

Eucalyptus Bark Lignin Substituted Phenol Formaldehyde Adhesives: A Study on Optimization of Reaction Parameters and Characterization

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ABSTRACT: The major adhesive resin worldwide used in the manufacture of plywood is phenol formaldehyde resole (PF) resin. The raw material for this kind of adhesive is derived from petroleum oil. Because of rising prices of crude oil and the scarcity of petroleum products, their replacement by natural resource-based raw material has become a necessity. In the present work, the possibility of replacing phenol in PF resin with lignin was explored. The parameters for preparation of bark lignin substituted PF (LPF) adhesive, such as lignin concentration, formaldehyde to phenol molar ratio, catalyst concentration, reaction time, and reaction temperature, were optimized. It was found that up to 50 wt % of

phenol can be substituted by lignin to give an LPF adhesive with better bonding strength compared to that of control PF resin. Prepared resins were characterized using IR, DSC, and TGA. IR spectra of LPF adhesive showed structural similarity with that of PF adhesives. Thermal stability of LPF adhesive was found to be lower compared to that of control PF (CPF) adhesive. DSC studies revealed a lower curing temperature for LPF resin than that for CPF resin. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 3514–3523, 2004

Key words: adhesives; resins; lignin; physicomechanical properties; thermogravimetric analysis (TGA)

INTRODUCTION

In the woodworking industry, an essential application of adhesive is in the manufacture of laminated products such as plywood panels. The major adhesive resin worldwide for plywood is phenol formaldehyde resole (PF) resin.^{1–3} PF adhesives are more significant for the production of weather- and boiling-resistant products.⁴ A large number of resins with dramatically different properties are possible, depending on the type of phenol used, formaldehyde to phenol molar ratio, type and amount of catalyst and/or hardener used, and the total reaction time. PF resole resins have been studied extensively in relation to formaldehyde to phenol molar ratio^{5,6}; catalyst to phenol ratio^{7,8}; reaction temperature, time, and pH.^{9,10} Marie et al.⁷ studied various resole model compounds by IR and applied the results on industrial-grade resole resin. Christiansen and Gollob⁶ used a differential scanning calorimeter to study the effect of resin formulation on thermal curing. Kim and Neih⁹ examined the effect of temperature and resin composition on resole cure. Although these adhesives are in adequate supply today, scarcity of petroleum products could affect future cost and availability of these petroleum-based adhe-

sives, making it imperative to develop adhesives by replacing petroleum-based raw materials with those from natural resources.

In recent years, use of biomass, such as wood, tree bark, and others, in material applications has been reported.^{11,12} Lignin is one such type of renewable polymer and constitutes about 20–30% of wood and vascular plants.¹³ In the context of natural waste utilization, for production of lignin, eucalyptus tree bark waste has proved to be a suitable resources. Lignin is a natural binder in wood and structurally it resembles PF resin condensate. It contains both aromatic and aliphatic hydroxyl groups, which can be used as potential reactive sites for chemical modification.¹⁴ All these factors have attracted researchers worldwide to explore the possibility of using lignin alone or as a comonomer for preparation of adhesives.^{15–18} Lignin can be incorporated into PF resin mainly in three ways: (1) it can be reacted with formaldehyde to provide methylol functionalities and then added to PF resins,¹⁴ where lignin acts as an extender; (2) condensing lignin directly with phenol and formaldehyde¹⁹; and (3) derivatizing lignin either with phenol or formaldehyde to enhance its reactivity toward PF resins.²⁰ The most practical way to incorporate lignin into phenol formaldehyde resin is still a subject of debate. Substitution of phenol by lignin reduces the cost and curing time and improves strength and water resistance.

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Olivares et al.¹⁶ substituted 15% of phenol with lignin to achieve 9.5% cost reduction compared to that of commercial PF resin. Plywood prepared from lignin substituted phenolic adhesive was found to have a lower wood failure level than that of a control PF (CPF) resin, and the shear strength of lignin substituted adhesive was found to be as good as, or better than, that of control PF adhesives.²¹ Lignin substituted PF (LPF) resin condensates have been studied in great detail. Although a number of references on use of lignin in PF resin condensates are available in the literature,^{19–25} only scant work has been reported on the effect of varying various parameters on prepared adhesive properties.

The objective of this article was to explore the possibility of replacing phenol with eucalyptus bark lignin in PF adhesives. Various reaction parameters, such as lignin to phenol ratio, formaldehyde to phenol lignin adduct ratio, catalyst concentration, polymerization time, and temperature, were studied. The conditions for preparation of LPF adhesives were optimized on the basis of physicomechanical properties of the prepared adhesives. The optimized LPF and CPF adhesives were characterized for structural and thermal properties by IR, DSC, and TGA.

EXPERIMENTAL

Materials

Phenol (99%; M/s Qualigens, India), formaldehyde solution (37%; M/s Merck, India), methanol (99%), sulfuric acid (98%; M/s S. D. Fine Chemicals, Mumbai, India), and sodium hydroxide (97%; M/s Rankem, India) were used for experimental work. Eucalyptus bark was collected from University Campus, Delhi (India). It was washed with distilled water, dried in an oven at 100°C, ground using a conventional mixer grinder, and subsequently used for delignification.

Lignin extraction

Delignification was performed in a two-neck round-bottom flask, equipped with a condenser and a thermometer. Ground bark (250 g) and 2.5 kg of 5 mol/L sodium hydroxide were charged to a flask. The temperature was maintained at 100 ± 1°C for 7 h. A black liquor so obtained was filtered to remove suspended pulp fibers and then neutralized with 50% H₂SO₄ solution under constant stirring. The precipitated lignin was filtered under vacuum and washed repeatedly with hot distilled water until neutral. A lignin cake (166.5 g) was obtained having 33% solid content.

Adhesive preparation

Both phenol formaldehyde (PF) and lignin phenol formaldehyde (LPF) were prepared in a four-neck

round-bottom flask, equipped with a stirrer, thermometer, reflux condenser, and dropping funnel.

Preparation of PF adhesive

Molten phenol (11.64 g), formaldehyde solution (20.27 g), and 10 g each of distilled water and methanol were charged to a flask. The mixture was heated and the temperature was then maintained at 80 ± 1°C. Sodium hydroxide (1.16 g) was added dropwise within 15 min, and the reaction was continued for 4 h.

Preparation of LPF adhesive

LPF adhesive was prepared in two steps: the first step consisted of the preparation of lignin phenol adduct (PL) and the second step consisted of the preparation of LPF adhesive (i.e., polymerization step). In the first step, 85 g of lignin cake, having 33% lignin content, was introduced to a beaker, after which 28 g of phenol, equal to lignin content in the lignin cake, was added to the mixture. The lignin–phenol mixture was mixed and stirred for 1 h at 40°C to obtain a homogeneous mass. The resulting adduct contained 50% moisture.

In the second step, 25 g of LP adduct (prepared in the first step), additional phenol (to the desired lignin : phenol ratio), 21.75 g of formaldehyde solution, and 10 g methanol were mixed and heated at 80°C. A 50% NaOH solution (1.16 g) was then added and the reaction was continued for 4 h.

Adhesive characterization

The percentage of nonvolatile content (solid content) of the adhesives was measured according to ASTM D 4426-93.

The gel time of adhesives was determined using an indigenous gel meter. Samples of 1 to 2 g of adhesive were placed into the grooves at 100 ± 1°C, and the time for the formation of fiber was observed.

Close contact joint or adhesive strength of all the samples was tested according to IS 851-1978. Teak wood–teak wood interface was used for this testing.

The shear properties were measured by tension loading of adhesives according to ASTM D 2339-94A.

The IR spectra of lignin, PF, and optimized LPF adhesive were taken using KBr pellets on a Nicolet Impact 410 FTIR spectroscope (Nicolet Analytical Instruments, Madison, WI).

Thermal transitions were measured using a differential scanning calorimeter (DSC 2910, TA Instruments, New Castle, DE). The sample was heated at the rate of 10°C/min from ambient to 250°C in a nitrogen atmosphere.

Thermal stabilities of CPF and optimized LPF adhesives were measured using a thermogravimetric analyzer (TGA, DTA 2960; TA Instruments). The CPF and

TABLE I
Various Prepared Adhesives

Sample no.	Adhesive code	Lignin substitution (%)	F to PL adduct (ratio)	Catalyst concentration (%)	Reaction time (h)	Reaction temperature (°C)
1	A	0	2.0	10	4	80
2	B	10	2.0	10	4	80
3	C	25	2.0	10	4	80
4	D	35	2.0	10	4	80
5	E	50	2.0	10	4	80
6	F	60	2.0	10	4	80
7	G	50	1.5	10	4	80
8	H	50	2.5	10	4	80
9	I	50	3.0	10	4	80
10	J	50	2.0	5	4	80
11	K	50	2.0	15	4	80
12	L	50	2.0	10	2	80
13	M	50	2.0	10	6	80
14	N	50	2.0	10	4	60
15	O	50	2.0	10	4	90

LPF samples were heated from ambient to 700°C, whereas lignin was heated to 500°C at the rate of 10°C/min in a nitrogen atmosphere.

RESULTS AND DISCUSSION

Optimization of reaction parameters

Different reaction parameters studied were lignin to phenol ratio, formaldehyde to phenol–lignin adduct ratio, catalyst concentration, reaction time, and reaction temperature. The parameters were varied and their effects on gel time, nonvolatile content, adhesive strength, and shear strength were studied. The various adhesives prepared are listed in Table I.

Lignin to phenol ratio

Figure 1 shows the effect of lignin substitution on nonvolatile solids, gel time, adhesive strength, and shear strength. The concentration of lignin was varied by 10, 25, 35, 50, and 60% (w/w). The values are compared with control PF adhesive. As observed from the figure, the amount of nonvolatile solids decreases with increase in lignin content and becomes constant after 25 wt % lignin substitution. Gel time was measured at 100°C. Gel time decreases with increase in lignin content up to 50 wt % lignin substitution and then increases slightly for 60 wt % lignin substituted adhesive. Adhesive strength and shear strength both increase proportionally with lignin content. A sharp increase in adhesive strength and shear strength of 10 wt % lignin substituted adhesive over that of control PF is evident. On progressive incorporation of lignin, up to 50 wt % in PF, adhesive strength and shear strength increase progressively. With 60 wt % incorporation of lignin, adhesive strength was found to

decrease slightly. It is well known that adhesive strength and shear strength are dependent on crosslink density. The increase in adhesive strength and shear strength of the PF adhesive on substitution by lignin can be explained by the fact that crosslinking between the polymer chains is enhanced, which provides better reinforcement structurally. The decrease in gel time with increase in the loading of lignin shows that the crosslinking rate has noticeably increased and,

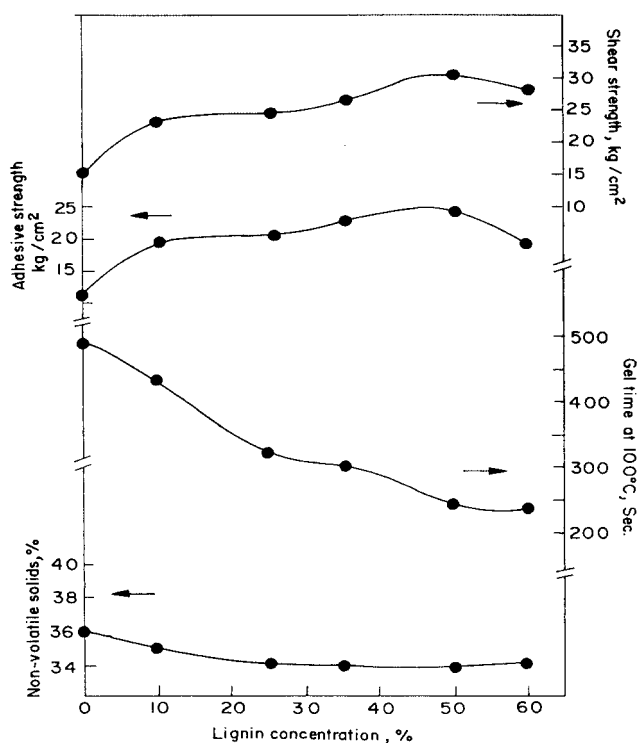


Figure 1 Effect of lignin concentration on physicochemical properties of LPF adhesives.

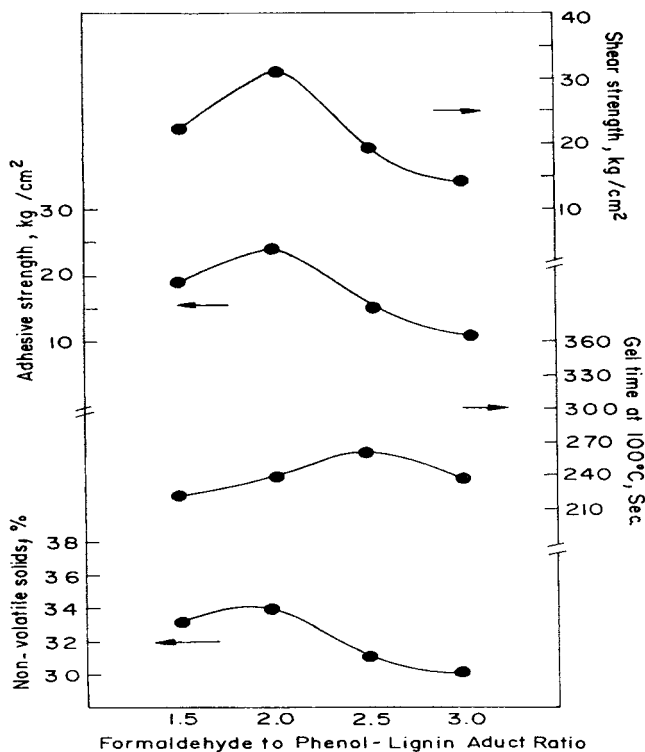


Figure 2 Effect of formaldehyde to phenol-lignin adduct ratio on physicochemical properties of LPF adhesives.

as a result, better structural alignment of lignin and phenol occurs. This also results in increased adhesive strength. This structural alignment, achieved by a decrease in gel time, continues up to 50 wt % loading of the lignin. It is observed that beyond 50 wt % loading of lignin in PF, gel time still decreases, showing that crosslinking between the two moieties is still continuing, but that adhesive strength and shear strength decrease. This is attributed to the fact that lignin is now in excess, causing a loss in both adhesive strength and shear strength. The results are in good agreement with the literature.^{21,26}

Comparing the control PF and lignin substituted PF resins, it is concluded that lignin substituted PF resin progressively improves the shear strength and adhesive strength up to 50 wt % substitution of phenol by lignin, with a simultaneous decrease in gel time. Thus, for preparation of lignin substituted PF resole adhesives, 50 wt % bark lignin incorporation is optimal.

Formaldehyde to phenol-lignin adduct ratio

Figure 2 depicts the effect of formaldehyde to phenol-lignin adduct ratio (F : PL) on various properties of the adhesives. The effect of formaldehyde concentration on properties of the adhesives was studied by varying the formaldehyde to phenol-lignin adduct ratio from 1.5 to 3.0. As observed from the figure, nonvolatile solid content increases up to a F : PL ratio of 2.0, and

then decreases sharply. An increase in gel time is observed with increase in the F : PL ratio. The values of nonvolatile content are dependent on the extent of crosslinking and network formation. It is observed that, at higher values of F/PL ratio, the nonvolatile content decreases, which indicates that crosslink formation is hindered at higher ratios. This results in a decrease in the rate of crosslink formation, leading to the increased gel time. It is observed that, between the F/PL ratios of 1.5 and 2.0, the nonvolatile content values are higher and gel time is lower. Above the F/PL ratio of 2.0, nonvolatile content values are lower and gel time values are higher. It is presumed that, at this higher F : PL ratio, some factor, such as excessive hydrogen bond formation between formaldehyde molecules, hinders the crosslink formation, leading to a lower rate of crosslinking. Adhesive strength and shear strength show similar patterns with maxima at the F : PL ratio of 2.0, beyond which a decrease in strength is observed. Comparing the four parameters, it is observed that an adhesive prepared at a F/PL ratio of 2.0 has higher adhesive strength and shear strength. The gel time and nonvolatile content values are found to be lowest and highest for the above ratio, respectively, indicating the highest rate of crosslinking and network formation, resulting in an increase in adhesive strength and shear strength of the adhesive, at this ratio.

Catalyst concentration

Effects of the catalyst on solids content, gel time, adhesive strength, and shear strength are given in Figure 3. The concentration of catalyst is expressed as weight in grams to the weight of phenol and lignin together and is varied from 5 to 15%. Figure 3 shows that nonvolatile content first increases and then become almost constant with catalyst concentration. Mahanta et al.²⁷ also observed an increase in solids content with catalyst concentration up to 8–10 wt % of concentration in the case of PF adhesive. A decrease in gel time is observed with increase in catalyst concentration, which is attributed to enhancement of the condensation reaction attributed to the effect of the catalyst. It has been shown that the presence of a catalyst accelerates the reaction involving dimethylene ether bridges or hydroxy methyl groups because of an increase in pH to the basic range.⁸ A maximum at 10 wt % catalyst concentration is observed for adhesive strength and shear strength. This shows that 10 wt % of catalyst concentration is optimal, with respect to adhesive strength and shear strength, for preparing LPF adhesive. It appears that 5 wt % catalyst concentration is inadequate for preparation of homogeneous three-dimensional network structures. Although a lower gel time is observed for adhesive prepared with 15% catalyst concentration, the adhesive obtained has

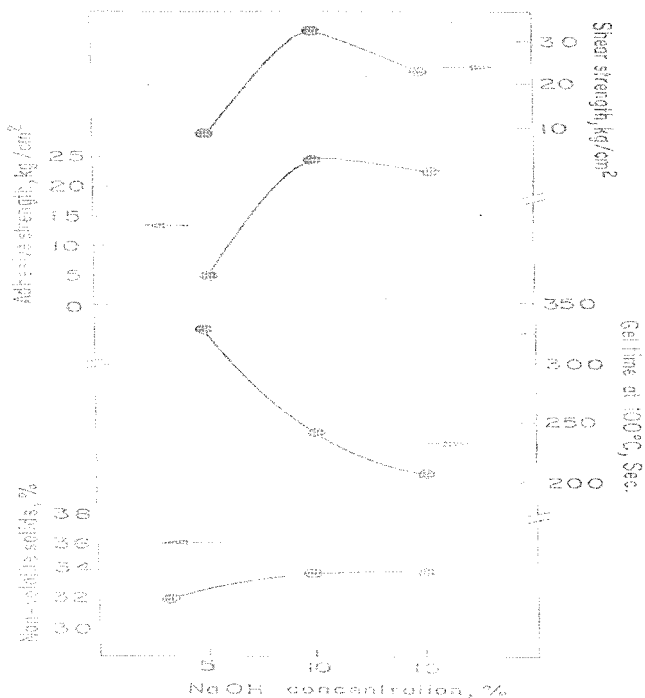


Figure 3 Effect of catalyst concentration on physico-mechanical properties of LPF adhesives.

lower strength. The optimal catalyst concentration for the preparation of LPF adhesive is thus 10 wt %.

Reaction time

The effect of reaction time on adhesive properties is presented in Figure 4. An increase in nonvolatile solids is observed, as reaction time is increased from 2 to 4 h, beyond which no significant effect of time is observed on solids content. Figure 4 shows that gel time increases with reaction time. Adhesive strength and shear strength both show similar patterns, with maxima at 4 h. For adhesive prepared at 2 h of reaction time, the values of both adhesive strength and shear strength are very low. A drastic increase in adhesive strength and shear strength is observed on increasing reaction time to 4 h. The lower values of adhesive strength and shear strength, for adhesive prepared at 2 h reaction time, reflect inadequate crosslinking. On comparing the adhesives prepared at three different reaction times, it is observed that adhesive strength and shear strength values are at a maximum for the adhesives prepared at 4 h reaction time. Resin yield is also at a maximum at this reaction time. At 2 h reaction time resin yield, adhesive strength, and shear strength values are low, which indicates that in this time the reaction failed to reach completion. On increasing the reaction time to 6 h, a decrease in shear strength and adhesive strength is observed. The resin still sets to gel but the prolonged reaction time appears

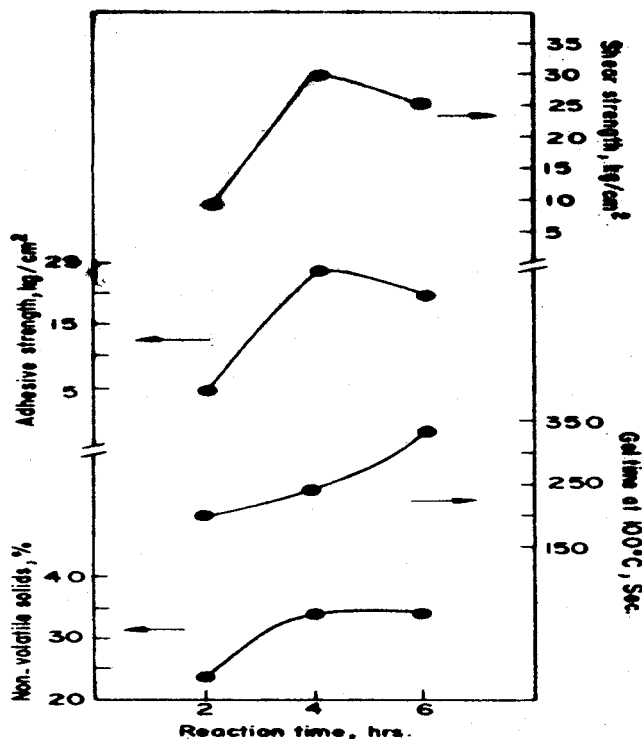


Figure 4 Effect of reaction time on physico-mechanical properties of LPF adhesives.

to cause a breakdown of a fraction of crosslinks, or some other deformation in the structure occurs, which results in decreased adhesive strength and shear

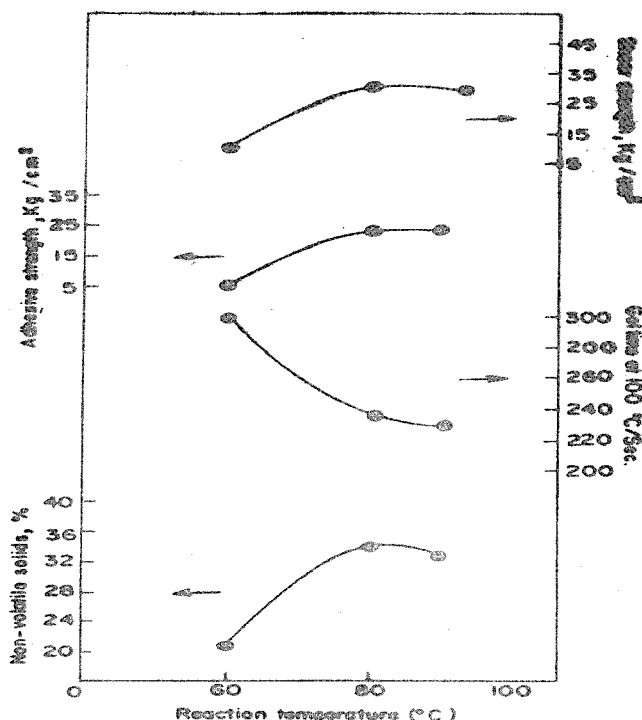


Figure 5 Effect of reaction temperature on physico-mechanical properties of LPF adhesives.

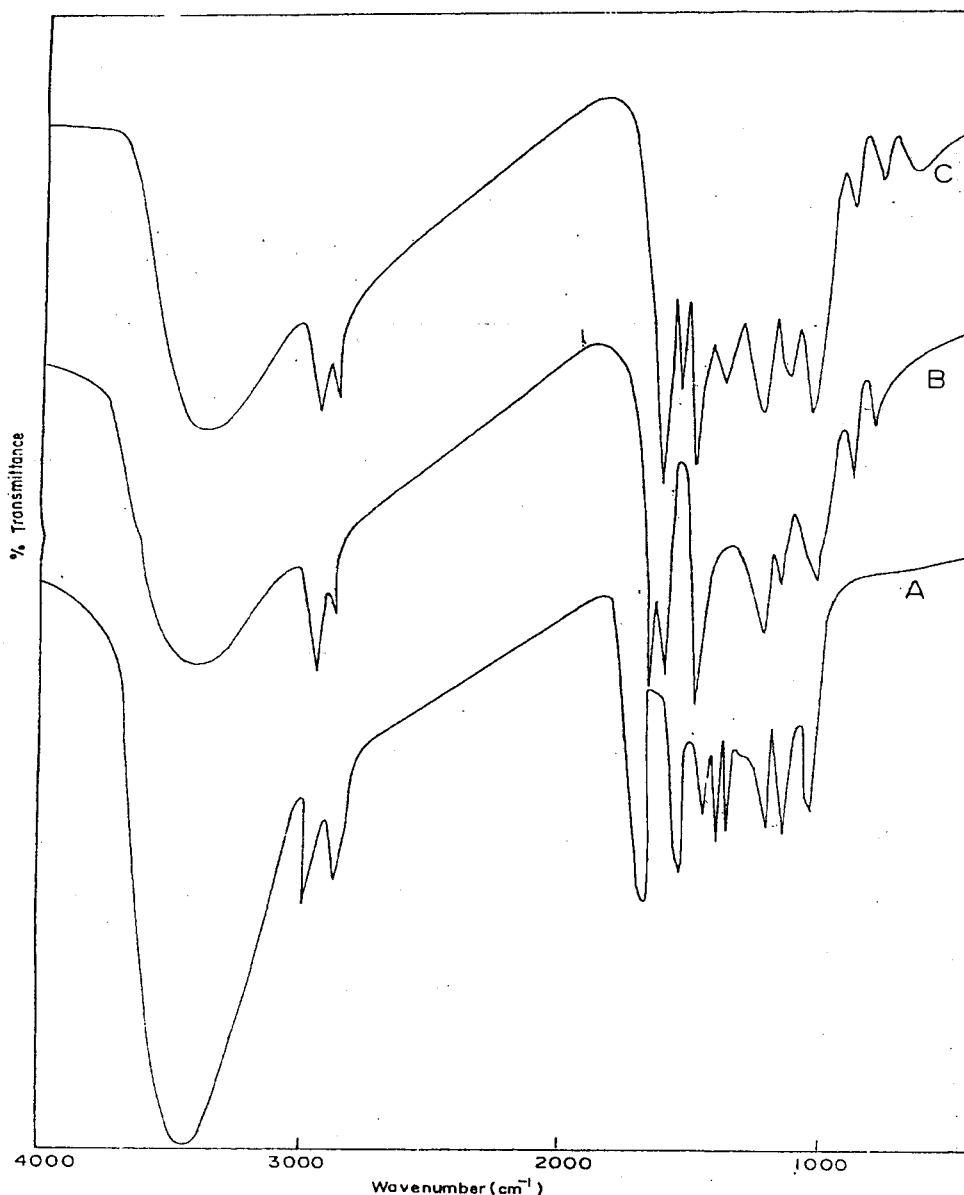


Figure 6 IR spectra of eucalyptus bark lignin (A), CPF (B), and LPF (C) adhesives.

strength. From the above observations, it is concluded that, for the preparation of lignin phenol formaldehyde resin, a reaction time of 4 h appears to be optimal.

Reaction temperature

The effects of reaction temperature on gel time, non-volatile solids, adhesive strength, and shear strength are presented in Figure 5. Reactions were carried out at 60, 80, 90, and 100°C; at 100°C gelling occurs. From 60 to 80°C the resin yield (i.e., solid content) increases sharply, 21 to 34%, and then decreases slightly to 33%. Gel time decreases from 300 to 230 s. Adhesive strength and shear strength also increase sharply on

increasing the temperature from 60 to 80°C, and then decrease slightly. It appears that crosslink formation starts from 60°C. However, at this temperature both the rate of crosslink formation and extent of crosslink formed are low. With the increase in temperature, the rate of crosslink formation and extent of crosslinking both increase. This causes an increase in resin yield, adhesive strength, and shear strength. At 80°C both the shear strength and adhesive strength are at their highest. At 90°C the resin yield decreases. The gel time was also found to decrease at this temperature. The small decrease in gel time shows that the extent of network formation is slightly less, which caused a small decrease in nonvolatile content. Our earlier observation, that shear strength and adhesive strength

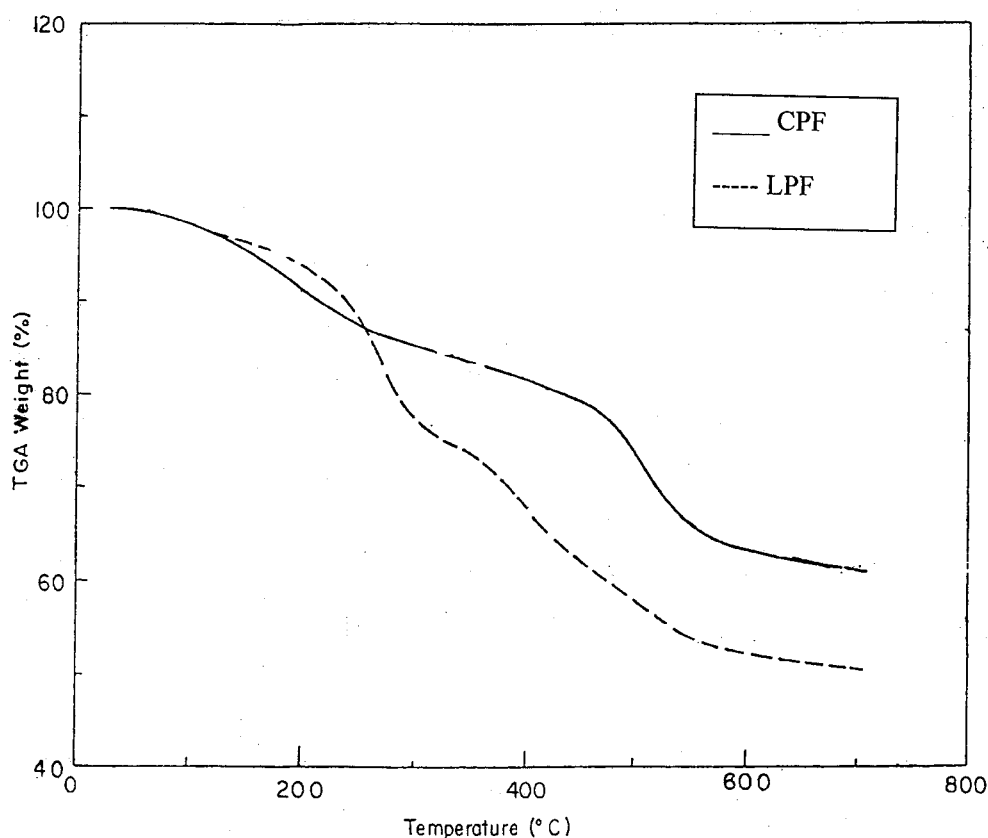


Figure 7 TGA thermograms of CPF and LPF resins.

are proportional to the nonvolatile content, is also confirmed by the result of this study. The above observations indicate that 80°C is the optimal polymerization temperature for preparation of LPF adhesives.

All the foregoing observations lead to the conclusion that optimal conditions for preparation of bark lignin substituted phenol formaldehyde resin are as follows: 50 wt % lignin substitution for phenol, a formaldehyde to phenol lignin ratio of 2.0, a catalyst concentration of 10 wt %, reaction time of 4 h, and reaction temperature of 80°C.

Characterization of adhesives

LPF adhesive, prepared under optimized conditions, was characterized by IR, DSC, and TGA and compared with CPF adhesive.

IR analyses

Figure 6 shows the IR spectra of bark lignin, PF, and LPF resin. All three spectra are characterized by the presence of a broad band of OH stretching in the 3300 cm^{-1} region, two bands of CH stretching at 2900 and 2800 cm^{-1} , and aromatic ring vibrations in the region 1600–1500 cm^{-1} . Bark lignin shows bands at 1550 and 1500 cm^{-1} , attributed to aromatic skeleton vibrations. The band at 1459 cm^{-1} is assigned to C—H deformation in the $-\text{CH}_3$ of a methoxyl group. The band at 1380 cm^{-1} is attributed to C—O of a syringyl unit. The bands at 1119 and 1042 cm^{-1} are assigned to C—H stretching in syringyl and C—O of primary alcohol. In CPF, a band at 3378 cm^{-1} is observed, which shows the presence of OH group. This band, appearing at lower frequency, indicates strong hydrogen bonding.

TABLE II
Thermal Properties of CPF and LPF Resins

Adhesive code	TGA analysis								DSC analysis		
	First thermal event				Second thermal event				Endothermic event		
	T_i (°C)	T_{\max} (°C)	T_f (°C)	Wt. loss (%)	T_i (°C)	T_{\max} (°C)	T_f (°C)	Wt. loss (%)	T_p (°C)	T_o (°C)	ΔT (°C)
A	124	190	242	14	468	503	552	22	125	90	35
E	214	267	291	25	374	393	493	24	92	85	07

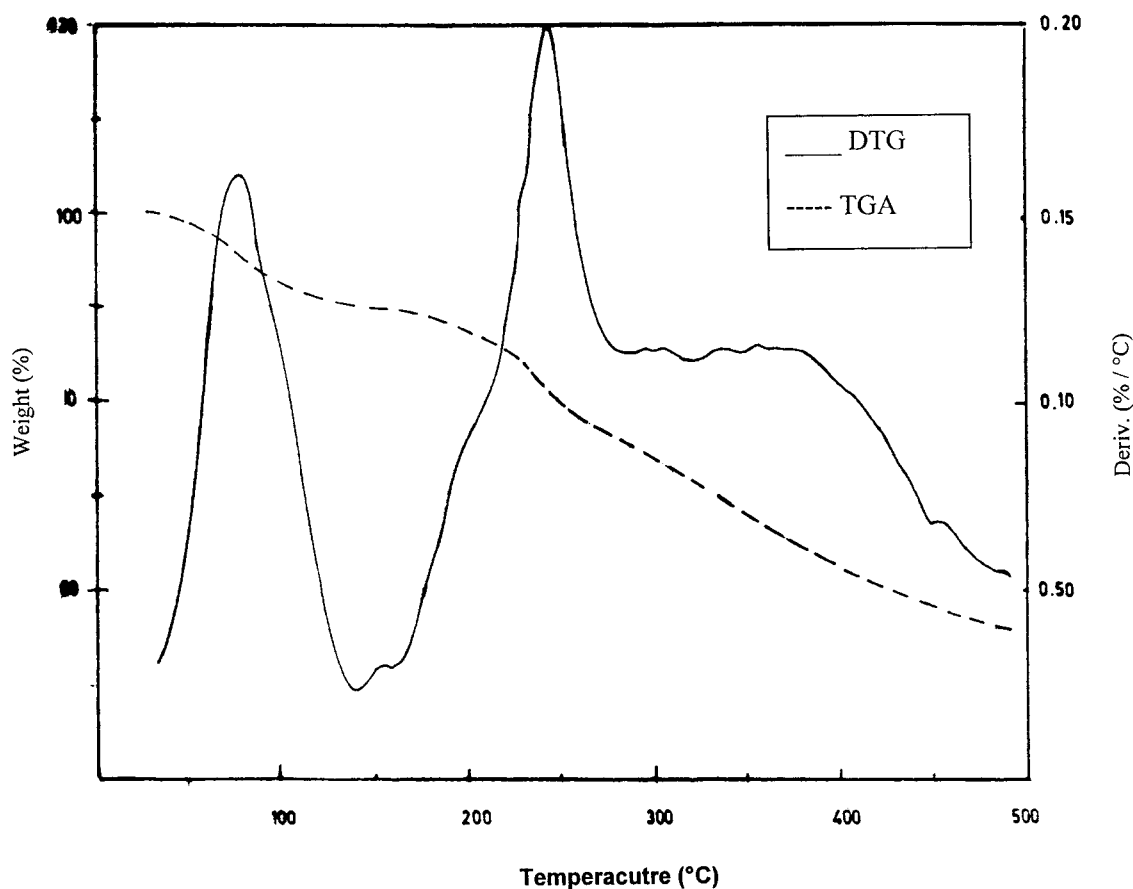


Figure 8 TG-DTG thermogram of bark lignin.

Bands at 2927 and 2842 cm^{-1} are a consequence of in-plane and out-of-plane stretching of aliphatic CH_2 . Similarly, these bands are also present in LPF resin.

Spectral differences in CPF and LPF resins are observed in the fingerprint region (1800–900 cm^{-1}). Bands at 1591 and 1404 cm^{-1} are assigned to $\text{C}=\text{O}$ stretching of a benzene ring. The band at 1480 cm^{-1} is assigned to CH deformation in $-\text{CH}_2$ groups. Rocznik et al.²⁸ identified the region between 1500 and 1400 cm^{-1} as characteristic of the deformation vibration of $-\text{CH}-$ bands in a $-\text{CH}_2$ group and observed some difference from the spectra of resins.

These differences can provide information as to the structure of a methylene bridge. In LPF resin the appearance of bands at 1480 and 1450 cm^{-1} indicates the presence of a methylene bridge. CPF shows a band at 1378 cm^{-1} , which is attributed to in-plane deformation of phenolic OH . The band observed at 1372 cm^{-1} in LPF is attributed to lignin, which is assigned to the $\text{C}-\text{O}$ of a syringyl unit present in bark lignin. The bands at 1208 and 1225 cm^{-1} are attributed to in-plane vibration of $\text{C}-\text{O}$ of the phenolic group present in CPF and LPF, respectively. In CPF the bands at 1170 and 1051 cm^{-1} are characteristic for in-plane deformation of aromatic $\text{C}-\text{H}$, whereas the band at 1170 cm^{-1}

in LPF is attributed to $\text{C}-\text{H}$ stretching in a syringyl unit and is attributed to the presence of lignin. The band at 1038 cm^{-1} in LPF is characteristic of lignin and is attributed to the $\text{C}-\text{O}$ of primary alcohol. Saad et al.^{29,30} identified this band as a lignin band.

Thermogravimetric analysis

Figure 7 shows the TGA thermograms of CPF and LPF resins. The study was carried out up to 700°C in N_2 atmosphere. In the case of CPF, 67 wt % residue remains after 700°C, whereas, in LPF, the residue obtained is 53 wt %. Decomposition temperatures and percentage weight loss values for different thermal events are presented in Table II.

In the case of CPF resin, two thermal events are observed, one in the range of 120–240°C and the other in the range of 450–550°C. The initial weight loss, in the range of 120–240°C, is believed to arise from post-curing reactions of phenolic resin. Christiansen and Gollob⁶ reported a DSC transition in the range of 139–151°C, which they attributed to crosslinking in phenolic resin. In the DSC thermograms of CPF and LPF adhesives, an endotherm is observed in the temperature range of 90–125°C, which further confirms

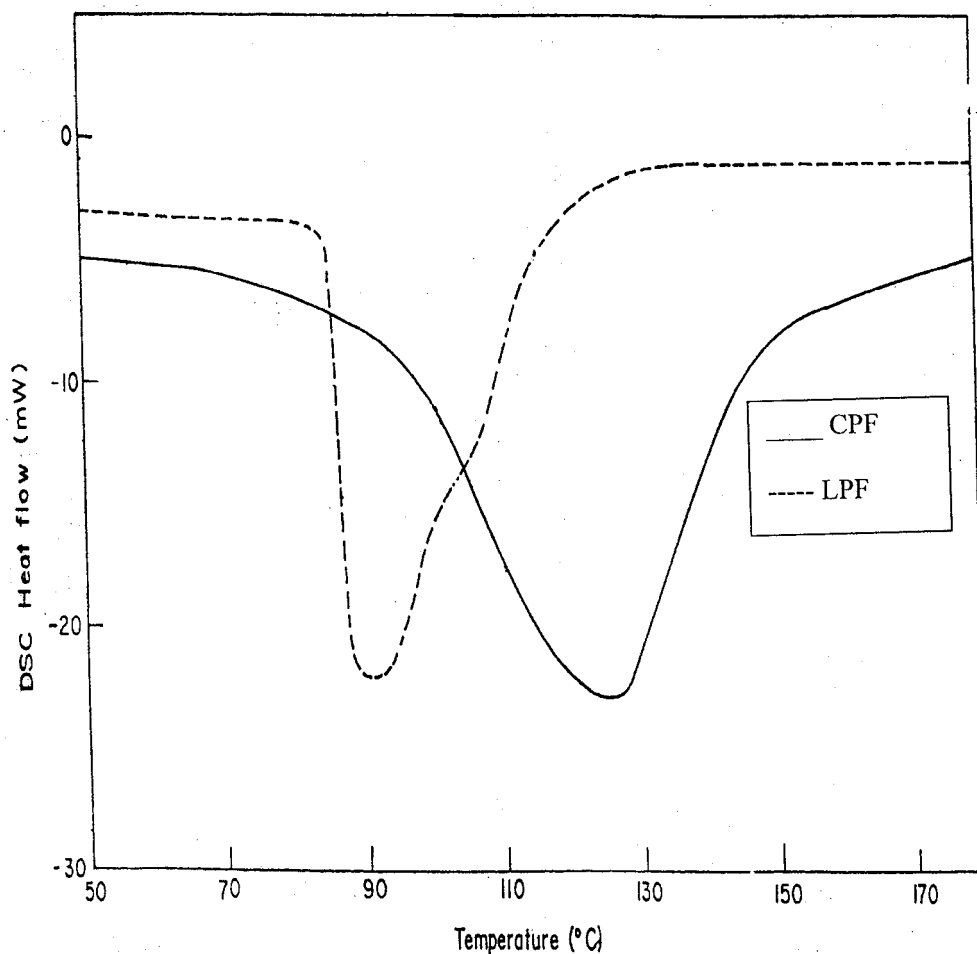


Figure 9 DSC thermograms of CPF and LPF adhesives.

the postcuring reactions in the resin. The second major weight loss event is observed in the range of 450 to 552°C. A 22% weight loss is observed in this event and is attributed to the breakdown of methylene linkages in phenolic resin.

In the case of LPF, two weight loss events are also observed. The first event starts at 214°C and ends at 291°C, with T_{\max} at 267°C: LPF loses 25% weight in this event. The second event is observed in the temperature range of 374 to 493°C: a 24% weight loss is observed in this transition, which is attributed to a breakdown of methylene linkages in LPF adhesive. It is observed that the first transition, in the case of LPF, starts at a higher temperature but the weight loss is greater in LPF compared to that in CPF resin. In the case of LPF adhesive, the weight loss is a consequence of both postcuring reactions in the resin and degradation of side alkyl chains in lignin. The DSC thermogram of LPF resin (see Fig. 9) shows an endothermic event between 85 and 92°C, which is attributed to a postcuring reaction in this case.

Figure 8 shows the TG-DTG thermogram of bark lignin. In the case of bark lignin, a 9% weight loss is

observed up to 100°C. In the temperature range of 100 to 200°C, a 4% weight loss is observed. Further, an appreciable weight loss of 13 wt % is observed in the temperature range of 200 to 250°C. The first thermal event, observed in the DTG thermogram of bark lignin, starts at 56°C and ends at 102°C, with T_{\max} at 76°C: weight loss in this event is 9%. A second thermal event starts at 206°C and ends at 254°C, with T_{\max} at 241°C, resulting in an 18% weight loss. This weight loss is attributed to breakdown of side chains present in lignin. This further confirms our interpretation of lignin breakdown in this temperature range in LPF resin. It is concluded, from the above observations, that initial thermal stability of LPF adhesive is higher but, as degradation proceeds, CPF becomes more stable.

DSC analysis

DSC thermograms of CPF and LPF adhesives are presented in Figure 9. In both cases an endotherm in the temperature range of 80 to 130°C is observed. In the case of CPF resins many conflicting results are pre-

sented in the literature. Some workers have reported only exothermic peaks in the ranges of 60–75 and 135–180°C during cure of base-catalyzed PF resins.^{31,32} Others have observed only endothermic peaks at 60, 125, and 180°C for both acid- and base-catalyzed resins.³³ However, Chow et al.³⁴ showed that a novolac-type resin always gives an exothermic peak, whereas the resole type of adhesives gives an endothermic peak for curing of PF resin. Thus the endotherm, obtained in this case, is attributed to the curing of CPF resin. The peak temperatures (T_p) and onset temperatures (T_o) for both adhesives are presented in Table II. In the case of CPF the transition is observed at 125°C and, for LPF, at 92°C. T_o for CPF is 90°C, which decreases to 85°C for LPF. This shows that curing of LPF starts at a lower temperature than that of CPF but later cures more slowly, giving a broad transition curve. These observations show that incorporation of lignin accelerates the curing of PF resin. ΔT ($T_p - T_o$) is the measure of rate of curing. For CPF adhesive the value is 35°C, which decreases drastically on substitution of 50% phenol by lignin. The lower value of ΔT shows a higher rate of curing in the case of LPF adhesives. These results are in good agreement with the result of gel time, which decreases with increase in lignin content.

CONCLUSIONS

The following conclusions are drawn from the study:

1. Up to 50% of phenol in phenol formaldehyde adhesive can be substituted by bark lignin with improved adhesive properties.
2. Adhesive strength and shear strength of lignin phenol formaldehyde adhesive was found to be better than phenol formaldehyde resin: this reflects the copolymerization of lignin with phenol formaldehyde resin resulting in better binding strength.
3. The optimized parameters for preparation of LPF adhesive are F : PL ratio 2.0, a catalyst concentration of 10%, reaction time of 4 h, and reaction temperature of 80°C.
4. IR spectra of LPF resin show characteristic peaks of both lignin and phenol formaldehyde resin.
5. Thermal stability of LPF resin is lower than that of PF resin.
6. Curing temperature of LPF is lower than that of PF adhesive, whereas the rate of curing is higher in the case of LPF.

References

1. Sellers, R., Jr. *Plywood and Adhesive Technology*; Marcel Dekker: New York, 1985; pp. 271, 349, 422, 514.
2. Keulgen, W. A. *Encyclopedia of Polymer Science and Technology*; Wiley: New York, 1969; Vol. 10, p. 1.
3. Knop, A.; Scheib, B. *Chemistry and Application of Phenolic Resins*; Springer-Verlag: New York, 1979.
4. Mittal, M.; Sharma, C. B. *Polym Int* 1992, 29, 7.
5. Haupt, R. A.; Sellers, R., Jr. *Ind Eng Chem Res* 1994, 33, 693.
6. Christiansen, A. W.; Gollob, L. *J Appl Polym Sci* 1985, 30, 2279.
7. Grenier-Loustalot, M. F.; Larrque, S.; Grenier, P. *Polymer* 1996, 37, 639.
8. Chow, S.; Steiner, P. R.; Troughton, G. E. *Wood Sci* 1975, 8, 343.
9. Kim, M. G.; Neih, W. L. S. *Ind Eng Chem Res* 1991, 30, 798.
10. Pizzi, A.; Stephanou, A. *J Appl Polym Sci* 1993, 49, 2157.
11. Alma, M. H.; Yoshioka, M.; Shiraishi, N. Ph.D. Thesis, Kyoto University, Japan, 1996.
12. Alma, M. H.; Kelley, S. S. *Polym Degrad Stab* 2000, 68, 413.
13. Kirk, T. K.; Farrell, R. L. *Ann Rev Microbiol* 1987, 41, 465.
14. Forss, K. G.; Fuhrmann, A. *Forest Prod J* 1979, 29, 39.
15. Amass, W.; Amass, A.; Tighe, B. *Polym Int* 1999, 47, 89.
16. Olivares, M.; Aceituno, H.; Neiman, G.; Rivera, E.; Sellers, T., Jr. *Forest Prod J* 1995, 45, 63.
17. Doering, G. A. U.S. Pat. 5,202,403, 1993.
18. Benar, P.; Adilson, R. G.; Dalmo, M.; Schuchardt, U. *Bioresour Technol* 1999, 68, 11.
19. Janiga, E. R. U.S. Pat. 4,423,173, 1983.
20. Oh, Y.; Seller, T., Jr.; Kim, M. G. *Forest Prod J* 1994, 47, 25.
21. Gardner, D. J.; Sellers, T., Jr. *Forest Prod J* 1986, 36, 61.
22. Sellers, T., Jr. *Panel World* 1990, 31, 26.
23. Nada, A. M. A.; El-Saied, H.; Ibrahim, A. A.; Yousef, M. A. *J Appl Polym Sci* 1987, 33, 2915.
24. Pizzi, A.; Mtsweni, B.; Parsons, W. *J Appl Polym Sci* 1994, 52, 1847.
25. Shiraishi, N.; Kishi, H. *J Appl Polym Sci* 1986, 32, 3189.
26. Lee, G. V.; Park, B. K.; Lee, B. G. *J Korean Chem Soc* 1976, 20, 240.
27. Mahanta, D.; Rahman, A.; Chaliha, B. P. *Indian Pulp Paper* 1980, June–July, 9.
28. Rocznaik, C.; Biernacka, T.; Skarzynski, M. *J Appl Polym Sci* 1983, 28, 531.
29. Saad, S. M.; Issa, R. M.; Fahmy, M. S. *Holzforchung* 1980, 34, 218.
30. Saad, S. M.; Metwally, N. E.; Shaaban, S. M. *Acta Polym* 1968, 39, 10.
31. Ezrin, M.; Claver, G. C. *Appl Polym Symp* 1969, 8, 171.
32. Katovic, Z. *J Appl Polym Sci* 1967, 11, 58.
33. Nakamura, Y. *Kogyo Kagaku Zasshi* 1961, 64, 392.
34. Chow, S.; Steiner, P. R. *J Appl Polym Sci* 1979, 23, 1973.