

Lignins for Phenol Replacement in Novolac-Type Phenolic Formulations, Part I: Lignophenolic Resins Synthesis and Characterization

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Received 2 April 2007; accepted 17 June 2007

DOI 10.1002/app.26941

Published online 25 July 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Several lignin (L)-based novolac-type phenolic prepolymers with two phenol (P) substitution degrees have been synthesized using three L from different origin (kraft pine L, soda/anthraquinone (AQ) flax L, and sulfonated kraft softwood L). These lignophenolic (LPF) resins have been characterized by means of free P and formaldehyde (F) analysis, viscosity, chemical structure (FTIR), and thermal behavior (DSC). Temperature at which curing reaction begins (DSC), hardening time at several curing temperatures (rheology) and volumetric changes (PVT) have also been determined for the

curing process with 10 wt % hexamethylenetetraamine (HMTA). All the results have been compared to those obtained for a commercial novolac. Depending on the L type employed a homogeneous material with lower curing onset temperature and gelation time than reference PF can be obtained even at high P substitution level (45 wt %). © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 2313–2319, 2007

Key words: lignophenolic resins; synthesis; differential scanning calorimetry; glass transition; gelation

INTRODUCTION

Phenol-formaldehyde (PF) resins, also called phenolic resins, were first synthesized by Leo H. Baekeland in 1908, becoming the first completely synthetic resins to be created. Because of their excellent behavior and relatively low production costs, PF resins are currently one of the most used thermosetting resins, and their use is fundamental in diverse areas such as wood composites, isolating materials, adhesives, and many others. In fact, they differ from the rest of polymeric materials (either thermosets or thermoplastics) in terms of the wide variety of applications they can be used in.¹ The main drawback associated to the production of PF resins derives from their environmental impact, as P is a volatile aromatic compound and F has been classified as high-risk product,² which restricts more and more of their utilization. For this reason, there is an urgent necessity of designing new materials where the whole process (raw materials extraction, production, and degradation) are sustainable and respectful with the environment. Lignin (L) has been found to be a promising

natural alternative to phenolic resins to be used as a partial replacement of P in the formulations.

In the last decades of the 20th century, the utilization of L as a copolymer in the area of materials engineering began to be considered as possible. The structural similarity existing with PF resins led to several attempts of incorporating L into phenolic formulations as a partial substitute of P,^{3–5} with the double objective of lowering production costs and reducing toxicity problems. Since then, much research work has been done trying to optimize L incorporation in PF formulations, being most of the works dedicated to resole-type resins^{6–21} and only a few of them to novolac-type lignophenolic resins.^{22–26} In both cases, L from different origins have been tested either nonmodified^{12–18,23–25} or after several modifications such as fractionation,^{3,8,9,27–31} hydroxymethylation,^{10,11,20,22,26,32,33} or phenolation.^{6,7,34,35} These previous treatments are applied with the aim of improving L reactivity, so that L-based systems fulfil all the requirements of commercial PF, but it seems that there is a great inconsistency among existing data and the utilization of both modified and nonmodified L leads to dissimilar results. This fact, which is undoubtedly a consequence of the huge variability of L structure derived from its natural origin, suggests that much work must still be done to completely understand the real possibilities of L as a component in PF resins.

With the aim of contributing to this search, three types of unmodified L, namely kraft pine L, soda/anthraquinone (AQ) flax L, and sulfonated kraft

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Contract grant sponsors: Hexion Ibérica, Gobierno Vasco (Spain).

softwood L, have been used for partially replacing P in the synthesis of novolac-type lignophenolic (LPF) resins. Each L has been incorporated at two different P substitution levels (25 and 45 wt %) resulting in six LPF prepolymers that, together with an unmodified commercial novolac system used as reference, have been characterized in terms of free P and F levels, viscosity, structural analysis (FTIR), and thermal behavior (DSC). Curing process of such prepolymers has also been analyzed, and their respective hardening time (rheological analysis) and volumetric variation, by means of pressure–volume–temperature (PVT) measurements, have been determined. All the results obtained from these analyses have been discussed focusing on L characteristics and compared with those derived from control PF system.

EXPERIMENTAL

The analysis of L-modified phenolic resins suffers from an inherent drawback; because of the extremely complicated L structure and its uncertain functionality, it is impossible in practice to prepare stoichiometric formulations. This can be attributed to the high weight average molecular weight (M_w) and wide molecular weight distributions (MWD), as well as to the existence of about 10 types of intermolecular linkages and as many more different functional groups in most L samples. Therefore, this work has been focused on the effects of the direct replacement of P with L, as we think it can be more interesting from an industrial point of view. Molar ratio between F and the phenolic part (now constituted by P and L) has been estimated to consider its effect over the different variables.

Materials

Three different types of L, namely kraft pine L (L1), soda/AQ flax L (L2), and sulfonated kraft L from mixed softwoods (L3) were used for lignophenolic resins synthesis. Physicochemical characterization of L1 and L2, which were isolated from industrial black liquors, was reported in a previous article³⁶ while L3, a commercial product called Diwatex 40P, was gently supplied by Basf Curtex and used as received. P (99%), oxalic acid (99%), HMTA, and commercial PF resin were gifts from Hexion Ibérica while F (30 wt % aqueous solution) was supplied by Aldrich.

Resin preparation

LPF prepolymers have been synthesized by substituting a P percentage (25 or 45 wt %) by L while F and oxalic acid amounts were kept constant (Table I). F/(P + L) molar ratio has been roughly estimated from guaiacyl/syringyl composition of L1 and L2

TABLE I
Resins Composition and Estimated F/(P + L) Molar Ratio

Resin	F ^a (g)	P (g)	L (g)	Oxalic acid (g)	F/(P + L) ^b
PF ^c	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

^a 30 wt % aqueous solution.

^b Estimated molar ratio.

^c Extrapolated composition from industrially used percentages.

that was determined by ¹H NMR in a previous work³⁶; for this purpose, L3 has been assumed to be equal to L1 as both are coniferilic kraft L. Resins nomenclature has been adopted as follows: the first number indicates the type of L that has been incorporated into the formulation (L1, L2, or L3), and the second one shows the P substitution degree (by weight); e.g., LPF-3-45 represents a modified phenolic resin where 45 wt % P has been substituted by L3.

Synthesis procedure for novolac-type LPF resins reproduces the method commonly used by the industry and mentioned elsewhere,¹ with the only difference of a previous step where P and L are mixed together. The desired quantity of L was added over molten P (~ 50°C) in a batch reactor connected to a condenser to avoid any loss and mechanically stirred for 1 h until a homogeneous mixture was obtained. In those cases, where the increase in viscosity was too high at this point, water had to be added to ensure a correct stirring. After heating the reaction mixture to 90–100°C, F solution was poured in drop by drop. Polymerization and postcondensation reactions were allowed to take place in these conditions for 180 min, after which water and unreacted P were removed by distillation under atmospheric pressure in the initial steps and then under vacuum during the last stages of the process. Finally, LPF resin was poured into a glass plate and allowed to cool down before grinding it to a fine powder. All samples were then kept in a fridge at 4°C until they had to be used.

Resin analysis

Resin viscosity was measured at 150°C using an ICI cone and plate viscosimeter following ISO 3219 standard. Free F present in LPF resins was determined according to the hydroxylamine hydrochloride method (ISO 9397). After diluting 10 g of resin in methanol, the pH was adjusted to 3.5 by adding 1M NaOH. Ten milliliters of hydroxylamine hydrochlor-

TABLE II
Free P, Free F, and Viscosity Values Determined for Each System

Resin	Free P (%)	Free F (%)	Viscosity (mPa s/10 ³)
PF	0.25	0.24	3.7
LPF-1-25	0.27	0.13	8.8
LPF-2-25	0.17	0.18	7.4
LPF-3-25	0.20	0.21	5.7
LPF-1-45	0.41	0.08	16.7
LPF-2-45	0.23	0.15	13.2
LPF-3-45	0.32	0.06	10.8

ide solution were then added, and the mixture was titrated with 1M NaOH solution after 10 min. Residual phenol was measured by gas chromatography after dissolving samples in acetone. Capillary column of 50 m length with an inner diameter of 0.2 mm was employed while *p*-cresol and helium were used as an internal standard and a carrier gas, respectively.

Fourier transform infrared spectroscopy (FTIR) was used for resin characterization. FTIR spectra were obtained within 4000–400 cm⁻¹ range and a resolution of 4 cm⁻¹, using a Nicolet spectrometer. KBr pellet technique was used and 20 scans were carried out for every single measurement.

Thermal analysis was performed with a Mettler DSC20 differential scanning calorimeter (DSC) linked to a TC 15 TA processor. Low pressure pans with 2–5 mg samples and a temperature range from 30 to 300°C and 10°C/min heating rate were used for the determination of glass transition temperatures (T_g) of L samples. Concerning the resins thermal behavior, samples from 5 to 10 mg of LPF resins containing 10 wt % hexamethylenetetraamine (HMTA) used as curing agent were sealed in medium pressure capsules, which can withstand up to 20 bar pressures. Scanning temperature range from 30 to 300°C and heating rate of 10°C/min was employed for the determination of both T_g of the prepolymer and onset temperature (T_0) of the curing reaction (the latter representing the temperature at which the curing reaction begins). In all cases, T_g has been defined as the middle point of the temperature range where the transition takes place.

Gelation times (t_{gel}) of the resins, cured with 10 wt % HMTA, were determined through rheological experiments performed in a Metravib VA 815 type viscoanalyzer under annular pumping geometry. Curing behavior was tested for each resin at three different isothermal temperatures (145, 165, and 185°C) with a frequency of 10 Hz. From the rheological curves, t_{gel} was taken when $G' = G''$ ($\tan \delta = 1$), representing the effective curing rate of the system.

Dimensional changes occurring during the hardening of LPF resins (with 10 wt % HMTA) as well as

their final specific gravity were determined carrying out the cure process in a PVT analyzer (SWO/Haake PVT100). Experimental conditions were 145°C, 90 min, and 150 bar.

RESULTS AND DISCUSSION

A series of novolac-type lignophenolic resins have been synthesized after substituting an important part of P (25 or 45 wt %) with L. Technical specifications of these resins as well as for the nonmodified resin used as reference, including free P and F contents and viscosity, are presented in Table II. As novolac synthesis was carried out with an excess of P, so that all F reacts during polymerization reactions, free F levels are expectedly low in all cases. On the other hand, low free P levels have been obtained after repeating a vacuum distillation process several times. The incorporation of L into the phenolic formulation causes a noticeable increase in the viscosity of LPF resins, being more pronounced this effect when the L content is increased up to 45 wt %. This behavior is related to the macromolecular nature of L, presenting both high M_w and MWD, what results in the existence of L fractions of 10⁵ Da in the case of kraft L.³⁶

FTIR spectroscopy has been used to analyze the chemical changes occurring during the synthesis of LPF resins. Figure 1 shows a detail of FTIR spectra corresponding to P, L3, P + L3 reaction product, and LPF-3-25 prepolymer in the 1800–650 cm⁻¹ range. Concerning the resin spectra, though a precise identification of bands is found difficult due to the nature of the components, the disappearance of 690 and 900 cm⁻¹ band, which are related to monosubstituted phenolic rings from P, can be clearly observed while that from L guaiacyl-type rings

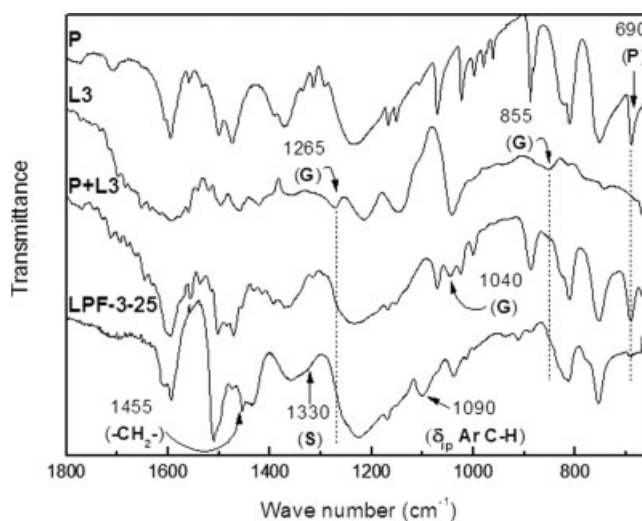


Figure 1 Detail of FT-IR spectra from P, L3, P + L3 reaction product and LPF-3-25 prepolymer.

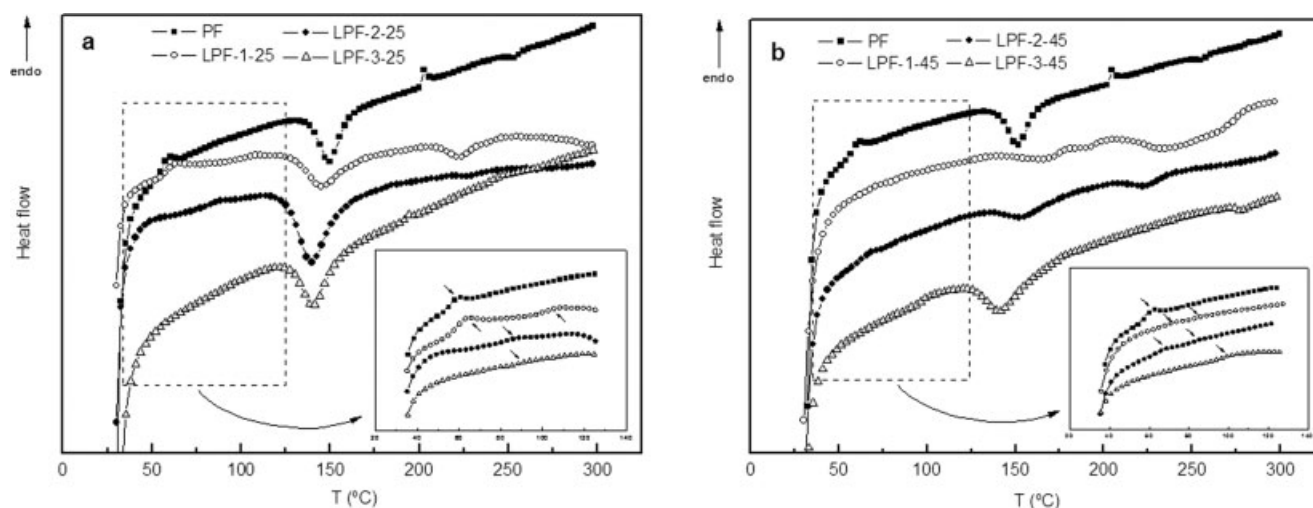


Figure 2 DSC thermograms and detail of the temperature range where glass transitions take place corresponding to the cure of (a) 25 wt % and (b) 45 wt % substituted LPF systems. In both cases, PF cure thermogram has also been added. T_g transitions are marked with arrows.

(1265, 1130, 1040, and 855 cm^{-1}) can only be supposed here. At the same time, the appearance of other signals corresponding to new ring substitutions (810–850, 910, and 1090 cm^{-1}), new methylene bridges (1455 cm^{-1}), and new L syringylic groups (1330 cm^{-1}) suggests the participation of both P and L in the creation of LPF polymeric network. Also, the appearance of 1430 cm^{-1} signal, related to L aromatic skeleton, indicates the formation of a different aromatic structure. A blank experiment was carried out with P and L3 after reproducing synthesis conditions (except for the absence of F) to evaluate the possible reaction between them. In view that resulting spectra exactly corresponds to the sum of P and L ones, it can be concluded that P and L do not suffer any structural changes when they are allowed to react in such conditions, meaning that the evolution observed during LPF polymerization is only derived from their reaction with F.

Figure 2 shows DSC thermograms corresponding to the cure of 25 wt % [Fig. 2(a)] and 45 wt % [Fig. 2(b)] substituted LPF systems obtained from DSC dynamic scans. In both cases, PF cure thermogram has also been added for better comparison. T_g transitions are marked with arrows and corresponding values, as well as those determined for L samples alone (in brackets), have been recorded in Table III. There are some remarkable differences with respect to the T_g observed for each system. Commercial PF resin presents a single transition localized at 60°C, what is in agreement with the available data from literature.¹ In a similar way, LPF-2-25, LPF-3-25, and LPF-3-45 systems show single T_g appearing at intermediate temperatures between those from unmodified PF and original L. It can be concluded that homogeneous materials in which L incorporation leads

to an increase of T_g have been obtained in these cases. Moreover, such increases result proportional to the L addition.

On the other hand, some LPF systems (LPF-1-25, LPF-1-45, and LPF-2-45) have two well-defined T_g showing therefore that an heterogeneous prepolymer has been created. In these cases, the first T_g appears in the 60–70°C range and suggests that a polymer fraction exclusively composed of P and F units has been formed. The second T_g is situated at higher temperatures and associated to lignophenolic fractions containing different L proportions. In the case of L1, this behavior can be attributed to its high M_w (8.7×10^3 g/mol), which is also reflected in a high T_g (144°C), that would obstruct its incorporation into the network during the synthesis. In spite of this, lignophenolic fractions with T_g of 102 and 85°C are formed in, respectively, 25 and 45 wt % L1-substituted systems. With respect to L2 addition, the second T_g (87°C) appears at the same temperature range as that from LPF-2-25. In this case, LPF-2-45 resin seems to have exceeded the L limit in which L2 can be incorporated without further modification in a homogeneous way.

TABLE III
Glass Transition Temperatures Obtained for the Different L and Resins Analyzed, and Onset Temperatures Determined for the Curing Reaction of Prepolymers

	PF	LPF-1-25 (L1)	LPF-2-25 (L2)	LPF-3-25 (L3)
T_g (°C)	60	61–102 (144)	88 (138)	87 (133)
T_0 (°C)	128	126	115	122
		LPF-1-45	LPF-2-45	LPF-3-45
T_g (°C)		67–85	65–87	98
T_0 (°C)		142	136	119

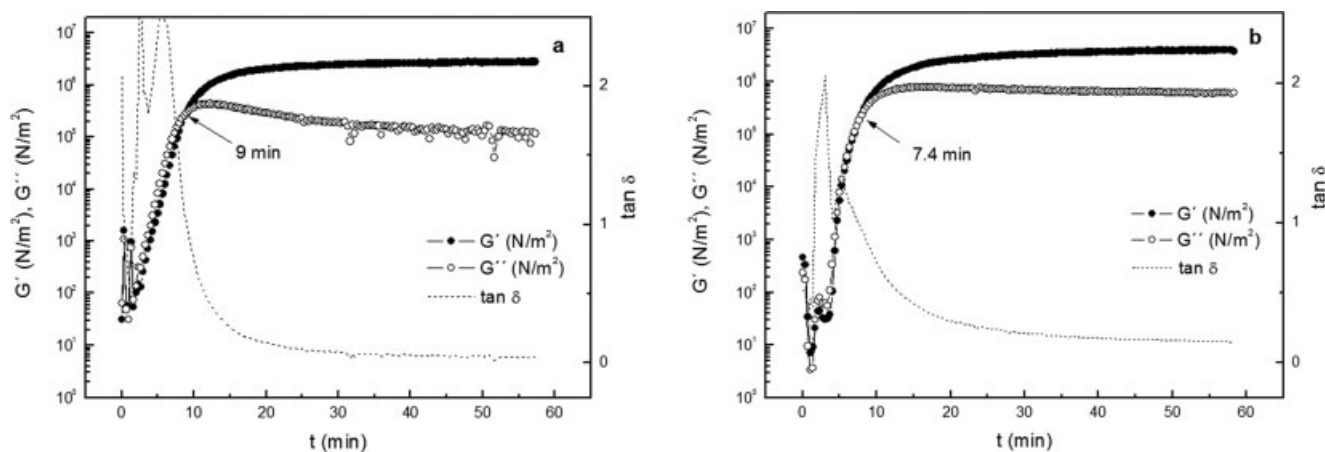


Figure 3 G' , G'' and $\tan \delta$ curves obtained through rheological analysis for (a) PF and (b) LPF-3-45 cure at 145°C .

The temperature at which the curing process begins, called onset temperature (T_0), has also been determined from DSC thermograms (Table III). In a dynamic scanning test, T_0 is related to the easiness of such reaction to proceed and, in relation to phenolic resins cure, this parameter is influenced by F/P molar ratio (inversely proportional). As mentioned earlier, the complex structure of L impedes the preparation of stoichiometric formulations but, despite this fact, it is possible to obtain some valuable information based on the estimated $F/(P + L)$ ratio shown in Table I. In view of those values (~ 0.8 and ~ 0.9 respectively for 25 and 45 wt %-substituted resins), LPF-25 systems, and even more LPF-45 systems, should have lower T_0 than control PF if no other effect were affecting the cure processes. As can be seen in Table III, the first group follows this trend despite LPF-1-25 shows little variation with regard to PF. From this fact, it can be inferred that the presence of L1 in the formulation hampers to some extent the curing reaction, what is probably due to its high M_w that causes both the increase of resin viscosity and the hindering of reactive positions. This effect acquires more relevance in LPF-1-45 and LPF-2-45 systems in which T_0 suffer noticeable increases despite the higher $F/(P + L)$ molar ratio. The homogeneous incorporation of L in LPF-3-45 system, as in LPF-2-25 and LPF-3-25, seems to minimize the increment of viscosity caused.

The hardening time of PF and LPF resins with 10 wt % HMTA has been analyzed by means of isothermal rheological experiments at three different temperatures (145, 165, and 185°C). As an example, Figure 3 shows G' , G'' , and $\tan \delta$ curves obtained for PF [Fig. 3(a)] and LPF-3-45 [Fig. 3(b)] cured at 145°C , while all the results are shown in Table IV. It can be noted that in most LPF systems, t_{gel} increases when compared with commercial PF though differences are rather little. It has to be considered again that $F/(P + L)$ molar ratio is inversely proportional to t_{gel}

while other aspects like viscosity increase would affect gelation times in the opposite way. On the other hand, the high M_w of L may cause the rapid formation of infinite-sized species, leading therefore to the early gelation of the material. This hypothesis justifies the low t_{gel} determined for LPF-1-45 resin, which has been shown to be very influenced by L1 high M_w . Gelation of LPF-1-45 and LPF-2-45 systems does not take place at 145°C due to the proximity of their respective T_0 , and so they could not be evaluated.

Concerning the rest of the systems, LPF-3-45 stands out as the most reactive one. Although t_{gel} of LPF-3-25 at 185°C is nearly the same as for PF commercial resin, it is increasingly higher as the curing temperature is lowered. When 45 wt % of L3 is incorporated, gelation at 185°C presents again little deviation with respect to that of control PF but it decreases when the curing temperature becomes lower. The higher molar ratio and probably the catalytic effect of $-\text{CH}_2\text{OH}$ groups¹⁰ present in L3 structure, which have good accessibility due to its homogeneous incorporation into the resin, seem to prevail in this case over the increase in viscosity and provide LPF-3 with a significant reactivity. This effect becomes more relevant at lower temperature, and it is related to the lower T_0 shown by this system.

TABLE IV
Gelation Times of PF and LPF Systems Cured with 10 wt % HMTA at 185, 165, and 145°C

	t_{gel} (min, $^\circ\text{C}$)		
	185	165	145
PF	3.8	5.6	9
PFL1-25	5.6	10	12
PFL2-25	6	6.7	10.3
PFL3-25	3.7	6.3	10.9
PFL1-45	4.4	7.1	—
PFL2-45	5.6	9	—
PFL3-45	3.9	4.2	7.4

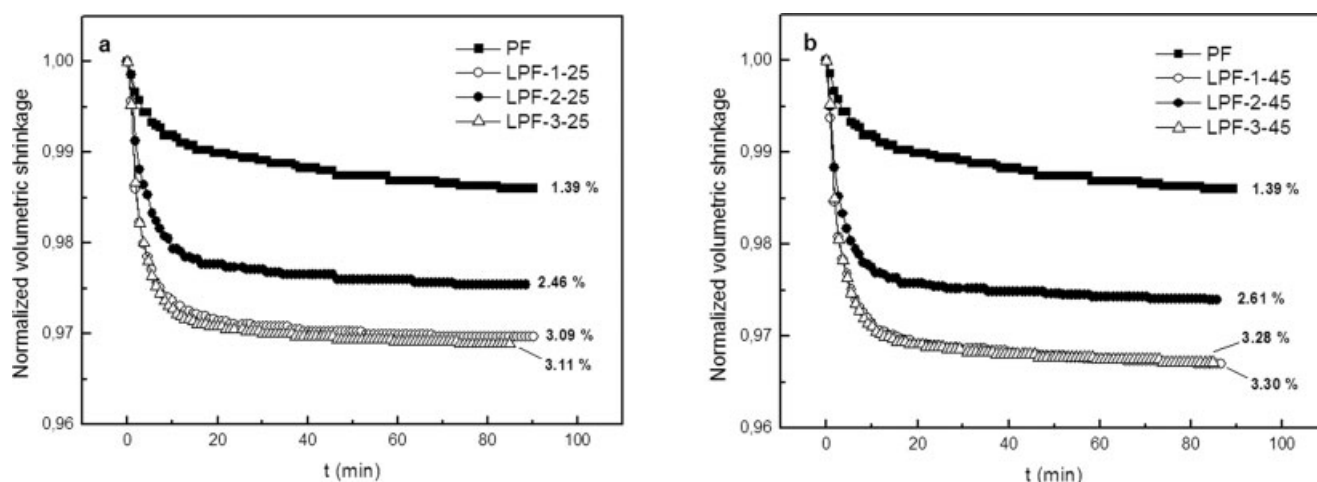


Figure 4 Normalized volumetric shrinkage versus time curves obtained for (a) 25 wt % and (b) 45 wt % substituted LPF systems during the curing process. PF curve has been added in both graphs.

Volumetric variations that occur during the hardening of polymeric materials are of great importance from an industrial point of view, as they determine the dimensions the mould should have. Curing reactions and also postcure cooling to ambient temperature lead to a notable shrinkage of the material. These variations have been evaluated for synthesized LPF resins and compared to that of reference PF. Figure 4 shows normalized volumetric shrinkage versus time curves obtained for 25 wt % [Fig. 4(a)] and 45 wt % [Fig. 4(b)] substituted LPF resins. PF curve has been added in both graphs for better comparison. As can be noticed, all LPF systems show around two times higher variations than commercial PF what should be taken into account prior to a possible industrial exploitation. This behavior, which is more pronounced in 45 wt %-substituted systems, could be related to the branched structure of L that would increase the free volume inside the polymeric chains. During the curing process, the reaction of L fragments would provoke the loss of part of such free volume, leading to the higher shrinkage observed.

Dimensional changes during the postcure cooling of all the systems (including PF and LPF) are very similar instead, regardless the type of L or the substitution degree. They are all comprised between 5.3 and 6.3% showing that this aspect is not influenced by L.

CONCLUSIONS

Several novolac-type LPF resins, where 25 or 45 wt % P has been substituted with three different types of L, have been synthesized and subjected to characterization by means of free P and F, viscosity, chemical structure (FTIR) and thermal behavior (DSC). Although the chemical structure and the amount of unreacted P and F show no remarkable differences

in LPF resins with respect to commercial PF, a noticeable rise in viscosity is observed regardless the type of L employed. Furthermore, some LPF systems present two well-defined T_g indicating that heterogeneous materials are created. Curing process of LPF systems with 10 wt % HMTA has also been analyzed, and respective onset temperature (DSC), hardening time at several curing temperatures (rheology) and volumetric changes (PVT) have been determined. Depending on the L characteristics, a homogeneous material with lower onset temperature and gelation time than reference PF can be obtained even at a high P substitution level (45 wt %). Volumetric shrinkage occurring during the hardening of LPF resins is in all cases approximately twice higher than that of commercial PF, what has been associated to the branched structure of L.

References

- Gardziella, A.; Pilato, L. A.; Knop, A. In *Phenolic Resins*; Gardziella, A., Ed.; Springer-Verlag: Berlin, 2000; Chapters 2 and 5.
- OSHA. Regulated Hazardous Substances, Occupational Safety and Health Administration, Department of Labour; Noyes data: Park Ridge, US, 1991.
- Forss, K. G.; Führmann, A. *Forest Prod J* 1979, 29, 39.
- Lapiere, C.; Montles, B.; Vassal-Gonthier, A.; Dworkin, A. *J Appl Polym Sci* 1986, 32, 4561.
- Northey, R. A. In *Materials and Chemicals From Biomass*; Rowell, R. M., Schultz, T. P., Narayan, R., Eds.; American Chemical Society: Washington, DC, 1992; ACS Symposium Series 476. p 146.
- El-Saied, H.; Nada, A. M. A.; Ibrahim, A. A.; Yousef, M. A. *Die Angew Makromol Chem* 1984, 122, 169.
- Nada, A. M. A.; El-Saied, H.; Ibrahim, A. A.; Yousef, M. A. *J Appl Polym Sci* 1987, 33, 2915.
- Olivares, M.; Guzmán, J. A.; Natho, A.; Saavedra, A. *Wood Sci Technol* 1988, 22, 157.
- Pranda, J.; Brazny, R.; Kosick, M.; Micko, M. M. *Tappi J* 1991, 74, 176.

10. Peng, W.; Riedl, B. *Polymer* 1994, 35, 1280.
11. Benar, P.; Gonçalves, A. R.; Mandelli, D.; Schuchardt, U. *Bioresour Technol* 1999, 68, 11.
12. Turunen, M.; Alvila, L.; Pakkanen, T. T.; Rainio, J. *J Appl Polym Sci* 2003, 88, 582.
13. Khan, M. A.; Ashraf, S. M.; Malhotra, V. P. *J Appl Polym Sci* 2004, 92, 3514.
14. Kazayawoko, J. S. M.; Riedl, B.; Poliquin, J.; Barri, A. O.; Matuana, L. M. *Holzforschung* 1992, 46, 257.
15. Kazayawoko, J. S. M.; Riedl, B.; Poliquin, J.; Barri, A. O.; Matuana, L. M. *Holzforschung* 1992, 46, 349.
16. Sarkar, S.; Adhikari, B. *Polym Compos* 2001, 22, 518.
17. Ysbrandy, R. E.; Gerischer, G. F. R.; Sanderson, R. D. *Das Papier* 1995, 49, 162.
18. Danielson, B.; Simonson, R. *J Adhes Sci Technol* 1998, 12, 923.
19. Vázquez, G.; Antorrena, G.; González, J.; Mayor, J. *Bioresour Technol* 1995, 51, 187.
20. Vázquez, G.; González, J.; Freire, S.; Antorrena, G. *Bioresour Technol* 1997, 60, 191.
21. Alonso, M. V.; Oliet, M.; Pérez, J. M.; Rodríguez, F. *Thermochim Acta* 2004, 419, 161.
22. Simitzis, J.; Karagiannis, K.; Zoumpoulakis, L. *Polym Int* 1995, 38, 183.
23. Kharade, A. Y.; Kale, D. D. *Eur Polym J* 1998, 34, 201.
24. Ysbrandy, R. E.; Gerischer, G. F. R.; Sanderson, R. D. *Cell Chem Technol* 1994, 28, 153.
25. Ysbrandy, R. E.; Gerischer, G. F. R.; Sanderson, R. D. *Cell Chem Technol* 1997, 31, 213.
26. Pérez, J. M. Ph.D. Thesis, Universidad Complutense de Madrid, Spain, 2005.
27. Wada, S.; Iwamida, T.; Iizima, R.; Yabe, K. *Chem High Polym Jpn* 1962, 19, 699.
28. Lange, W.; Faix, O.; Beinhoff, O. *Holzforschung* 1983, 37, 63.
29. Van der Klashorst, G. H. In *Wood Adhesives Chemistry and Technology*; Pizzi, A., Ed.; Dekker: New York, 1989; Chapter 6.
30. Villar, J. C.; Caperos, A.; García-Ochoa, F. *Sep Sci Technol* 1996, 31, 1721.
31. Gonçalves, A. R.; Benar, P. *Bioresour Technol* 2001, 79, 103.
32. Alonso, M. V.; Rodríguez, J. J.; Oliet, M.; García, J.; Gilarranz, M. A. *J Appl Polym Sci* 2001, 82, 2661.
33. Alonso, M. V. Ph.D. Thesis, Universidad Complutense de Madrid, Spain, 2002.
34. Schweers, W. H. M.; Vorher, W. *Soil Org Matter Stud Proc Symp* 1977, 85.
35. Alonso, M. V.; Oliet, M.; Rodríguez, F.; García, J.; Gilarranz, M. A.; Rodríguez, J. J. *Bioresour Technol* 2005, 96, 1013.
36. Tejado, A.; Peña, C.; Labidi, J.; Echeverría, J. M.; Mondragon, I. *Bioresour Technol* 2007, 98, 1655.