

Fortified Mangrove Tannin-Based Plywood Adhesive

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SYNOPSIS

Mangrove bark tannin adhesives are based on a renewable resource. They are potential substitutes or supplements for phenol-formaldehyde (PF) wood-bonding adhesives which are derived from petroleum, a finite natural resource. However, mangrove tannin adhesives exhibit poor adhesive properties including poor wet strength, brittleness, and poor wood penetration. These problems were addressed by treating tannin extract with acetic anhydride and then sodium hydroxide followed by modification with 20% resole-type PF resin. Significant structural changes occurred after the chemical treatment. Heat of reaction of tannin with formaldehyde was increased while the activation energy was drastically reduced. Premature cure was also reduced. The fortified formulations had good plywood adhesive properties. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

There have been several attempts to replace part of the petroleum-derived phenolic compounds in wood bonding adhesives with phenolic-type compounds obtained from renewable sources. Principal among these efforts is the development of adhesives from tannin.^{1,2} Tannin-based adhesives have in the past been heavily fortified with urea, urea-formaldehyde (UF), phenol-formaldehyde (PF), and resorcinol-formaldehyde (RF) with encouraging results.¹⁻⁵ However, very little work has been done on tropical forest mangrove tannin. In Nigeria, where mangrove forests abound on the south coast, Ohunyon and Ebewele attempted to develop mangrove tannin-based plywood adhesive.^{6,7} Their efforts were concentrated on using metal acetates to induce participation of the "B" ring of the tannin flavonoid molecule in the tannin formaldehyde condensation reaction. This B is normally inert except at pH > 8, at which the reactivity of the "A" ring becomes very high. High level (55%) fortification with methylol phenol was still necessary to achieve good adhesive properties. However, the adhesives developed have a number of shortcomings including brittleness,

poor wood penetration, and poor wet strength. Reasons advanced for these shortcomings *inter alia* include the following.^{1,2,6,7}

1. The tannin molecules are big and therefore cannot rotate freely about their backbone. This results in the observed inherent brittleness.
2. The high reactivity of tannin molecules causes premature cure. Consequently, the residual active centers become too far apart for formaldehyde molecules to bridge.^{3,5-7} The resulting incomplete crosslinking enhances loss of structural integrity in adverse environments.

The aim of this study therefore was to improve the adhesive properties of mangrove bark tannin adhesive. Specifically, the objective was to reduce the size of the polyflavonoid molecules to enhance molecular flexibility and then modify the resulting structure with resole-type PF resin to reduce the tendency for premature cure and encourage a higher degree of crosslinking. Nuclear magnetic resonance spectroscopy (¹³C-NMR) was used to monitor the probable chemical changes while differential scanning calorimetry (DSC) was used to determine the relative cure response and kinetic characteristics of the unmodified and modified mangrove tannin adhesives.

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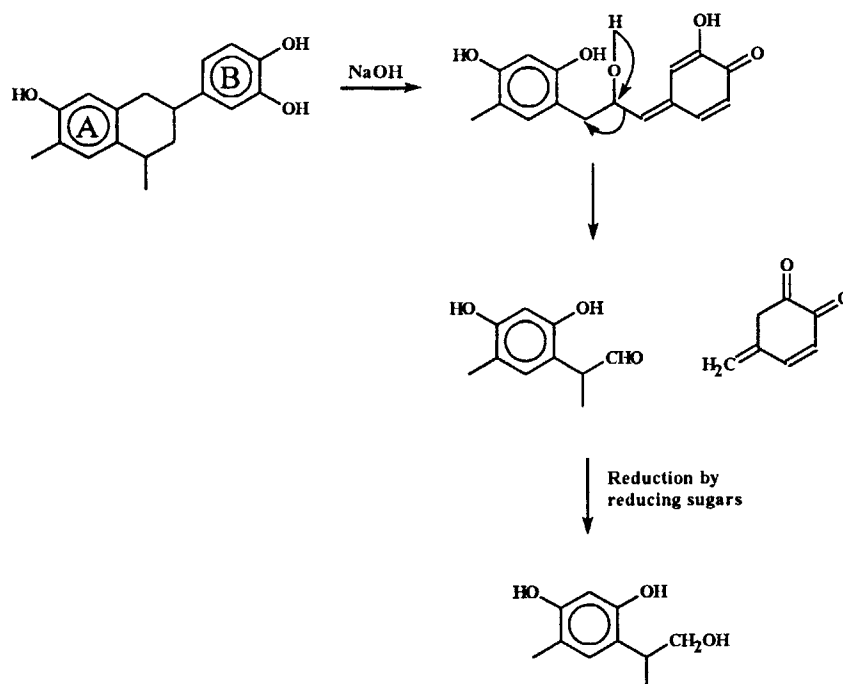


Figure 1. Proposed caustic hydrolysis reaction.

Chemistry of Condensed Tannin

The tannin polyflavonoid molecule essentially consists of five to 11 monoflavonoid units. In the monoflavonoid unit, two phenolic rings (A and B), are joined by a heterocyclic ring (Fig. 1). Tannin, being phenolic, reacts with formaldehyde in a manner similar to that for the reaction of formaldehyde with phenol. However, unlike most synthetic phenolic compounds, on heating tannin degrades rather than melts. Therefore, during the condensation reaction of tannin with formaldehyde, especially at high temperatures, tannin molecules become immobile due to evaporation of water. The result is that condensation does not go far enough to give the required adhesive properties. It therefore appears that the size and the non-melting nature of the tannin, and not just the

reactivity of the A ring, are most probably responsible for the poor adhesive properties. In addition, the presence of nontannin compounds such as gums, which are highly branched polysaccharides, affects the properties of tannin-based adhesive, particularly its moisture resistance.

Hydrolysis of Tannin

Caustic hydrolysis of resorcinolic tannin has been reported to cleave the interflavonoid bond and open the etherocyclic ring joining the A and B ring of the flavonoid unit.⁸ A proposed mechanism based on this study is shown in Figure 1.

Acid hydrolysis has been shown to easily open the etherocyclic ring of polyflavonoids with the formation of a carbocation, which is capable of reacting

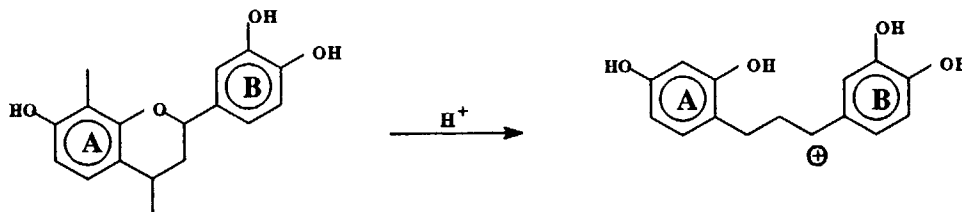


Figure 2. Acid hydrolysis of the polyflavonoid.

with another nucleophile present.⁵ This is represented by Figure 2.

Pizzi and Stephanou⁹ reported an improvement in the performance of a nonfortified mimosa tannin-based adhesive developed by subjecting tannin extracts to anhydride and subsequent alkaline treatment. The following were suggested as probable reasons for the improved adhesive performance.⁹

1. Cleaving of the tannin interflavonoid bond: This results in smaller, more mobile tannin flavonoid compounds. Therefore, the level of condensation is enhanced with formaldehyde.
2. Opening of the heterocyclic ring joining the A and B rings of the tannin flavonoid compound leads to a more flexible compound and reduces the stiffness of the tannin molecules and consequently the brittleness of the adhesive.
3. Hydrocolloid gums are hydrophilic, and very viscous, even at moderate concentrations. The presence of these gums in tannin extract tends to promote high solution viscosity and poor moisture resistance of the tannin-based adhesive. On the other hand, their corresponding sugars (of low molecular weight) do not have much effect on the viscosities of solutions. The destruction of these gums will therefore improve moisture resistance of the resulting tannin-based adhesive. In addition, because of its reduced viscosity, penetration of adhesive into wood substrate will be enhanced.

Fortification of Tannin-Based Adhesive

Some longer crosslinking agents have been tried on wattle (resorcinolic) tannin. These include some phenolic and amino-plastic resins.^{2,4,5} The relatively large molecules were used in part to replace formaldehyde, with evident improvement in resulting wattle tannin-formaldehyde adhesive.

Resorcinol, resorcinol-formaldehyde, and phenol-resorcinol-formaldehyde resoles of different types have been used²⁻⁴ to improve the level of condensation of wattle tannin-formaldehyde-based adhesives. Resorcinol capped resoles were mostly used as bridging agents. In one instance, resorcinol capped resorcinol-formaldehyde resole was first prepared. This was then reacted with flavonoid and formaldehyde. In another instance, a methylol capped phenol-formaldehyde resole was first pre-

pared and later reacted with resorcinol to give a resorcinol terminated phenol-resorcinol-formaldehyde resole, which was then used as a bridging agent. The use of fortifying agents like PF resoles is therefore expected to help bridge the reactive sites on the large tannin flavonoid molecules.

EXPERIMENTAL

Acid and Subsequent Alkaline Hydrolysis of Tannin

Modification of mangrove tannin was essentially by anhydride and sodium hydroxide treatment. Fifty parts of mangrove tannin extract were heated with 95 parts of distilled water, 2.5 parts of acetic anhydride, and 2.5 parts of (6 : 10) phenol : acetic acid mixture to about 90°C. The reaction mixture was then held under reflux at 90°C for 1 h. After that, the pH of the reaction mixture was brought to 8 by adding about 22.5 parts of 33% NaOH solution. The reaction was allowed to go on for 3 h while monitoring the pH profile of the medium as the reaction progressed. Acid hydrolysis time, acid concentration, and alkaline concentration were varied to determine their effect on the degree of modification of the tannin.

PF Resole Preparation

Forty parts of phenol, 60 parts of 37% formalin solution, and 22 parts of distilled water were charged into a reaction vessel. The temperature of the medium was raised to 90°C, and three parts of 33% NaOH solution was gradually added with continuous stirring. This was followed by double addition of three parts of 33% NaOH solution at 20-min intervals. The reaction was stopped 1 h after the first addition of NaOH solution by rapidly cooling the reaction product. Reaction time and interval of NaOH addition were varied to obtain PF resoles of varying degree of condensation.

NMR Analysis

NMR (¹³C-NMR) was used to study the acid and subsequent alkaline hydrolyzed samples. D₂O was used as the solvent for the NMR runs.

DSC

DSC was carried out in a Perkin-Elmer 7 Series Thermal Analysis System. One part of tannin ex-

tract or modified-treated tannin was dissolved in four parts of water, and paraformaldehyde was added to the tannin solution. For the first set of runs, which were intended to determine the optimum amount of paraformaldehyde needed for the condensation reaction of tannin with paraformaldehyde, paraformaldehyde content of each batch was varied. For each run, a sample weight of between 5 and 8 mg was weighed into the sample capsule pan, sealed hermetically, placed in the calorimeter sample capsule holder with an empty reference capsule in the calorimeter reference capsule holder, and heated at 10°C/min, up to an upper limit of 200–230°C. To obtain a baseline for the computation of the heat of reaction, and other kinetic data, the sample was run again. Heat of reaction and other kinetic data were automatically calculated and stored in the thermal analysis system.

Bond Strength Tests

Adhesive formulations, based on acid and subsequent alkaline hydrolyzed tannin, and the different PF fortifiers, are shown in Table I. Three-ply plywood shear specimens were prepared using loblolly (Southern) pine veneer. Bonded panels were subjected to dry and wet (vacuum pressure soak, VPS) bond strength tests. Test specimens, with a bond area of 6.45 cm² (1 in.²), were bonded using a hy-

draulic hot press at a press temperature of 170°C and pressure of 160 psi for 7 min. A glue spread of about 5 g/316.14 cm² (0.158 kg/m²) was used, making sure that glue spread was as even as possible. Bonded panels were subjected to dry, VPS tests. An Instron testing machine (model 1000) was used to determine bond strength of the plywood specimens produced. A shear rate of 2 mm/s was used.

RESULTS AND DISCUSSION

NMR

From the NMR spectroscopy (Fig. 3), there is an indication that some low molecular weight aromatic compounds were produced. This is evident from the appearance of new narrow peaks in the 115–135 ppm region, characteristic of aromatic compounds. The production of these low molecular weight aromatic compounds is presumably from the hydrolysis of the tannin flavonoid compounds. It is believed that this is an indication of interflavonoid bond cleavage resulting in smaller tannin flavonoid molecules.⁹ There was no change observed in the 60–90 ppm band region, which is characteristic of plant gums. This does not, however, rule out hydrolysis of the plant gums.

Table I Adhesive Formulations for Acid and Subsequent Alkaline Hydrolyzed Tannin

Components	Composition									
	1	2	3	4	5	6	7	8	9	10
Untreated tannin	22.7									
Acid and subsequent alkaline hydrolyzed tannin		22.7	16.0	16.0	16.0	22.7	22.7	22.7		
Paraformaldehyde	4.54	4.54	3.0	3.0	3.0	4.54	4.54	4.54		
Water	40.75	40.75	27.0	27.0	27.0	40.75	40.75	40.75		
PF1				4.0						
PF2					4.0					
PF5						6.0				
PF8							6.0			
PF11								6.0		
Phenol			4.01							
Bond strength (MPa)										
Dry	1.46	2.41	2.53	2.30	2.58	2.94	2.70	2.29	2.85	3.55
Wet	0.11	1.34	2.44	1.16	1.94	1.59	1.40	1.00	1.9	2.24
Wood failure (%)										
Dry	0	20	73	50	88	73	29	11	41	23
Wet	0	0	61	8	82	37	13	0	59	83

PFs are the different laboratory prepared phenol formaldehyde resoles. Formulations 9 and 10 are commercial PF resins (cascophen and SPC52, respectively).

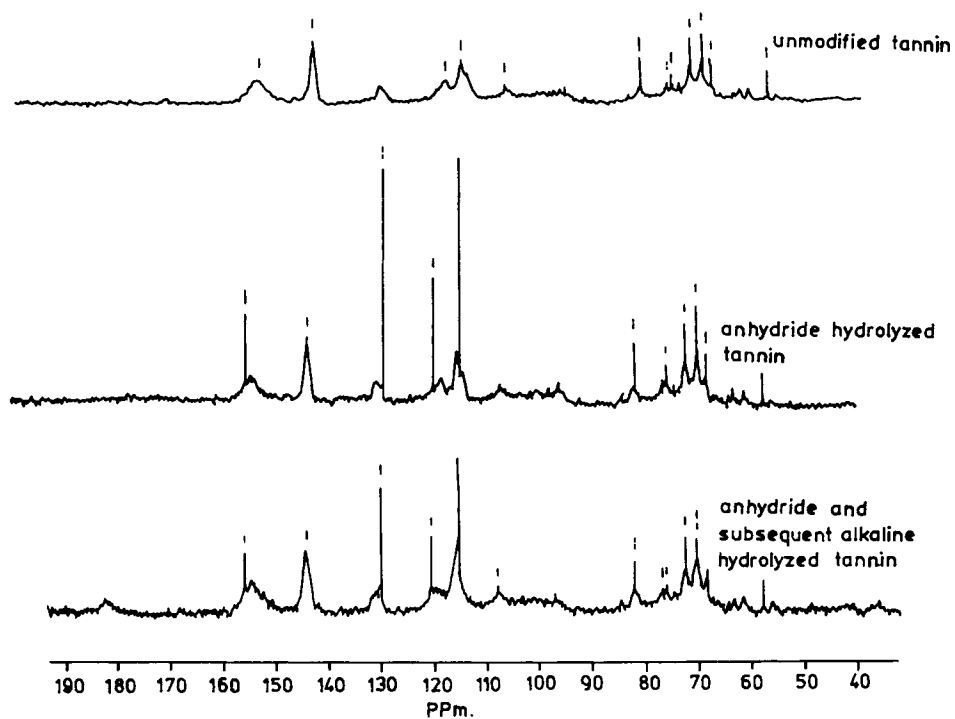


Figure 3. ¹³C-NMR spectra for treated and untreated tannin.

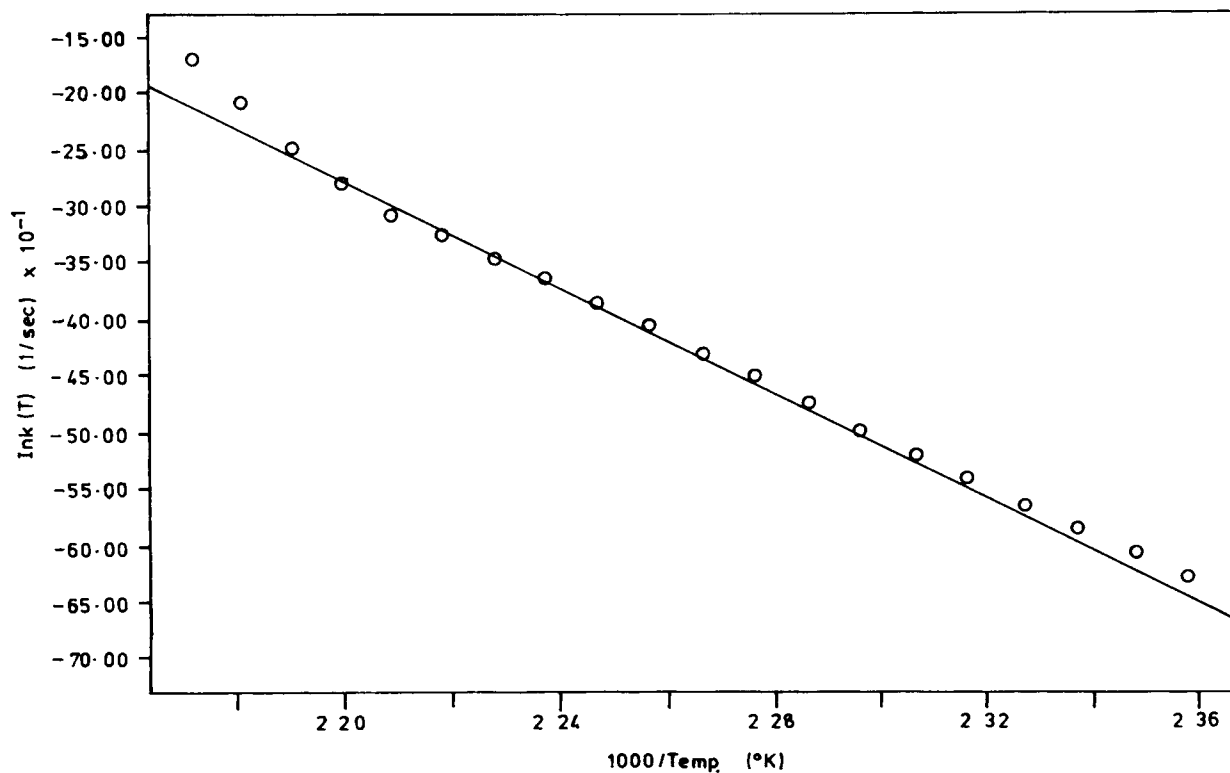


Figure 4. Arrhenius plot for untreated tannin reaction with formaldehyde.

DSC

DSC analysis, for both treated and untreated tannin, shows a great improvement in the overall kinetic properties of hydrolyzed tannin over the untreated tannin (Figs. 4–7). For example, the heat of reaction increased by over 100% when tannin was hydrolyzed (52.1 J/g for untreated tannin and 118.6 J/g for hydrolyzed tannin). Arrhenius plots generated for both the modified and unmodified tannin adhesive also showed a drastic reduction in activation energy when tannin was hydrolyzed: 193 kJ/g for untreated tannin (Fig. 4) and 84.7 kJ/g for hydrolyzed tannin (Fig. 5).

Figure 6 shows how the extent of reaction varies with time at different temperatures (140–180°C) for the untreated and treated tannins, respectively. The slope of the curve is a measure of the reactivity of the adhesive. For the untreated tannin, the reactivity was observed to be very high, especially at high temperatures. This dropped to a near zero value after 5 min, confirming a cessation of further reaction, probably due to premature cure. However, at temperatures about 150°C or below this initial reactivity was not as high as for temperatures above 150°C. The situation is different for treated tannin (Fig. 7). The initial reactivity for the treated tannin was ob-

served to be lower than that of untreated tannin at temperatures above 150°C. The duration of reactivity was much longer while the drop in reactivity was also found not to be as sharp as untreated tannin. These observations suggest that treatment of tannin enhances overall molecular flexibility that in turn slows down the rate of vitrification. This permits a greater level of condensation between molecular active sites. This is consistent with the value for the heat reaction and activation energy for both tannins. But at temperatures below 150°C, the initial reactivity for treated tannin was observed to be higher than for untreated tannin. Therefore, the tendency for premature cure exhibited by untreated tannin is low in treated tannin at elevated temperatures.

Bond Strength

Formulation 1 and 2 (Fig. 8) are nonfortified unhydrolyzed and hydrolyzed tannin, respectively. Comparing the two, hydrolysis of tannin results in a marked improvement in bond strength and wood failures. The wet strength and wet wood failure of hydrolyzed tannin is almost the same as the dry bond strength and wood failure of the untreated tannin. However, when formulation 2 (hydrolyzed tannin)

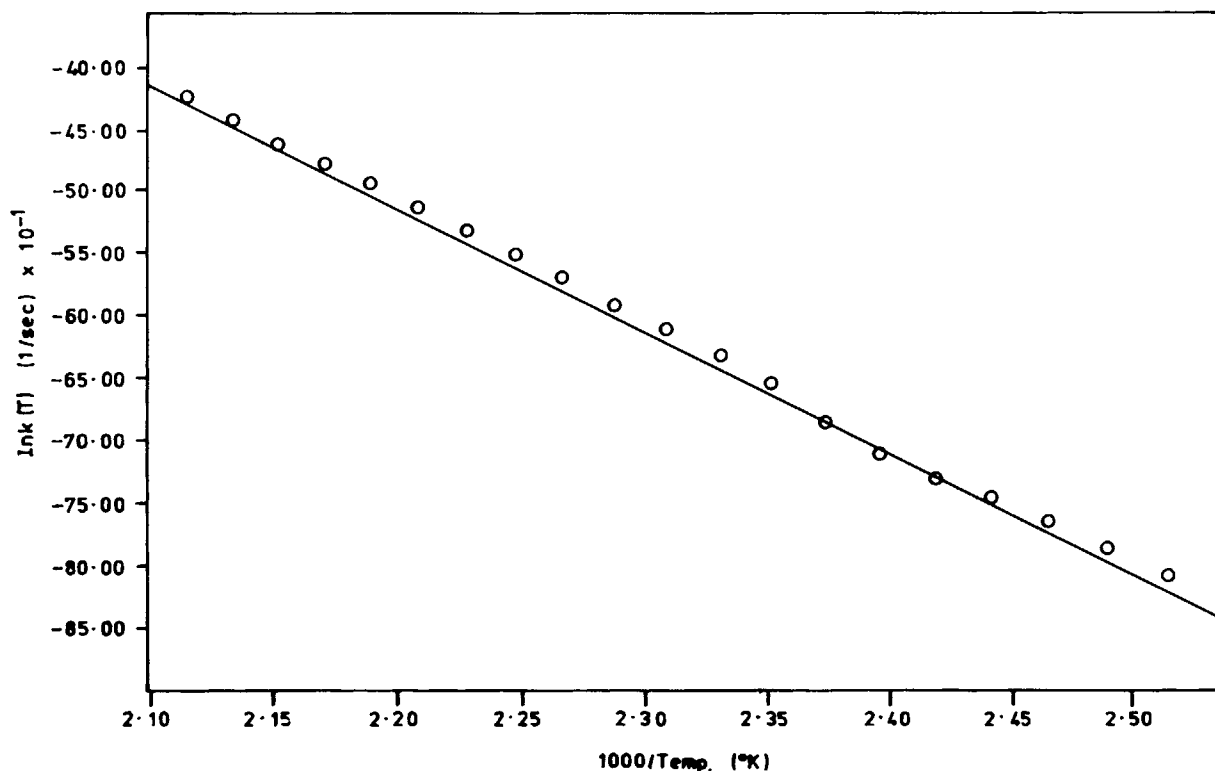


Figure 5. Arrhenius plot for hydrolyzed tannin reaction with formaldehyde.

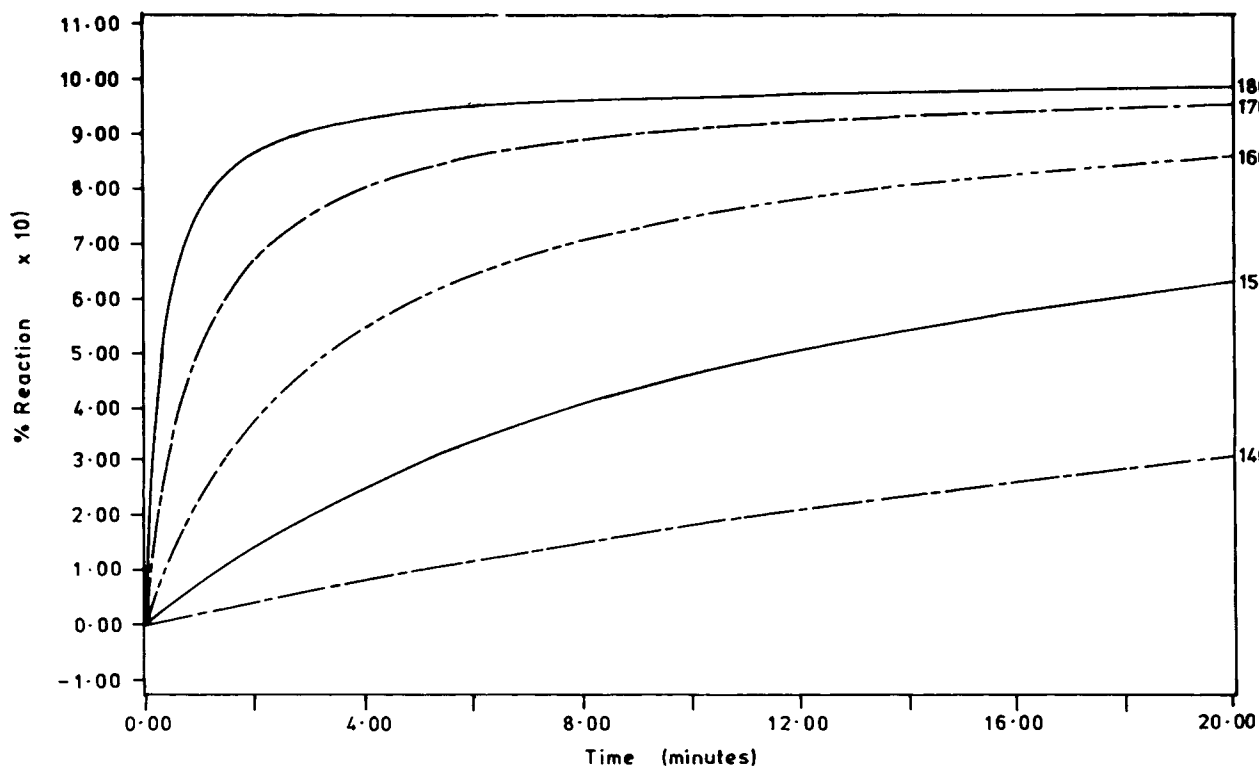


Figure 6. Degree of conversion of untreated tannin with time.

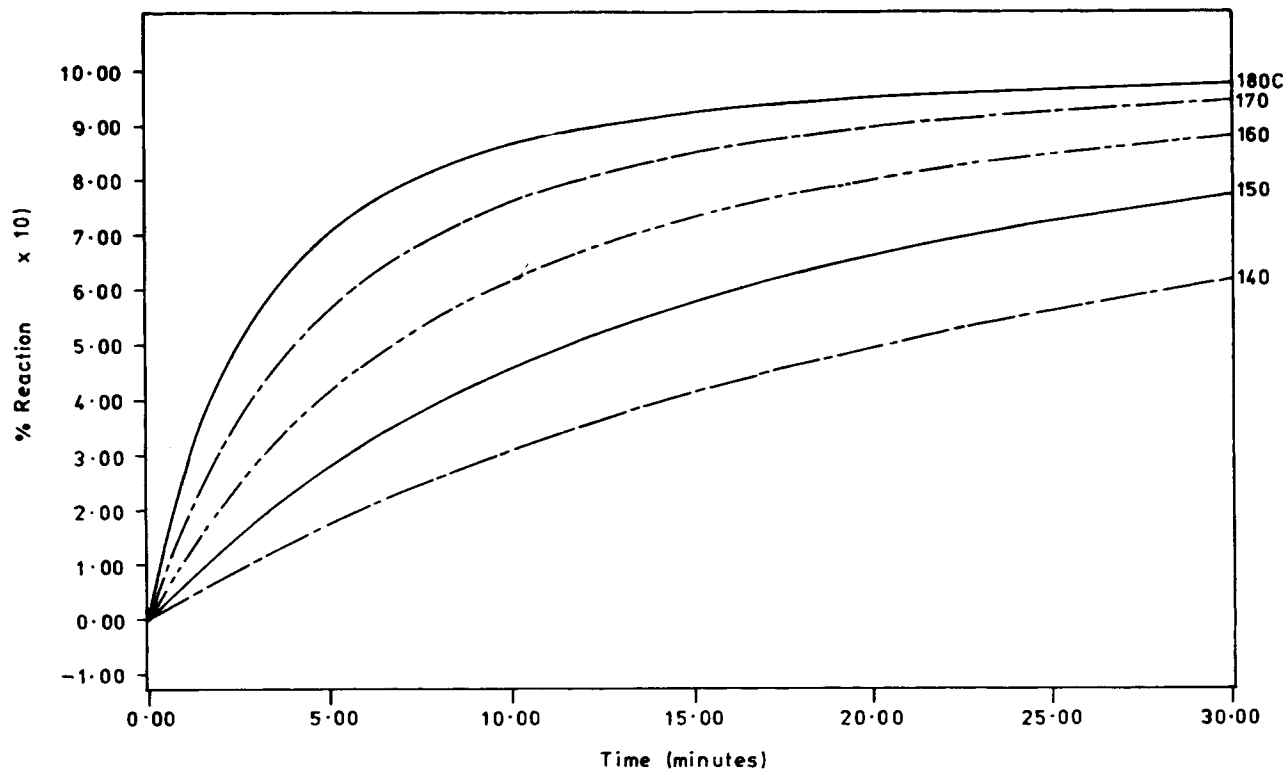


Figure 7. Degree of conversion of hydrolyzed tannin with time.

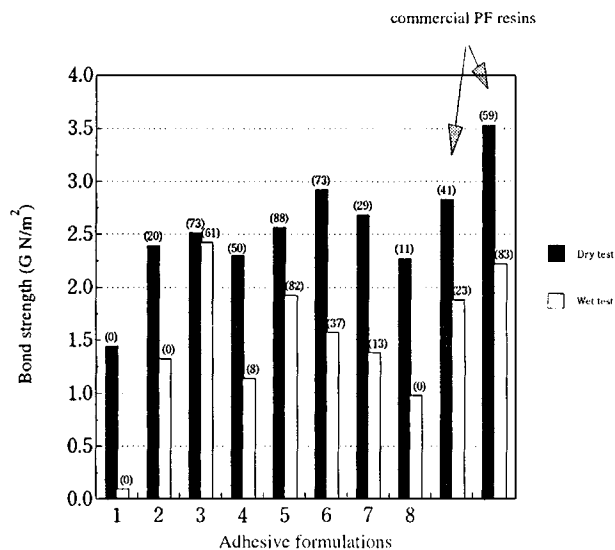


Figure 8. Bond strength of modified and untreated tannin, formaldehyde, and commercial PF resin. Note: wood failures (percentages) are shown in parentheses above each bar.

was compared with either formulation 9 or 10 (commercial PF resin), it was observed that despite the improvement in adhesive properties of hydrolyzed tannin, its bond strength and wood failure were still relatively inferior. This is probably due to the characteristic dry-out problem of tannin in which tannin dries up and degrades rather than melt on heating. However, when fortified with 20% phenol (formulation 3) or with PF resoles (formulations 4–8), the adhesive performance was enhanced. Formulations 3 (hydrolyzed tannin fortified with phenol), 5 (fortified with PF2), and 6 (fortified with PF5) particularly compared favorably with the two commercial PF resins in both dry and wet strength and wood failure. Unlike tannin, these PF resoles and phenol melt at elevated temperatures and would therefore promote a higher level of condensation and penetration of tannin into a wood substrate.

CONCLUSIONS

Anhydride and subsequent alkaline hydrolysis of mangrove tannin caused significant changes in the adhesive properties of mangrove tannin. Activation energy was lowered while heat of reaction was increased, thus promoting a greater level of condensation and reducing the tendency to cure prematurely. Fortifying hydrolyzed mangrove tannin with 20% phenol or PF resin produced plywood with bond strength as good as those derived from some commercial PF resins.

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