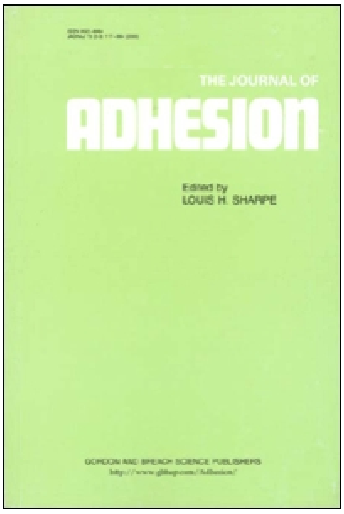

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Engineering Plastics from Lignin. IX. Phenolic Resin Synthesis and Characterization

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The performance of phenol-formaldehyde (PF) resins, formulated with lignin derivatives previously synthesized as phenolic resin prepolymers, was evaluated by thermal analysis of the curing process, and by a hard maple shear block test. At 54 and 60% phenol replacement levels, respectively, kraft (KL) and steam explosion lignin (SEL)-based resoles exhibited cure behavior very similar to a standard PF resin. Acid hydrolysis lignin gelled prematurely, and was found to be incompatible with the normal synthesis procedure. Differential scanning calorimetry (DSC) was used to compare kinetic parameters for the curing process of neat and lignin derived phenolic resins. Activation energies and cure rates determined by DSC showed no difference between adhesives. High lignin contents had no inhibitory effect on resin cure. Shear strength properties were evaluated in a compression test, and results illustrate that both lignin-based resins have acceptable strength properties, both in a dry and accelerated aging test. Of the lignins tested, kraft lignin consistently demonstrated superior performance as a prepolymer in phenolic adhesives. This was attributed to differences in the chemical structure of the two lignins, which had been found to vary in terms of their reactivity with formaldehyde and phenol. KL had been noted to be more amenable to derivatization with formaldehyde and phenol, hence its ability to crosslink with a phenol-formaldehyde fraction during resin synthesis was increased. Positive structural features in KL are a high phenolic guaiacyl (3-methoxy, 4-hydroxy phenyl) content, low carbon-to-carbon bonding between aromatic rings, high solubility in alkali, and a higher number average molecular weight than SEL.

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INTRODUCTION

Characterization of the curing process in phenol-formaldehyde (PF) resins has traditionally been limited by the lack of analytical methods capable of investigating the condensed, intractable structures present during the latter stages of resin advancement. Events which occur during the resin cure are of primary concern since the formation of a network structure is essential to the success of adhesion in bonded products[1]. A determination of the effects of prepolymer structure on cure characteristics could provide insight into the relationship between chemical structure and material properties. This information would lead to the prediction of adhesive performance on the basis of molecular structure. The structure-property relationship is important in lignin-based plastics, where lignins from different genetic or industrial origins with differing chemical character, could be screened for polymeric utility on the basis of individual structural features or cure properties. This would eliminate the time consuming task of testing glued composite materials. Since the chemical features displayed by lignins from different origins can be quantitatively described in terms of the composition of an average repeat (C_9) unit, the evaluation of the structure-property relationship in lignin based polymeric material systems becomes a technical possibility[2,3].

One method of monitoring the process of cure is by thermal analysis. Differential scanning calorimetry (DSC) is one technique of thermal analysis that has shown great promise in the characterization of thermoset resin cure[4]. DSC is especially applicable to thermoset materials where chemical changes which occur during cure are marked by the release of heat. Quantitative information regarding heats of reaction and cure rates is easily determined by DSC.

Dynamic methods of thermal analysis have previously been employed in the characterization of PF resins. The curing reaction was found to be marked by characteristic endothermic peaks near 110 and 150°C. These peaks were assigned to the endothermic evaporation of water produced during the initial and final stages of cure[5-7]. Other researchers have reported two exothermic peaks in the DSC thermogram of phenolic resoles. These peaks were attributed to the addition of formaldehyde to a phenolic nucleus and the condensation of methylol phenols respectively[8,9]. Hermetically sealed stainless steel capsules were used to suppress the volatilization of reaction product so that the reaction exotherms were resolved. It was found that the addition of formaldehyde followed first order kinetics while the condensation reaction was second order. Activation energies can also be abstracted from the dynamic scan. Attempts to correlate thermal reaction characteristics with bond properties showed that the second exothermic peak was critical to a strong bond[10,11]. Isothermal cure of phenolic resins can also reveal pertinent kinetic information. Reaction rates can be directly related to the rate of heat generation. Through this relationship, cure levels or extent of conversion to network gels can be determined[12].

This study represents phenolic resin synthesis procedures involving stoichiometric adjustments to formulation parameters based on structural details of the lignin prepolymer. This allows for maximum covalent bond formation between the derivatized lignin adduct and a PF fraction. Both dynamic and isothermal methods of DSC were applied to the evaluation of the influence of the presence of lignin and lignin derivatives (resole prepolymers) on resin advancement. The final measure of lignin utility in phenolic resins was determined by a hard maple shear block test. The strength values of neat and lignin based adhesives were correlated with thermally determined kinetic parameters and general thermal profiles. A chemical structure characterization described in the previous paper[13] provides the basis for evaluating the influence of lignin structure on thermal behavior and thermoset phenolic properties.

MATERIALS AND METHODS

I. Materials

Sequentially hydroxymethylated (CH_2O) and phenolated derivatives of kraft, steam explosion, and acid hydrolysis lignins were used. Derivatization included reaction with formaldehyde at room temperature for 72 hours, or at 70°C for 20 hours followed by reaction with phenol (in aqueous alkali at 170°C) according to a previous study[13].

Kraft Lignin (KL): The kraft lignin used in this study was Indulin ATR from Westvaco Corp., Charleston, SC. The commercially available material was purified by dissolution in aqueous alkali, acid precipitation, washing with distilled water, and centrifugation.

Steam Explosion Lignin (SEL): This preparation was isolated by Iotech Corp. of Ottawa, Canada, from steam exploded aspen wood chips.

In this process, the wood was subjected to steam hydrolysis (240°C) at 600 psi. followed by explosive decompression and extraction with ethanol or aqueous alkali[14]. Lignin preparations were received as dry brown powders and were used as received.

Resin Synthesis: In a 400 ml beaker, phenolated lignin (25 g), water (40 g) and 37% formalin (31.6 g) were mixed. NaOH (3.8 g at 50%) was then added to dissolve the lignin. The solution was transferred to a 250 ml 3-neck flask. Phenol (40 g at 89%) and the remainder of the

TABLE I

Composition of neat and lignin-based PF resin formulations

	NEAT PF	KL–PF	SEL–PF
Formaldehyde (F), g	99	99	99
, moles	3.3	3.3	3.3
Phenol (P), g	140.9	104.3	104.3
, moles	1.5	1.11	1.11
Lignin prepolymer, g	0	208.7	208.7
—Degree of phenolation, per C_9[a]	0	0.43	0.21
—Phenolated C_9-units, moles[b]	—	1.13	1.09
—Phenolic equivalents, moles[c]	0	0.33	0.15
—Phenolic OH equivalents, moles[d]	—	1.16	0.77
Total P equivalents, moles	1.5	1.44	1.26
Total phenolic OH equivalents, moles	1.5	2.27	1.88
Total (*t*-) NaOH, g	36	55.6	55.6
, moles	0.9	1.39	1.39
i-NaOH, g[e]	15	32.3	32.3
2nd NOH, g[e]	12	13.3	13.3
3rd NaOH, g[e]	9	9.7	9.7
F/P ratio	2.2	2.3	2.6
NaOH/P ratio	0.6	0.61	0.74
Total solids, g	275.9	467.6	467.6
Lignin Content,			
of prepolymer, %	0	80.5	89.9
of PF resin solids, %	0	35.9	40.1
of P fraction, %	0	53.7	59.9
Water[f], g	377.3	575.2	575.2
PF resin (wet), g	653.2	1042	1042
Solids content of wet resin, %	42.2	44.8	44.8

[a] Determined by H–NMR according to ref. 13.

[b] On the basis of ave. C_9-unit weights of 190 gmol^{-1} and 205 gmol^{-1} for KL and SEL, resp.

[c] On the basis of 2 reactive (with F) sites per phenol substituent.

[d] On the basis of 0.6 and 0.5 phenolic OH groups per C_9-unit for KL and SEL, resp.[2], and degree of phenolation.

[e] Initial, second, and third charge, resp., of caustic.

[f] Including the water content of the formaldehyde, phenol, and caustic solutions.

initial alkali (i-NaOH) were then charged. The resin flask was equipped with reflux condenser, thermometer and sealed glass stirring rod. Resin synthesis followed a cooking schedule determined by viscosity advancement. Neat PF resin was prepared analogously by reacting phenol and formaldehyde at an F/P of 2.2. The cook schedule used in resin synthesis was the same as that used in lignin-PF resin synthesis. For detailed synthesis parameters, see Table I.

Viscosity: Resin viscosity was measured with a Brookfield Synchro Lectric Viscometer (LVT). Resin samples (7 ml) were pipetted from the resin flask and immediately cooled to 25°C in an acetone cold bath. A correction factor for sample vessel size using LV spindle 4 was used to determine absolute viscosities.

Maple Shear Blocks: Shear blocks were prepared from freshly planed hard maple stock (12″ × $2\frac{1}{2}$″ × $^5/_{16}$″). Moisture content was six percent and specific gravity was 0.62. Two shear blocks per adhesive type were assembled from the hard maple stock. Each board was machined by bandsaw with a yield of 10 shear samples per board or 20 total shear samples per adhesive type. The samples were tested 48 hours after machining.

II. Methods

Shear Sample Preparation: Hard maple shear blocks were parallel laminates prepared with a glue spread of 12 lbs/thousand square feet of single glue line (MSGL) on a neat resin basis. Glued boards were allowed a closed assembly time of 3 minutes. The samples were machined 48 hours after pressing.

Accelerated Aging: Shear samples were immersed in boiling water for 4 hours, and then tested immediately in the wet condition.

Adhesive Shear Test: All shear blocks were tested on a Tinius Olson testing machine in a compression shear test as recommended in ASTM D905–49 for measuring adhesive strength in wood laminates. Loading rate was 0.015 inches per min.

Differential Scanning Calorimetry (DSC): DSC analyses were performed with a Perkin–Elmer System 4 instrument equipped with a

Thermal Analysis Data Station (TADS). Samples of approximately 20 mg were used in the thermal analysis. In the dynamic scans, heating rates of 5, 10 and 20°C per minute were used in the determination of activation energy. Adhesive samples in the isothermal test were heated at the maximum rate to the isothermal cure temperature of 150°C. All analyses were performed under dry nitrogen. Large volume, sealable stainless steel capsules were used in all cases.

RESULTS AND DISCUSSION

Resin Formulation

Resins were formulated using a procedure which promotes covalent bond formation between lignin and the phenolic network. To derive the greatest possible benefit from the activated (phenolated) lignin derivative, stoichiometric adjustments of formulation parameters must be made. This approach was aimed at achieving a homogeneous crosslink network between lignin and the PF resin. Recent work has revealed that formaldehyde and NaOH levels have a dramatic effect on molecular weight and relative branching, which are related to bond performance[15]. Although it was not the goal of this study to determine optimal resin synthesis parameters, some adjustments of formulation parameters in accordance with specific prepolymer chemistry were necessary.

Normal levels of formaldehyde, determined on the basis of number of reactive sites per average phenolic nucleus, are in the range of 1.5–2.2 formaldehyde to phenol (F/P). High F/P ratios are to be avoided because they result in objectionable release of gaseous formaldehyde during hot pressing. However, since high F/P ratios allow for complete hydroxymethylation during resin synthesis, a high F/P ratio was selected for the synthesis of lignin-based PF resoles so as not to limit lignin incorporation. Thus all resins were formulated in accordance with the parameters given in Table I.

The acid hydrolysis lignin (AHL) prepolymer was found to be limited by its compatibility in a normal synthesis procedure. The required dissolution of the AHL prepolymer could not be achieved at a 45% solids content and a total NaOH/P of 0.60. AHL, which is a considerably condensed material with high content of carbon-to-carbon interunit linkages[2], only formed unmanageable gels under the reaction conditions selected. Therefore, AHL must be considered a material unattractive as a component in phenolic resins.

The formulation parameters for KL and SEL are shown in Table I. Their effective F/P ratio was calculated to be 2.4 for KL and 2.6 for SEL. The requisite amount of catalyst (NaOH), based on a target NaOH/P ratio of 0.60[15–17], must also be adjusted for a lignin derived phenolic resin. Extra alkali must be added to neutralize lignin's phenolic hydroxy groups although they do not participate in any reaction during resin synthesis. Based on degree of phenolation, adjusted formulation parameters were calculated.

True lignin content (underivatized lignin) in the two phenolic resins is 36 and 40% for KL and SEL, respectively, based on total solids. This amounts to 54 and 60%, respectively, for phenol substitution levels. The synthesis of lignin-based phenolic resins was conducted following procedures commonly employed in the preparation of industrial plywood resole adhesives. Stepwise addition of caustic was used to control resin advancement closely during the cook. Caustic was added in accordance with viscosity, and this was monitored at regular intervals with a Brookfield viscometer specially adapted for testing small sample aliquots.

By monitoring viscosity during resin synthesis, a viscosity-time profile was generated for each cook. A typical viscosity-time profile for a lignin based phenol-formaldehyde resin is shown in Figure 1. The staged addition of caustic is determined by viscosity advancement attaining certain viscosity "windows". The first viscosity window is in the 32,000–48,000 cps range. The second window lies between 12,000 and 16,000 cps. The cook is terminated when the final viscosity reaches 1000 cps after the third addition of caustic.

Both KL and SEL-based PF resins gave similar traces in the viscosity/time profile. This compares favorably with that of an unextended (neat) phenolic resin. Indeed, the lignin based phenolic resins achieved higher viscosities slightly more quickly than the neat PF resin. This is probably due to the initial charge of a polymeric fraction in the lignin based phenolic resin[18]. This is a positive characteristic in a lignin based PF resin since industrial cooking schedules could be shortened, resulting in reduced energy costs and higher through-put.

The objective of following a regimented synthesis schedule with the lignin fraction charged simultaneously with phenol and formaldehyde was to promote a maximum of chemical bonding or crosslinking between derivatized lignin and a PF prepolymer. Lignin is not being

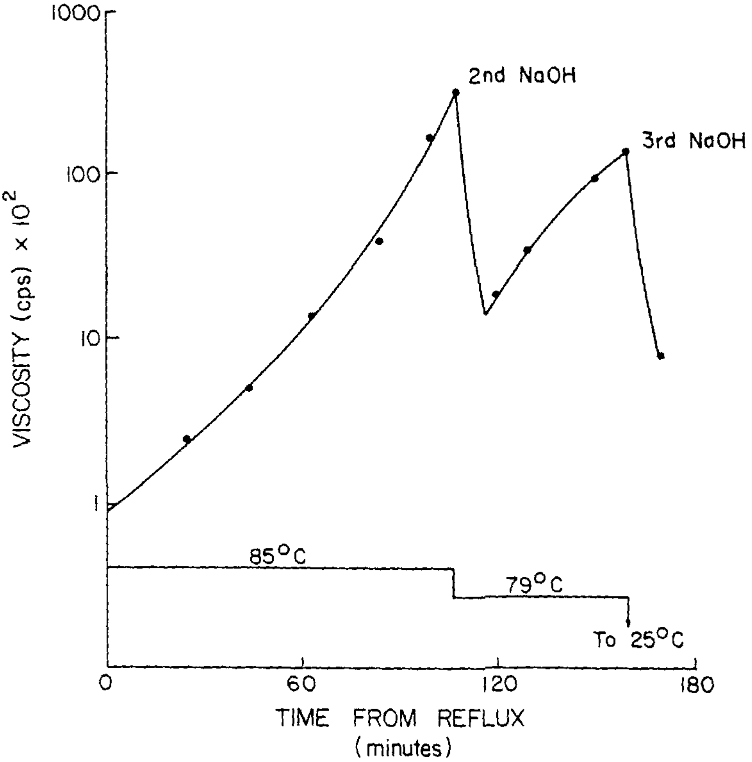

FIGURE 1 Typical viscosity-time profile for lignin-based phenolic resins.

viewed as an inert extender, but as an integral part of the network structure covalently bound through functionalities introduced to the PF fraction. An idealized network structure of a lignin derived PF resin is illustrated in Figure 2. The ability of the phenolated lignins to perform in a synthesis procedure dictated by the reaching of narrow viscosity windows is an initial indication that KL and SEL are suitable materials for use in a PF resin system.

Cure analysis of lignin/phenol-formaldehyde resins

Thermal analysis, and in particular DSC, is an analytical technique which is currently demonstrating its utility in characterizing the progress of network formation in thermoset systems. Not only can heats

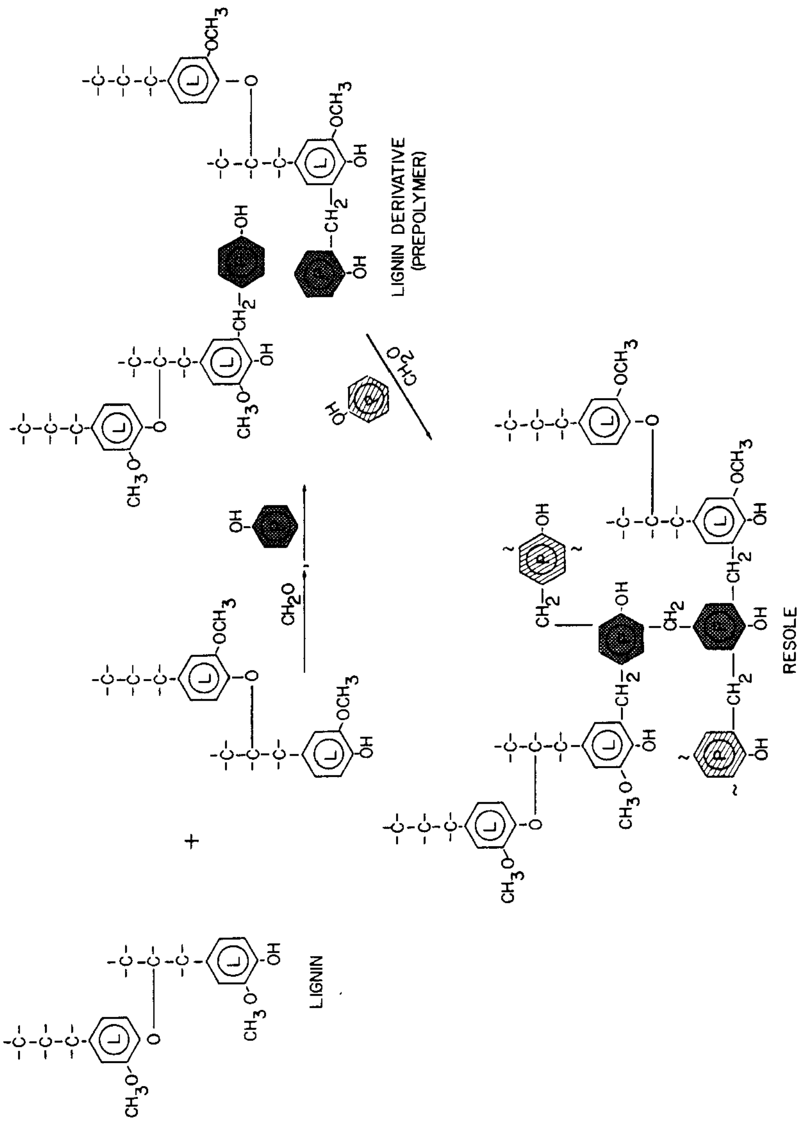

FIGURE 2 Structural scheme of a lignin-based phenolic resin.

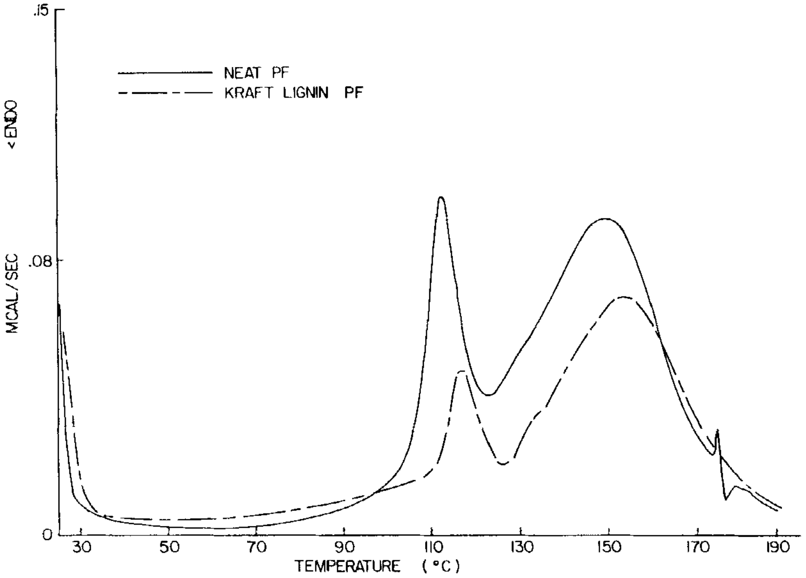

FIGURE 3 Dynamic DSC thermograms of a neat and a kraft lignin-based phenolic resin.

of reaction be resolved with DSC, but useful data regarding kinetic parameters such as relative reaction rates and degree of polymer conversion, can also be deduced. Since the process of wood adhesion is a function of many factors, such as wetting, penetration and diffusion, any study investigating the effects of these factors on bond performance is hindered by the complex interaction of a large number of variables. Thermal analysis is capable of characterizing the actual curing process itself by thermally monitoring chemical changes within the resin irrespective of the above-mentioned variables. Kinetic parameters for the curing process can be obtained from both isothermal and dynamic methods. Activation energy is one such parameter which provides insight into the effects of various additives (*e.g.* lignin) on the chemistry of cure.

Dynamic thermograms of a neat and a lignin-based PF resin are shown in Figure 3. The initial peak, which occurs around 115°C, has been attributed to the exothermic addition of formaldehyde to a phenolic nucleus[8] and is indicative of free formaldehyde present in the resin. This free formaldehyde peak was observed in all thermograms.

TABLE II
Kinetic results from dynamic DSC scans of several PF-resins

Sample	Peak maximum (°C)	Heating rate (°C/min)	Slope[c]	Activation energy (KJ mole^{-1})
NEAT PF	141	5		
NEAT PF	150	10	−5139	−93.5
NEAT PF	169	30		
SEL-PF[a]	144	5		
SEL-PF[a]	153	10	−5324	−96.3
SEL-PF[a]	164	20		
KL-PF[b]	144	5		
KL-PF[b]	154	10	−5436	−98.9
KL-PF[b]	165	20		

[a] Phenolated steam explosion lignin-based PF resin.

[b] Phenolated kraft lignin-based PF resin.

[c] From the Arrhenius plot of log ϕ vs. $1/T_p$ where ϕ is the heating rate and T_p is the temperature of the peak maximum.

The larger second peak is the result of a condensation reaction between methylol phenols, which produces an insoluble network (termed "resit"), mainly through the formation of methylene bridges. The characteristics of this crosslinking exotherm are important for the comparison of kinetic parameters between neat and lignin based phenolic resins. Despite the fact that the thermoset cure process represents a complex multi-step reaction, accurate kinetic data can be determined from the position of the crosslinking peak.

Dynamic DSC was used to generate the kinetic information in Table II. Because peak position in a thermogram varies in a predictable manner with heating rate, and because the extent of cure is constant at the peak exotherm, activation energies (E_a) can be calculated with accuracy[19–21]. E_a results from an Arrhenius plot and the relationship

$$E_a = -\frac{R}{0.457}\frac{\Delta \log \phi}{\Delta \frac{1}{T_p}} \qquad \text{(Equation 1)}$$

where ϕ is the programmed heating rate
T_p is the temperature at peak maximum, and
R is the gas constant.

This method of monitoring peak position as a function of heating rate has been shown to be well suited for the analysis of thermoset systems where multiple exotherms or unreliable baselines are a problem[22-24]. The values for E_a for the two lignin based phenolic resins, Table II, were insignificantly higher than the control (neat PF). These agree with values determined similarly for standard phenol-formaldehyde resins[8]. It can be concluded from these E_a values that high lignin contents have no inhibitory effect on cure mechanism or cure rate. On a more pragmatic note, press times and temperatures used in an industrial process would not have to be modified to accommodate these lignin-extended adhesives.

Figure 4 compares a neat PF resin with one in which underivatized KL was physically mixed (about 1:1 ratio) immediately prior to DSC analysis and yielding a partially heterogeneous mixture with a PF resole in the DSC sample holder. Clear differences between the thermograms are apparent, with a noticeable lack of a formaldehyde peak which may have been shifted (by about 45°C) to a higher temperature, and which may be masked by the immediately following crosslinking peak.

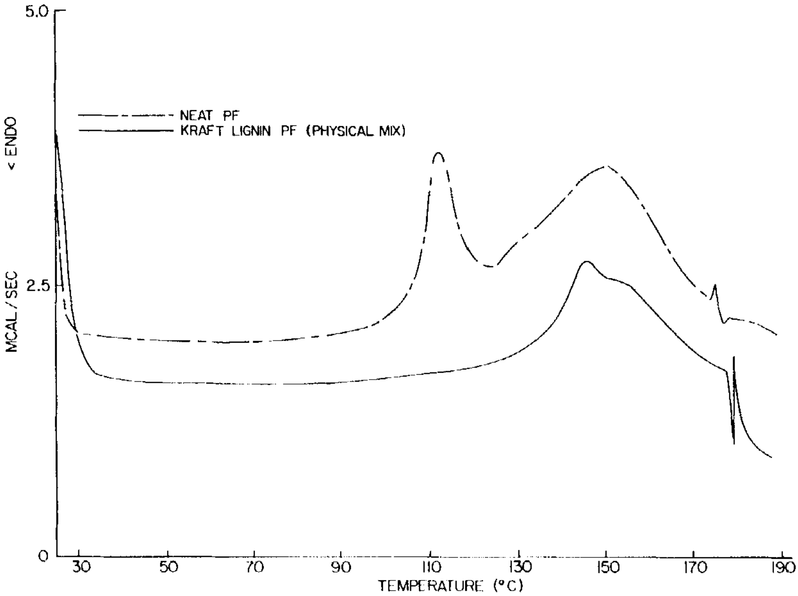

FIGURE 4 Dynamic DSC thermograms of a neat and a lignin-based phenolic resin produced as a physical mixture.

This suggests that lignin, when added as a physical mix to a phenolic prepolymer, affects network formation during cure.

An isothermal method for the determination of cure kinetics was used to generate information on the time-degree of conversion relationship for phenolic resins. This relationship can be described[22] by

$$\alpha_t = \frac{\Delta H_t}{\Delta H_{rxn}} \qquad \text{(Equation 2)}$$

where α_t is degree of conversion at time (t),
ΔH_t is the heat of reaction at time (t), and
ΔH_{rxn} is the total heat of reaction.

DSC is well suited to monitor degree of conversion since ΔH can be derived from the DSC thermogram as the area under the peak exotherm. In an isothermal cure (at T_{150} = 150°C, at the top of the curing peak),

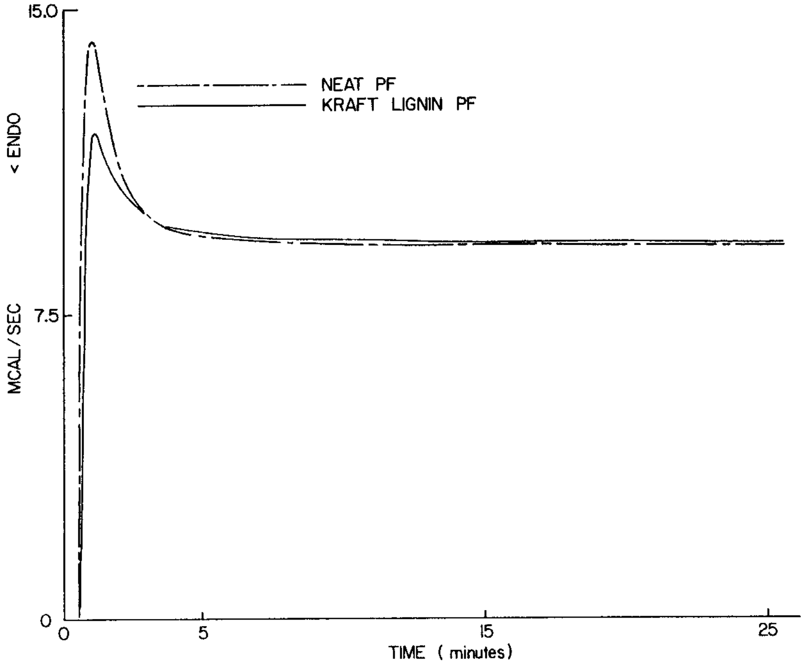

FIGURE 5 Isothermal cure of a neat and a lignin-based phenolic resin.

the sample is placed in the calorimetric cell and heated at the maximum rate to the cure temperature. The thermogram then measures liberated heat as a function of time at cure temperature.

A thermogram for the isothermal cure of a neat and a lignin derivative-based PF resin is shown in Figure 5. A baseline is drawn to determine the point of isothermal temperature equilibration for the sample. The determination of ΔH does not include the heat generated before the sample is equilibrated at the isothermal cure temperature. Therefore, any kinetic parameters obtained from the isothermal cure will be a relative measure. Figure 5 reveals that during an isothermal cure, a lignin-based phenolic resin behaves similarly to a neat PF resin. Differences can be detected in total ΔH represented by the total area under the isothermal cure curve (at constant sample weights). There is less condensation in the PF resins formulated with phenolated lignin since approximately half of the free phenol has been replaced with the unreactive lignin portion of the prepolymer. (No analogous tests were conducted with the underivatized lignin-PF resole mixture).

To quantify the similarities between thermal profiles for the different phenolic adhesives, kinetic parameters were calculated from the isothermal cure experiments. Using the relationship in equation 2, degree of conversion (α_t) with respect to time was calculated for all resins. Because thermal behavior before temperature equilibration was ignored, a new parameter, α_{app}, is defined as apparent degree of conversion. A graphical representation of the α_{app}-time relationship is presented in Figure 6. These curves were generated using the "cut and weigh" method where area under the exothermic curve at time (t) is directly proportional to the heat of reaction at time (t). Within the accuracy of the experiment (measuring relative kinetic parameters), the neat resin showed slightly higher degrees of conversion at shorter times than the two lignin based PF resins which exhibited no difference in their isothermal thermograms or their α_{app} values. All three resins achieved well over 80% apparent degree of conversion in <4 min. It has been shown previously that a typical resole plywood adhesive achieves maximum wood failure and strength at a degree of cure between 65 and 75%[25]. This level of degree of cure is reached in <2.5 min by both lignin based PF resins during a 150°C isothermal cure. This fact illustrates that lignin prepolymer-based PF resins are not limited by long cure times, a notion that has discredited much earlier lignin-PF research[26]. These data again suggest that when lignin is covalently bound within a PF network by cooking it during a typical resole

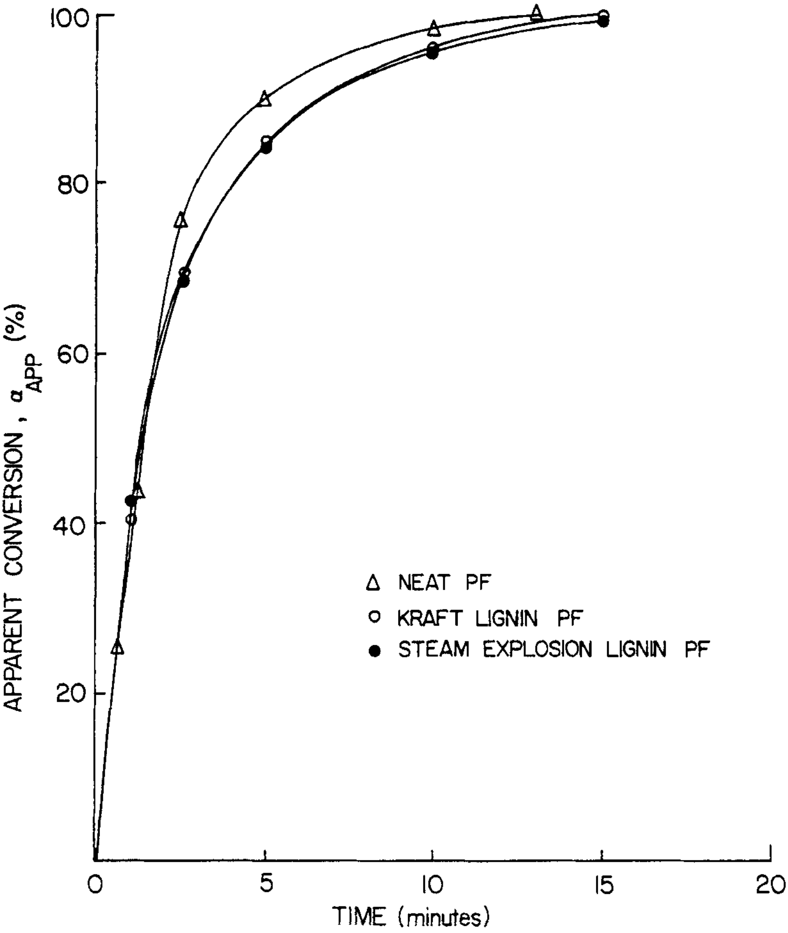

FIGURE 6 Apparent degree of conversion for three phenolic resin types.

synthesis, lignin does not act as an inhibitor (or retarder) to cure, but in fact the cure behavior of a lignin-based phenolic resin is essentially identical to that of a standard resole.

Evaluation of adhesive strength

The final test of a lignin-based phenolic resin is its performance as an adhesive in a bonded wood system. A hard maple shear block test was

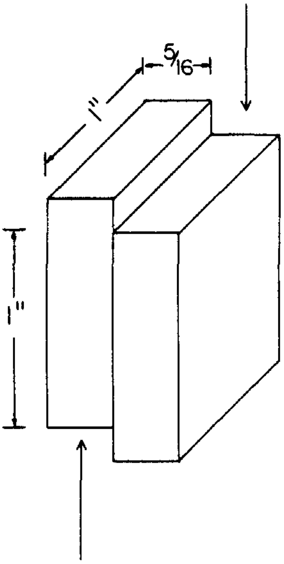

FIGURE 7 Shear block specimen for adhesive testing.

chosen and this employed modified shear blocks as illustrated in Figure 7. This modification of the ASTM shear test D905–49 is also applicable as an accelerated aging test[27]. Shear strengths were determined in the dry state and after a 4-hour boil schedule.

The results of the dry shear test for the three adhesive types are compared in Figure 8 by use of a box and whisker plot[28]. Sample medians are represented by the dashed lines, sample means by the solid dots, and upper and lower quartiles are marked by the respective box boundaries. Thus, the box represents the middle 50% of the data. The whiskers are a measure of the range of the data, and the open ovals in Figure 9 are moderate outliers (within 1.5 times the interquartile range of the upper and lower quartiles). Twenty replications were conducted for each test representing 5 test specimens from 4 boards, each.

Figure 8 illustrates that the lignin-based PF resins (especially the KL sample) show more dispersion than the neat PF resin. The mean dry strength values for the neat PF, KL–PF, and SEL–PF are 3400 psi, 3240 psi and 2840 psi, respectively.

Corresponding strength values for neat and lignin based PF resins

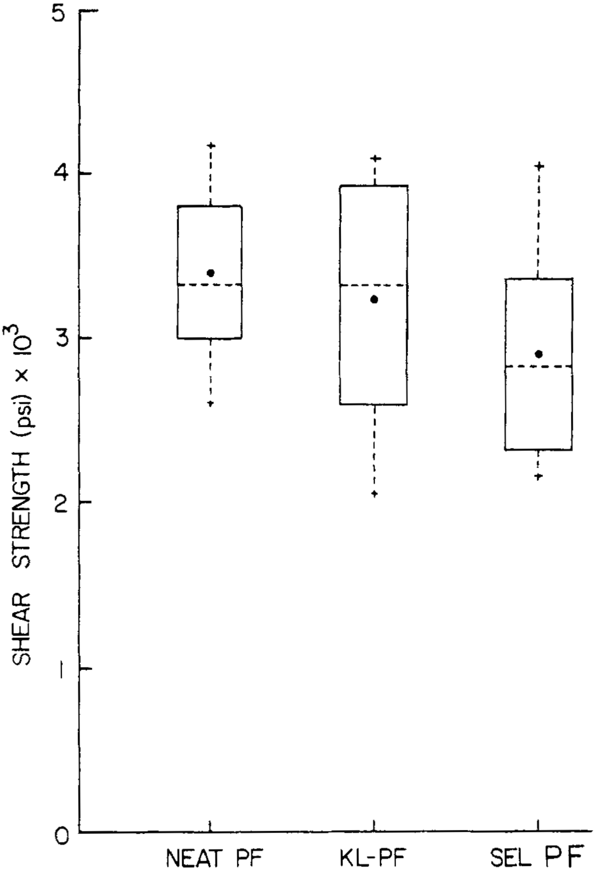

FIGURE 8 Box and whisker plots of dry strength values for neat and lignin based phenolic resins.

subjected to accelerated aging by boiling for 4 hours are shown in Figure 9. The samples were tested in the wet condition. The trends for wet strength are consistent with those for the dry test by showing the neat PF resin to give again the highest strength values. Mean strength values for the neat, KL and SEL–PF resins are 1600 psi, 1425 psi and 1080 psi, respectively. The within group variation for wet strength values was considerably less than that of the dry test. Based on results from both the dry and wet shear tests, high lignin contents and high strength values are not mutually exclusive. Of the two lignins evaluated,

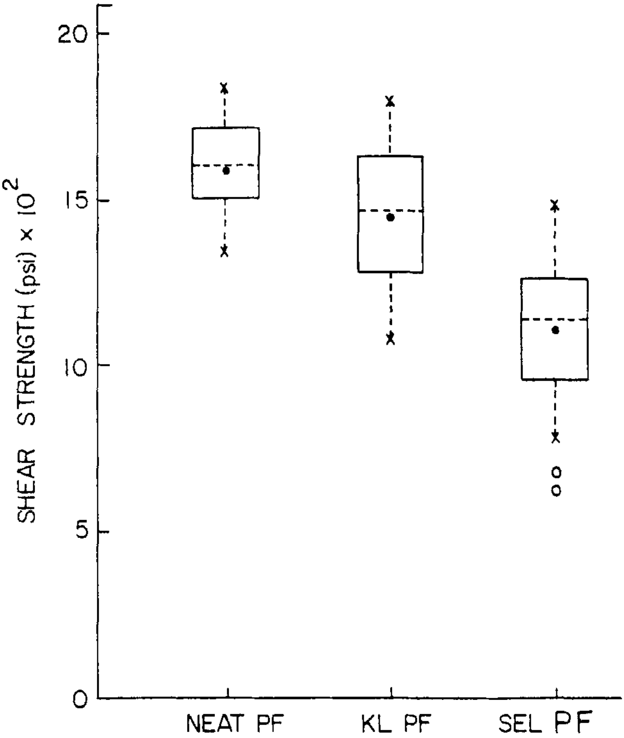

FIGURE 9 Box and whisker plots of wet strength values for neat and lignin-extended phenolic resins subjected to a 4-hour boil test.

KL is the material showing superior performance in a PF resin as compared to SEL, and chemical structure is likely to be held responsible for this phenomenon[13].

In order to make definitive statements comparing lignin-based adhesives to unextended phenolic adhesives, statistical multiple comparison tests were conducted. A modified version of the Least Significant Difference Test (LSDMOD) and Scheffe's tests[29,30] were employed to group adhesive mean strength values.

Test results indicate that only the neat PF resin and the SEL—PF are significantly different at the .05 level for the dry shear test (Table III). No significant differences were noted at the .01 level. These results agree fairly well with the box and whisker plots (Figure 8), suggesting that lignin-based phenolic resins can perform well in a dry shear test and

TABLE III
Test results for dry and wet shear tests

	LSDMOD[a]		Scheffe's	
Adhesive type	.05	.01	.05	.01
Neat PF	+	No significant difference	+	No significant difference
KL–PF	+ +		+ +	
Dry SEL–PF	+		+	
Neat PF	All groups significantly different	+	All groups significantly different	+
Wet KL–PF		+		+
SEL–PF				

[a] Least Significant Difference test.

that bond performance may indeed be affected by lignin type.

Multiple comparison test results for adhesives subjected to a 4-hour boil show that all groups are significantly different at the .05 level (Table III). Strength values for both the neat and the KL–PF resin are significantly higher ($\alpha = .01$) than SEL–PF resin values. Wet strength characteristics have traditionally been a limiting factor in the development of lignin based wood adhesives. The statistical results from the wet shear tests also suggest that wet strength may be a function of lignin type since the SEL was shown to be significantly different from the neat PF resin.

Correlation between chemical structure, thermal properties and bond performance

Chemical structure analysis performed on the derivatized and non-derivatized lignins showed KL (softwood) to possess structural features which are more conducive to hydroxymethylation and phenolation than SEL[13]. The resulting high degree of substitution by phenol allows for more crosslinking with the PF fraction. SEL (hardwood), by contrast, had a significantly lower degree of phenolation than KL, hence its reactivity in phenolic systems was lower. An examination of KL and SEL derivatives revealed structural differences relating to the number of reactive sites per prepolymer fragment of average size (as determined by M_n). KL prepolymer was recognized to possess >2 phenolic entities per number-average fragment, whereas the corresponding SEL derivative has <1. It appears that the absence of a minimum of 2 reactive phenolic units per average lignin fragment contributes to the below-standard performance of the (hardwood) SEL preparation[13]. This point needs some further experimental exploration. Since the number of crosslinks between polymer chains has a profound influence on mechanical strength, it can however not surprise that the shear strength trends for the dry and accelerated aging test demonstrate that KL produces a superior adhesive. This illustrates that lignin structure has a major influence on material properties when incorporated into polymeric systems.

The characterization of lignin-based phenolic resins by dynamic and isothermal thermal analysis shows that cure mechanism and cure rates are nearly identical to those of an unextended phenolic resin. An attempt to correlate thermal behavior with bond quality reveals that both shear testing (dry and wet) and thermal analysis fail to produce signs of significant differences between the two lignin adhesives and the neat PF sample. Thermal behavior in terms of cure rates and activation energies were nearly identical. Based on the statistical results of the strength tests and the similarity in thermal profiles, it can be concluded that thermal analysis shows promise as a screening tool for revealing reactivity differences, which are an important element of bond performance of lignin-based phenol-formaldehyde resins.

CONCLUSIONS

KL and SEL both show similar resin synthesis behavior as judged by the viscosity-time profile. Chemical derivatization and adjustment to formulation parameters have resulted in lignin-based phenolic resins with acceptable performance in resin formulation.

Thermal analysis has proved to be valuable in the characterization of the curing process of phenolic resins. Important kinetic information can be obtained by dynamic and isothermal DSC methods. Cure kinetics provide insight into the effects of lignin content on cure advancement.

KL and SEL prepolymers, when chemically modified with formaldehyde and phenol, have no inhibitory influence on resin cure at the 50–60% phenol substitution level. This conclusion is based on activation energies and cure rates.

Shear strengths of KL and SEL-based PF resins compare favorably with strength values of the neat resin. Statistical analysis failed to reveal significant differences between mean wet and dry strength values for the KL-extended and neat resole adhesives. The phenolic resin formulated with SEL exhibited strength values which were slightly lower than those of the neat and kraft lignin-based resins.

This study shows that unfractionated lignin can indeed be incorporated into PF resins with equal performance as their unextended counterparts. However, this incorporation into the network structure may require (expensive) prepolymer synthesis by derivatization with formaldehyde and phenol. The degree of derivatization required appears to increase with decreasing molecular weight.

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