

# Lignins for Phenol Replacement in Novolac-Type Phenolic Formulations. II. Flexural and Compressive Mechanical Properties

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**ABSTRACT:** Several hexamethylenetetraamine-cured novolac-type lignophenolic resins have been subjected to mechanical analysis to check the influence of the addition of different types of lignins (kraft pine lignin, soda/anthraquinone flax lignin, and sulfonated kraft lignin from mixed softwoods) and the influence of different phenol substitution levels. Both flexural and compression tests have been performed to evaluate the influence of the curing temperature and pressure. The results have been compared with those from a commercial novolac system. Flexural tests show that lignin incorporation leads to systems with increased rigidity, whereas up to 82%

of the maximum strength can be retained with respect to a commercial phenolic (phenol-formaldehyde) at a 45 wt % substitution degree. Compression analyses show that modified prepolymers are not significantly affected by the presence of lignin at a medium curing pressure (150 bar), but their deformability results considerably increase at high curing pressures (400 or 600 bar). © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 159–165, 2008

**Key words:** mechanical properties; polyaromatics; renewable resources; resins; structure-property relations

## INTRODUCTION

Phenol-formaldehyde (PF) resins were the first completely synthetic resins employed in the production of molding compounds. They are well known to possess excellent properties, but their inherent brittleness makes necessary, in most cases, the use of additives in formulations. By means of mixtures with other compounds (reinforcement agents, accelerators, pigments, etc.), PF resins can be employed for the production of a wide variety of products that have to be subjected to different mechanical requirements during their lifetime. In this way, organic (cotton, cellulose, etc.) and inorganic (glass) fibers can be incorporated to enhance mechanical and impact resistance, wood flour can be incorporated for modifying the hardness and final appearance, silicate minerals can be incorporated for enhancing thermal resistance and decreasing postcuring shrinkage, mica can be incorporated for increasing insulating properties, and so forth.<sup>1</sup>

The use of lignin as a partial substitute for phenol in the formulation of lignin-phenol-formaldehyde (LPF) resins assumes the introduction of bulky structures with limited reactivity, which results in an increase in the resins' brittleness.<sup>2–5</sup> A mechanical analysis of LPF resins seeks to minimize this adverse effect, trying to maintain the mechanical properties with little variation with respect to conventional resins. The best results have been obtained when lignin is added at the beginning of the synthesis procedure.<sup>4,6</sup>

In this work, several novolac-type LPF resins, in which 25 or 45 wt % phenol has been substituted by lignin, have been subjected to mechanical analysis after being hexamethylenetetraamine (HMTA)-cured. Both flexural and compression tests have been performed to evaluate the effects derived from the incorporation of lignin into polymeric formulations.

## EXPERIMENTAL

### Materials

Three different types of lignins [kraft pine lignin (L1), soda/anthraquinone flax lignin (L2), and sulfonated kraft lignin from mixed softwoods (L3)] were used for lignophenolic resin synthesis. The physicochemical characterization of L1 and L2, which were isolated from industrial black liquors, has been

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TABLE I  
Compositions of the Synthesized LPF Prepolymers

Resin	Formaldehyde (g) <sup>a</sup>	Phenol (g)	Lignin (g)	Oxalic acid (g)	Formaldehyde/(phenol + lignin) <sup>b</sup>
PF <sup>c</sup>	373	500	—	2.5	0.70
LPF-1-25	373	375	125	2.5	0.80
LPF-2-25	373	375	125	2.5	0.81
LPF-3-25	373	375	125	2.5	0.80
LPF-1-45	373	275	225	2.5	0.90
LPF-2-45	373	275	225	2.5	0.92
LPF-3-45	373	275	225	2.5	0.90

An industrially used PF composition is included for comparison.

<sup>a</sup> A 30 wt % aqueous solution.

<sup>b</sup> Estimated molar ratio.

<sup>c</sup> Extrapolated composition from industrially used percentages.

reported elsewhere,<sup>7</sup> whereas L3, a commercial product called Diwatex 40P, was kindly provided by Basf Curtex and used as received. Phenol (99%), oxalic acid (99%), HMTA, and a commercial PF resin were gifts from Hexion Ibérica (Hernani, Spain), whereas formaldehyde (a 30 wt % aqueous solution) was supplied by Aldrich.

### Resin preparation

The LPF resins used in this work have been fully described elsewhere.<sup>7</sup> The extremely complicated lignin structure and its uncertain functionality made it impossible in practice to prepare stoichiometric formulations. For this reason, the molar ratio of formaldehyde to the phenolic part [formaldehyde/(phenol + lignin)], now consisting of phenol and lignin, was put aside, and this work focused on the effects of the direct replacement of phenol with lignin, as we thought this could be interesting from an industrial point of view. Therefore, LPF prepolymers were synthesized by the substitution of a percentage of phenol (25 or 45 wt %) by lignin, whereas the formaldehyde and oxalic acid amounts were kept constant (Table I). The formaldehyde/(phenol + lignin) molar ratio was roughly estimated from the guaiacyl/syringyl composition of L1 and L2, which was determined by <sup>1</sup>H-NMR in a previous work;<sup>7</sup> for this purpose, L3 was assumed to be equal to L1 as both were coniferilic kraft lignin. The resin nomenclature has been adopted as follows: the first number indicates the type of lignin that has been incorporated into the formulation (L1, L2, or L3), and the second one shows the phenol substitution degree (by weight). For example, LPF-3-45 represents a modified phenolic resin in which 45 wt % phenol has been substituted by L3.

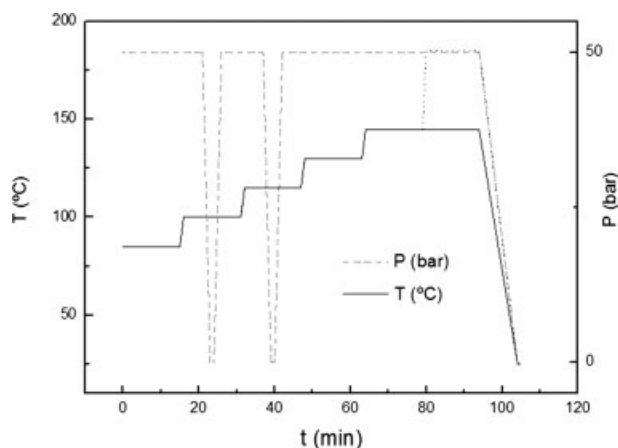
The synthesis procedure for the novolac-type LPF resins reproduced the method commonly used by the industry and mentioned elsewhere,<sup>1</sup> with the only difference being a previous step in which phenol and lignin were mixed together.

### Specimen preparation

The specimens employed for the flexural tests were shaped from plates obtained by the compression molding of resins cured with 10 wt % HMTA, as this is usually the method employed for molding phenolic resins.<sup>1</sup> The temperature first causes the softening of the material, which fills the mold, and then the curing process takes place. The pressure acts as a force against the appearance of bubbles in the material, which originate from water and ammonia emissions generated during the cure. The evaporation of these volatile compounds during the hardening of the resin causes the formation of bubbles inside the material. This problem is of vital importance when the mechanical properties of phenolic resins are analyzed because these defects are weak points at which the early fracture of the piece can be produced. Such effects would invalidate the mechanical parameters that are being determined.

To minimize the negative effect mentioned previously, the curing cycle represented in Figure 1 was designed, leading to satisfactory results after several attempts. The temperature was gradually increased in 15°C steps and kept constant at each value for 15 min. After the final temperature (145°C) was reached, the conditions were maintained for 30 min more to obtain fully cured materials. A pressure of 50 bar was employed during the entire process. Two decompression stages were also included in the first steps of the curing process with the aim of facilitating the exit of volatile compounds and, therefore, improving the quality of the resulting pieces. The effect of the temperature on the flexural behavior was also evaluated for LPF-2-25 and LPF-3-45 resins together with the reference PF. In these cases, curing was carried out with the same procedure but with the addition of a new postcuring stage at 185°C, as shown in Figure 1 by a dotted line.

The specimens employed in compression tests were obtained by the hardening of the resins with 10 wt % HMTA in a cylindrical pan (7.4 mm in diameter and 100 mm high) of an SWO/Haake PVT



**Figure 1** Scheme of the curing cycle employed for compression molding ( $T$  = temperature;  $P$  = pressure;  $t$  = time).

100 pressure–volume–temperature analyzer. The experimental curing conditions were 145°C, 150 bar, and 90 min. PF, LPF-3-25, and LPF-3-45 systems were also employed to study the effect of the curing pressure on the mechanical properties. With this aim, the curing process was carried out at 400 and 600 bar, with constant temperature and time conditions maintained. In all cases, cylindrical pieces obtained from the pressure–volume–temperature analyzer were shaped until the required dimensions, according to ASTM D 695, were obtained (length/diameter = 2). Special care was taken to obtain perfectly parallel sides.

### Mechanical characterization

Flexural tests were carried out in an Instron model 4026 universal testing machine with a three-point bending device. The conditions employed for the analysis were set according to the ASTM D 790M standard with a span ratio of 16 and a crosshead rate of 1 mm/min.

A minimum of five specimens were tested for each system, and the mean value was presented. The flexural properties were calculated from the graphics obtained with the equations of the ASTM D 790M standard:

$$\varepsilon_f = \frac{6Dd}{s^2} \quad (1)$$

$$\sigma_f = \frac{3P_R s}{2bd^2} \quad (2)$$

$$E_f = \frac{s^3 m}{4bd^3} \quad (3)$$

where  $\varepsilon_f$  is the maximum strain,  $D$  is the maximum deflection (mm),  $s$  is the length between supports

(mm),  $d$  is the depth of the specimen (mm),  $\sigma_f$  is the flexural strength (MPa),  $P_R$  is the maximum load (N),  $b$  is the width of the specimen (mm),  $E_f$  is the apparent flexural elastic modulus (MPa), and  $m$  is the slope in the elastic zone of the load–deflection curve.

Compression tests were also carried out in an Instron universal testing machine with the appropriate supports. The crosshead displacement rate was fixed to 1 mm/min in accordance with the ASTM D 695 standard. The following expressions were employed:

$$\varepsilon_c = \frac{l_0 - l_R}{l_0} \quad (4)$$

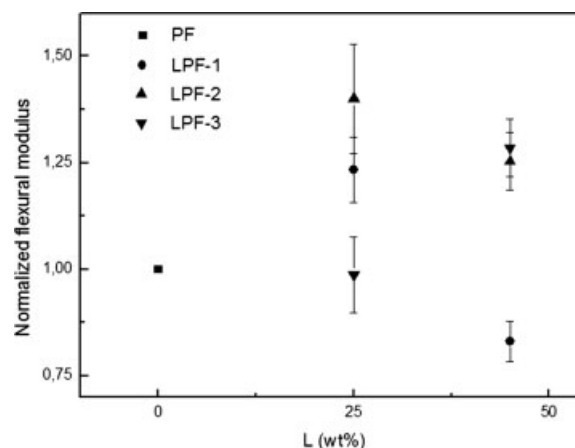
$$\sigma_c = \frac{P_r}{a} \quad (5)$$

$$E_c = \frac{\sigma_{c,2} - \sigma_{c,1}}{\varepsilon_{c,2} - \varepsilon_{c,1}} \quad (6)$$

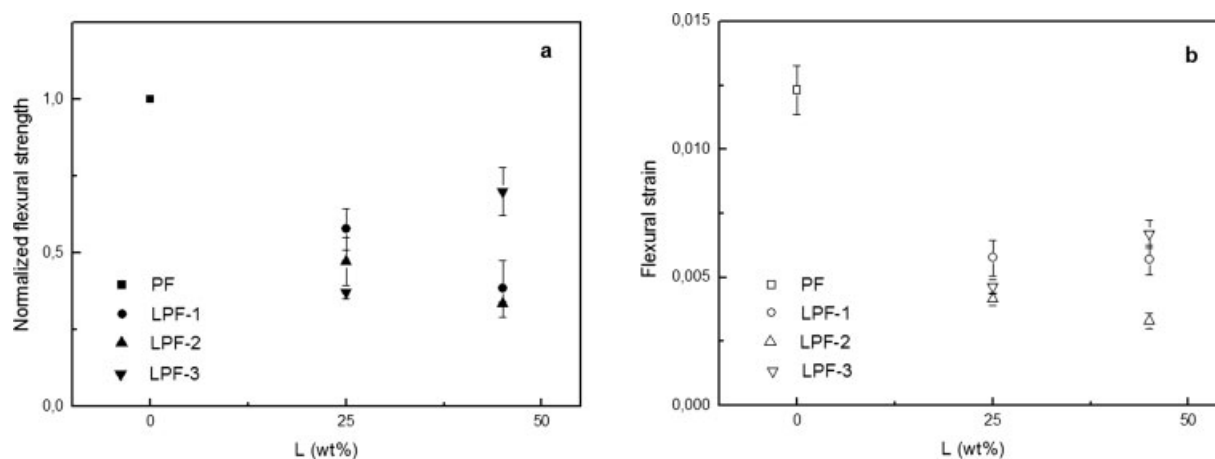
where  $\varepsilon_c$  is the maximum compressive strain,  $l_0$  is the initial length of the specimen (mm),  $l_R$  is the length of the specimen at rupture (mm),  $\sigma_c$  is the compressive strength (MPa),  $P_r$  is the maximum load (N),  $a$  is the transversal section of the specimen (mm<sup>2</sup>),  $E_c$  is the compressive elastic modulus (MPa), and  $\sigma_{c,i}$  and  $\varepsilon_{c,i}$  are the compressive stress and strain measured at points 1 and 2 in the elastic zone of the curve. The values correspond to averages of at least three measurements.

## RESULTS AND DISCUSSION

Cured lignophenolic resins, like phenolic resins, present the characteristic mechanical behavior of a brittle solid, with practically linear stress–strain curves in which all the deformation is elastic.<sup>1,9</sup> This breaking mode has been defined as strain-controlled



**Figure 2** Normalized flexural modulus as a function of the type and content of lignin (L).



**Figure 3** (a) Normalized flexural strength and (b) flexural strain as functions of the type and content of lignin (L).

rupture,<sup>10</sup> which means that the fracture occurs when the deformation capacity of the material is not enough to resist the normal stresses appearing in the direction tangential to the load application. For both cases, that behavior is related to the high crosslinking density and the reduced mobility caused by methylene linkages. On the other hand, because of their geometry, three-point bending tests create compression stresses on the upper side of the sample (where the stress is applied) and tensile stresses on the lower side. The latter, because of the low deformability of the system, lead to the premature breaking of the sample.

### Flexural tests

Initially, the results obtained for a cure cycle up to 145°C were analyzed. The flexural moduli of the different systems were normalized with respect to that of the PF resin (Fig. 2) for a better comparison between them. As can be seen in Figure 2, most of the LPF systems show higher modulus values than PF resin. Despite some lignin phenylpropanic (C9) units forming covalent bonds during the LPF resin cure, the high molar mass and the complex structure of lignin cause the existence of low-crosslinking-density zones at the end of the process. In this way, the presence of highly substituted lignin aromatic rings, which are often linked to other C9 units through

C—C bonds, can be observed. These kinds of structures show very low mobility and thus high rigidity that is transferred to the general behavior of the material and leads to the observed modulus increase.

The only exception to this behavior is the LPF-3-25 system, which shows modulus values similar to that for the reference resin, and LPF-1-45, which shows much lower values. As reported in a previous article,<sup>8</sup> the LPF-1-45 system shows very low reactivity during curing because of the presence of lignin aggregates in the prepolymer as a result of the difficulty of homogeneously incorporating L1 into the resin, which also justifies the low modulus of this resin.

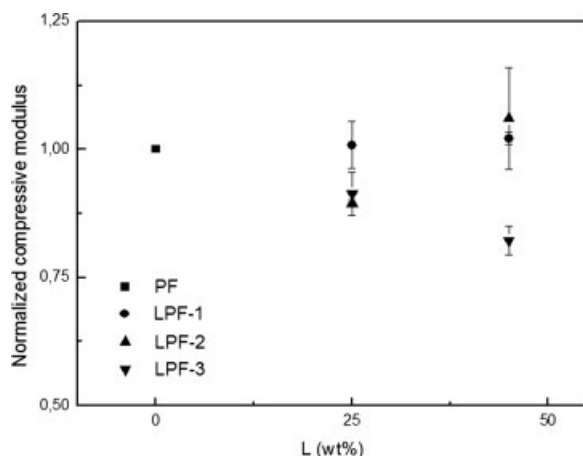
It can be concluded that the substitution of some of the phenol by a type of lignin that can be homogeneously incorporated into the phenolic formulation leads to an improvement in the rigidity of the material. This is a valuable feature that, in addition to economic and environmental profits derived from the use of lignin, converts these lignin-modified mixtures into very interesting systems to be industrially used.

In Figure 3(a,b), the strength and strain values, respectively, are presented. The existence of zones with low reactivity in the lignin, which are not able to form links during the cure process, is reflected in the low deformability of the systems modified with lignin. These zones are weak points from which the

**TABLE II**  
Retained Flexural Resistance of LPF Prepolymers for Two Lignin Concentrations

Resin	145 °C			185 °C		
	$E_f^*$	$\sigma_f^*$	$\varepsilon_f$ (mm/mm)	$E_f^*$	$\sigma_f^*$	$\varepsilon_f$ (mm/mm)
PF	1	1	0.012 ± 0.001	1.29 ± 0.05	0.86 ± 0.12	0.008 ± 0.001
LPF-2-25	1.40 ± 0.13	0.47 ± 0.08	0.004 ± 0.001	1.36 ± 0.02	0.73 ± 0.02	0.007 ± 0.001
LPF-3-45	1.28 ± 0.06	0.70 ± 0.08	0.007 ± 0.001	1.19 ± 0.06	0.82 ± 0.05	0.009 ± 0.001

\* Normalized values.



**Figure 4** Normalized compressive modulus of 150-bar-cured systems as a function of the type and content of lignin (L).

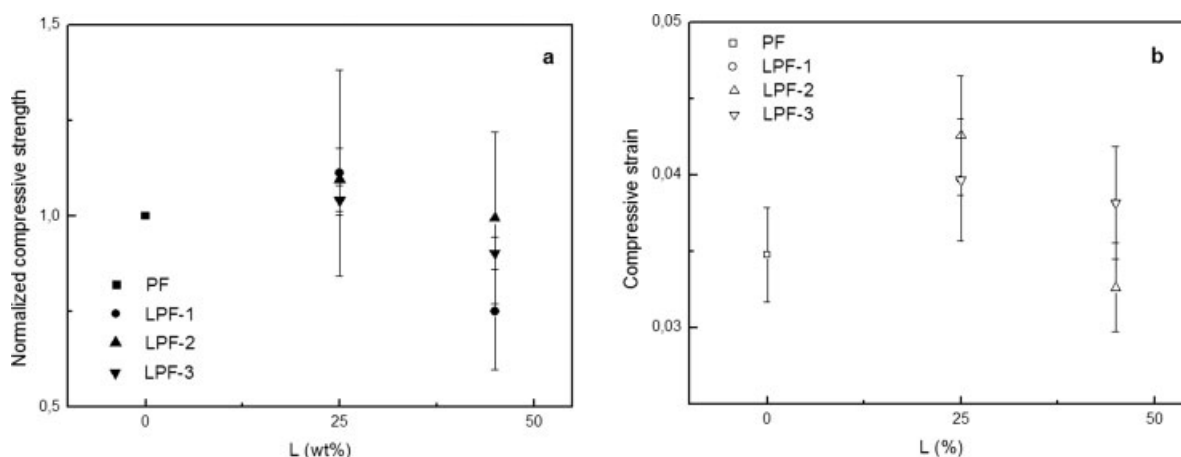
material starts to break prematurely when stress is applied. As a result, the maximum strength of the material is notably reduced. Several authors<sup>5,11</sup> have related this behavior to the low content of lignin reactive groups and also to the voluminous structure. The strength loss becomes higher with increasing lignin content, except for the LPF-3 system; LPF-3-45 shows an improvement of the properties, reaching a retention of 70% with respect to that of the PF resin. This result confirms the higher reactivity observed for this system in a previous work,<sup>8</sup> which was related to the higher molar ratio and probably to the catalytic effect of  $-\text{CH}_2\text{OH}$  groups<sup>12</sup> present in the L3 structure.

In the following, lignin-modified mixtures with a cure cycle up to 185°C are analyzed to evaluate the effect of the cure temperature on the mechanical properties of LPF resins. With this aim, LPF-2-25 and LPF-3-45 resins were selected as they showed higher reactivity in a previous work,<sup>7</sup> which was

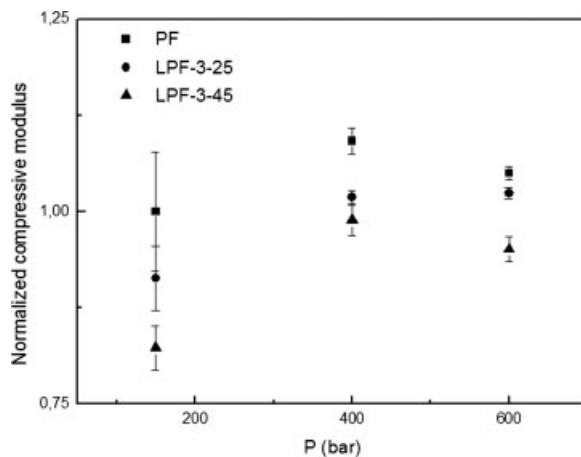
related to the more homogeneous distribution of lignin in both systems. A commercial PF resin was also tested as a reference.

Table II shows the normalized flexural modulus and strength and maximum strain of these systems. Values for cure at 145°C have also been included for a better comparison. As the cure temperature increases, the control PF resin shows an increase in the flexural modulus, whereas a decrease is observed in the maximum deformation and strength. Phenolic resins are well known to form highly crosslinked networks during curing,<sup>1</sup> which provide them with excellent mechanical properties.<sup>1,11</sup> However, when the density of crosslinking is too high, cured phenolic resins become extremely brittle because of the low deformation capacity of their inner structure. In the same way, the strong increase in the modulus and the decrease in the strain at break suggest that the cure cycle applied to the PF resin gives a highly crosslinked structure.<sup>13–15</sup>

On the other hand, for both lignonovolacs, the flexural moduli remain nearly constant, whereas the strength and deformation values increase in a similar way, as the cure temperature increases. The retained strength increases up to 73.4 and 82.3% with respect to that of the control resin cured at 145°C for LPF-2-25 and LPF-3-45, respectively. Lignin presents glass transitions that are extended along a wide range of temperatures<sup>8</sup> as a result of their high polydispersity. Specifically, for L2 and L3, this range is extended up to  $\sim 150$  and  $\sim 170^\circ\text{C}$ ,<sup>8</sup> respectively, thus indicating the existence of some fractions (with highest molar masses) that are not softened up to this point. The increase in the curing temperature from 145 to 185°C can lead to the softening of the polymeric fractions with a higher glass-transition temperature, thus making possible their reaction with the subsequent formation of new links in the network. This possibly helps the disappearance of



**Figure 5** (a) Normalized compressive strength and (b) compressive strain of 150-bar-cured systems as functions of the type and content of lignin (L).



**Figure 6** Normalized compressive modulus at different curing pressures ( $P$ ).

weak zones that lead to the early breaking of the material at a low cure temperature, with the consequent higher strength and deformation at break.

### Compression tests

LPF and PF systems cured at 150 bar were initially analyzed. The normalized compressive modulus (Fig. 4) and strength [Fig. 5(a)] and maximum strain [Fig. 5(b)] values, determined as functions of the type and content of lignin, are presented. The mechanical behavior shows little variation with the incorporation of lignin into the formulation, regardless of its type and the percentage of substitution.

It is well known that the mechanical properties of a thermoset system, particularly deformability, can be modified by the introduction of compounds having mobile groups in their structure.<sup>10,16,17</sup> The lignin structure is composed of hydroxyphenylpropane units that are connected to each other mainly through ether-type linkages.<sup>18</sup> Once lignin is integrated into the network, both aliphatic chains and ether bonds

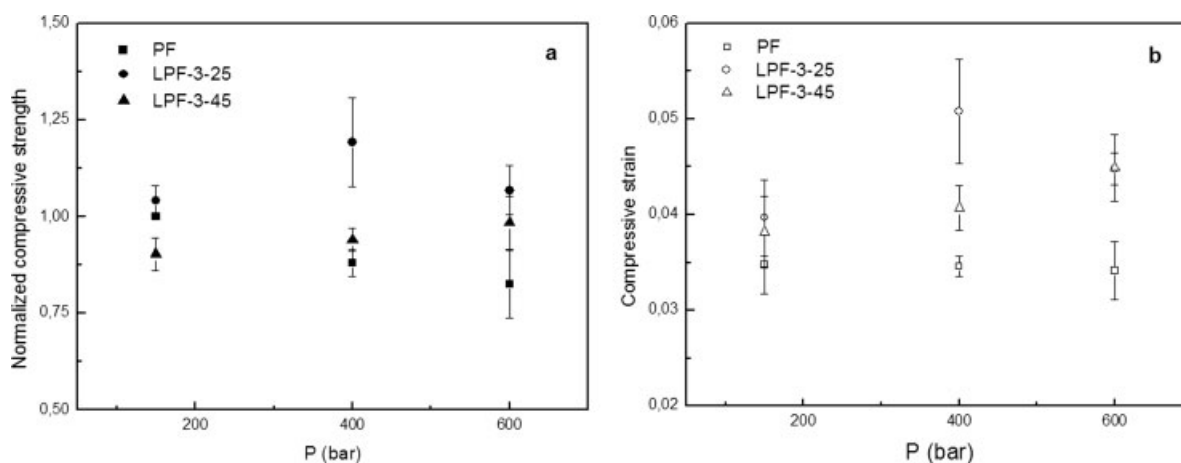
are expected to enhance the overall deformability of LPF resins.<sup>6</sup> This would explain the slightly higher deformation observed in LPF systems.

The results obtained in compression tests for both 400- and 600-bar-cured LPF-3 systems, together with the reference one, are presented in Figures 6 and 7. Values corresponding to the same systems cured at 150 bar have been also included in the plots. The increase in the curing pressure does not have a relevant influence on the PF resin properties, as none of the analyzed properties suffers remarkable variations. Such an influence is not observed in the compressive modulus from lignin-modified resins (Fig. 6), which present values similar to those of the PF resins, whereas the increase in the curing pressure causes a slight growth in the LPF-3 resin strength, which is especially relevant in the 400-bar-cured LPF-3-25 system [Fig. 7(a)].

A greater influence has been found to exist on LPF deformability [Fig. 7(b)], which significantly rises in both LPF-3-25 and LPF-3-45 systems; this results in a 28% increase in the 400-bar-cured LPF-3-25 system. The increase is smaller in the LPF-3-45 resin but shows an upward dependence with pressure, with 18% higher deformation at 600 bar. These improvements could be related to the influence of  $-\text{CH}_2\text{OH}$  groups from the L3 structure on the curing process, which would react to a higher extent as a result of the drastic conditions. Again, new linkages involving aliphatic lignin chains are suggested to be formed, causing an increase in LPF deformability. The LPF-3 strain results show increments of 46 and 30% for the LPF-3-25 and LPF-3-45 systems, respectively, when they are compared with PF.

### CONCLUSIONS

Several HMTA-cured novolac-type LPF resins have been subjected to mechanical analysis to analyze the



**Figure 7** (a) Normalized compressive strength and (b) compressive strain at different curing pressures ( $P$ ).

influence of incorporating different types of lignin and different phenol substitution levels into the polymeric formulations. Experimental results obtained by flexural tests show that in most cases lignin addition leads to systems with increased rigidity, which results in a flexural modulus up to 1.4 times higher than that from unmodified PF. Furthermore, with an increase in the curing temperature, up to 82% of the flexural strength can be retained in some cases with respect to that of a commercial phenolic at a 45 wt % phenol substitution level. Compression analyses show that the modified prepolymers were not significantly affected by the presence of lignin at a medium curing pressure (150 bar), whereas their deformability results considerably increased at high curing pressures (400 or 600 bar).

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