SYNTHESIS AND MECHANICAL PROPERTIES OF LAMINATES BASED ON PHENOLIC RESINS MODIFIED WITH SODIUM LIGNOSULFONATE

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***Abstract*—The reduction of phenol and/or formaldehyde consumption during phenolic resin synthesis is of great technological and scientific interest because of its economic and environmental implications.**

In this work, the addition of sodium lignosulfonate as partial replacement of phenol in the phenolic resol base resins used for decorative laminates production is experimentally studied. The work involves: i) the characterization and reactivation of lignosulfonate, ii) the industrial synthesis of traditional and modified resoles by replacement of 10%w/w of phenol, iii) the industrial impregnation of Kraft-type papers with the produced resins, iv) the production of laminates at laboratory and industrial scale, and, v) the measurement of their final properties. Tensile, bending and impact strength were evaluated. Modified laminates exhibited mechanical properties statistically comparable with those of traditional laminates.

Industrial tests were carried out at Centro S.A, San Francisco, Córdoba.

***Keywords*—**Laminate; Resol; Lignosulfonate; Mechanical Properties**.**

I. INTRODUCTION

Phenol-formaldehyde (PF) resins are the oldest synthetic polymers and are commercialized since 1910. Due to their excellent physical and mechanical properties (Gardziella ***et al***., 1999), they are used in a wide variety of applications such as the production of decorative laminates, adhesives, coatings, molded plastics, and aerospace components.

The reduction of phenol (P) and/or formaldehyde (F) consumption during phenolic resin synthesis is of great technological and academic interest because of the economic and environmental implications. P and F are no renewable toxic substances, with LD50 values in rats of 317 mg/kg and 65 mg/kg, respectively (Dongre *et al.*, 2015). One alternative to replace P in PF resins is to use lignins, due to the structural similarity between lignins and PF resins (Forss and Fuhrman, 1979). Lignin and its derivatives are natural and renewable poly-phenolic polymers obtained mainly as a waste from the pulp industry. It presents a complex structure that depends on the wood type and the pulping process adopted to separate cellulose. Lignosulfonates are water soluble commercial lignins containing sulfur and high ash and sugars contents. Lignin reactivity is low (Falkehag, 1975) due to the increased lignin ring substitution respect to P that generates steric impediment (Kuo *et. al.*, 1991). In order to increase the reactivity, lignin requires a chemical modification (Forss and Fuhrman, 1979; Dolensko and Clarke, 1978) that is vital to produce resins with good quality. Different techniques of lignin modifications have been reported but the hydroxymethylation with F in alkaline conditions is the most used method for resols synthesis (Alonso, 2001; Ungureanu *et al*., 2009).

In the literature there is a lot of information about the use of PF resins modified with lignins as adhesives for the production of particleboard (Vazquez *et al.*, 1999). However, the use of LPF resols for paper impregnation has been scarcely studied (Siedl, 1944; Sibalis and Rosario, 1980; Seidl and Fuller, 1984; Mahendran *et al.*, 2010). A decorative laminate comprises a decorative surface and a substrate. The decorative surface consists on an α-cellulose paper impregnated with melamine-formaldehyde resin (MF) and the substrate consists on a set of Kraft- type papers impregnated with a resol type PF resin. The industrial production of decorative laminates requires three basic steps: i) synthesis of the base resins, ii) impregnation and drying of papers, and iii) compression moulding of the sandwich structure composed by the impregnated papers and the MF surface at high pressure and temperature (T=146 °C and p=70 kg/cm^2).

In this work, resol type PF resins (traditional and modified by partial replacement of P with 10%w/w sodium lignosulfonate) were synthesized and use for the production of laboratory and industrial laminates. A replacement of 10%w/w of P was adopted following the composition used in the commercial particleboards production process (Çetin and Özmen, 2002). The industrial work (synthesis and characterization of resols, impregnation and pressing of papers) was carried out in Centro S.A. (San Francisco, Córdoba, Argentina) and the final properties of the laminates produced were determined from industrial tests. For the laminates obtained in the laboratory, industrial impregnated papers were used. The mechanical properties (such as tensile, bending and dart impact) were measured and statistical

methods were employed for the interpretation of the results.

II. METHODS

A. Raw materials

The following materials were used for this work: F 37%w/w (Alto Paraná, Argentina), P (Dalgar SA, Argentina), sodium lignosulfonate powder (Vixilex SDX, Brazil), Kraft-type paper of180g/m^2 (Stora Enso), and α-cellulose-type paper impregnated with MF resin (Centro S.A.).

B. Characterization of sodium lignosulfonate

The characterization of sodium lignosulfonate includes the following determinations: moisture and ash by gravimetric analysis, carbohydrates by High Performance Chromatography [HPLC]), C, H, N and S content by Elemental Analysis, phenolic hydroxyl groups by UV-vis Spectroscopy, and functional groups by Fourier Transform Infrared Spectroscopy[FTIR].

C. Synthesis of industrial resols

A traditional resol (T) and a modified resol (L) by replacing a 10 %w/w of P by commercial sodium lignosulfonate were synthesized in a stirred batch reactor. The resol T was obtained by reaction between a 91 %w/w solution of P and a 37%w/w solution of F (formalin) at T=90 °C and pH=9.

The synthesis of the L resol involved the lignosulfonatehydroxymethylation as a first step; and a co-condensation of P with the hydroxymethylated lignosulfonate at pH=9 and T=90 °C as a second stage. Samples were taken along the hydroxymethylation to determine the free total F [F_T] by the technique of hydroxylamine hydrochloride (ISO 14001:2002). In addition, the density, viscosity and solids content were measured at the end of the synthesis.

D. Industrial impregnation papers

The impregnation was carried out according to industrial procedures in a GORDON 3-bodies impregnation machine (resin bath, tunnel-type drying and guillotine). Kraft-type papers of 180g/m^2 were impregnated with a 38% (wet basis) of T and L resols, prior addition of 6 %w/w carbohydrates for L resin. Industrial impregnated papers are anisotropic due to lamination conditions. The in-plane mechanical properties show two main directions: parallel and perpendicular to the rolling directions.

E. Preparation and characterization of laminates

Laboratory laminates were obtained without decorative surface (α cellulose-type paper impregnated with MF) in order to evaluate the mechanical performance of the substrate (paper impregnated with resol). Also, properties of industrial decorative laminate were measured.

E.1.Laboratory laminates

A traditional laminate (LT) and a modified laminate (LL) were fabricated by pressing 26 Kraft papers impregnated with L and T, respectively, in a laboratory hydraulic press heated with steam. Laminates of 400 mm in width, 400mm in length and 50mm of thickness were pressed for 10 minutes at T=150 °C and p=35 kg/cm^2 and then cooled down during 10 min using water at T= 25 ºC.. The pressure employed corresponds to the maximum operating pressure of the equipment.

Finally mechanical properties such as tensile strength (ASTM D3039), flexural strength (ASTM D790) and impact strength (D5628) were measured taking into account the fiber orientation of paper.

Tensile test

Uniaxial tensile tests were carried out according to ASTM D3039 in order to obtain the strength and elastic modulus of the materials studied, taking into account the orientation of the laminates. To show such effects, 7 and 6 longitudinally-oriented specimens of LT and LL, respectively; and 3 transversely-oriented specimens of LT and LL were tested. Rectangular specimens of 120 mm in length, 10.7 mm in width and 49 mm of thickness were examined.

The tests were performed on a 4467 Model Instron universal testing machine with controlled displacement. A 30kN load cell and an INSTRON extensometer were used to obtain the elastic modulus of the material. The determinations were carried out at room temperature and with a crosshead speed of 2 mm/min. A calibrated length of 50 mm was set. Supplements tabs were employed to reduce stress concentration in the region of gagging as recommended in ASTM D3039.

Point flexural test

3-Point flexural tests were performed according to ASTM D790. The values of flexural strength and elastic modulus in longitudinal and transverse directions were obtained. 6 specimens of LT and LL longitudinally- and transversely-oriented, respectively were measured. Rectangular specimens of 100 mm in length, 15 mm in width and a thickness of 48 mm were used. The tests were performed on a 4467 Model Instron universal testing machine at room atmosphere and with a crosshead speed of 2 mm/min. For each sample tested a span of 76 mm was set taking into account the relative span / thickness ratio of 16:1.

Dart drop impact test

Tests were carried out following the ASTM D5628 in order to characterize the fracture behavior against impact dart loads. A CEAST 6789 Fractovis Gravity Drop machine, equipped with a steel dart of 12.7 mm in diameter and a support of 76mm in diameter was used. 4 samples of LT and LL were tested, respectively. Square specimens with a size of 100×100 mm and 4.8 mm of thickness were performed. Because of laminates size was insufficient to cut the specimens with the dimensions required, tests were made directly in different parts of the original sample of size 180×180 mm. An enough distance was kept between successive tests in order to ensure no influence from previous impacts. The tests were carried out at room temperature with 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.

E.2.Industrial laminates

Decorative laminates LTi and LLi of 3060×1220 mm and 0.6 mm of thickness were obtained by compression of 1 α-cellulose paper impregnated with base MF resin and 2 Kraft-type papers impregnated with T and L resoles, respectively. The pressing was carried out in a FJELLMAN discontinuous press (with a hot-cold cycle) at 70 kg/cm^{2}with a heating time of 6 min. to reach T=146 ºC. Then, the temperature was maintained during 45 min. Finally, the system was cooled for 20 min. Final properties such as boiling water resistance (IRAM 13367), and impact by ball (IRAM 13370) were measured.

Boiling water resistance test

Tests were performed according to the standard IRAM 13367. Three square pieces of 50 mm were cut and edges were sanded. The specimens were dried for 24 hours in an oven at 50 °C and then cooled in a desiccator and weighed. The thickness was measured in the four edges of each specimen. Then, the specimens were immersed in boiling water for 2 h and allowed to cool in distilled water at room temperature for 15 min. Finally, they were dried, re-weighted, and the four vertices thicknesses were measured. Average (mass and thickness) increments for each specimen were determined.

Ball drop impact test

Following IRAM 13370, rectangular specimens of 240×320 mm were cut. The stainless steel ball (38.1 mm diameter and 226.80 g) was drop from a fixed height (h) above the surface of the laminate. Four impacts at a distance of at least 60 mm from the edges of the specimen were done. The ball must hit only once on the surface of the specimen. The visual change of surface finish (break, depression) in the area of the ball hitting determines whether the laminate is affected or not.

III. RESULTS AND DISCUSSION

The composition of lignosulfonate is shown in Table 1 and its corresponding spectrum in Fig. 1.

Table 1 – Composition of sodium lignosulfonate.

Determination		Result
Moisture [%]		8.89
Ash [%]		23.45
Carbohydrates [%]		13.63
Phenolic hydroxyls [%]		2.03
Elemental analysis [%]	C	39.99
	H	5.34
	N	0.18
	S	4.14

Ash and carbohydrates are high in sodium lignosulfonate.

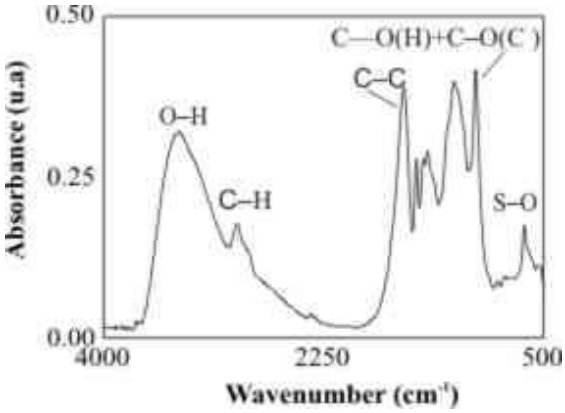

Fig. 1 – FTIR of sodium lignosulfonate

The band at 3400 cm^{-1} is assigned to hydroxyl groups (O-H). The band (C-H) from methyl and methylene groups appears at 2840-2850 cm^{-1}. Bands corresponding to aromatic skeleton and due to alcohols, carboxyl groups and ethers appear at 1600 cm and 1030 cm^{-1}, respectively. The distinct band appearing at 620 cm^{-1} in the spectrum is assigned to the sulfonic groups (S-O stretching vibration).

Fig. 2a) shows the evolution of F_T and Fig.2b) presents the reacted F (Fr) expressed as the difference between the initial total F (F*i*) and F_T per kg of lignosulfonate (ash and sugars free). As expected, $F_T$decreases at the expense of an increase in Fr. The measurements indicate that Fr (14.0 mol/ g lignosulfonate) is higher than the total OH reacted (OHr= 0.20 mol/ Kg lignosulfonate assuming a complete hydroxymethylation) at the end of the hydroxymethylation, suggesting the presence of side reactions of F.

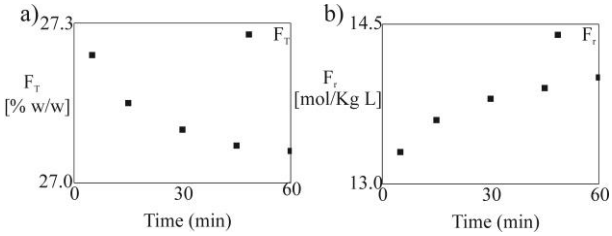

Fig 2 - Hydroxymethylation of lignosulfonate.Evolution of (a) Free F_T and (b) F_r.

Table. 2 shows the final properties of L and T resins. Density, viscosity and percent solids show no appreciable differences. F_T content is a little higher for L resin in comparison with T resin, due to the lower reactivity of lignins in comparison with phenol as it was reported in literature (Çetin and Özmen, 2002).

Table 2- Final properties of L and T resins

Final properties	L	T
Density, g/ml	1.06	1.05
% Dry Matter (2h 105ºC)	49.2	48.2
Viscosity, (Ford Cup#4, 30ºC), s	16.3	15.6
% Final F_T (w/w)	1.42	1.01

For laboratory laminates, all samples in traction broke outside the calibrated length determined by the exten-

someter, so no break elongation could be determined. Tests were performed using supplements in the grips. However, the adhesive failed in all cases and data was not recorded. All samples failed in the same way. It was observed that there is poor adhesion between the sheets near to the surface, since when using a lower clamping pressure on the jaws during testing, slippage of the specimen occurs. This behavior was observed in both, traditional and modified laminates.

Fig. 3shows the stress-strain curves obtained from LT and LL laminates in longitudinal and transverse directions, respectively. In all cases an elastic linear behavior is observed followed by a small non-linear zone towards the end of the curves. There are considerable differences between the curves for the tests in the longitudinal and transverse directions. The materials present similar behavior for transverse testing. However, differences where observed in samples tested in longitudinal orientation.

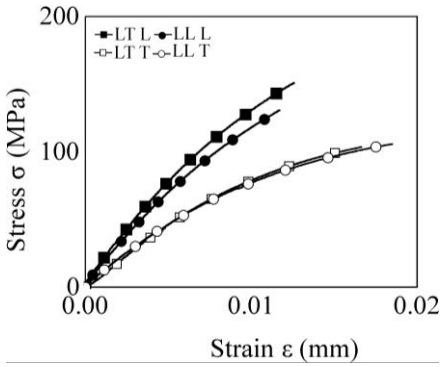

Fig 3 - Stress-strain curves in tensile test for laboratory laminates.

The main mechanism of failure in flexural test is traction developed in the sheets on the surface opposite to the contact. Large cracks in the thickness direction across the sample were seen in all samples of LL and some of LT due to poor adhesion between the layers (Fig. 4).

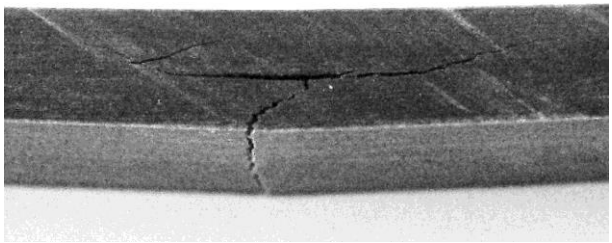

Fig 4 - Photograph of a specimen LL tested in flexural test.

Fig. 5 shows the stress-strain curves for LT and LL for the longitudinal and transverse test. Initially, the sample shows a linear behavior, followed by a slope reduction due to non-visible damage taking place. Damage is accumulated up to the peak load, which corresponds to the maximum bending resistance (strength). Note that although sudden failure occurs due to the presence of reinforcing fibers, the specimen retains a partial ability to withstand loads after failure.

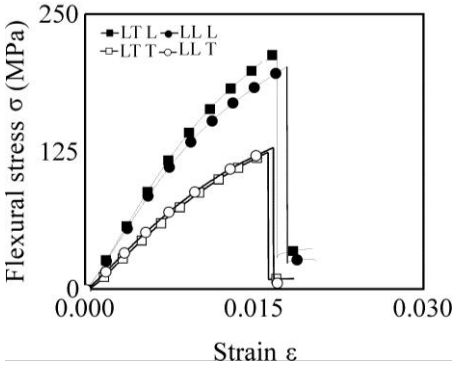

Fig 5- Stress-strain curves in flexion test for laboratory laminates.

Regarding the impact tests, no observable differences were found between modified and traditional samples. The material near to the bottom surface (opposite to the load application point) delaminated without being completely perforated by the dart (Fig. 6) suggesting an insufficient adhesion between the layers. Fig. 7shows the load-displacement curve for LL. Similar curves were obtained for LT.

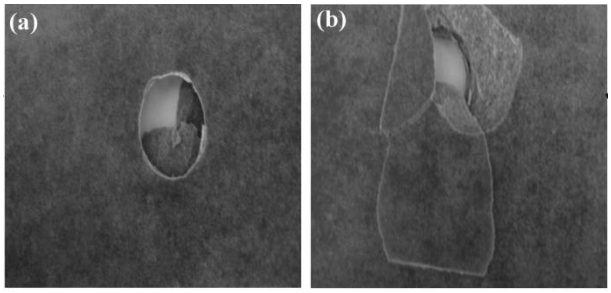

Fig 6- Photographs of a LL specimen rebuilt after the impact. (a) Bottom surface (traction). (b) Surface in contact with the dart

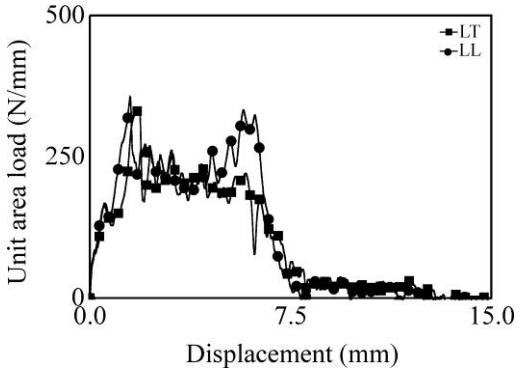

Fig 7– Load-displacement curves in impact test.

Fig. 8a), b) andFig. 8c)-d) show the strength (σ_t) and the elastic modulus (E_t) obtained from stress-strain curves in tension.

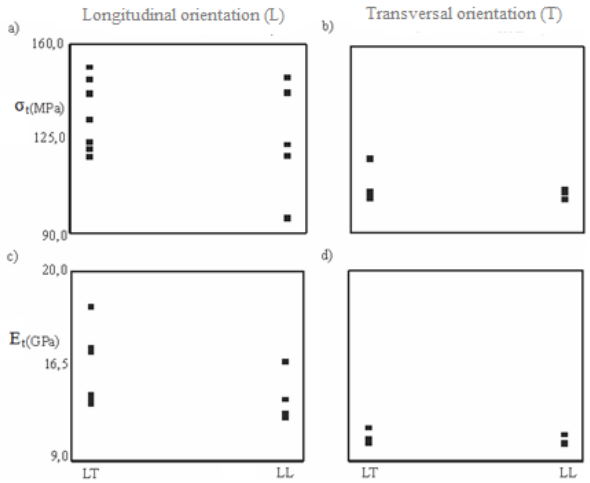

Fig 8– Tensile tests for LT and LL: a, b) strength, c, d) module of elasticity.

Similarly, flexural strenght (σ_F) and modulus of elasticity (E_F) were calculated from the stress-strain curves for flexural tests, [Fig. 9a)-b), and Fig. 9c)-d), respectively], and the energy absorbed in fracturing (EI) and maximum load (CI) from impact test [Fig. 10a)-b) and Fig. 10c)-d), respectively].

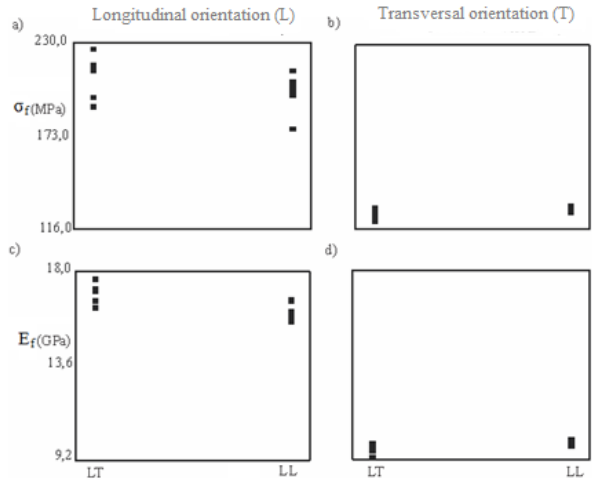

Fig 9 - Flexural test for LT and LL: a, b) strength, c, d) modulus of elasticity.

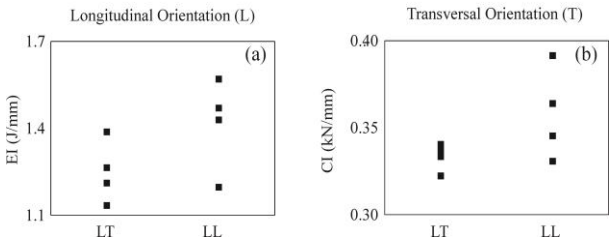

Fig 10 - Impact Test Dart Drop for LT and LL: a) energy absorbed in fracturing, and b) maximum load.

Mechanical properties of laminates show noticeable differences when loaded in the two main directions. These differences were attributed to the anisotropy of the impregnated papers, which is retained in the composite plates. In all cases, the values corresponding tolongitudinal direction of the paper were higher than the transversal.

The results were statistically compared by analysis of variance (ANOVA) at a level of 95% confidence implementing free software R program version 2.15.1.p is the level of significance (p =0.05 for a confidence level of 95%). If p <0.05 there are significant differences between samples. If p>0.05, no significant differences between samples are observed.

For flexural and tensile measurements a 2×2 bifactorial design was proposed, where factors correspond to the type of laminate (LT and LL) and the fiber orientation (longitudinal and transverse). For impact measurements a completely unifactorial randomized design was proposed because measurements are independent of the direction of the fiber (Montgomery, 1991).

The suitability of the models (independent errors normally distributed with mean zero and constant variance for all factor levels) were checked but the flexural strength and tensile modulus measurements did not satisfy the assumptions of homoscedasticity and residuals normality. Therefore, a modified nonparametric ANOVA was adopted for these measurements that employ the theory of test permutations (Venables, 2000).

Table 3 shows the *p* level of significance [p =0.05 for a confidence level of 95%. If p <0.05 there are significant differences between samples. If p>0.05, no significant differences between samples are observed], obtained from the tests in combination with statistical processing.

Table 3–p-value from ANOVA test

Test	Property	*p**	
		Type of laminate	**Orientation**
Tensile	Strength (MPa)	0.226	1.20×10^{-2}
	Elastic-modulus (GPa)	0.168	4.00×10^{-4}
3 point-flexure	Strength (MPa)	0.573	2.00×10^{-16}
	Elastic-modulus(GPa)	0.200	2.00×10^{-16}
Impact	Absorbed energy (J/mm)	0.125	––
	Maximum impact load (kN/mm)	0.111	––

The mechanical properties for both laminates resulted statistically equal for a confidence level of 95% ($p>0.05$). These results show that the replacement of P by 10%w/w of lignosulfonate did not produce effects that were detrimental to the overall performance of the decorative laminates. However, statistically significant differences were observed when changing the orientation of the laminate ($p<0.05$).

Finally, Table 4 shows the measurements of the final properties of the industrial laminates LTi and LLi.

Table 4 - Final properties of the industrial decorative laminates

Test	Increment	LTi	LLi
Boiling Water Resistance	Mass, %	8.43	10.78
	Thickness %	11.73	14.44
Ball drop impact test		Not affected	

The LLi presents higher mass and thickness increments compared to the LTi. However delamination and blister formation after 2 hours in boiling water were not observed indicating a good adhesion between the sheets. Probably the observed result is a consequence of hygroscopicity of sodium lignosulfonate that contains high sulfur content due to the presence of the hydrophilic sulfonic acid groups. Good ball impact resistance is observed for both laminates.

IV.CONCLUSIONS

The synthesis of base phenol-formaldehyde resins using sodium lignosulfonate as partial replacement of phenol was studied. The resins obtained were used for the production of industrial and laboratory laminates. The properties of the modified laboratory laminates were evaluated and compared with those of traditional laminates. For this purpose, tests such as tensile, bending and impact resistance were performed and final properties such as boiling water resistance and ball drop impact were measured. The mechanical tests were combined with statistics techniques to a better assessment of the mechanical properties. Materials with good properties according to the industrial specifications were obtained employing a weight ratio lignosulfonate:phenol of 10:90.

In comparison to traditional laminates, the laminates based on sodium lignosulfonate exhibited higher tensile, flexural and impact properties.

In a future communication the experimental work will be extended in order to optimize the process of synthesis maximizing the replacement of phenol, minimizing the consumption of F and holding the final properties in the expected values.

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