high temperatures (90-180 °C) for non-derivatized lignins^{27,28}. In this case, T_g values for isolated lignins were 116.5 °C for OE and 122.7 for OS, as was demonstrated in a previous work²². However, lignin-ester derivatives presented an interesting change in its thermal behavior. Fig. 2 shows the obtained thermograms for both lignin-ester derivatives. In the case of OE_{12C}, T_g of the sample was not clearly observed. However, based on the glass transition temperature is defined as the midpoint of the lineal variation of the polymer heat capacity, and taking into account this inflexion point is a maximum of the curve first derivative, it was possible to obtain a clearer information to indentify this parameter. So, based on this basic concept, it is possible to assume that the modification of OE generated a great reduction of the glass transition temperature for OE_{12C}, which began to soften at temperatures below room temperature (10.5 °C) due to the internal plasticizing effect of the introduced ester groups. However, OS_{12C} did not show the same behavior. In this case, a clear endothermic peak at 38.5 °C was observed. Although at first, it was thought that this endothermic peak was related to melting of the material, this conclusion was rejected because this material is totally amorphous and the thermogram never showed a crystallization peak. Therefore, it could be confirm that this endothermic peak is associated with the glass transition temperature of the material, which is usually presented as endothermic peak due to enthalpy relaxation. This usually happens when the sample has been stored under the glass transition temperature for a "long time". Thus, the replacement of hydroxyls groups by ester substituent produced the reduction of the number of hydrogen bonding in lignin molecule and implied an increase free volume in the molecule and thus the mobility of the chains^{15,17}. Therefore, the use of esterification to elaborate lignin derivative products by attaching long aliphatic chains proved that it is a suitable method to obtain lignins with different thermal behaviors. The differences on

their physical appearance are mainly due to the change on their softening point. Isolated lignins were a brown thin powder ($T_g \sim 115\text{-}125\text{ }^\circ\text{C}$) while esterified lignins exhibited different appearance. OE_{12C} showed a soft and sticky dark resin appearance because its new T_g was below room temperature. Although OS_{12C} also has undergone a drastic reduction of its softening point, is not as malleable and seems more brittle not having such resinous appearance as its T_g remained above room temperature.

On the other hand, contact angle with water measurements of isolated and esterified lignins were performed in order to confirm the change in the hydrophobicity. After chemical modification, hydroxyl groups present in lignins are substituted with non-polar groups $[-CO(CH_2)_{10}CH_3]$ increasing the hydrophobicity¹⁶. Fig. 3 shows how esterified lignins presented higher hydrophobicity than isolated lignins. Moreover, it can be observed that modified lignins displayed a greater stability in contact angle values through time.

3.2. Thermal behavior of composites. The thermogravimetric (TGA) first derivative (DTG) curves of isolated, synthesized lignin-ester derivatives and composites under nitrogen atmosphere are presented in Fig. 4 (a and b). Thermal stability of the samples was assessed as the onset temperature (referred to 5% weight loss on a dry basis), maximum degradation temperature as well as the amount of residual char and the obtained results are summarized in Table 2. Isolated lignins had a small weight loss (2-4%) below $100\text{ }^\circ\text{C}$ due to the gradual evaporation of moisture. The main weight loss stage occurs in the temperature range between $200\text{-}600\text{ }^\circ\text{C}$ ²⁹ but Eucalyptus lignin (OE) presented lower thermal stability than Spruce lignin (OS) with the main weight loss temperature values at $353.4\text{ }^\circ\text{C}$ for OE and $385.8\text{ }^\circ\text{C}$ for OS. Generally, it is common that hardwood lignins present lower thermal stability than softwood lignins³⁰. It depends mainly on the chemical

structure, molecular weight properties as well as the applied extraction processes²². On the other hand, considering that thermal degradation of polymers is usually an important parameter to know during thermal processing and to establish the service life conditions³¹, it was very important to determine the thermal degradation profile of synthesized lignin-ester derivatives as well as elaborated composites. Thermograms of esterified lignins were indicative of the alterations in chemical structure and as a result in the thermal stability. Synthesized lignin-ester derivatives presented more stable profiles at the beginning as they do not show any weight loss due to moisture, confirming that they expressed less affinity for water and higher hydrophobicity than isolated lignin samples. However, thermal stability of lignins decreased after chemical modification. The initial degradation temperature ($T_{5\%}$) was lower with 184.0 °C for OE_{12C} and 188.5 °C for OS_{12C} while both isolated lignin samples began to degrade around 260 °C. The same happened in other studies in which cellulose was esterified with fatty acids³². Moreover, two degradation steps were observed for both samples. The first one occurred at around 200 °C being more noticeable for OS_{12C} and the second one was between 350-400 °C (see Table 2). The first weight loss is associated with the cleavage of the C-O bond present in the ester linkage and the consequent loss of the introduced long aliphatic chain. In other studies, where other biomass components like cellulose was modified with the same reactive (dodecanoyl chloride), there were also observed two degradation steps^{33,34}. The first one could be observed at similar temperatures to this study. About elaborated composites made from OE₁₂, in general a slight improvement on initial degradation temperature was observed as the acetate cellulose content increased. However, a small reduction of the main degradation step was found. Moreover, no clear evidence on the trend of the degradation step which occurred between 180-250 °C was observed.

Although it could not be tested mechanically, OS_{12C} composites were prepared in the absence of plasticizer in order to study the influence of the plasticizer on thermal behavior of the material (data not shown). The results showed that TEC had important influence on thermal degradation profile creating a small reduction on both initial degradation temperature and the main degradation temperature at higher contents. In any case, the same trend as the OE_{12C} composites was noticed; the cellulose acetate content increased the temperature of the degradation step which happened around 200 °C. Furthermore, in both cases, the cellulose content involved a small reduction of the main degradation step. On the other hand, esterified lignin as well as composites exhibited higher weight loss than original lignins due to the lower phenolic OH group contents in its structure. The char residue was 15-20% OE_{12C} and 20-27% for OS_{12C} and its composites respectively, while isolated lignins remained over 40%. Hence, thermal degradation profiles demonstrated that synthesized lignin-ester derivatives and its composites presented thermal degradation temperatures so remote from the temperature at which the material can be processed.

Table 2. Thermal degradation temperatures and char residue characteristics of isolated lignins, esterified lignins and elaborated composites.

	T_{5%}	T_{max}	Residue at 800°C	
OE	261.6	----	353.4	40.8
OE _{12C}	184.0	180-250	370.4	18.2
OE _{12C} 5%	183.9	180-250	363.2	17.5
OE _{12C} 10%	187.9	180-250	357.3	17.1
OE _{12C} 25%	192.6	180-250	356.2	18.1
OE _{12C} 50%	187.6	180-250	361.2	16.2
OS	257.8	----	385.8	48.7
OS _{12C}	188.5	216.2	393.1	26.6
OS _{12C} 5% (5% TEC)	184.7	214.1	383.6	25.2
OS _{12C} 25% (5% TEC)	185.1	217.2	368.6	22.0
OS _{12C} 5% (10% TEC)	179.3	207.6	381.3	24.7
OS _{12C} 25% (10% TEC)	182.8	216.4	367.6	20.9

DSC was used in order to understand the thermal transitions of elaborated composites. The DSC curves of elaborated composites are reported in Fig. 5 (a and b). Both types of composites presented similar thermal behaviors. In both systems two T_g values are appeared. The first one corresponds to T_g of the lignin-ester derivative while the second is related with T_g of the acetate cellulose which was found at 115.2°C (data not shown). In general, the addition of cellulose acetate did not show any influence on the softening temperature of the matrices. Only when the cellulose acetate content was low (5%) in OE_{12C}, the T_g of the matrix increased from 10.5°C to 21.9°C. This suggested that the presence of low contents of cellulose acetate as reinforcement promoted some molecular restrictions on lignin molecule. Although the addition of cellulose acetate as reinforcement did not cause important changes in thermal behaviors of produced lignin-ester derivatives, its use help during processing and an important improvement was observed on mechanical properties. The addition of plasticizer had not influence these thermal transitions.

3.3. Composites appearance and surface properties. The addition of cellulose acetate as reinforcement created more consistent products which enhanced their ability to be processed and manipulated, especially for composites with OE_{12C} as matrix. These types of composites were able to form a continuous material without the addition of any kind of plasticizer. However, elaborated composites using OS_{12C} as matrix, presented too high fragility and great difficulty of handling. Therefore, TEC was used as plasticizer at 5% and 10 %. Higher plasticizer content hindered the composites processing. As the cellulose acetate content increased in the material, a color change could be observed in composites made from OE_{12C}. Moreover, the material became less sticky and more malleable. For composites with OS_{12C} as matrix, the color change with the addition of cellulose acetate

was not visually appreciable, showing all composites the same black color. Fig. 6 shows the visual aspect of both of elaborated composites.

Fig. 7 shows the most representative SEM images where it could be observed some morphology differences between composites. In the case of composites made from OE_{12C} as matrix and different cellulose content (5% and 25%), it was observed a homogeneous and smooth surface, in which an even dispersion of cellulose acetate in the matrix is noticed. Other studies where softwood Kraft lignin was chemically modified with stearyl chloride to introduce a long aliphatic chain (18 carbons), showed similar morphology after press moulding than composites made from OE_{12C}.³⁵ Cellulose acetate is presented both as fibers with diameters around 10 μm as well as particles with lower sizes. Most of the fibers are appreciated inside the matrix with some of them emerging to the surface of the OE_{12C} matrix at one end. On the other hand, composites elaborated with OS_{12C} presented a completely different morphology that does not correspond to the usual morphology of melted plastic materials. Composites with 5% TEC content showed a non-continuous and rough surface. This suggests that although the material has visual aspect of a softened material, at microscale it can be observed that this process did not take place. However, the increase of TEC content to 10% caused a higher softening of the material at processing temperature, which is clearly noticeable on surface roughness. The porous structure was reduced in composites with 10% TEC when compared to 5% TEC composites and is more similar to those of OE_{12C} as matrix obtaining a material with a smoother surface. Therefore, the different morphologies of composites could be due to the differences on thermal behavior between them and the used processing conditions. Moreover, it is well known that the morphology of the materials has a great influence on the final mechanical properties. So, composites made from OE_{12C} as matrix had higher

ductility due to the absence of imperfections than composites made from OS_{12C}. However, the macro porous structure revealed by SEM of composites made from OS_{12C} as matrix, especially in the case in which lower plasticizer content was added, could be responsible of the high fragility of these type of composites.

In addition, the dynamic contact angles with water (WCA) of composites surfaces are shown in Fig. 8. The contact angle of liquids on solid surfaces provides direct information about the wetting behavior of the surface. All composites were quite stable against water with values above 80 ° after two minutes of analysis, showing the most hydrophobic behavior for composites made from OE_{12C}.

3.4. Mechanical properties. Mechanical properties of the elaborated composite materials were characterized using tensile testing at room temperature. The Young modulus (E), elongation at break (ϵ) and tensile strength (σ) are shown in Table 3. It was not possible the elaboration of control films made from original isolated lignin samples and cellulose acetate as reinforcement due to their shape (powder) and their high softening point (115-125 °C). However, the studied composites clearly showed a thermoplastic behavior; on the other hand, the cellulose acetate content into the material had an important influence on it, probably due to an appropriate dispersion of fibers and good compatibility between synthesized lignin-ester derivatives and cellulose acetate which both have a hydrophobic character. Young modulus and tensile strength of elaborated composites increased with the increase of cellulose acetate content, confirming the high reinforcement potential of the cellulose fibers as already has been demonstrated by other authors^{18,19}.

High differences on mechanical behavior between composites were found. In case of composites made with OE_{12C} as matrix and different contents of cellulose acetate, very high elongation at break (up to ~130%) could be observed, but it was decreasing (up to

~5%) as the cellulose acetate content increased, as expected taking into account the results obtained by other authors³⁶⁻³⁸. Although, low elongations at break are usually related to properties such as stiffness and fragility, in this case OE_{12C} 50% maintained its malleability without being brittle. With regard to composites elaborated with OS_{12C}, different percentages of cellulose acetate and TEC as plasticizer, is remarkable the higher strength and stiffness of composites with tensile strength and Young modulus values larger than composites made from OE_{12C}. However, lower elongations at break values were noticed. Moreover, the addition of TEC also presented an important influence, showing higher tensile strength and Young modulus values at lower TEC contents. Other author studied the obtention of lignin-based thermoplastic copolyester synthesized via copolymerization of sebacoyl dichloride with alkali lignin and poly(ethylene glycol) with similar mechanical values up to 1.3 MPa of tensile strength and modulus of 16 MPa but with elongations at break up to 60 %³⁹.

Table 3. Average values of tensile strength, elongation at break and Young modulus of composites.

	σ (KPa)	ϵ (%)	E (MPa)
OE_{12C} 5%	136.3 ± 27.8	129.2 ± 16.8	2.8 ± 0.6
OE_{12C} 10%	185.5 ± 11.9	98.2 ± 20.7	6.5 ± 1.2
OE_{12C} 25%	424.0 ± 18.1	54.1 ± 9.6	13.4 ± 1.3
OE_{12C} 50%	906.8 ± 19.9	4.8 ± 1.6	47.8 ± 1.2
5% TEC			
OS_{12C} 5%	707.0 ± 57.0	1.5 ± 0.2	53.7 ± 9.4
OS_{12C} 10%	968.5 ± 36.2	1.0 ± 0.4	86.1 ± 5.9
OS_{12C} 25%	1429.0 ± 74.0	1.6 ± 0.3	111.9 ± 7.6
10% TEC			
OS_{12C} 5%	317.0 ± 57.9	1.7 ± 0.1	57.3 ± 1.4
OS_{12C} 10%	756.2 ± 30.8	6.0 ± 1.3	45.1 ± 4.3
OS_{12C} 25%	946.8 ± 51.2	4.0 ± 1.1	47.1 ± 4.1

CONCLUSIONS

The esterification process at studied conditions was successful to synthesize lignin-ester derivatives to be used as matrix for composites elaboration. Chemically modified lignins

showed a significant decrease of glass transition temperature. The thermal degradation temperature was far from the temperature at which the material can be processed, making them a suitable product to use as thermoplastic matrix. Ten new composites based in two different lignins were evaluated. The addition of cellulose and also the plasticizer improve their ability to be manipulated and processed. The use of TEC as plasticizer generated a small reduction of thermal stability. Appearance differences between different composites as well as stiffness and brittleness were visually appreciable. Composites made from OE_{12C} and different cellulose contents presented the highest and more stable dynamic contact angle for water. Reinforced OS_{12C} composites showed the most rigid and tough behavior as well as brittleness. However, OE_{12C} composites exhibited higher ability to deform. In both cases, the reinforcement potential of cellulose acetate was demonstrated, suggesting that the final properties of the material were less dependent on the cellulose acetate content and more dependent on the lignin intrinsic characteristics.

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Figures

Fig. 1. FTIR spectra of isolated and esterified lignins, (a) organosolv spruce lignin (OS) and (b) organosolv eucalyptus lignin (OE).

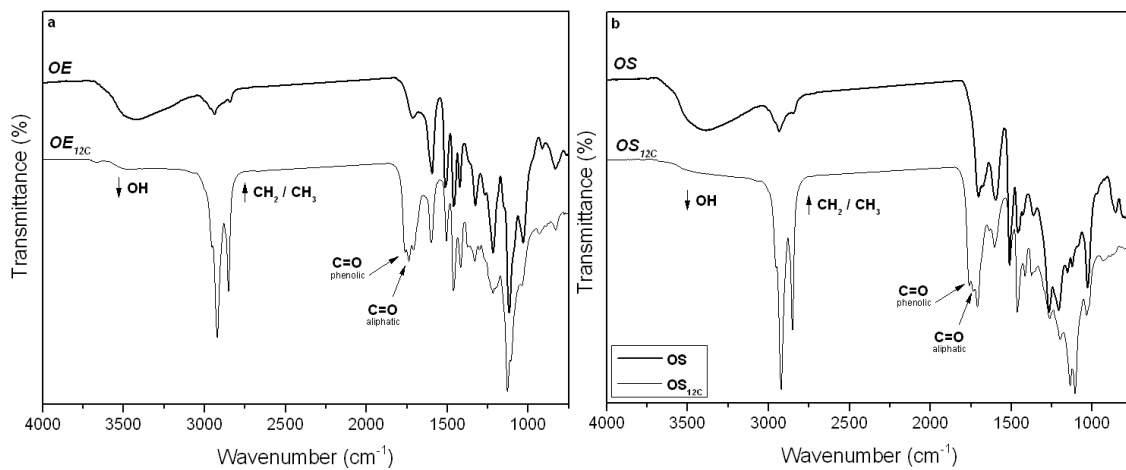


Fig. 2. DSC thermograms of lignin-ester derivatives.

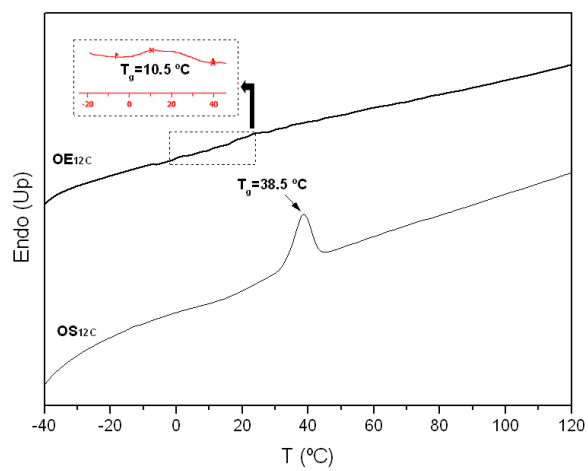


Fig. 3. Contact angle of isolated and esterified lignins and with images of contact angle of isolated and esterified lignins after 120 s.

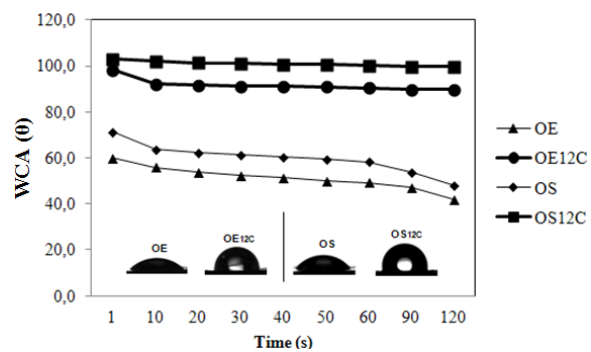


Fig. 4. TG and DGT curves of (a) Eucalyptus lignin (OE), OE_{12C} and its composites and (b) Spruce lignin (OS), OS_{12C} and its composites.

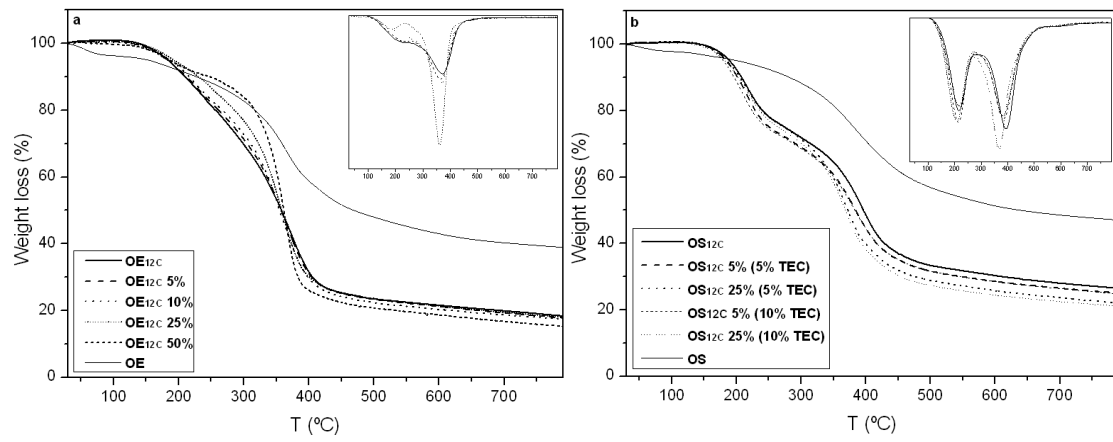


Fig. 5. DSC thermograms of composites (a) made from OE₁₂C as matrix and (b) made from OS₁₂C as matrix.

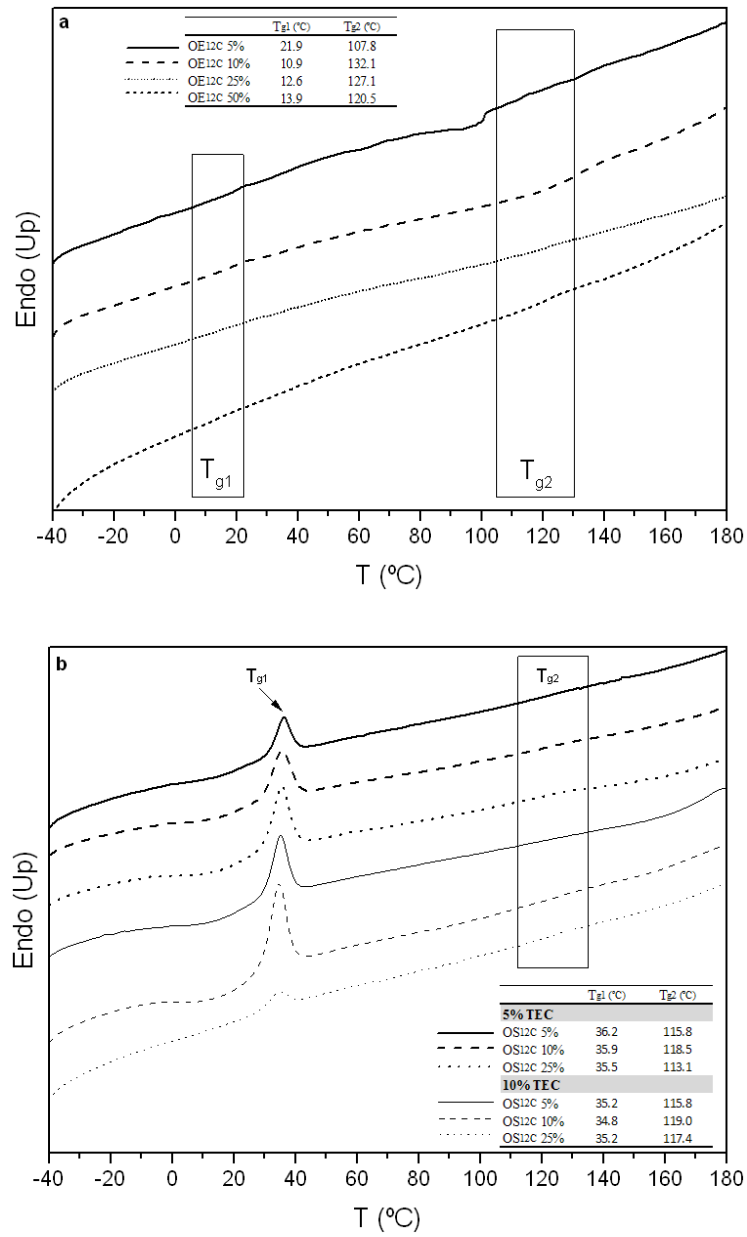


Fig. 6. Composite a) with 75% of OE_{12C} and 25% of cellulose acetate and b) with 75% of OS_{12C}, 25% of cellulose acetate and 10% TEC.



Fig.7. SEM micrographs of composites.

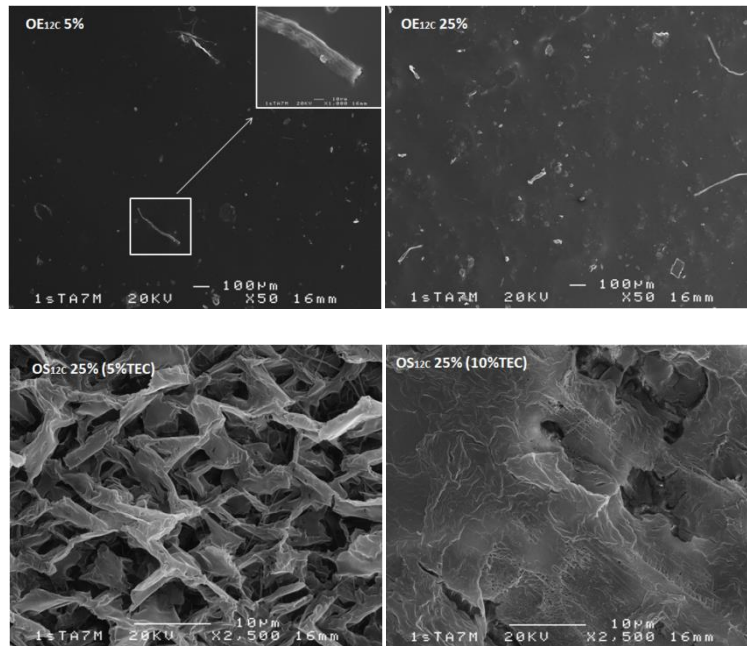
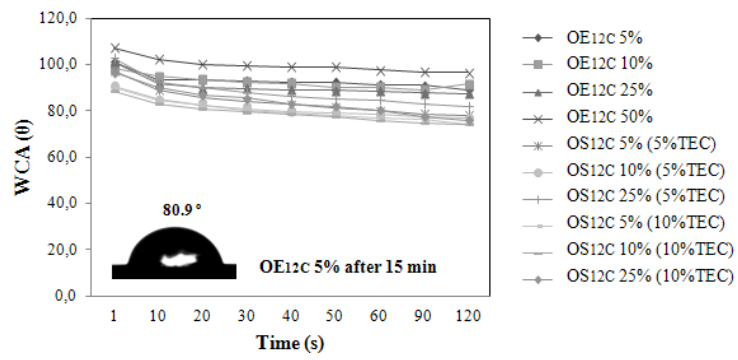
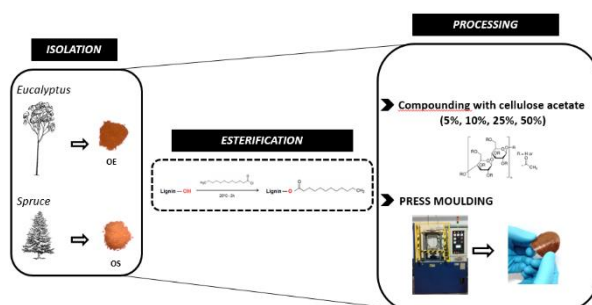


Fig. 8. Dynamic contact angles with water (WCA) of composites.



Graphical abstract (TOC)



Bio-based products such as lignin and cellulose were used to elaborate eco-friendly thermoplastic composites with interesting thermal and mechanical properties.