Differential scanning calorimetry of hydrolysed mangrove tannin

S Sowunmi,[1]* RO Ebewele,[2] O Peters[3] and AH Conner[4]
[1] *Department of Chemical Engineering, Ahmadu Bello University, Zaria, Nigeria*
[2] *Department of Chemical Engineering, University of Benin, Benin City, Nigeria*
[3] *Department of Chemistry, Ahmadu Bello University, Zaria, Nigeria*
[4] *Forest Products Laboratory, One Gifford Pinchot Drive, Madison, WI 53705, USA*

Abstract: Mangrove-bark-tannin adhesives are potential substitutes for phenol-formaldehyde (PF) wood-bonding adhesives which are derived from petroleum, a finite natural resource. However, mangrove-bark-tannin adhesive exhibits poor adhesive properties, including brittleness, poor wet strength, and poor wood penetration. These shortcomings are due to its high reactivity and structural features. To reduce these shortcomings, the structure of the adhesive was modified by subjecting tannin to (a) caustic hydrolysis and (b) consecutive acetic anhydride and caustic hydrolysis. The effectiveness of these hydrolyses was determined by using differential scanning calorimetry (DSC) to monitor the reaction and cure characteristics of hydrolysed and unhydrolysed tannin with formaldehyde. These hydrolyses resulted in lowering both the activation energy and collision frequency of the cure reaction. Consequently, the initial reactivity of tannin towards paraformaldehyde, which was usually very high, was reduced. The resulting longer reaction time enhanced the extent of reaction, as was evident in the increase in heat of reaction of the hydrolysed tannin.
© 2000 Society of Chemical Industry

Keywords: tannin hydrolysis; initial reactivity; premature gelation

INTRODUCTION

There have been several attempts to replace part of petroleum-derived phenolic compounds with phenolic-type compounds (Mimosa tannin) obtained from renewable sources in wood-bonding adhesives. [1-4] However, tannin-formaldehyde adhesive exhibits brittleness, poor wet strength, and poor wood penetration. Therefore tannin-formaldehyde adhesives needed to be heavily fortified with urea-formaldehyde, phenol-formaldehyde, or resorcinol-formaldehyde to achieve the desired adhesive properties.[2,3,5] However, very little work has been done on tropical forest mangrove tannin.

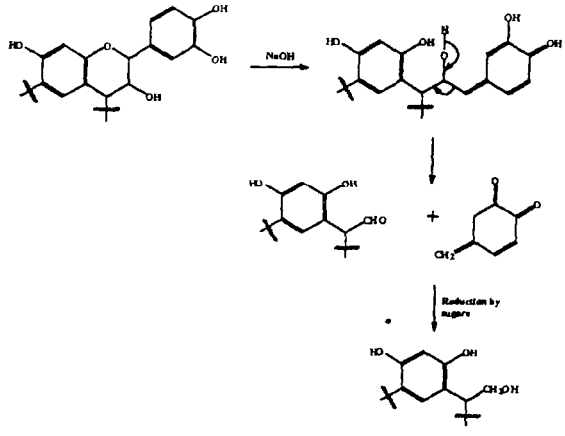
In Nigeria, where mangrove forests abound on the south coast, Ohunyon and Ebewele have attempted to develop mangrove-tannin-based plywood adhesive.[6,7] Their efforts were concentrated on using metal acetates to induce participation of the 'B' ring of the tannin flavonoid molecule in the tannin-formaldehyde condensation reaction. The 'B' ring is normally inert towards formaldehyde except at pH>8, when the reactivity of the 'A' ring towards formaldehyde becomes unacceptably high. High-level (55%) fortification with methylol phenol was found necessary to achieve good adhesive properties. Recent work on mangrove-tannin-based adhesive has shown that the level of adhesive fortification with either phenol or phenol-formaldehyde can be reduced drastically (to about 15%) by hydrolysis with sodium hydroxide and acetic anhydride.[8]

The aim of this study, therefore, was to compare effectiveness of the extent of hydrolysis of tannin by monitoring the relative cure response of the reaction of formaldehyde with hydrolysed and unhydrolysed tannin with differential scanning calorimetry (DSC).

CHEMISTRY OF CONDENSED TANNIN

The tannin polyflavonoid consists essentially of 5-11 monoflavonoid units. In the monoflavonoid unit, two phenolic rings ('A' and 'B'), are joined by a heterocyclic ring (see Scheme 1 below). 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, tannin has a high reactivity towards formaldehyde, and is larger in size. Therefore, during the condensation reaction of tannin with formaldehyde, especially at high temperatures, tannin-formaldehyde resoles become rapidly immobilized due to premature gelation as a result of its high reactivity and molecular size. The result is that condensation does not go far enough to achieve the required adhesive properties. It can therefore be said that the size and the reactivity of the 'A' ring, are most probably responsible for the poor adhesive properties. In addition, the

*Correspondence to: S Sowunmi, Department of Chemical Engineering, Ahmadu Bello University, Zaria, Nigeria
Contract/grant sponsor: Tropical Forest Research Program; contract/grant number: PF-92-1836
(Received 15 June 1999; revised version received 4 November 1999; accepted 12 January 2000)



Scheme 1

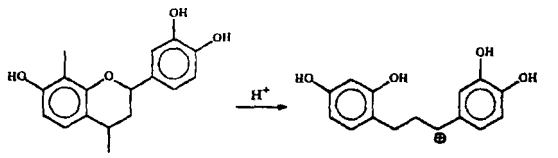
presence of non-tannin compounds such as gums, which are highly-branched polysaccharides, affects the properties of tannin-based adhesive, particularly its moisture resistance.

Hydrolysis of tannin

Caustic hydrolysis of tannin has been reported to cleave the interflavonoid bond and open the heterocyclic ring, joining the 'A' and 'B' rings of the flavonoid unit.[9] A proposed mechanism based on this study is shown in Scheme 1.

Acid hydrolysis has been shown to open the heterocyclic ring of polyflavonoids easily, with the formation of a carbo-cation which is capable of reacting with another nucleophile present.[4] This is represented by Scheme 2.

Pizzi and Stephanou[10] reported an improvement in the performance of a non-fortified mimosa-tannin-based adhesive developed by subjecting tannin extracts to acetic anhydride and subsequent alkaline treatment. They suggested the following as probable reasons for the improved adhesive performance.[10] (i) Cleavage of tannin interflavonoid bond. This results in smaller, more mobile tannin flavonoid compounds and therefore enhances the level of condensation with formaldehyde. (ii) Opening of the heterocyclic ring joining the 'A' and 'B' rings of tannin flavonoid compound leads to a more flexible compound, reduces the stiffness of the tannin molecules and consequently the brittleness of the adhesive. (iii) 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 tannin-based adhesive. However, their corresponding sugars (of low molecular weight) do not have much effect on 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.



Scheme 2

EXPERIMENTAL

Extraction of tannin

The hot water extraction adopted in this work essentially entails heating 500g of bark in 3L of water at 90°C for 5h, and filtering the extract from the bark through a 100 circles per inch^2 filter paper, and drying the filtrate in an oven at about 40°C

Caustic hydrolysis

Fifty parts by weight of mangrove tannin extract were heated with 95 parts of distilled water, to about 90 °C. The reaction mixture was brought to pH 8 by gradually adding 33% NaOH solution. The reaction was allowed to go on for 1-5h. The reaction products were cooled and dried, after which they were subjected to DSC analysis.

Consecutive acetic anhydride and caustic hydrolysis

In this hydrolysis, the method used by Pizzi and Stephanou[11] was adopted, as described below. Fifty parts by weight 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 1h (this acid hydrolysis time was varied between 1 and 3 hours). After that, the reaction mixture was brought to pH 8 by adding about 22.5 parts of 33% NaOH solution. The reaction was left to proceed for another 3h, after which it was cooled and dried by vacuum evaporation at about 40°C. The resulting hydrolysed tannin is hereafter referred to as doubly-hydrolysed tannin. This was also subjected to DSC analysis.

Differential scanning calorimetry (DSC)

One part of unhydrolysed tannin extract or hydrolysed tannin was dissolved in four parts of water, and paraformaldehyde added to the tannin solution. For each run, a sample weight of between 5 and 8 mg was weighed into a sample capsule pan, which was sealed hermetically and placed in the calorimeter sample capsule holder. An empty reference capsule was placed in the calorimeter reference capsule holder. The heating rate and an upper temperature limit were set at 10 °C per minute and 200-230°C, respectively. To obtain a baseline for the computation of the heat of reaction and other kinetic data, the sample was run again. The heat of reaction and other kinetic data were

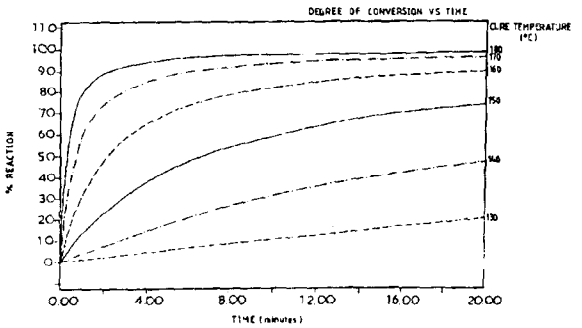


Figure 1. Cure characteristics of unhydrolysed tannin reaction with formaldehyde (10%).

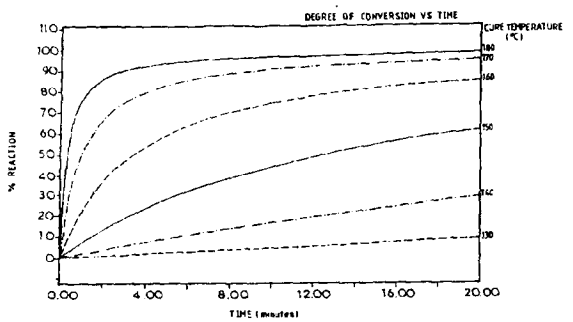


Figure 2. Cure characteristics of unhydrolysed tannin-fomlaldehyde reaction (with 20% paraformaldehyde).

automatically calculated and stored in the Perkin Elmer 7 Series thermal analysis system.

For the unhydrolysed tannin, paraformaldehyde contents corresponding to 5, 10, 15, 20, 25 and 30 wt% based on weight of dry tannin were used, while for the caustic hydrolysed and the doubly-hydrolysed tannin, 2wt% paraformaldehyde was used.

RESULTS AND DISCUSSION

Figures 1 and 2 show the typical variation of the extent of reaction with time and temperature for unhydrolysed tannin-formaldehyde adhesives. We observe that for reaction temperatures of 160°C and above, the initial reactivity was very high as shown by the steepness of the thermogram. This was followed by a plateau in the thermogram after about 5 min reaction time. The plateau represents a cessation of the reaction of tannin with formaldehyde. However, at a temperature of 150°C and below, the observed initial reactivity, as represented by the steepness of the thermogram, was considerably reduced; in fact, for the cure carried out at 130°C, the reactivity was very low.

Figures 3-6 are typical thermograms for the reaction of hydrolysed tannins with formaldehyde at various temperatures. We observed a number of significant differences between the cure kinetics of the hydrolysed and unhydrolysed tannin adhesives,

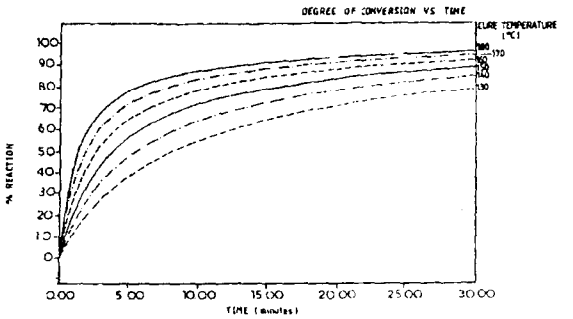


Figure 3. Cure characteristics of 2h caustic hydrolysed tannin reaction with formaldehyde (20 wt%)

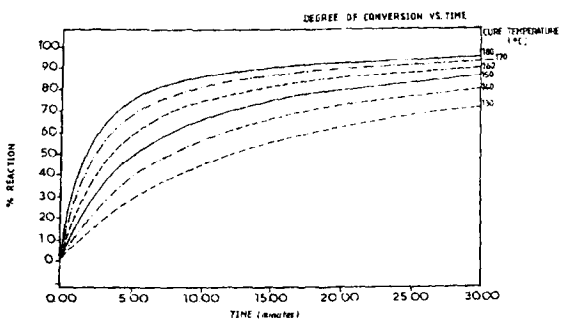


Figure 4. Cure characteristics of 5h caustic hydrolysed tannin reaction with formaldehyde (20 wt%).

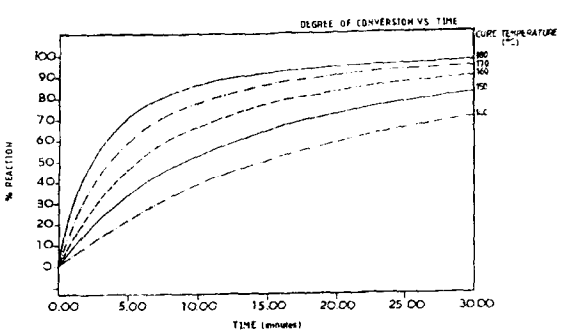


Figure 5. Cure characteristics of 2h acetic anhydride and subsequent caustic hydrolysed tannin reaction with formaldehyde (20wt%)

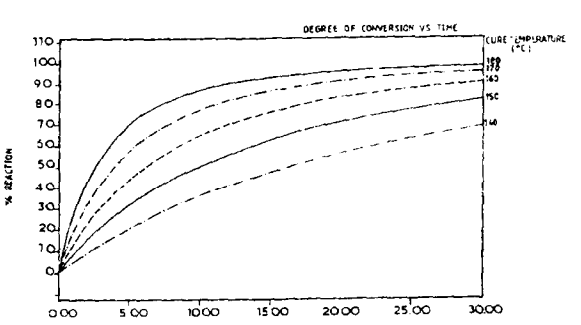


Figure 6. Cure characteristics of 3h acetic anhydride and subsequent caustic hydrolysed tannin reaction with formaldehyde (20wt%)

Table 1. Initial reactivities of unhydrolysed and hydrolysed tannin towards formaldehyde

Temperature (°C)	Unhydrolysed tannin	Initial reactivity[a]							
		Caustic hydrolysis time (h)					Anhydride hydrolysis time (h)		
		1	2	3	4	5	1	2	3
180	3323	840	850	980	930	930	520	539	580
170	1564	630	810	740	630	700	340	370	400
160	422	410	540	510	480	450	210	240	300
150	131.6	270	390	350	350	330	120	160	170
140	36	160	290	250	250	220	72	100	100
130	8	99	190	150	164	140			

[a] $\left(\frac{dr}{dt}\right) \times 10^3 s^{-1}$.

(1) The initial high reactivity of the unhydrolysed tannins at temperatures above 160°C has been significantly reduced in the hydrolysed tannins.
(2) For the hydrolysed tannin adhesives, there is no clearly defined plateau in the thermograms even at high cure temperatures (above 160 °C), indicating that there is no complete cessation of reaction between the hydrolysed tannin and formaldehyde.
(3) The clear demarcation in the cure behaviour of unhydrolysed tannin adhesives cured at high temperatures (above 160°C) and those cured at lower temperatures (below 150°C) was not evident in the hydrolysed tannin adhesives.

The slope of the thermogram denotes the reactivity of tannin with formaldehyde. Table 1 shows the initial reactivities (slopes) of the unhydrolysed and hydrolysed tannin adhesives at various cure temperatures. The initial reactivities for the caustic hydrolysed and doubly-hydrolysed tannin adhesives are observed to be much lower than the corresponding reactivity of the unhydrolysed tannin-formaldehyde adhesives at temperatures greater than 150°C. The doubly-hydrolysed tannin-formaldehyde adhesives exhibited the least initial reactivity. Furthermore, the drop in reactivity with decreasing cure temperature for the hydrolysed tannin adhesives was not as sharp as that for the unhydrolysed tannin adhesives. Indeed, at temperatures below 150°C, the initial reactivities for the hydrolysed tannin-formaldehyde adhesives were higher than for the corresponding unhydrolysed tannin-formaldehyde adhesives.

Two molecular phenomena occur as most liquid thermosetting polymers cure. The first is gelation, which corresponds to incipient formation of an infinite network. The second is vitrification, which occurs when the glass transition temperature (T_g) of the reaction mixture rises to the cure temperature. At gelation, resin fluidity decreases substantially even though the reaction rate is still kinetics-controlled. With continued cure, the T_g reaches the cure temperature and vitrification occurs. At this point, the reaction rate becomes diffusion-controlled and is drastically reduced. The observed differences in the cure characteristics between the hydrolysed tannin

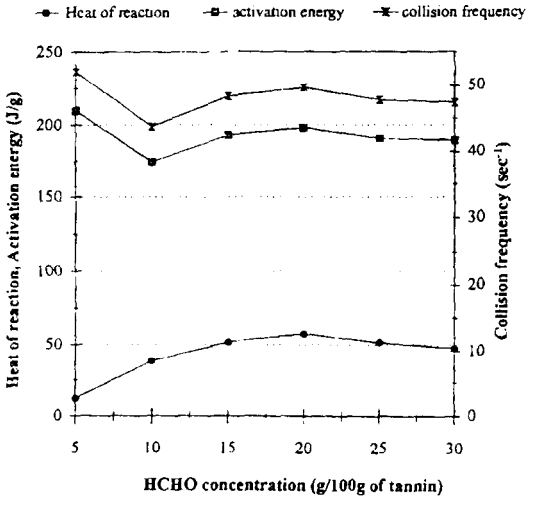


Figure 7. Kinetic parameters of unhydrolysed tannin-formaldehyde reaction

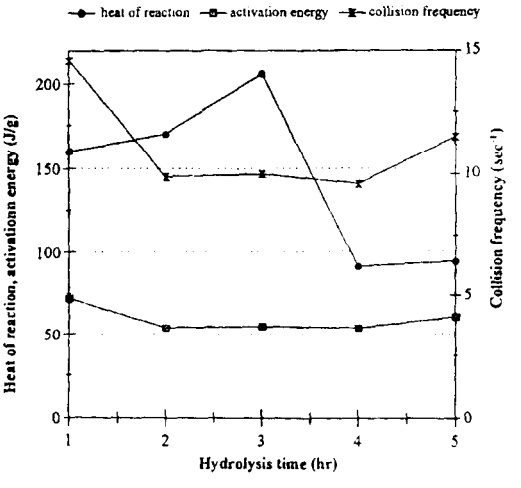


Figure 8. Kinetic parameters of caustic hydrolysed tannin-formaldehyde reaction (using 20% HCHO).

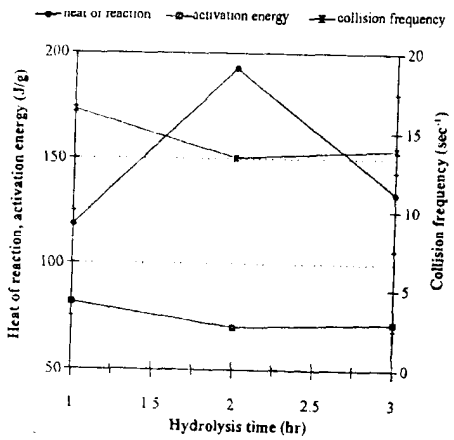


Figure 9. Kinetic parameters of doubly hydrolysed tannin-formaldehyde reaction (using 20% HCHO).

adhesives and the unhydrolysed tannin adhesives can be explained on the basis of these views. It is apparent that for the reaction of the unhydrolysed tannin with formaldehyde at high temperature, the high initial reactivity resulted in early vitrification, thus rapidly immobilizing the large and stiff tannin molecules. The resulting adhesive would only be partially cured and be internally stressed. Such an adhesive would be susceptible to physical breakdown and consequently exhibit poor adhesive performance. In contrast, for the reaction of the hydrolysed tannins with formaldehyde, the reduction in the initial cure rate precluded early vitrification, thus increasing the extent of cure.

The above observations are consistent with the kinetic data derived from the DSC runs. Figures 7-9 show the variation of kinetic parameters for the reaction of unhydrolysed and hydrolysed tannins with formaldehyde. The DSC runs for the hydrolysed tannins were carried out at a paraformaldehyde concentration of 20wt%. It is instructive, therefore, to compare the kinetic parameters for the hydrolysed tannin and unhydrolysed tannin adhesives at this concentration of paraformaldehyde. Irrespective of the duration of hydrolysis, the collision frequencies and activation energies of the hydrolysed tannin adhesives were consistently lower than those of the unhydrolysed tannin adhesives, whereas the heats of reaction of the hydrolysed tannin adhesives were higher than that of the unhydrolysed tannin adhesive. For example, the maximum observed heats of reaction for the caustic-hydrolysed and doubly-hydrolysed tannin adhesives were 206 Jg^{-1} and 193 Jg^{-1}, respectively, compared with 52 Jg^{-1} for the unhydrolysed tannin adhesive. Similarly, the activation energy decreased from 198 Jg^{-1} for the unhydrolysed tannin adhesive to 54Jg^{-1} for the caustic-hydrolysed tannin adhesive and about 34Jg^{-1} for the doubly-hydrolysed tannin adhesive. The reduction in the collision frequencies for the hydrolysed tannin adhesives suggests a reduction in the overall mobility of the reacting species. This provides the reacting molecules with enough time to arrange themselves properly to engage in fruitful collisions. A proper orientation of the reacting species translates into a reduction in the activation energy. The overall consequence of these effects is an increased extent of reaction as reflected by the relative magnitudes of heat of reaction or cure extent of the hydrolysed and unhydrolysed tannin adhesives.

CONCLUSIONS

Consecutive acetic anhydride and caustic hydrolysis of mangrove tannin resulted in significant changes in the kinetic behaviour of tannin reaction towards paraformaldehyde. The heat of reaction of tannin was greatly increased by hydrolysing tannin. In addition, the initial reactivity and consequently the premature gelation of tannin adhesive was reduced. This ensured an increase in the heat of reaction or extent of cure. The activation energy was lowered by these hydrolyses.

ACKNOWLEDGEMENTS

This work was done at the Forest Products Laboratory, Madison, WI, under the Tropical Forest Research Program. The financial support provided by this programme (Contract PF-92-1836) is gratefully acknowledged.

REFERENCES

1 Pizzi A and Scharfetter HO, *J Appl Polym Sci* **22**:1745 (1978).
2 Pizzi A, *J Appl Polym Sci*, **22**:2717–2718 (1978).
3 Pizzi A and Roux DG, *J Appl Polym Sci* **22**:1945 (1978).
4 Pizzi A, in *Wood Adhesives: Chemistry and Technology* ed by Pizzi A, Marcel Dekker, New York, pp 177–231 (1983).
5 Pizzi A, *J Appl Polym Sci* **23**:2777 (1979).
6 Ohunyon PE, Ph D thesis Faculty of Science, Ahmadu Bello University, Zaria (1992).
7 Ohunyon PE and Ebewele RO, *Adhes Age*, **35**(3):35–40 (1992).
8 Sowunmi S, Conner AH, River BH and Ebewele RO, *J Appl Polym Sci* **62**:577 (1996).
9 Pizzi A, *Int J Adhesion Adhesives* **2**:213–214 (1981).
10 Pizzi A and Stephanou A, *Holzforsch Holzverwert* no **4**:(1992).
11 Pizzi A and Stephanou A, *Holzforsch Holzverwert* no **2**:(1993).