

## Mechanical Evaluation of Laminates Based on Phenolic Resins using Lignins as Partial Substitutes for Phenol

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Reducing the consumption of phenol during synthesis of phenolic resins is of great technological and scientific interest because of its economic and environmental implications. In this work, the use of hydroxymethylated lignins as a partial replacement for phenol in resol phenol-formaldehyde resins used for the production of decorative laminates was experimentally studied. The work involved: i) the industrial synthesis of traditional and modified resols with 10%w/w of sodium lignosulfonate and kraft-type lignin; ii) the industrial impregnation of kraft-type paper with the produced resins; iii) the production of laminates on both laboratory and industrial scales; and iv) the measurement of their final properties. The mechanical performance of the laminates was evaluated *via* the determination of the Young modulus, bending strength, biaxial impact strength, and Mode-I interlaminar fracture toughness. The (modified and traditional) laminates exhibited statistically significant differences in mechanical properties. However, the partial lignin replacement did not produce effects that were detrimental to the overall performance of the decorative laminates.

*Keywords:* Laminate; Resol; Lignin; Mechanical properties

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### INTRODUCTION

High-pressure decorative laminates (HPLs) are composite materials comprised of a paper-based decorative surface and a substrate impregnated with formaldehyde resins. The decorative surface consists of  $\alpha$ -cellulose paper impregnated with a base melamine-formaldehyde resin (MF), and the substrate consists of a set of kraft-type papers impregnated with a base resol-type phenol-formaldehyde (PF) resin. The curing of resins imparts special mechanical and physical properties to the laminates, enhancing the matrix properties. However, postforming HPLs are partially cured in order to impart some flexibility to the material, allowing for a tailored fit to curved surfaces. Currently, the use of environmentally friendly plasticizers is preferred over the use of high initial phenol-to-formaldehyde (P/F) molar ratios (Pilato 2010).

The industrial production of HPLs consists of three basic steps: i) synthesis of the base resins (MF and resol-type PF); ii) resin impregnation of (decorative and kraft-type) papers and drying; and iii) compression molding at high pressure and high temperature of the “sandwich” structure, composed of the impregnated papers.

The resols used for paper impregnation are typically produced by reacting a 37% w/w water solution of F (or formaline) with a 91% w/w water solution of P at pH=8 to 9. The characteristics of the resins, together with the operating conditions, are vital for

determining the final properties of the laminates. The standard industrial determinations do not give direct information about the microstructure of the material. To this end, Nordin (2001) studied the mechanical properties of laminates formed from kraft papers impregnated with PF resins and showed that the use of this type of paper led to good mechanical properties due to the presence of undamaged natural fibers within the paper structure. According to Coffin *et al.* (2011), the elastic modulus of kraft paper-based laminates with a high fiber fraction (above 70% w/w) is in the range of 16 to 25 GPa. The highest modulus values are achieved when kraft papers are manufactured with fibers of a high aspect ratio (length/diameter). Industrial impregnated papers are anisotropic due to their lamination conditions (Stenberg 1999), and this characteristic is inherited by the composite laminates thereby derived. For this reason, testing should be performed following the main in-plane anisotropy directions.

Nowadays, there is an environmental and economic interest in replacing (at least partially) some of the petrochemical raw materials, such as P, that are used in the synthesis of resol-type PF resin with renewable resources such as lignins, sugars, and other carbohydrates, tannins, and soy proteins, among others (Effendi *et al.* 2007; Pilato 2010; Quiao *et al.* 2015; Chen *et al.* 2015).

Lignin is a complex polyphenolic macromolecule found in the plant cell wall. Constituting 30% of the non-fossil organic carbon, and between a third and a quarter of the weight of dry wood, it is one of the most abundant organic polymers on earth. Lignin is also a waste product from the cellulose pulp industry, and its beneficial utilization would help reduce the contamination and oxygen demand of its effluents.

The type of lignin depends on the vegetable species and the isolation process. Technical lignins (lignosulfonates and kraft-type lignin) contains sulfur, as well as impurities such as ash and carbohydrates, in its composition. Sulfur is present in the form of the sulfonic groups in lignosulfonates and in the form of inorganic sulfur in kraft-type lignin (Chávez-Sifontes and Domine 2013). Due to their structural differences, lignosulfonates are water-soluble, while kraft-type lignin is soluble in alkali or organic solvents (Laurichesse and Avérous 2013). Moreover, lignosulfonates have a higher average molar mass than do kraft-type lignin. The impurities present in lignins detract from their adhesion properties (Wang and Chen 2014). However, it has been reported that the bending strength of dry boards obtained with lignin-phenol-formaldehyde resins steadily increases with the sugar content of sodium lignosulfonate (Pizzi and Mittal 1994).

The aromatic (guayacyl, *p*-hydroxy phenyl, and syringyl) groups present in lignin structure have 1, 2, or no reactive site per ring, while P has three reactive sites (*-para* and *-ortho* positions). Note that the content of *p*-hydroxy phenyl groups is smaller than the content of guayacyl and syringyl groups in wood species (El Mansouri 2007). The low reactivity of lignin towards F due to the high substitution of their phenolic rings makes it necessary to carry out a preliminary structural modification. Hydroxymethylation is the most commonly used method for alkaline conditions (Alonso 2002). Due to the covalent binding that occurs, the chemical modification of lignin allow for high P replacement without affecting its material performance (Vázquez *et al.* 1997; Olivares *et al.* 1988; Çetin and Özmen 2002).

Several investigations into applications for lignin-phenol-formaldehyde resins, including the production of plywood, flakeboard, particleboard, and fiberboard, have been reported in previous publications (Olivares *et al.* 1988; Vazquez *et al.* 1995; Vázquez *et al.* 1997; Danielson and Simonson 1998; Çetin and Özmen 2002). However,

the use of lignin-phenol-formaldehyde resols for paper impregnation has scarcely been studied (Seidl *et al.* 1944; Sibalis and Rosario 1980; Seidel and Fuller 1984; Mahendran *et al.* 2010).

Seidl *et al.* (1944) and Sibalis and Rosario (1980) fabricated decorative laminates by adding lignin as a filler or extender without chemical modification. When Seidl *et al.* (1944) incorporated up to 60%w/w of lignin from the soda-pulp process in PF resins, no appreciable changes in the compression and tensile properties of the laminates were observed. Increases in the percentage of lignin resulted in decreases in the tensile and compressive strengths and increases in toughness. Sibalis and Rosario (1980) prepared decorative laminates by extending a PF resin with less than 15%w/w of ammonium lignosulfonate. Seidel and Fuller (1984) obtained moisture-resistant laminates by using a lignin-phenol-formaldehyde resol modified with 23%w/w softwood kraft-type lignin to replace P and a mixture of alkaline earth metals.

In this work, the synthesis and characterization of modified PF resins (by partial replacement of P with 10%w/w of sodium lignosulfonate and Kraft-type lignin) and their application to the fabrication of laminates based on Kraft-type papers was studied in order to evaluate the performance of these materials in comparison with the traditional laminates. A rigorous evaluation of mechanical properties was carried out, which included a tensile test, flexural test, biaxial impact test, and Mode-I interlaminar fracture test considering the different orientation of paper fibers. The effects of the presence of carbohydrates on the final properties were also studied. The industrial work (synthesis and characterization of resols, impregnation and pressing of papers) was carried out in facilities at Centro S.A. (San Francisco, Argentina).

## EXPERIMENTAL

### Materials

The following materials were used in this work: 37%w/w F solution (Alto Paraná, Argentina), P (Dalgas S.A., distributor in Argentina), sodium lignosulfonate (Vixilex SDX, Brazil), kraft-type lignin (Suzano, Brazil), Sucrodex (Productos de Maiz S.A., Argentina), kraft-type paper of 180 g/m<sup>2</sup> (Stora Enso),  $\alpha$ -cellulose-type paper impregnated with MF resin (provided by Centro S.A.), 0.01 N HCl (Cicarelli), hydroxylamine hydrochloride (Anedra), sulfuric acid 99.9% (Cicarelli), dioxane (Cicarelli), NaOH (Cicarelli), KH<sub>2</sub>PO<sub>4</sub> (Anedra), Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O (Anedra), and methanol (Cicarelli).

### Methods

#### *Characterization of lignins*

The characterization of lignins included the following measurements:

*Moisture content.* The moisture content of lignin was gravimetrically determined by drying samples at 105 °C to constant weight (Zakis 1994).

*Ash content.* The ash content of lignin was gravimetrically determined after in-furnace calcination at 575 °C for 3 h (Zakis 1994).

*Carbohydrates content.* Simple carbohydrates were measured by high performance liquid chromatography (HPLC) after two-step acid hydrolysis of samples with 72%v/v H<sub>2</sub>SO<sub>4</sub>.

A Waters chromatograph fitted with a (515 model) pump with refractive index and diode array detectors and a AMINEX-HPX87H (BIO-RAD) column was used. The carrier solvent was H<sub>2</sub>SO<sub>4</sub> (4 mM) at 0.6 mL/min, and the system was operated at 35 °C (Kaar *et al.* 1991). The assignment of peaks was done according to El Mansouri (2007).

*Phenolic hydroxyl groups.* Guayacyl and syringyl groups of lignins were measured by UV spectroscopy ( $\Delta\epsilon$  method). Then 10 to 15 mg of sample were dissolved in 10 mL of dioxane (lignosulfonate was previously dissolved in distilled water). Then 2 mL of the solution were transferred to three 10 mL flasks, and the volumes were completed with a buffer solution pH = 6, a buffer solution pH = 12, and 0.2 N NaOH, respectively. The buffer solution pH = 6 was prepared by mixing 495 mL of 0.1 N KH<sub>2</sub>PO<sub>4</sub> with 113 mL 0.1 N NaOH and completing 2 L volume with deionized water. The buffer solution pH = 12 was prepared by mixing 40 mL of 0.1 N Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> 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 nm and 360 nm employing the solution of pH = 6 as reference.

#### *Synthesis and characterization of industrial resols and paper impregnation*

Three syntheses of three resols were carried out: one standard resol (named PF) and two modified resols, obtained by substituting a 10%w/w of P for commercial sodium lignosulfonate and kraft-type lignin (named LPF and KPF, respectively). For the reactions, a stirred batch reactor of 3000 L was used. The PF resin was obtained by reacting a 91% w/w P solution with a 37%w/w F solution in a molar ratio F/P $\approx$ 1.1. The pH was adjusted to 9.0 by addition of NaOH, and during the first step of reaction, the temperature was raised from room temperature to 90 °C at 2 to 3 °C/min. The reaction was carried out at 90 °C for around 2 h. As condensation proceeds, oligomers turn immiscible in water. Finally, water is vacuum-removed, and the base resin is cooled and dissolved in alcohol for storage.

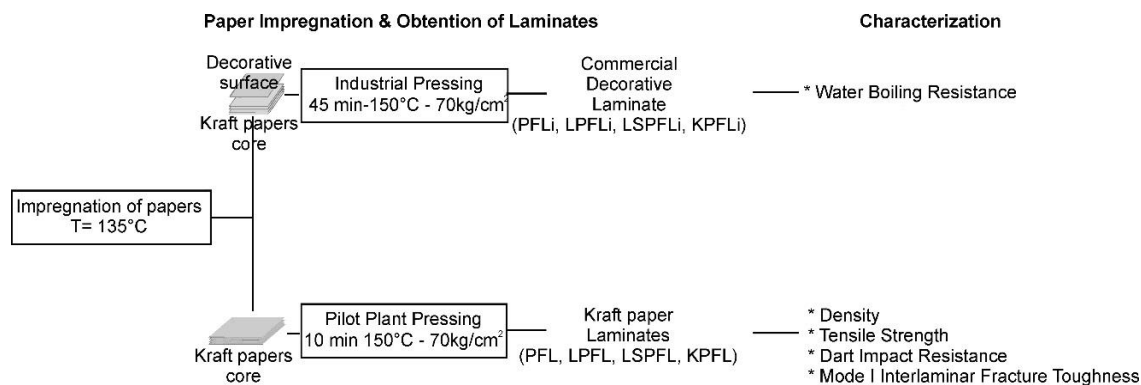
The synthesis of the resols LPF and KPF involved two main steps. In the first one, the lignosulfonate and the kraft lignin were dissolved and then reactivated *via* hydroxymethylation (Alonso 2002) at T=50 °C and pH= 9 and 11, respectively. In the second stage, a co-condensation of P with the hydroxymethylated lignin was carried out at pH=9 and T=90 °C. The final properties, such as viscosity index, pH, density, solids, and total free formaldehyde were determined following the industrial tests. The viscosity index was measured in a Ford Cup 4 at 30 °C. The density and pH were measured with a glass densitometer and with a Hanna HI 8424 pH-meter, respectively. To measure the solids content, the samples were dried in an oven at 105 °C until they had reached a constant weight. The total free F was measured by means of the hydroxylamine hydrochloride potentiometric method (ISO 11402:2004).

The effects of the presence of carbohydrates were evaluated by the addition of 6%w/w SucroDEX to the LPF resin (LSPF in what follows). The composition of the SucroDEX was 20%w/w fructose, 33%w/w dextrose, 9%w/w maltose, 4.5%w/w maltotriose, 2.5%w/w maltodextrose, and 31%w/w other sugars.

Kraft-type papers weighing 180 g/m<sup>2</sup> were impregnated with a 38%w/w (wet basis) of either PF, LSPF, LPF, or KPF in a GORDON 3-body impregnation machine (composed of a resin bath, tunnel-type drying, and guillotine).

### Fabrication and characterization of laminates

Laboratory and industrial laminates were obtained from the industrially impregnated papers. The laboratory laminates were fabricated without their decorative surfaces in order to evaluate the mechanical performance of the substrate. The procedure of laminates fabrication is shown in Fig. 1.



**Fig. 1.** Procedures of the production of laminates

A standard laboratory laminate (PFL) and three modified laminates (LSPFL, LPFL, and KPFL) were obtained by pressing twenty-six kraft-type papers, which had been industrially impregnated with PF, LSPF, LPF, and KPF, respectively, in a laboratory hydraulic press heated with steam. Laboratory laminates measuring 400 mm in width, 400 mm in length, and 5 mm in thickness were pressed over the course of 10 minutes at  $150^{\circ}\text{C}$  under a pressure of  $70\text{ kg/cm}^2$ . Industrial decorative laminates (PFLi, LSPFLi, LPFLi, and KPFLi) measuring  $3060 \times 1220\text{ mm}$  and 0.8 mm in thickness, were obtained via the compression of one  $\alpha$ -cellulose paper impregnated with base MF resin and two Kraft-type papers impregnated with resols (PF, LSPF, LPF, or KPF). The pressing was carried out in a Fjellman discontinuous press at  $70\text{ kg/cm}^2$  over the course of 45 min at  $150^{\circ}\text{C}$  after a heating time of 6 min.

The characterization of the laboratory laminates consisted of the measurement of density, tensile modulus [ASTM D3039/D 3039M-00 (2000)], flexural modulus, flexural strength [ASTM D790-00 (2002)], impact strength [ASTM D5628-06 (2006)], and Mode-I interlaminar fracture toughness [ASTM D5528-01 (2001)]. The mechanical properties were measured, taking into account the fiber orientation of the paper (parallel or longitudinal and perpendicular or transversal to the rolling direction). The thickness of the samples was determined for each laminate (about 5 mm). The selected tests were intended to reproduce the most typical load a laminate would experience over its service life.

The density of the different composite laminates was determined using the ratio between the weight and the volume of the  $100\text{-mm}^2$  samples.

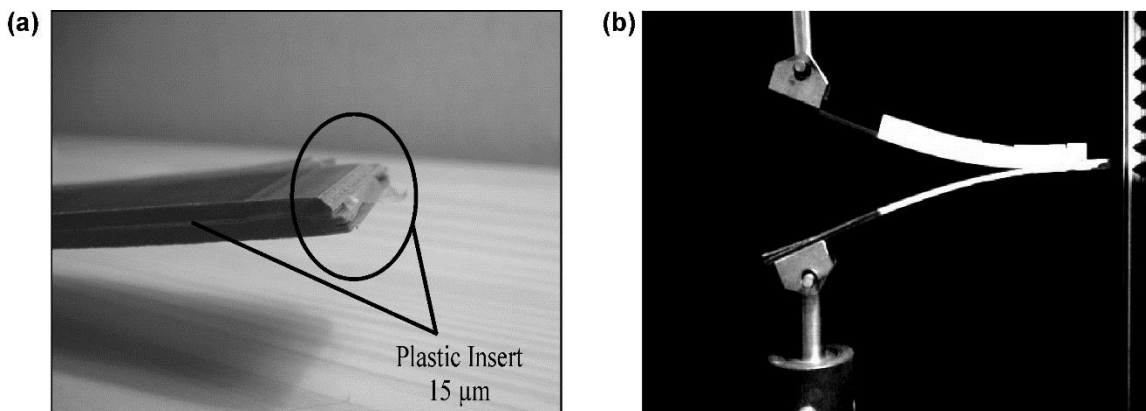
For the tensile test, at least 5 longitudinally-oriented specimens and at least 3 transversely-oriented specimens of PFL, LSPFL, LPFL, and KPFL were machined from the laminates. Rectangular specimens measuring 120 mm in length and 10.5 mm in width were examined. The tensile tests were performed on a 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 calculated.

For the flexural test, at least 6 longitudinally-oriented specimens and 4 transversely-oriented specimens of PFL, LSPFL, LPFL, and KPFL were tested. Rectangular specimens measuring 100 mm in length and 15 mm in 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.

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 4 samples of PFL, LSPFL, LPFL, and KPFL 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.

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 6 longitudinally-oriented specimens and 4 transversely-oriented specimens of PFL, LSPFL, LPFL, and KPFL 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 (Fig. 2a). The tests were performed in an Instron universal testing machine at a crosshead speed rate of 2 mm/min. The loads were applied to the composite specimens through aluminum loading blocks, as shown in Fig. 2b.



**Fig. 2.** (a) Detail of a DCB sample showing the artificial defect that produces the starting of delamination and (b) stable growth of crack

The interlaminar fracture toughness ( $G_{IC}$ ) and the flexural elastic modulus ( $E_{DCB}$ ) were determined in both the longitudinal and transversal directions. The classical beam

theory can be applied to obtain  $G_{IC}$  (Diehl 2008). However, in practice, beams are not perfectly built, and some rotation at the delamination front may occur, which could lead to overestimation of the calculated  $G_{IC}$  (Robinson and Hodgkinson 2000). The ASTM standard suggests three data reduction schemes for correcting this error. In this work, the Modified Beam Theory (MBT) was adopted (ASTM D5528-01(2001)). This method assumes that the DCB contains a slightly longer delamination than the measured one ( $a + \Delta$ ,  $a$  = crack length). The  $\Delta$  value was determined experimentally by generating a least squares plot of the cube root of compliance ( $C^{1/3} = (\delta/P)^{1/3}$ ,  $\delta$  = load point deflection, and  $P$  = load) as a function of delamination length. The use of a slightly longer value of delamination length leads to smaller values of calculated  $G_{IC}$ , as this is a conservative approach.

For industrial laminates, resistance to boiling water was evaluated in accordance with ISO 4586-2:2004, which establishes their capacity to withstand contact with boiling water without blistering or delaminating. Three test square pieces of 50 mm were cut, and edges were sanded. The specimens were dried for 24 h in an oven at 50 °C and then cooled in a desiccator and weighed. Thickness was measured at the four vertices of each specimen. Then, the specimens were immersed in boiling water for 2 h and afterwards allowed to cool in distilled water at room temperature for 15 min. Finally, the specimens were dried with tissue paper, re-weighted, and the thickness of the four vertices was measured. The average increments in mass and thickness were obtained.

## RESULTS AND DISCUSSION

The compositions of the sodium lignosulfonate and kraft-type lignin are shown in Table 1.

**Table 1.** Characterization of Lignins

	%Moisture	%Ash (dry basis)	% Carbohydrates (dry basis)	Phenolic hydroxyl groups	
				Guayacyl	Syringyl
<b>Sodium Lignosulfonate</b>	8.89	23.45	13.63	1.47	0.56
<b>Kraft-type Lignin</b>	4.48	21.67	5.16	2.76	0.93

Kraft lignin is more reactive and pure than sodium lignosulfonate due to the high content of guayacyl groups and the low moisture, ash and carbohydrates contents in comparison with lignosulfonate.

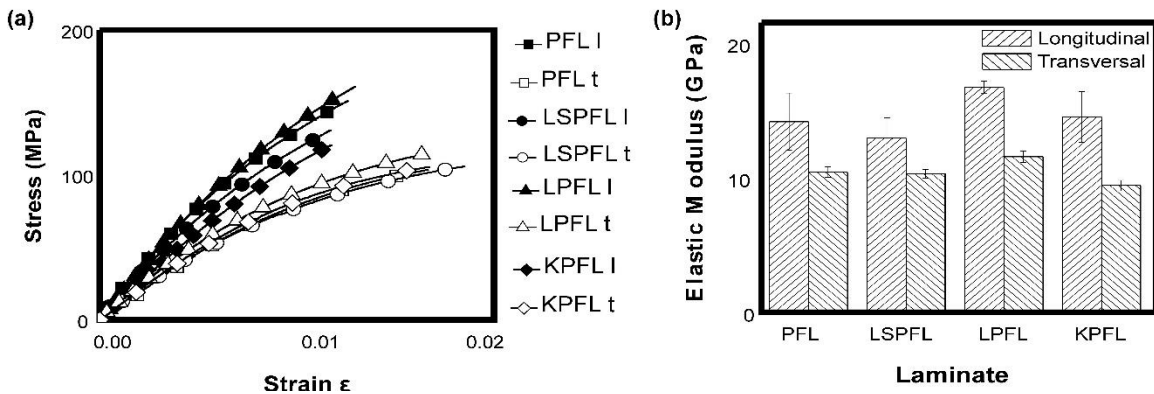
Table 2 shows the density, pH, percent solids, viscosity index, and total free F of the PF, LPF, and KPF resins. No appreciable differences were observed, with the exception of total free F, which was a little higher for the LPF and KPF resins in comparison with that of the PF resin. This result can be attributed to the lower reactivity of lignins in comparison with phenol and it was also reported in the literature (Çetin *et al.* 2012). In order to reduce the F content of resins, an optimization of reaction conditions (F:P:lignin ratio) could be performed.

**Table 2.** Properties of the PF, KPF, and LPF resins

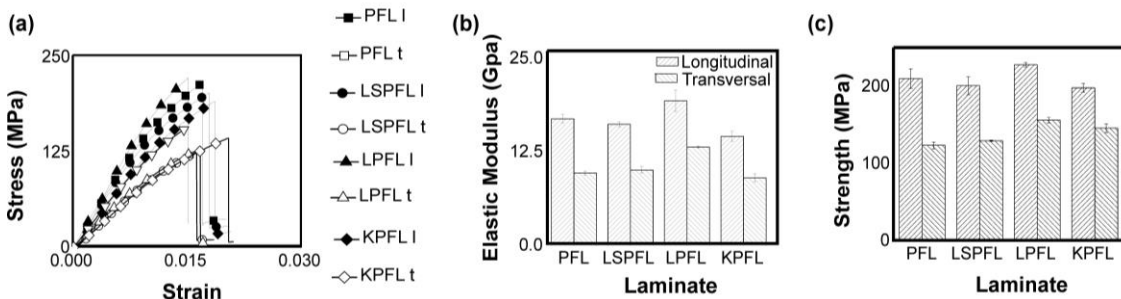
Property	Density (g/ml)	pH	Solid (% w/w)	Viscosity (s)	Total free F (% w/w)
PF	1.05	8.05	48.3	15.6	1.01
LPF	1.06	8.02	49.2	16.3	1.42
KPF	1.05	8.12	50.81	15.81	1.31

The values of density were 1.36 ( $\pm 0.02$ ), 1.41( $\pm 0.02$ ), 1.40 ( $\pm 0.02$ ), and 1.41 ( $\pm 0.02$ ) g/cm<sup>3</sup> for the PFL, LSPFL, LPFL, and KPFL, respectively. No significant differences were found among the materials and negligible effects on the mechanical performance of decorative laminates are expected. The variation of densities can be attributed to the porosity level originated during the fabrication process (Nordin 2001).

The results of the tensile tests, presented in Fig. 3a, show the tensile stress-strain curves for all specimens of PFL, LSPFL, LPFL, and KPFL tested in the longitudinal (l) and transverse (t) directions. In all cases, an elastic linear behavior was observed, which was followed by a small non-linear zone towards the end of the curves. There were considerable differences between the curves for the tests in the longitudinal direction and the curves for the tests in the transverse direction, the former showing considerably higher responses and smaller elongation-at-break values. The average and standard deviation values are presented in Fig. 3b. LPFL exhibited the highest elastic modulus.



**Fig. 3.** Tensile test for laboratory laminates: (a) stress-strain curves of specimen and (b) average tensile modulus

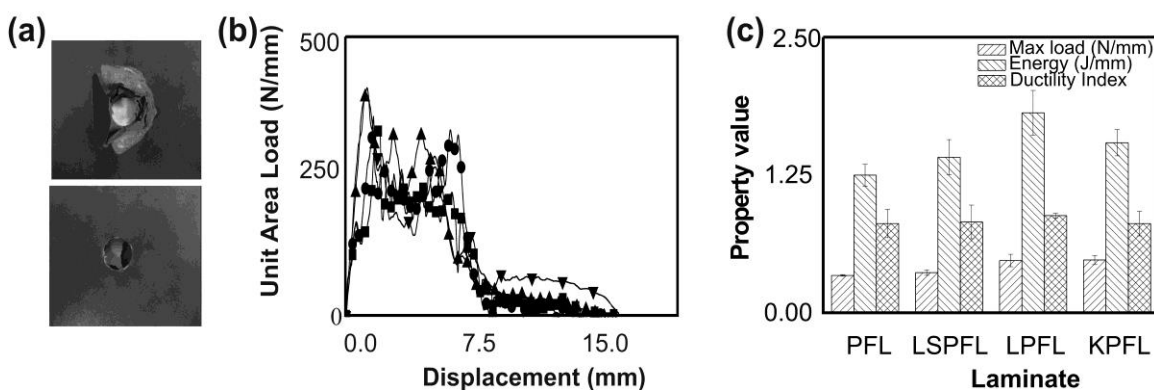


**Fig. 4.** Flexural test for laboratory laminates: (a) stress-strain curves of specimen, (b) average flexural modulus, and (c) average flexural strength



For tests in both the longitudinal and transverse directions, the flexural stress-strain curves of PFL, LSPFL, LPFL, and KPFL, shown in Fig. 4a, indicated an initially linear behavior, followed by a reduction in slope due to the occurrence of invisible damages. Again, LPFL showed the highest resistance and elastic modulus in flexure, as seen in Fig. 4b and c.

The impact tests showed a similar failure mode for all laminates. The impacted side experienced a clear fracture, while on the opposite surface many pieces were partially torn apart (delaminated) from the laminate (Fig. 5a). A very sharp linear initiation region was observed up to the maximum load. Afterwards, a gradual rupture, presenting relatively high loads at high displacements, could be observed. This effect corresponded to the elevated impact energy values exhibited by the composites and physically represented by the delamination effects (Fig. 5b).

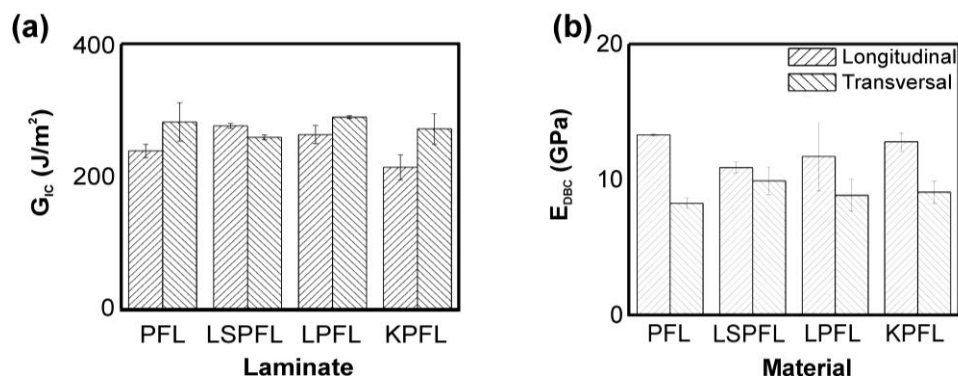


**Fig. 5.** Dart Impact test for laboratory laminates: (a) impacted and opposite surface of KPFL; (b) load-displacement results for specimen, and (c) average mass load, energy, and DI

The ductility index (DI) was calculated for all the samples in accordance with the suggestions of Driscoll (1986). DI represents the relation between the energy required for crack initiation ( $E_i$ ) and that required for crack propagation ( $E_p$ ). In all cases, DI was close to 0.9 without distinction between different laminates. The greatest portion of  $E_p$  was consumed during delamination. The LPFL laminates exhibited the highest energy absorption values as well as the highest loads, as shown in Fig. 5c. It is worth noting that thicker laminates presented larger delamination zones and higher energy absorption values. This could be attributed to changes in the loading condition due to geometrical constraints.

All the laminates studied exhibited stable crack growth under the applied testing conditions in the mode-I interlaminar fracture test, suggesting that the tests were valid for determining  $G_{IC}$ . Usually, experimental  $G_{IC}$  values start at lower values and gradually approach an asymptotic critical value, which is determined at the delamination lengths above 100 to 150 mm. However, in some cases, at the delamination onset, high  $G_{IC}$  values can be obtained, which was the case of the tested laminates. This is usually attributed to resin-rich regions close to the artificial defect, and these  $G_{IC}$  values are not representative of the interface between laminas (Moore *et al.* 2001). A considerable number of tests were discarded when the cracks propagated out-of-plane. All laminates presented similar  $G_{IC}$  values, around 250 J/m<sup>2</sup>, as can be observed in Fig. 6a. No noticeable differences were found between the different orientations. This could be

attributed to the fact that the load was applied in the thickness direction, which was perpendicular to paper laminas. The  $E_{DBC}$  values, calculated from the delamination tests, are presented in Fig. 6b. Values comparable to those from the flexural tests were observed (Fig. 4c).



**Fig. 6.** Mode-I interlaminar fracture toughness test for laboratory laminates: (a) average interlaminar fracture toughness ( $G_{Ic}$ ) and (b) average flexural elastic modulus ( $E_{DBC}$ )

Significant differences between the means were found after performing analysis of variance (ANOVA) at the confidence level of 95%. To this effect, the free software program R, Version 2.15.1, was employed. For the tensile, flexural, and interlaminar fracture measurements, a  $2 \times 2$  bifactorial design was adopted, where the factors were laminate type (PFL, LSPFL, LPFL, and KPFL) and fiber orientation (longitudinal and transverse). For the impact measurements, a completely unifactorial randomized design was proposed, due to the fact that measurements were independent of the direction of the fiber. The suitability of each model was investigated (such that the independent errors were normally distributed with mean zero and constant variance for all factor levels), but the flexural resistance and tensile modulus measurements did not satisfy the assumptions of homoscedasticity and residual normality. Therefore, a modified nonparametric ANOVA that employed the theory of test permutations was adopted for these measurements. According to the  $p$  level of significance obtained from the ANOVA ( $p < 0.05$ ), the mechanical properties of the laminates showed significant differences when loaded in the two different directions. In all cases, the values from tests performed in the longitudinal direction of the paper were higher than those in the transversal.

An inclusive analysis of the obtained results permitted the identification of the contribution of the partial substitution of P by lignin to the mechanical performance of the studied materials. The tensile and flexural tests measure in-plane mechanical properties, which are determined by the anisotropy of the paper sheets, as anisotropy strongly influences the response of the laminates. The results of the impact tests demonstrated the influence of resin adhesive failure, which occurred due to the greater interaction between the partially substituted resins and the paper laminas. On the other hand, there were no significant differences in the interlaminar fracture among laminates ( $p > 0.05$ ); rather, the fracture behavior of the resin appeared subject to the geometrical constraints of its surrounding laminas. Thus, the results of the delamination tests constituted resin adhesive failure.

Finally, in order to obtain multiple comparisons between the laminate materials, a non-parametric Tukey Test was implemented to determine the changes in average tensile, flexural, and impact values and mechanical properties in the following order:

- Tensile modulus PFL=LSPFL=KPFL; LSPFL=KPFL<LPFL
- Elastic Modulus KFPL< PFL=LSPFL< LPFL
- Flexural resistance LSPFL=PFL< KPFL< LPFL
- Absorbed energy PFL=LSPFL< KPFL< LPFL
- Maximum load PFL=LSPFL< KPFL=LPFL

As expected, the LPFL exhibited the best tensile, flexural, and impact performance, probably as a consequence of its ash content and of the structurally larger lignosulfonate in comparison to the kraft-type lignin and P. An increase in carbohydrate content caused a decrease in the mechanical properties of LSPFL in comparison to those of LPFL. The mechanical properties of LSPFL were similar to those of traditional laminates, but inferior to those of KPFL; the only exception was the elastic modulus, and this was probably due to the smaller molecule size of lignin in comparison to the lignosulfonate molecule. Similarly, the mechanical performance of KPFL was worse than that of LPFL, in spite of the higher sugar content of lignosulfonate. The results indicated that both KPFL and LSPFL would be suitable for postforming applications; however, KPFL would be more appropriate than LSPFL due to its lower elastic modulus and higher flexural resistance.

Among the industrial laminates, the average mass and thickness increments were 8.43%, 7.66%, 10.78%, and 11.12% and 11.63%, 9.69%, 12.44%, and 11.94% for PFLi, KPFLi, LSPFLi, and LPFLi, respectively. According to ISO 4586-2:2004, the mass and thickness increments must be lower than 12%. Although the LSPFLi and LPFLi increments were higher than those of the PFL, the delamination blister formation was not observed, indicating good adhesion between the sheets. It seemed likely that the observed results were a consequence of the hygroscopicity of sodium lignosulfonate due to the presence of the hydrophilic sulfonic acid groups.

## CONCLUSIONS

1. Laboratory and industrial HPLs were obtained by employing a commercial weight ratio lignin:P of 10:90. Mechanical tests were combined with statistical techniques in order to better assess the mechanical properties.
2. Due to paper anisotropy, the mechanical properties, when tested in longitudinal direction of the paper, were superior to those tested in the transversal direction. No differences between laminates were observed for the interlaminar fracture, and delamination was the result of resin adhesive failure.
3. The laminates based on sodium lignosulfonate (LPFL) exhibited higher tensile, flexural, and impact properties, whereas laminates based on kraft-type lignin (KPFL) showed a decrease in the elastic modulus in comparison to traditional laminates. Due to the flexibility of KPFL, it was deemed most suitable for curved surface applications. The mechanical properties of the LPFL were similar to those of traditional laminates, making this laminate more suitable for plane applications.

4. For modified LPF, the addition of carbohydrates during paper impregnation caused a decrease in the performance of mechanical properties.

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