

Effect of Kraft Lignin from Hardwood on Viscoelastic, Thermal, Mechanical and Aging Performance of High Pressure Laminates

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Abstract In this work, the synthesis and characterization of phenol-formaldehyde resols modified with 10, 20 and 30 wt% of Kraft lignin (a waste from pulp industry) from hardwood were studied. In all cases, the Kraft lignin was activated by hydroxymethylation. The resols characterization involved industrial measurements of free formaldehyde, viscosity, total solids and density. The resins were used for the industrial impregnation of Kraft-type paper and the production of laboratory laminates. The mechanical and thermal properties of the laminates were determined. Mechanical measurements included tensile, flexural, impact and inter-laminar tests. Thermogravimetric and dynamic mechanical analysis were used for the thermal characterization. In addition, the aging of materials in water was studied. No significant differences in mechanical and thermal properties between traditional and modified materials were found with replacement up to 20 wt% of phenol. Modified laminates

exhibited better water resistance due to the lignin hydrophobicity. This work was carried out in collaboration with Centro S.A., San Francisco, Córdoba, Argentina, a high pressure-laminates industry.

Keywords Biobased materials · Kraft lignin · Laminates

Introduction

Nowadays, 15–20 million tons of synthetic resins including phenolic resins are produced worldwide and used as adhesives [1]. In the wood industry, phenolic resins have wide applications and high market prospects [2]. These adhesives are used in the production of wood-based panels, decorative laminates, and other engineered wood products.

High pressure laminates (HPL) are composite materials with a decorative surface and a core impregnated with formaldehyde resins. The decorative surface consists of an α -cellulose paper impregnated with a melamine-formaldehyde resin (MF), and the core consists of a set of Kraft-type papers impregnated with a resol phenol-formaldehyde resin (PF). The industrial production of HPL consists of three basic steps: (i) production of MF and resol PF resins (prepolymers); (ii) impregnation of decorative surface and core with prepolymers (MF and PF resins, respectively) followed by drying of impregnated papers; and (iii) curing by compression molding at high pressure and high temperature. After curing stage, a thermosetting material is obtained which provides special mechanical and physical properties to the laminates, by enhancing the matrix properties. However, for curved surfaces post-formable HPL are required and for this reason partial curing of prepolymers is carried onto to obtain more flexible materials.

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Phenolic resins used in the synthesis of HPL are derived from petroleum (phenol–P–) and natural gas (formaldehyde–F–) resources. The replacement of P by natural resources such as lignins promises environmental gains and economic benefits [3]. Lignins are amorphous polyphenolic polymers, obtained as a byproduct from pulp and paper production processes. Lignins are mainly used as internal energy source for pulping and biorefinery processes [4, 5]. However, the amount of technical lignins produced exceeds (in about 60%) the requirements of energy.

The production of adhesives based on lignins has been well explored in the last decades [6–14]. The publications related to the use of phenolic resins modified with lignins for the production of HPL are relatively scarce and mainly involve softwood lignins [15–18]. Although lignins from softwood are more suitable for the formulation of phenolic resins due to their low impurities content and the high reactivity [4], *Eucalyptus* spp. species from hardwood constitute the main fiber source for pulp and paper industry in South America [19]. Non-activated lignins were employed as fillers [16–18]. Chemical modification of lignin is a way to improve lignin performance for different applications including materials with good mechanical properties [12, 20–22]. Hydroxymethylation is the most common activation method used for alkaline conditions [12, 20, 21].

Curing conditions affect viscoelastic and thermal properties of final materials. Dynamic mechanical analysis (DMA) is an important technique used to study the effect of temperature of curing on the viscoelastic properties of composite materials. Several works have been reported on the viscoelastic properties of epoxy resins [23–25]. The typical parameters associated to DMA are elastic modulus (E'), loss modulus (E'')—that indicate elastic and viscous behavior of material, respectively—; and loss tangent ($\tan \delta$) which is the ratio between E' and E'' . Also, DMA allows to determinate the glass temperature (T_g) of materials. Prime and Turi [26] measured elastic modulus and $\tan \delta$ for uncured, partially cured and cured phenolic resins. The results indicated that the cured phenolic resin exhibited highest stiffness and T_g above 250 °C. The uncured sample showed a large damping peak at T_g and a smaller, well-separated damping peak associated with cure. The partially cured sample exhibited a broad, single damping peak that was a combination of peaks associated with the glass transition and curing.

Thermal and viscoelastic properties of phenolic resins modified with lignins were scarcely studied [27, 28]. Danielson [28] performed DMA for wood panels based on phenolic resins modified with non-activated commercial Kraft lignin from softwood with replacement up to 80 wt% of P. In general E' decreased when temperature increases (40–200 °C), which means that the resin softens in the temperature range studied. Similar results were

obtained for traditional and modified resins. In a recent paper, Mahendran et al. [15] studied the curing of traditional and modified resins (with replacements of 20 wt% of P with non-activated Kraft lignins from softwood) for paper impregnation applications by differential scanning calorimetry analysis. The curing time of the modified resin was lower than that of the traditional one.

In our previous works, the effect of hardwood (sodium lignosulfonate and Kraft) lignins activated by hydroxymethylation on the mechanical performance of laminates was investigated [29, 30]. The results indicated that partial P replacement up to 10 wt% did not produce effects that were detrimental to the overall performance of the HPL.

Another important feature of laminates is the sensitivity of their mechanical properties to moisture uptake. The absorption of water in polymers is related to the free volume and the polymer–water affinity. The amount of free volume depends on the molecular packing and is affected by both the crosslink density (and therefore the extent of curing) and physical aging. Swamy et al. [31] analyzed the water absorption of areca PF composites. The areca composite showed excellent moisture absorption (about 6–7%) in comparison with conventional wood-based particle boards that exhibited high water absorption (more than 40%). Çetin et al. [11] and Cavdar et al. [9] studied the water absorption of particle boards and oriented strand boards modified with lignins, respectively. Çetin et al. [11] used non-activated and modified (by phenolation) commercial Organosolv lignin with replacement up to 40 wt% of P, and observed that particleboards with replacement of 20 and 25 wt% absorbed less water than traditional materials. Cavdar et al. [9] used Kraft lignin from softwood as filler and observed that the water absorption was 13% lower than the corresponding to conventional PF panels. These results can be associated to chemical bonding between the lignin and the surface of the strands.

As far as the authors know, publications about thermal, viscoelastic and aging tests for HPL or Kraft-type papers impregnated with modified resins is not available in the literature. In this work, resins modified with 10, 20 and 30 wt% of Kraft lignin from hardwood were synthesized and characterized. In all cases, Kraft lignin was previously activated by hydroxymethylation. The resins were employed for the industrial impregnation of Kraft-type paper and the production of laboratory HPL. In order to study the effect of Kraft hardwood lignin on the final properties, laminates were mechanically (tensile, flexural, impact and interlaminar test) and thermally (thermogravimetric and dynamic mechanical analysis) characterized. Also, water uptake tests were carried out. Industrial syntheses of resins were performed at Centro S. A., San Francisco, Córdoba, Argentina.

Materials and Methods

Materials

The following materials were used: 37 wt% F solution (Alto Paraná, Argentina), P (Dalgas S.A., distributor in Argentina), Kraft lignin (Suzano, Brazil), Kraft-type paper of 180 g/m² (Stora Enso), and BF2001 resol (Centro S. A.) named PF in the text.

Characterization of Kraft Lignin

The characterization of lignin included the following measurements:

Moisture Content

The moisture content was gravimetrically determined by drying samples at 105 °C to constant weight [32].

Ash Content

The ash content was gravimetrically determined after in-furnace calcination at 575 °C for 3 h [32].

Carbohydrates Content

Simple carbohydrates were measured by high performance liquid chromatography (HPLC) after two-step acid hydrolysis treatment with 72 wt% H₂SO₄ solution. A (Waters) chromatograph fitted with a (515 model) pump with refractive index and diode array detectors and an AMINEX-HPX87H (BIO-RAD) column was used. The carrier solvent was H₂SO₄ (4 mM) at 0.6 mL/min, and the system was operated at 35 °C [33]. The peaks assignment was done according to the literature [34].

Phenolic Hydroxyl Groups

Total phenolic hydroxyls were measured by UV spectroscopy ($\Delta\epsilon$ method) [32]. About 10–15 mg of sample were dissolved in 10 mL of dioxane. Then 2 mL of the solution were transferred into three 10 mL flasks, and the volumes were completed with a pH 6 buffer, a pH 12 buffer, and a 0.2 N NaOH solutions, respectively. The pH 6 buffer was prepared by mixing 495 mL of 0.1 N KH₂PO₄ with 113 mL of 0.1 N NaOH and completing to 2 L volume with deionized water. The pH 12 buffer was prepared by mixing 40 mL of 0.1 N Na₂B₄O₇ with 60 mL of 0.1 N NaOH. A Perkin Elmer Lambda 25 UV–Vis spectrophotometer was used. The absorbances of the alkaline solutions were

measured at 300 and 360 nm employing the pH 6 buffer as reference.

Elemental Analysis

Carbon (C), hydrogen (H), sulfur (S) and nitrogen (N) contents were determined using a Perkin Elmer Series II Analyzer. Data were acquired using the EA 2400 Data Manager software.

Functional Groups

About 2 mg of the dried sample were carefully mixed with 300 mg of dried KBr and pressed into a self-supporting pellet. Fourier transform spectroscopy (FTIR) measurements were performed using a Shimadzu FTIR-8201 PC between 4000 and 400 cm⁻¹. Hyper IR software was used to analyze the spectra.

Thermal Stability

Thermal stability was studied by thermogravimetric analysis (TGA) on a Toledo 812e instrument under N₂ atmosphere using air as a purge. The samples were placed in aluminum crucibles and heated from 30 to 900 °C at 10 °C/min.

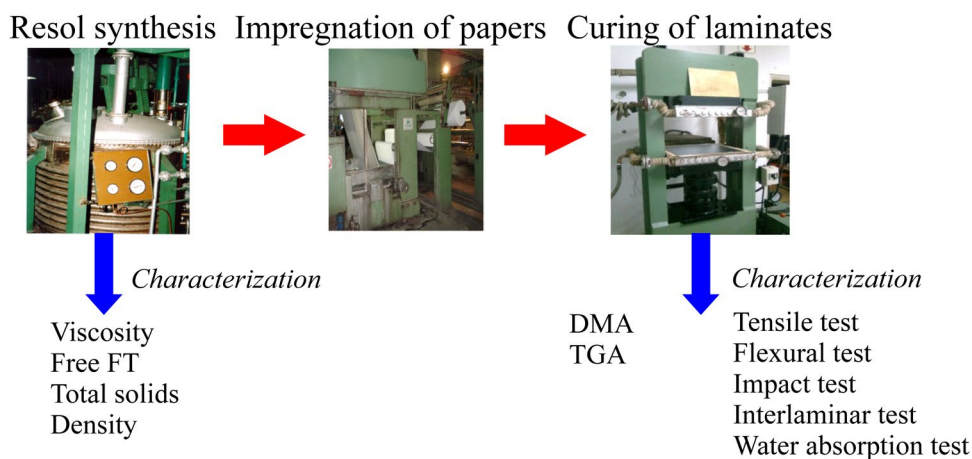
Laminates Production

A scheme of the experimental methodology is presented in Fig. 1. It involved: (i) the industrial syntheses and characterization of the modified resols using replacement up to 30 wt% of P for Kraft lignin; (ii) the industrial impregnation of papers with the resins followed by drying, and (iii) the assembly and curing of laminates at laboratory scale and their characterization.

Synthesis and Characterization of Modified Resins

Three modified resols with substitution of 10, 20 and 30 wt% of P by commercial Kraft lignin (PF10, PF20, and PF30; respectively) were synthesized in a batch stirred-tank reactor by a two-step process. First, lignin was activated by hydroxymethylation. The hydroxymethylated lignin was analyzed by FTIR using the same procedure included in the “[Characterization lignin](#)” section. Lignin hydroxymethylation was performed by addition of 37 wt% F solution using an initial weight ratio of F/lignin = 1.2 (correspond to an approximate molar ratio = 53.6) at T = 50 °C and pH 10 ± 0.5 adjusted with NaOH 34 wt% for 30 min. Then, the hydroxymethylated lignin was mixing with a 91% wt P. The weight ratio of P/hydroxymethylated lignin was 8.1; 3.6 and 2.9 (corresponding to molar ratio of 128, 57 and 44) for substitution of 10, 20 and 30 wt% of P. For all solutions, the pH

Fig. 1 Schematic representation of the production of laminates and their characterization at each stage of the process



was adjusted to 9.0 by addition of 34 wt% NaOH solution, the temperature was raised at 2–3 °C/min. from room temperature to 90 °C, and maintained at 90 °C for around 2 h. Note that recipes were reformulated to take into account the addition of lignin in replacement of P and the F employed in the first stage.

Final properties such as viscosity index, density, pH, solids, and total free formaldehyde (F_T) were determined following industrial measurements. The viscosity index was measured in a Ford Cup 4 at 30 °C. The density and pH were obtained by a glass densitometer and a Hanna HI 8424 pH-meter, respectively. For the solids content, the samples were dried in an oven at 105 °C until constant weight while F_T was measured by the hydroxylamine hydrochloride potentiometric method (ISO 11402:2004).

Impregnation and Drying of Papers

The base resins (PF, PF10, PF20 and PF30) were used for the industrial impregnation of Kraft-type papers. The impregnation was carried out according to the plant procedures in a GORDON 3-body impregnation machine (composed of a resin bath, tunnel-type drying, and guillotine).

The residence time of impregnated paper, the air velocity and temperature in the drying tunnel were adjusted to obtain a final resin and volatile contents of 33–38 wt% and 4–6 wt%, respectively.

Curing and Characterization of Laminates

Laboratory laminates of 400 × 400 mm without decorative surface (α -cellulose paper impregnated with MF base resin) were obtained in order to evaluate viscoelastic, thermal, mechanical and aging performance of the substrate (Kraft-type papers impregnated with resols). The assembly of laminates was performed according to thickness requirements. Table 1 shows the composition and curing conditions

Table 1 Laminate systems. The number of impregnated papers is indicated in parentheses

Laminates			Curing conditions	Resin
PF (3)	—	—	150 °C; 35 kg/cm ² 120 °C; 70 kg/cm ² 170 °C; 70 kg/cm ²	PF
PF(3)	PF(10)	PF(26)	150 °C; 70 kg/cm ²	PF
PF10(3)	PF10(10)	PF10(26)	150 °C; 70 kg/cm ²	PF10
PF20(3)	PF20(10)	PF20(26)	150 °C; 70 kg/cm ²	PF20
PF30(3)	PF30(10)	PF30(26)	150 °C; 70 kg/cm ²	PF30
Nominal Thickness (mm)				
0.8*	2.0**	5.0***		

*From TGA and DMA measurements, **From DMA measurements, ***From mechanical measurements and aging test

of HPLs. Note that the number of impregnated papers varies according to the specific requirement of each test.

The curing was carried out in a laboratory press employing vapor as heating medium and water for cooling. The pressing was carried out in a laboratory press (with a hot–cold cycle) with a heating time of 10 min. to reach the curing temperature (120, 150, 170 °C) at two pressing conditions (35 and 70 kg/cm²). Finally, the system was cooled for 10 min for all.

Fiber orientation was taken into account (longitudinal –l– o transversal –t–) due to the known anisotropy in materials [29] except for TGA and impact tests.

The characterization of the materials involved thermal (TGA) and mechanical (DMA, tensile, bending, impact, and interlaminar fracture) analysis. Also, aging characterization was performed by bending test after water uptake.

Thermogravimetric Analysis

The equipment and methodology for TGA measurements were described above in *Characterization lignin section*.

Dynamic Mechanical Analysis (DMA)

DMA tests were carried out on a DMA 25150 MetraVIB 01dB. The measurements were carried out in a bending mode using a heating rate of 4 °C/min for a temperature range from 30 to 250 °C, using frequencies of 1, 5 and 10 Hz. At least one specimen longitudinally and transversally oriented of 3.6 mm (width) and 22 mm (length) of laminates of 2.0 mm of nominal thickness were cut with a diamond disk.

The crosslinking density of a thermosetting material can be estimated by the E' in the rubber state, using the theory of rubber elasticity or Flory's rubber elasticity [35]. This theory is strictly valid for materials with low crosslinking, and therefore it could only be used in thermosetting materials for semi-quantitative comparisons of the cross-linking degree.

Tensile Test

For the tensile test of laminates, at least five longitudinally-oriented specimens and at least three transversely-oriented specimens of 5 mm of nominal thickness were machined. Rectangular specimens of 120 mm (length) and 10.5 mm (width) were examined. The tensile tests were performed in a Model 4467 Instron (USA) universal testing machine under controlled displacement. A 30 kN load cell and a 5 mm gauge Instron extensometer were used in order to obtain the elastic modulus of the material. The determinations were carried out at room temperature at a crosshead speed of 2 mm/min. A calibrated length of 50 mm was set. Supplementary tabs were employed to reduce the concentration of stress near the clamps, as is recommended in ASTM D3039/D 3039M-00 (2000). Failure outside the calibrated length was observed for all tensile tests, even though sandpaper tabs were used in order to reduce the clamping effects. For this reason, no valid results for tensile strength could be obtained.

Flexural Test

For the flexural test, at least six longitudinally-oriented specimens and four transversely-oriented specimens of laminates of 5 mm of nominal thickness were tested. Rectangular specimens of 100 mm (length) and 15 mm (width) were used. The flexural tests were performed on a Model 4467 Instron universal testing machine under atmospheric conditions at a crosshead speed of 2 mm/min. For each sample tested, a span of 76 mm was set, taking into account the relative span-to-thickness ratio of 16:1.

Impact Test

The biaxial impact resistance of laminates was assessed by performing instrumented dart tests in accordance with ASTM D5628-06(2006) standard recommendations. A CEAST 6789 Fractovis Gravity Drop machine (Italy), equipped with a steel dart 12.7 mm in diameter and a support of 76 mm in diameter was used. At least four samples of laminates of 5 mm of nominal thickness were tested. Measurements were performed on 100 × 100 mm plates. The tests were carried out at room temperature at a speed of 3.5 m/s, corresponding to the speed at the moment of dart impact against the sample. The dart was located at a height of 0.625 m from the surface of the sample. The total mass was adjusted with a value of 18.490 Kg. An energy value of 113.25 J was imposed. This energy was in all cases more than 50 times the energy absorbed during the impact tests, which ensured a quasi-constant dart speed during penetration.

Interlaminar Test

The Mode-I delamination tests were carried out in accordance with the ASTM D5528-01 (2001) standard. In order to account for the material anisotropy, at least six longitudinally-oriented specimens and four transversely-oriented specimens of laminates of 5 mm of nominal thickness were tested. Standard size rectangular double cantilever beam (DCB) specimens measuring 20 mm × 200 mm were used. A non-adhesive 15 µm-thick polypropylene film was inserted between the central lamina to simulate a starting artificial defect.

Aging Test

Aging test involved two steps: water absorption of samples and the bending analysis after water uptake. Water absorption test was carried out taking into account the recommendations included in ASTM D-570-98. Six oriented longitudinally specimens measuring 20 mm × 200 mm × 5 mm were submerged in distilled water at 60 °C. The specimens were removed from the water at certain periods of time and weighted in a high precision balance and then submerged again in water. After that, flexural properties of specimens were measured under the same conditions and using the same procedure as described before.

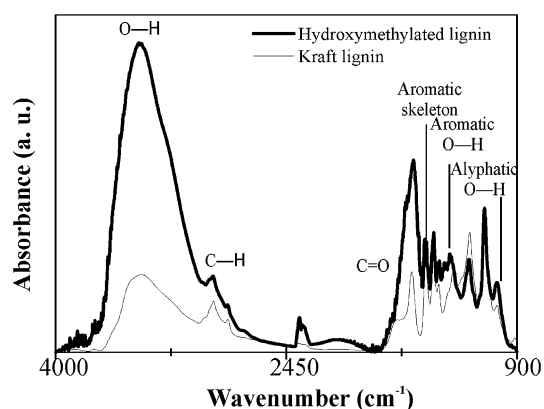
Results and Discussion

Table 2 shows the composition of the commercial hardwood Kraft lignin. Moisture and carbohydrates are similar to the values reported for softwood Kraft lignin [10]

Table 2 Characterization of commercial Kraft hardwood lignin

Determination	Value
Moisture (wt%)	4.48
Ash, dry basis (wt%)	21.67
Carbohydrates, dry basis (wt%)	5.16
Purity* (wt%)	73.17
Total phenolic hydroxyls (wt%)	3.69
Elemental analysis (wt%)	C: 49.1; H: 3.7; N: 0.22; S: 1.90

*Purity (wt%) = 100 – % sugars (dry basis) – % ash (dry basis)

**Fig. 2** FTIR spectrum of Kraft lignin

while ash content is higher due to differences in lignin treatments. El Mansouri et al. [10] treated commercial softwood Kraft lignin with sulfuric acid (1%) and washed extensively with deionized water until the ash content fell to 0.5%. In this work, no treatment was used before the determination. Total phenolic hydroxyls are in the range reported by Brodin et al. [36] for a hardwood Kraft lignin.

According to elemental analysis, C and H contents are lower than the values reported by El Mansouri et al. [10], but N and S contents are similar.

The FTIR spectra of lignin and hydroxymethylated lignin together with the assignment of signals are shown in Fig. 2. The bands at 3411 and 2840–2850 cm^{-1} are assigned to total hydroxyl groups (O–H) and methyl and methylene groups (C–H), respectively. Bands corresponding to carbonyl groups (C=O) appear at 1600 cm^{-1} and aromatic skeletal vibration around 1510 cm^{-1} . The FTIR of hydroxymethylated lignin was normalized at 1510 cm^{-1} and show an increment at 3400, 1370 and 1100 cm^{-1} due to the total, aromatic and aliphatic OH, respectively, indicating the incorporation of F. It is important to note that interpretation of bands below 1430 cm^{-1} is difficult [37].

Thermal properties of lignin are shown in Fig. 3a, b and Table 3. Three stages can be identified in the thermogram of Fig. 3a. In the first stage between 30 and 240 °C the weight loss of Kraft lignin is attributed to moisture content and the rupture of hydroxyl groups located to the benzyl groups [34]. Note that 5% of weight loss occurs near at 150 °C (Table 3) and this value is similar to the moisture content of lignin (Table 2). In the second stage from 240 to 400 °C mass loss is nearly 50%. In the interval between 400 and 800 °C, the weight loss is about 20% and at the end of the test, char of Kraft lignin is 36%. In Fig. 3b different degradation processes can be identified, associated to the moisture of the lignins [38] at 60 and 149 °C and to the rupture of the hydroxyl phenolic groups at 230 °C. The greatest degradation due to the cleavage of C–C bonds [38] takes place near to 400 °C.

In relation to the resins characterization, Table 4 shows the measurements of density, solids, viscosity and F_T both for lignin-modified resins and the control resin. No appreciable differences are observed in the density, solids and viscosity values but F_T content is higher for the modified resins as a result of the lower reactivity of lignin compared to P. Note that similar results were observed in a previous work [11]. The resin content of impregnated papers was 33, 33, 34 and 38%wt for PF, PF10, PF20 and PF30, respectively.

Thermal, viscoelastic, mechanical and aging tests were performed for HPL laminates with different lignin content (10, 20 and 30 wt%) and number of papers (3, 10 and 26). Results are shown in Tables 3, 4 and 5 and Fig. 3–9. Also, thermogravimetric measurements were carried out for Kraft-type paper for comparison purposes.

The main thermogravimetric results of Kraft-type paper and laminates are summarized in Fig. 3 and Table 3. The composites (Fig. 3e, f) exhibit thermograms similar to Kraft-type paper (Fig. 3c, d) up to 300 °C but then the profile is higher and similar to lignin (Fig. 3a, b). The thermal stability of PF30(3) is slightly higher than PF20(3), probably due to the higher resin content in PF30(3). Also, except for PF30(3), the final char for all laminates approximately corresponds to the sum of the char of paper (≈ 10 wt%) (Table 3) and lignin ash content (≈ 23 wt%) (Table 2), (Fig. 3e, f). The final char for PF30(3) is lower (Table 3) in comparison to the rest of the laminates possibly as result of a lower interaction between lignin and paper that promotes the degradation. Besides, the resin uptake for PF30(3) is higher, for this reason, an effect from resin is observed. The char increases in the following order PF(3) > PF20(3) \approx PF10(3) > PF30(3).

Regarding to DMA measurements, no significant changes were observed in the results when the frequencies of the tests were modified. For that reason the analysis were performed at 1 Hz. First, the effect of pressure and temperature on the curing of longitudinally-oriented traditional laminates (Figs. 4, 5) is evaluated.

Fig. 3 TGA of Kraft lignin, Kraft-type paper and laminates (containing three papers). Thermograms in (a, c, e) and first derivate—DTG—in (b, d, f) respectively

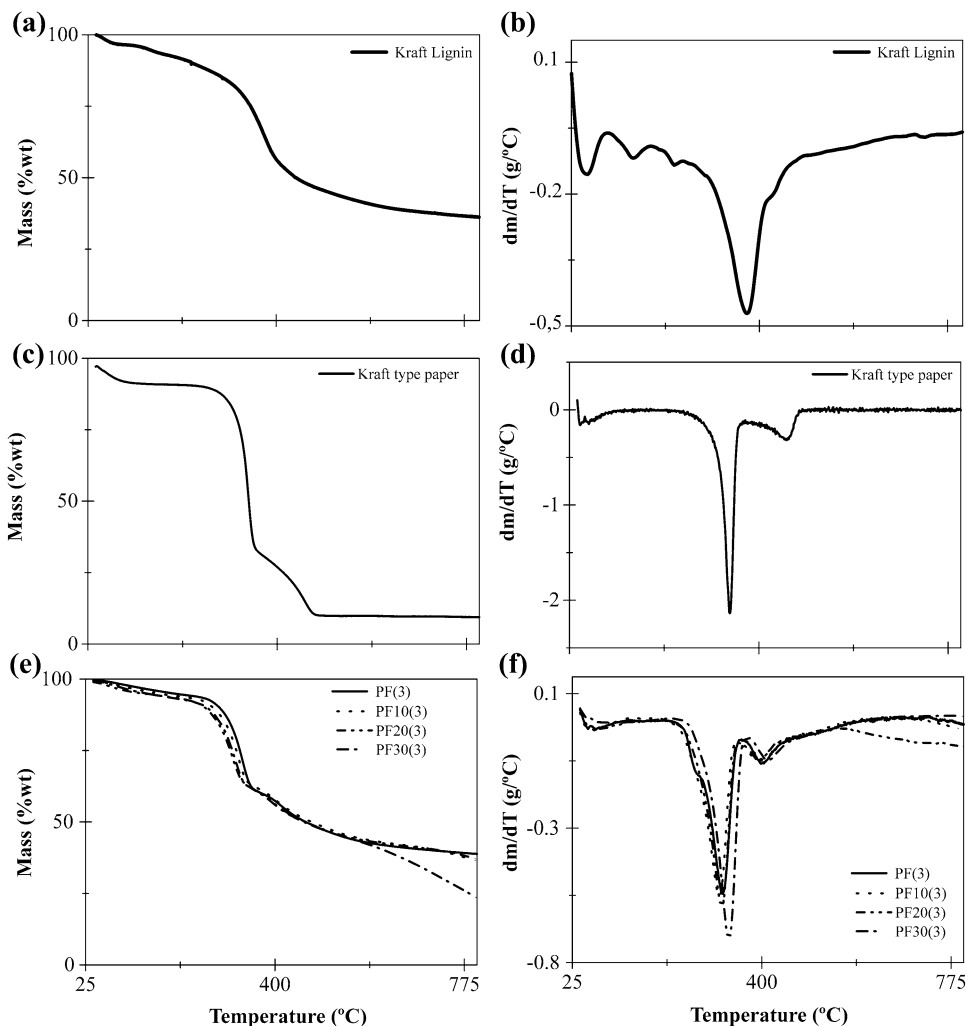


Table 3 Thermogravimetric properties

Samples	T _{5%} ^a	T _{10%} ^b	T _{50%} ^c	T _{máx} ^d	Char (800 °C)
Kraft lignin	148	236	438	376	36.0
Kraft-type paper	61	254	343	341	9.40
PF(3)	198	322	460	403	38.8
PF10(3)	168	313	472	326	36.3
PF20(3)	136	300	460	379	36.4
PF30(3)	144	305	457	319	23.3

^aTemperature of 5 wt% weight loss

^bTemperature of 10 wt% weight loss

^cTemperature of 50 wt% weight loss

^dMaximum mass loss temperature

Figure 4 shows the effect of pressure (35 and 70 kg/cm²) on the curing of longitudinally oriented traditional laminates at 150 °C. The increase of modulus after 150 °C as well as the high intensity of peak of tan δ for the laminate pressed at 35 kg/cm² indicate a post-cure of the material due to the

Table 4 Characteristics of base PF: traditional resin (PF) and modified with of 10 (PF10), 20 (PF20) and 30% (PF30) of P replacement

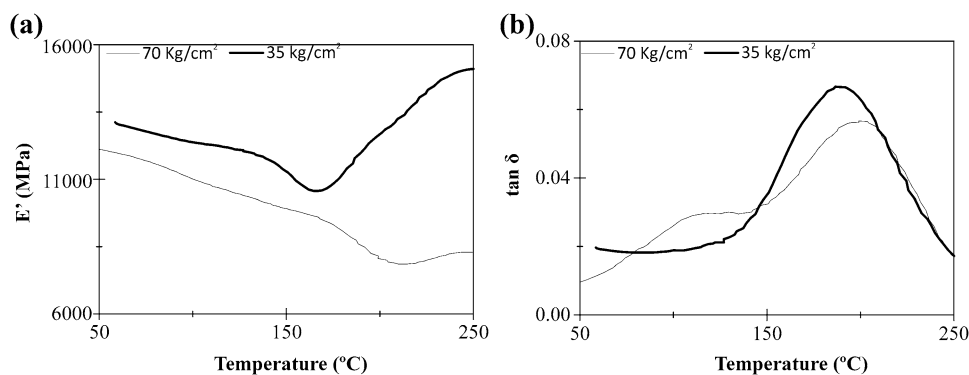
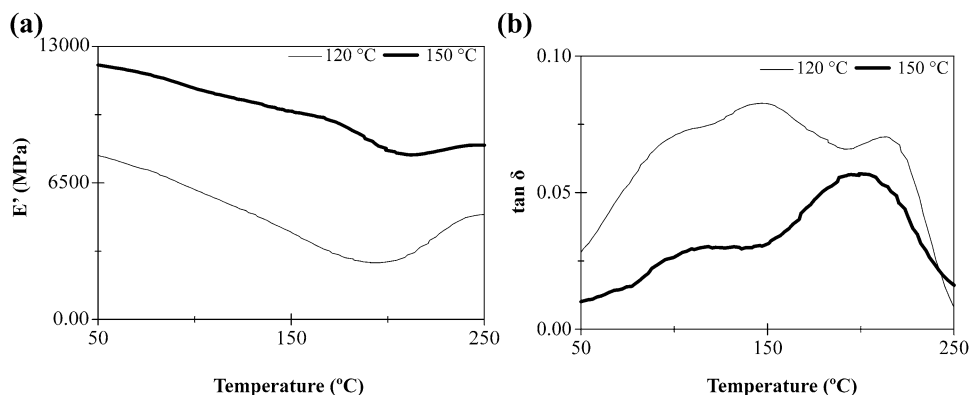
	PF	PF10	PF20	PF30
Density (g/ml)	1.05	1.05	1.05	1.04
Solids (2 h 105 °C) (wt%)	48.2	50.8	47.72	48.2
Viscosity (Ford cup N ^o 4, 30 °C) (s)	15.6	15.8	14.74	15.7
F _T (wt%)	1.01	1.42	1.30	1.40

uncompleted curing [26]. In addition, the heterogeneity of the composites (resin + paper) is evidenced by the wide and bimodal distribution of tan δ.

The effect of curing temperature (120, 150 and 170 °C) for longitudinally oriented traditional laminates pressed at 70 kg/cm² is studied. In Fig. 5, the results for 120 and 150 °C are shown. As expected, the crosslinking density of the materials increases with the curing temperature (Fig. 5a) and this observation is in agreement with the lower height of tan δ (Fig. 5b). At 170 °C the result obtained was not very

Table 5 Viscoelastic properties of laminates

	Longitudinal			Transversal		
	T _g (°C)		E' (MPa)	T _g (°C)		E' (MPa)
	tan δ	E''		tan δ	E''	
PF(3)	199	199	7700	185	170	4500
PF10(3)	194	152	5020	180	150	3700
PF20(3)	–	–	–	–	–	–
PF30(3)	182	142	3000	–	–	–
PF(10)	194	190	21,000	230	226	11,240
PF10(10)	–	–	–	193	180	12,894
PF20(10)	180	170	25,431	171	110	600
PF30(10)	132	130	3776	–	–	–

Fig. 4 DMA measurements: effect of pressure for longitudinal PF(3) (containing three papers) cured at 150 °C, **a** E', **b** tan δ**Fig. 5** DMA measurements: effect of temperature for longitudinal PF(3) (containing three papers) cured at 70 kg/cm², **a** E', **b** tan δ

good probably due to a degradation of the material during the curing stage.

The DMA measurements for the laminate systems containing three papers cured at 150 °C and 70 kg/cm² are shown in Fig. 6 and Table 5. Besides, results of laminates containing 10 papers are summarized in Table 5. Table 5 shows the T_g obtained as a maximum of tan δ, E' calculated in the minimum of E' curve and E''. As expected, E' is higher for longitudinal orientations in comparison to transversal orientations. All materials were heterogeneous (wide and bimodal tan δ peak). The degree of crosslinking (tan δ

peak intensity) and T_g (maximum of tan δ) of the materials decreased with the increase of Kraft lignin replacing P. In addition, E' increases with the thickness of laminates even though the lower crosslinking density.

Figure 7 shows a typical mechanical behavior of laminate test piece including tensile, bending, impact and interlaminar fracture tests that is in agreement with results reported in our previous work [30]. An elastic linear behavior was observed for tensile tests followed by a small non-linear zone towards the end of the curves (Fig. 7a). Flexural test (Fig. 7b) shows an initial linear

Fig. 6 DMA measurements: E' and $\tan \delta$ for laminates containing three papers (0.8 mm in thickness): longitudinally: (a, b); and transversally: (c, d); respectively

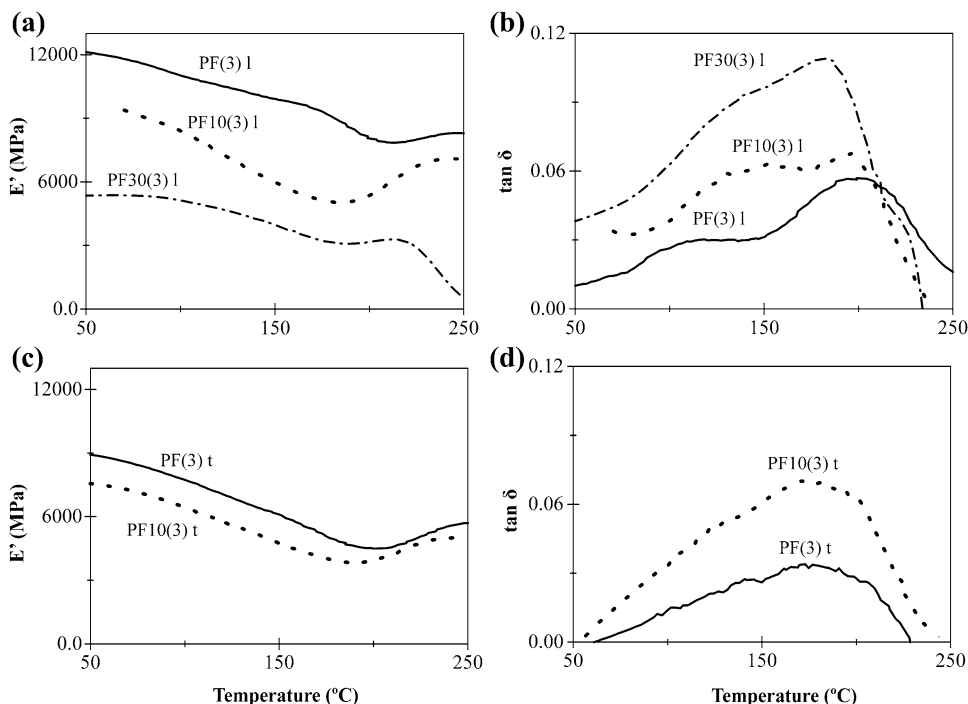
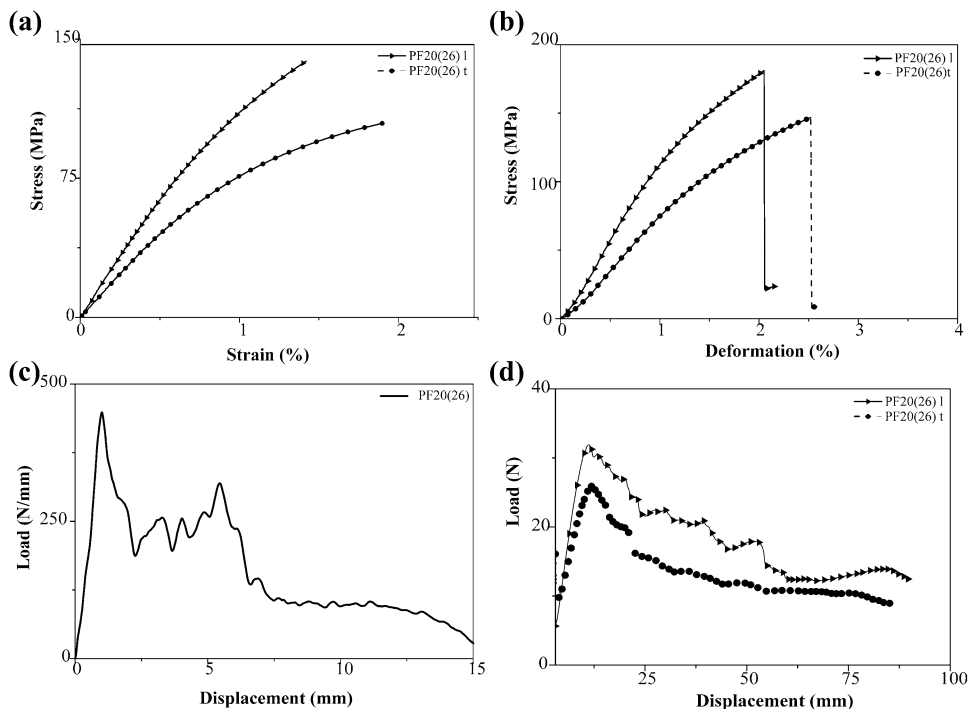


Fig. 7 Mechanical behavior of laminates with 20% replacement of P and 26 papers [PF20(26)], and longitudinal (l) and transversal paper (t) orientation: a tensile test, b flexural test, c impact biaxial test and d interlaminar fracture test



behavior followed by a reduction in slope due to the occurrence of invisible damages. For impact test a very sharp linear initiation region was detected up to the maximum load. Afterwards, a gradual rupture is observed (Fig. 7c). All the studied laminates exhibited stable crack growth under the applied testing conditions in the mode-I interlaminar fracture test, suggesting that the tests were valid

for determining interlaminar fracture toughness (G_{IC}) and the flexural elastic modulus (E_{DCB}) (Fig. 7d).

The results obtained by mechanical tests are statistically compared by analysis of variance (ANOVA) at a level of 95% confidence using a free software R program version 2.3.3.3. For measurements of tensile, flexural and interlaminar fracture tests, a 2×2 bifactorial design is proposed, where

factors correspond to the laminates [PF(26), PF10(26), PF20(26), PF30(26)] and the fiber orientation (longitudinal and transverse). For impact test, unifactorial randomized design is proposed because measurements are independent of the material anisotropy [39]. The suitability of the models (independent residues normally distributed with mean zero and variance for all factor levels) are checked but do not satisfy the assumptions of homoscedasticity and residuals normality. Therefore, a modified nonparametric ANOVA is adopted that employs the theory of test permutations [40]. Table 6 shows the average mechanical properties and the p level of significance for a confidence level of 95% $p = 0.05$. If $p < 0.05$ no significant differences between samples are expected.

The average mechanical properties of the laminates show significant differences according to the orientation of paper fibers. These differences are related to the anisotropy of the impregnated papers. In all cases, the values corresponding to longitudinal direction of the paper are higher than the transversal direction. On the other hand, no significant differences in the tensile test among laminates ($p > 0.05$) are observed.

In order to obtain multiple comparisons between the laminate materials, a Tukey Test was implemented to determine the changes in average flexural, impact and interlaminar fracture. In that follows the main results are presented.

Elastic modulus	PF10(26) = PF20(26) < PF30(26); PF20(26) < PF(26) = PF10(26) < PF30(26)
Flexural strength	PF10(26) = PF20(26) < PF30(26) PF20(26) < PF(26) = PF10(26) < PF30(26)
Absorbed energy	PF10(26) = PF20(26) = PF30(26) PF(26) = PF10(26) < PF20(26) = PF30(26)

Maximum load	PF30(26) = PF10(26) PF (26) = PF30(26) < PF10(26) = PF20(26)
G_{IC}	PF10(26) < PF20(26) = PF30(26) PF10(26) < PF(26) = PF20(26) < PF30(26)
E_{DCB}	PF30(26) < PF(26) = PF10(26) = PF20(26)

The mechanical properties of laminates are related to the structure of cured resin (lignin characteristics, lignin content, curing degree), type, orientation and number of papers, and interactions between papers and resins. From the experimental results and statistical analysis, it is observed that the mechanical performance of modified laminates is similar to the traditional ones. However, a slight improvement of the mechanical performance is observed for the laminate with 30% replacement of P, indicating a synergic effect in the composite.

Water absorption isotherms at 60 °C are shown in Fig. 8. The behavior of all absorptions isotherms of laminates in the experimental timeframe is similar exhibiting a linear increase (Fig. 8). For cellulose composites, an initial linear behavior followed by an exponential increase in water absorption is generally observed [41]. The obtained results suggest that the absorption was limited to the first part of the fickian behavior. The percentage of absorption of water, after 8 h, is clearly lower for modified materials with lignin suggesting hydrophobic effect that is more important than the decrease of the crosslinking degree. These results are consistent with the reports of Swamy et al. [31].

Finally, modulus and resistance on flexural test from longitudinally orientated materials after water absorption are measured and shown in Fig. 9. The flexural modulus and resistance decrease with time as a direct consequence of

Table 6 Average mechanical properties of different laminates and p value from ANOVA test

Test	Property	Orientation	PF(26)	PF10(26)	PF20(26)	PF30(26)	p value	
							Laminate	Orientation
Tensile test	E (GPa)	Longitudinal	14.0 (±2.0)	14.6 (±1.9)	13.3 (±0.6)	12.6 (±0.1)	0.41	< 2.0 × 10 ⁻¹⁶
		Transverse	10.5 (±0.4)	9.5 (±0.4)	9.6 (±0.2)	11.4 (±0.3)		
Point-flexure test	Strength (MPa)	Longitudinal	210 (±13.0)	197 (±5.6)	185 (±5.6)	240 (±4.2)	< 2.0 × 10 ⁻¹⁶	< 2.0 × 10 ⁻¹⁶
		Transverse	123 (±4.0)	145 (±5.3)	146 (±1.0)	175 (±2.5)		
	Elastic modulus (GPa)	Longitudinal	16.9 (±0.5)	14.5 (±0.2)	12.9 (±0.3)	21.6 (±0.5)	< 2.0 × 10 ⁻¹⁶	< 2.0 × 10 ⁻¹⁶
		Transverse	9.7 (±0.3)	9.0 (±0.5)	8.4 (±0.1)	13.7 (±0.2)		
Interlaminar test	G_{IC} (J/m ²)	Longitudinal	238 (±10)	215 (±19)	378 (±20)	319 (±60)	4.0 × 10 ⁻⁴	0.04
		Transverse	284 (±29)	273 (±23)	322 (±29)	391 (±60)		
	E_{DCB} (GPa)	Longitudinal	13.3 (±1.0)	12.6 (±1.0)	12.1 (±1.0)	8.91 (±4.0)	1.6 × 10 ⁻³	< 2.0 × 10 ⁻¹⁶
		Transverse	8.24 (±1.0)	8.56 (±1.0)	8.91 (±1.0)	(±4.0)		
Impact test	Absorbed energy (J/mm)		1.2 (±0.1)	1.5 (±0.1)	1.8 (±0.2)	1.7 (±0.2)	1.9 × 10 ⁻³	–
	Maximum impact load (N/mm)		330 (±8)	479 (±42)	538 (±102)	400 (±1)	< 2.0 × 10 ⁻¹⁶	–

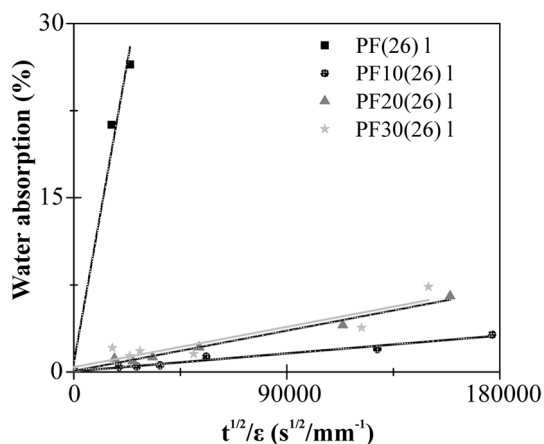


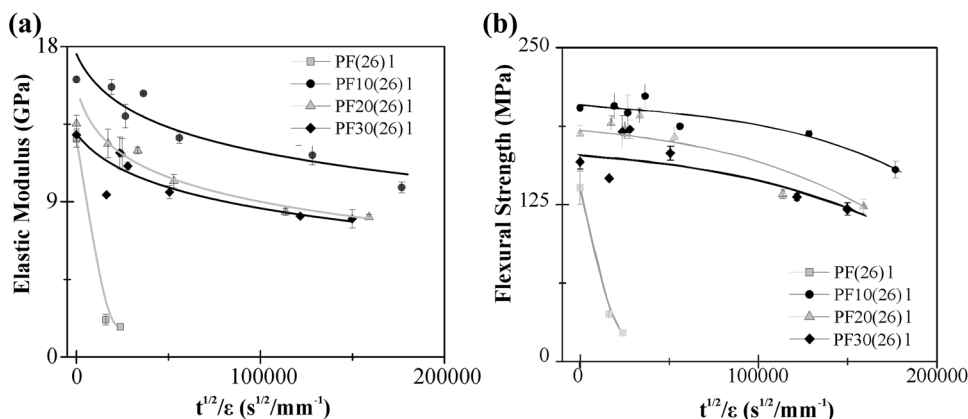
Fig. 8 Water absorption measurements: percentage of water absorbed by laminates containing 26 papers as a function of the absorption time and thickness

the percentage of water absorbed. The mechanical performance of PF10(26) was higher in comparison with PF20(26) and PF30(26). The reduction of elastic modulus and flexural strength was 27 and 10% for PF10(26). PF20(26) and PF30(26) showed similar behavior and reductions of 37 and 18% of elastic modulus and flexural strength, respectively. Probably, the better mechanical performance of PF10(26) is due to the minor content of lignin. As a higher content of lignin, the behavior is reduced. As expected, the traditional laminate exhibited more mechanical deterioration in presence of water.

Conclusions

Three industrial resins modified with commercial Kraft lignin were synthesized and used for the production of decorative laminates. Replacements of 10, 20 and 30 wt% of P were assessed. Lignins were activated by hydroxymethylation in alkaline medium at $T = 50\text{ }^{\circ}\text{C}$.

Fig. 9 Flexural measurements after water absorption: **a** elastic modulus and **b** flexural strength of the longitudinal laminates containing 26 papers as a function of the absorption time and thickness



The incorporation of lignins slightly decreased the thermal stability, the crosslink density, and the T_g of the materials. The best viscoelastic properties were achieved for the materials pressed at $150\text{ }^{\circ}\text{C}$ and 70 kg/cm^2 in the longitudinal direction of papers.

The mechanical properties of laminates are related to the structure of cured resin (lignin characteristics, lignin content, curing degree), type, orientation and number of papers, and interactions between papers and resins. Mechanical and thermal properties of materials with replacement up to 20 wt% of Kraft lignin were similar to those of traditional materials. A slight improvement of the mechanical performance was observed for laminates with 30 wt% replacement of P, indicating a synergic effect between paper, resin and lignin.

Modified laminates exhibited better water resistance due to the hydrophobicity of lignin.

For practical applications, this study suggests that resols modified with 20 wt% of Kraft lignin can be used for the production of HPL, while resols modified with 30 wt% of lignin for post formable laminates.

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