

Development of Wood-Products Adhesives from Mangrove Bark

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Synopsis

Mangrove bark was extracted using either water, ethanol, acetone, or various binary mixtures of these, as solvent. With plywood panels as substrates, joints prepared with adhesives derived from these extracts were tested for strength properties. In terms of the quantity of extracts from mangrove bark, water was the most effective solvent, followed sequentially by ethanol and acetone. However, in terms of the tannin content of these extracts, the order of extraction effectiveness of these solvents was reversed. The use of solvent mixtures in tannin extraction did not produce an observable synergistic effect. The quantity of extract and its tannin content were dictated primarily by the predominant solvent in the binary mixture. The reactivity of mangrove bark extracts is influenced significantly by formaldehyde concentration, cure temperature, type, and pH of the adhesive medium. Adhesive joints of significant bond strength were obtained from mangrove tannin adhesives. Prolonged cure periods, particularly at elevated temperatures, have deleterious effects on the strength properties of these adhesive joints.

INTRODUCTION

Over the last four or five decades phenolic adhesives for wood products have been derived largely from petroleum—a finite natural resource. Some efforts, of course, have been devoted to developing thermosetting phenol-formaldehyde-type adhesives from vegetable origins.¹⁻⁷ However, following the recent upsurge in the price of petroleum due to the 1973 Arab-Israeli war, the search for adhesives from renewable resources has acquired added impetus.⁸⁻¹⁷ The research efforts have been aimed at obtaining substitute phenolics whose quality and performance as adhesives for products from wood would equal those of phenolic adhesives. Tannin extracted from tree bark and other natural resources represent such potential substitute phenolics. Bark generally contains a high percentage of polyphenolic tannins. These are condensed tannins polymers of hydroxylated flavanoid constituents.¹⁸ Hillis and Urbach¹⁹ and Scharfetter²⁰ contend that the A-ring of polymeric flavanoids is the only one able to react with formaldehyde in conditions generally used in wood adhesives; the B-rings, which in flavanoid carry two hydroxyl groups, can react only at pH 10 where the extremely fast reactivity of the A-ring yields adhesives of little practical value.

The research effort described here is therefore geared towards exploiting the adhesive potential of Nigeria's rich forests. Our initial focus has been on the mangrove forests found in the coastal areas of the country. The overall objective is to determine the technical feasibility of using mangrove bark (*Rhizophora mucronata*) as the reactive component of phenol-formaldehyde (P-F)-type adhesives for wood products. The specific objectives are threefold:

- (i) Establish the best extraction method for mangrove bark that would yield effective tannins for P-F-type adhesives.
- (ii) Characterize the extracted tannins so as to establish the optimum bonding conditions for the adhesives derived from these extracts.
- (iii) Perform preliminary bonding tests with these adhesives using plywood panels as substrates.

EXPERIMENTAL

Bark Collection and Preparation. Fresh and dry barks from mangrove trees were collected from Ikoyi park in Lagos State of Nigeria. The samples were from the middle to lower portion of the tree trunk. The barks were stored in cellophane bags for about 4 days, and thereafter removed and air-dried in an open space in the laboratory for 8 days till they were crisp. The samples were then ground with a grinding machine to particle size 1-mm sieve screen.

Bark Extraction. In order to establish the most suitable length of time of extracting the useful substances for adhesive formulation from the samples studied (the properties of which might be different in some respects from those on which work has been carried out¹⁻⁵), extraction for selected lengths of time was decided. Cold leaching of the ground air-dried bark material was carried out using as solvents either single or binary mixtures of various composition chosen from among water, ethanol, and acetone. 250 cm³ of the pure solvent or solvent mixture, added to 25 g air-dried ground bark in a conical flask, was agitated in a mechanical shaker. At the end of the extraction period, which varied from 1 to 7 days, the bark was filtered from the extract using a Buchner's flask with whatman filter paper no. 540. The residue was vacuum oven-dried at 105°C to a constant mass. The filtrate (extract solution) was concentrated to about 50 cm³ using a Buchi rotor evaporator at a temperature below 40°C and then put in a thermostated vacuum oven operated at 20°C. The extract was finally obtained as a powdered mass. The process of obtaining the powdered extract was the same in all cases except for those solvent mixture whose water content exceeded 50%. In these cases, the temperature of the Buchi rotor evaporator was increased to 55°C. The percent extractive content of bark was computed on the basis of the original air-dried bark sample.

Determination of Tannin Content of Extract. Tannin content was determined according to the procedure established by Wissing.²¹

Characterization of Tannins. No attempt has been made here to elucidate the structural details of the tannin extracts. Instead, initial characterization efforts were confined to determining the effects of some pertinent variables on the reactivity of the extracts so as to establish optimum bonding conditions. Besides, only the extracts obtained with water as solvent were used in these tests.

Gelation Times of Mangrove Tannin-Formaldehyde Adhesives. The reaction between mangrove extract and formaldehyde (in the form of paraformaldehyde) under various reaction conditions were studied by observing the gelation time. Following Dalton,¹ the gelation time was taken as the period elapsing until the sample could support a 25 g glass rod of 0.375-in. diameter. The effects of the following variables on gelation time were considered:

- (i) *Type of Solvent and pH of Adhesive.* 45% aqueous solutions of mangrove bark extract (from 5 g of extract in water) were adjusted to the desired pH value

by adding either 10% NaOH or 5% sulfuric acid as required. The test tubes containing the solutions were then placed in a water bath maintained at 80°C. 10% paraformaldehyde powder, based on the total solids content of solutions, was added after the solution had reached the desired temperature of 80°C. The gelation time was then measured. The experiment was repeated using 50% aqueous ethanol instead of pure water as the solvent medium for the adhesive.

(ii) *Paraformaldehyde Concentration.* 6-g samples of tannin extract in 6 cm³ of water were mixed with 1 cm³ of glycerol and placed in a water bath maintained at 80°C. The samples were all maintained at a pH of 4.5 by the addition of 10% sodium hydroxide solution. Different amounts of paraformaldehyde (ranging from 2% to 30%) relative to the mass of the total solids were added after the solution had reached 80°C, and the gelation times were then measured.

(iii) *Reaction Temperature.* 5 g of mangrove bark extract in 5 cm³ of water was mixed in a test tube and placed in a water bath maintained at a required temperature (20°C, 40°C, 60°C, 70°C, and 80°C). The gelation times were measured at these temperatures. All the extract solutions were maintained at a pH of 4.5 and had a paraformaldehyde concentration of 10%.

Adhesive Preparation. 2 g of freshly prepared extract was introduced into a test tube containing 2 cm³ of the corresponding solvent used in the extraction. The test tube and its contents were heated at 60°C for 15 min in a water bath and then cooled. For the adhesive prepared from extracts obtained with binary solvent mixtures, 0.5 cm³ of glycerol was added to the mixture at this stage, and then heated for an additional two minutes. The cooled mixture was adjusted to pH 7.5 with 10% NaOH. Paraformaldehyde (10% total solids) was then added, and the contents of the test tube mixed thoroughly.

Bonding Procedure. Plywood specimens (hardwood surface) of dimensions 13.0 cm × 2.5 cm × 1.0 cm were roughened on the surfaces to be bonded. The adhesive was then applied finally by a brush on the surfaces to be mated. Open and closed assembly times were 8 and 5 min, respectively. The test specimens were of simple lap joint type with a 5-cm overlap.

Adhesive Curing and Fracture Tests. Adhesives joints derived from extracts obtained with pure water as solvent were cured for various lengths of time (1–13 h). Curing was carried out at various temperatures (80–140°C) using a Moor hand press machine with a pressure of 2 tons. For the adhesives joints prepared from extracts obtained from the various solvent mixtures, curing was done at 120°C for 4 h under a pressure of 2 tons using the same machine. All samples were tested in shear on a Denison testing machine of 50 tons capacity. The crosshead speed used was 2 cm/min.

For comparative purposes, some bonded test specimens were boiled in hot water for 3 h before fracture tests were carried out. These constituted the wet tests. For the dry tests, specimens were fractured without boiling.

RESULTS AND DISCUSSION

Bark Extractive Content of Single Solvents

Figure 1 shows the effect of duration of cold extraction with pure solvents (water, ethanol, and acetone) on the quantity of extractable material. The relative

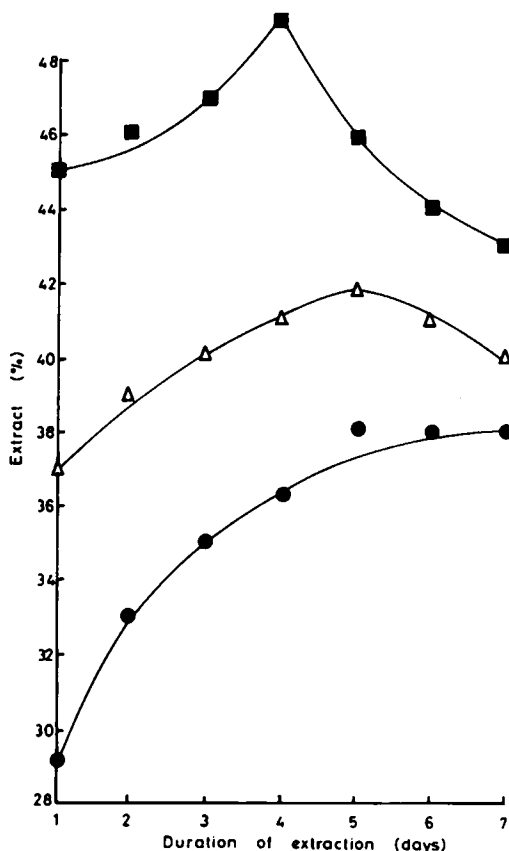


Fig. 1. The effect of duration of cold extraction with single solvents on quantity of total extractable material: (■) water; (Δ) ethanol; (●) acetone.

effectiveness of the solvents is in the order: water > ethanol > acetone. The plots for both water and ethanol extracts, however, showed a maximum (49% and 42%, respectively) after the fourth or fifth day of extraction. The downward trend in the amount of extract after the maximum was more drastic for water than ethanol. The corresponding plot for extraction with acetone exhibited a plateau (38%) after the fifth day of extraction.

Over the entire period of extraction, the tannin content of extract was highest for acetone extraction (max 76%) followed by ethanol (max 64%) and least for water (max 54%) (Fig. 2). Thus, even though acetone extractable material was least in quantity, acetone was decidedly most specific for tannin extraction.

Bark Extractive Content of Binary Solvent Mixtures

Figure 3 is a typical plot showing the effectiveness of binary solvent mixture in the extraction of mangrove bark. The corresponding typical plot for the tannin contents of extracts is shown in Figure 4. The trend of the two plots is similar to those of the pure single solvents. Compare with Figures 1 and 2, respectively. It should be specifically noticed that the behavior of a particular plot closely paralleled that for extracts obtained using the predominant solvent

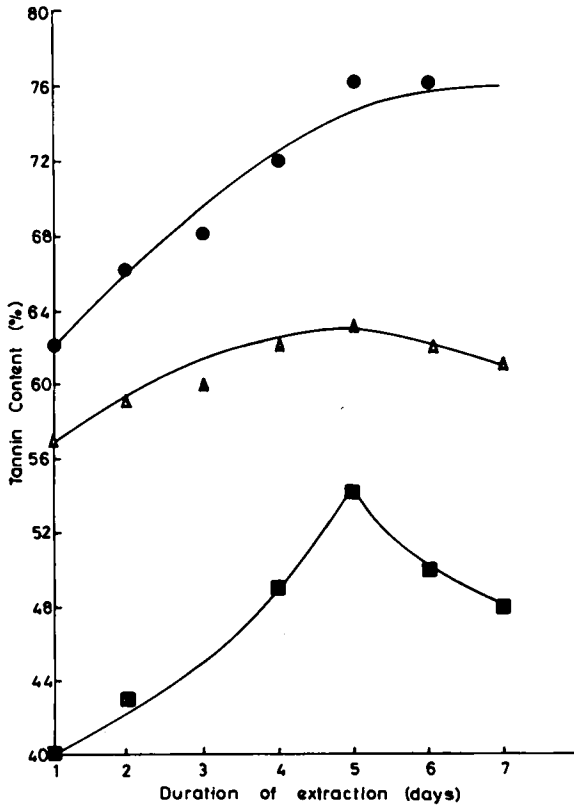


Fig. 2. Tannin content of the total extracts of bark with three different solvents: (■) water; (Δ) ethanol; (●) acetone.

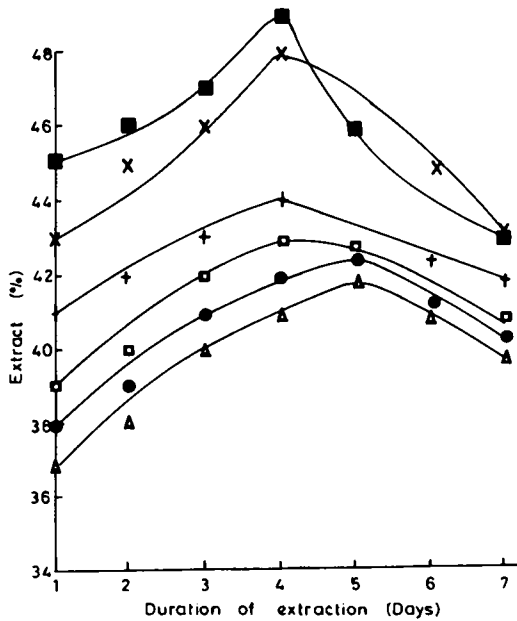


Fig. 3. The variation of total extractable materials from the barks with mixtures of water and ethanol. H₂O (vol %): (■) 100; (X) 90; (+) 50; (□) 30; (●) 10; (Δ) 0.

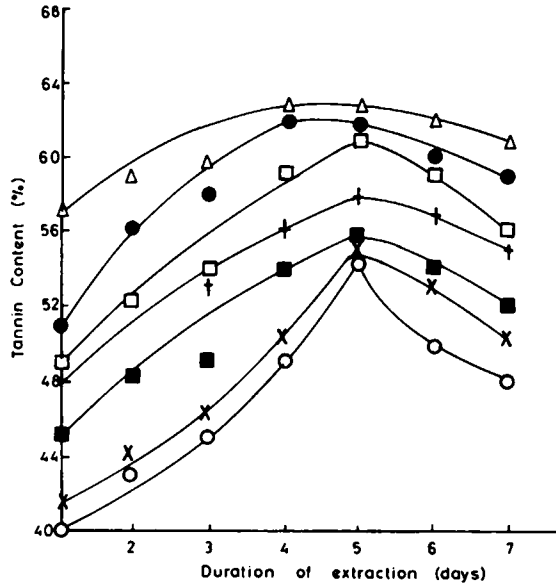


Fig. 4. Tannin content of total extracts from barks with mixtures of water and ethanol. H₂O (vol %): (○) 100; (×) 90; (■) 70; (+) 50; (□) 30; (●) 10; (Δ) 0.

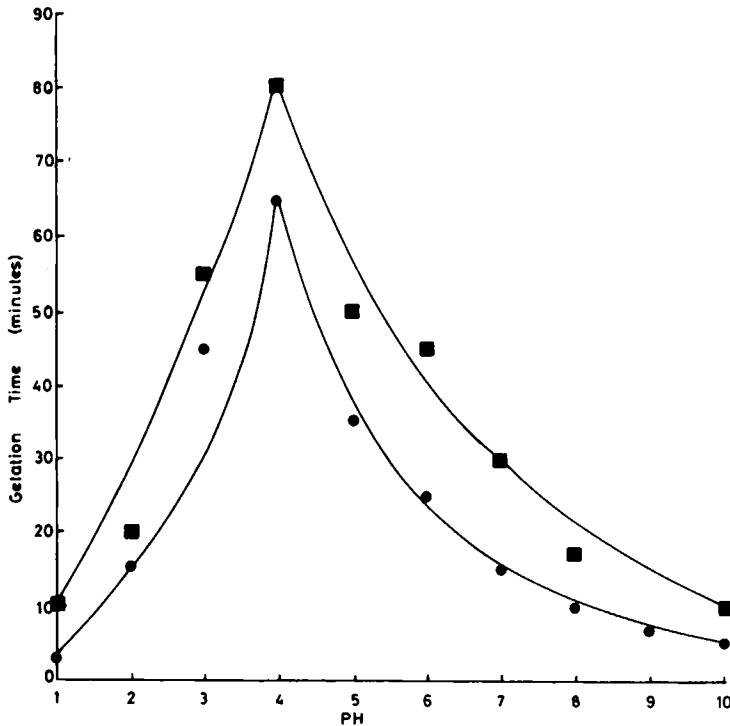


Fig. 5. The dependence of gelation time on the tannin solutions of mangrove bark extract on the type and pH of extraction medium: (■) 50/50 water/ethanol (v/v); (●) 100% water.

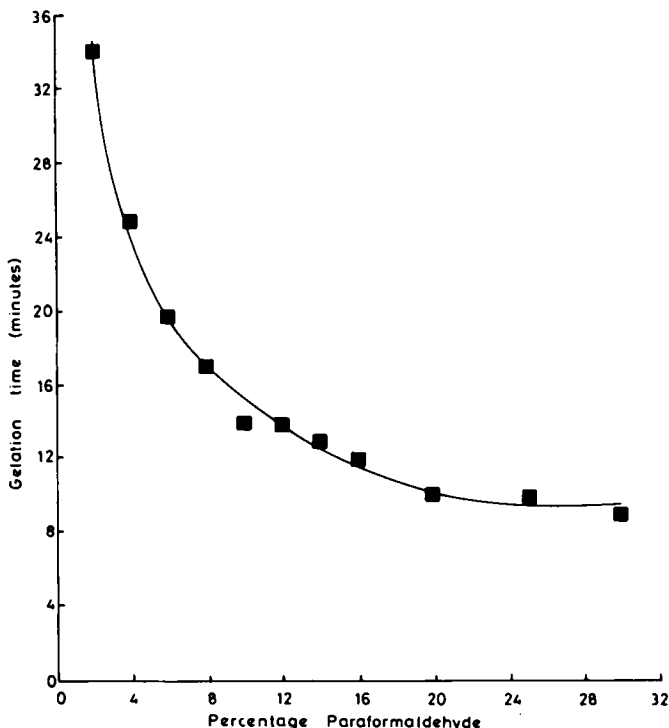


Fig. 6. Influence of paraformaldehyde on gelation time of a tannin extract of bark.

in the solvent mixture. The largest quantity of extracts and their tannin contents, for different compositions of the various solvent mixtures, occurred in the intermediate range between those of the pure solvents comprising the mixtures. The quantity of extract and its tannin content was dictated by the predominant solvent in the mixture except for extracts from ethanol-acetone system where this general trend was not strictly observed. Thus, for the solvents used in this investigation, the use of their binary mixtures did not necessarily improve the effectiveness, i.e., no synergistic effects were observed.

Reactivity of Mangrove Bark Extract Adhesives

The dependence of the reactivity of mangrove bark extract adhesives towards formaldehyde on the type and pH of medium is illustrated in Figure 5. It would be observed that the highest reactivity occurred at highly acidic and moderately alkaline conditions. From the pH values considered in our experiments, minimum reactivity, i.e., longest gelation time, occurred at about pH 4. It is also observable from Figure 5 that a change of medium from purely aqueous to aqueous ethanol resulted in a retardation of the reactivity of mangrove bark extract adhesives, in support of the earlier reports.^{1,5}

Figure 6 shows the influence of paraformaldehyde on the reactivity of adhesives from mangrove bark extracts. A rapid change in gelation time with increase in paraformaldehyde occurred up to about 20%. Beyond this point no change in reactivity was noticeable. Gelation time decreased very rapidly with cure

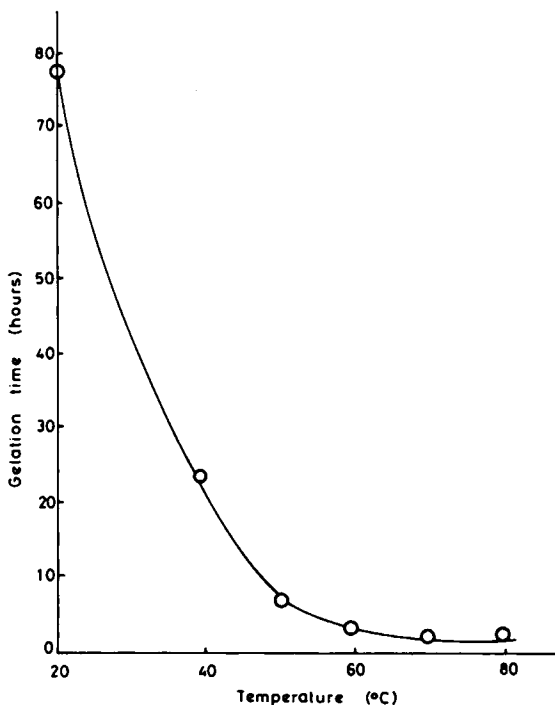


Fig. 7. Effect of temperature on gelation time for the tannin resins in Figure 6.

temperature: from about 78 h at ambient temperature to less than 1 h at temperatures equal to or greater than 70°C (Fig. 7).

Tests of Bond Strength

(i) **Cure Temperature and Time.** Both cure temperature and cure time were varied to determine their effects on the resultant adhesive bond strength of a simple lap joint with plywood as substrates. Dry and wet shear strength tests were carried out. A typical result is given in Figure 8 for dry and wet tests on samples cured at 80°C. Figure 9, however, compares the results for dry tests on specimens cured at four different temperatures. At a particular cure temperature, prolonged cure periods resulted in a drop in bond strengths for both wet and dry test specimens. The values of the maximum bond strength and the cure time at which the maxima occurred were higher for dry test specimens than for the corresponding wet test specimens. Very high cure temperatures did not necessarily result in adhesive joints with the highest bond strengths (Fig. 9). In fact, prolonged cure at very high temperatures resulted in a drastic reduction in bond strength. This was particularly obvious for specimens cured at 140°C, where the deterioration of bond strength occurred even at short cure periods of about 5 h. Thus, for bonds of good strengths, short times of about 3–4 h are needed when curing is done at high temperatures of 140°C and possibly above.

(ii) **Composition of Binary Solvent Mixtures (v/v).** Figure 10 shows the effects of the type and composition of solvent mixture on the bond strength of

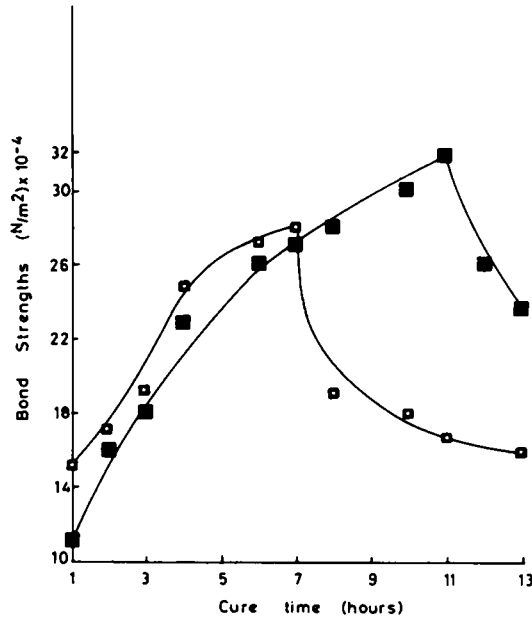


Fig. 8. Variation of bond strength of substrates bonded with adhesives from the tannins of mangrove bark on curing at 80°C: (■) dry test; (□) wet test.

mangrove tannin adhesive joints. Adhesive joints derived from water-ethanol solvent mixture extracts had the highest bond strengths followed by those from water-acetone and ethanol-acetone solvent mixtures, respectively. The strength of the joints derived from extracts from water-acetone and ethanol-acetone

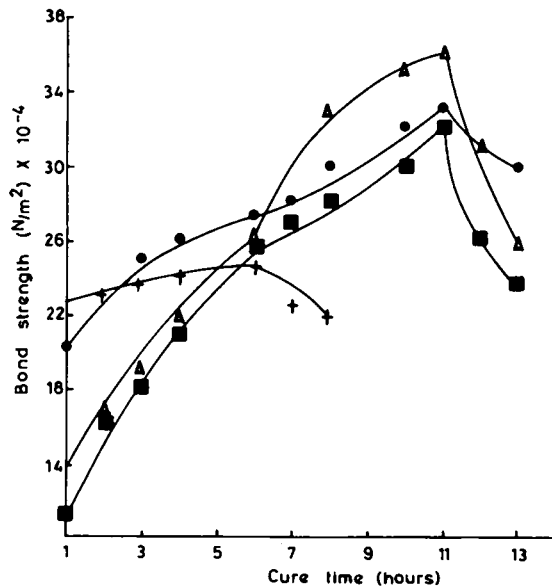


Fig. 9. Dependence of bond strength of substrates bonded with adhesives from the tannins of Mangrove bark on curing time, at different temperatures (°C) for dry tests: (■) 80; (▲) 100; (●) 120; (+) 140.

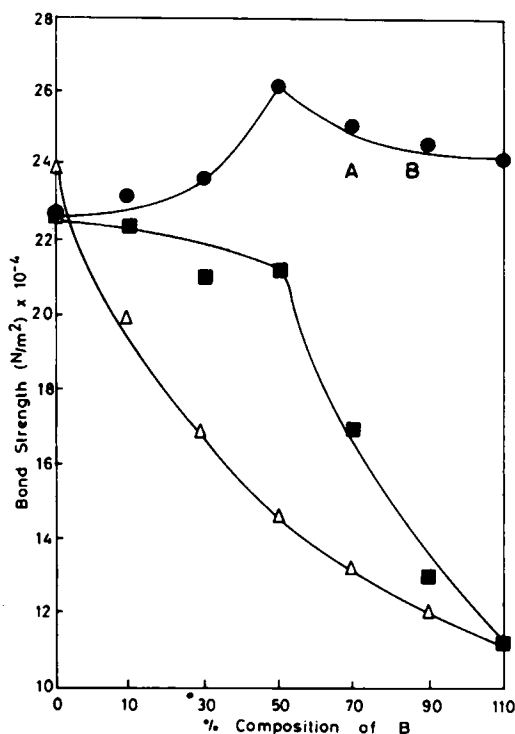


Fig. 10. Effect of the type and composition of solvent mixture on the bond strength of the adhesive joints.

solvent mixture generally decreased with increase in the amount of acetone in the mixture. The corresponding plot for the adhesive joints obtained from water-ethanol solvent mixture extracts showed a maximum at 50% ethanol.

The quantity of extractable material due to each of the pure single solvents is attributable to the combined effects of polarity and hydrogen-bond-forming ability of the individual solvent. Acetone may possess just sufficient polarity to exhibit specificity for polyphenolic tannin extraction. On the other hand, water and ethanol, both polar and with considerable ability to form hydrogen bonds, were less discriminatory in their extraction of bark materials: extracting both the polyphenolic tannins and possible other polyhydroxyl components of bark like carbohydrates. Apparently this accounts for the low tannin content of water and ethanol extracts relative to that of acetone extracts. The downward trend in the extractable material after the fifth day of extraction for both water and ethanol was possibly due to the promotion of chemical interactions between the chemical components of the extract. The occurrence of any form of polymerization or crosslinking of the constituents of the extract would undoubtedly result in high molecular weight and insoluble products which would be precipitated out of the extracting medium.

It is worth mentioning the peculiar behavior of ethanol-acetone extracts. Extracts from the pure solvents and other solvent mixtures were granular and readily soluble in water. Ethanol-acetone extracts were, however, platelike in shape, did not dissolve in water, and hence the stiasny tests could not be carried

out. These peculiar characteristics suggested that the ethanol-acetone solvent must have promoted some form of polymerization of the chemical constituents of the extracts during concentration of the solvent. Preliminary infrared analysis (not shown) of solid extracts from this solvent mixture has confirmed this suspicion.

The pH, type of solvents, paraformaldehyde content, and cure temperature were observed to have considerable influence on the reactivity of mangrove bark extracts. Similar observations have been made by Dalton.¹ The longest gelation time in both aqueous and water-ethanolic media occurred at about pH 4. This falls within the range pH 3-4.5 found to be the point of minimum reactivity for tannins from five different sources by Dalton. Dalton,¹ however, noted that Little and Pepper²² established pH 3 as the point of minimum reactivity for polyhydric phenols.

The observed trends in the strength properties of mangrove tannin adhesive joints are similar to those observed by Ebewele et al.,²³ who used Tapered Double Cantilever Beam (TDCB) test specimens and commercial phenol-resorcinol-formaldehyde (PRF) as adhesive. These authors claim that, for PRF adhesives, the fracture toughness is strongly dependent on cure temperature and cure time. They further reported that optimum strength properties of adhesive joints were obtained at the cure temperature which was determined for the adhesives from differential scanning calorimetry (DSC) measurements. The drastic deterioration in the bond strength of joints at prolonged cure periods and elevated temperatures is certainly due to wood embrittlement resulting from dehydration. The contention is supported by the extensive wood failure in these specimens. The reduction in strength properties as a result of boiling specimens (wet tests) has also been observed by several authors.^{1,10,11,13,14}

The different plots showing the effect of the composition of the solvent mixture used in mangrove bark extraction on the resultant adhesive bond strength are not directly comparable in terms of specific components of the adhesive since the joints were prepared from adhesives of different formulations. However, it appears that, for each plot, the joint influence of the adhesive components exceeds the separate effect of individual adhesive components. We pointed out earlier that ethanol-acetone extracts had peculiar characteristics, which was explained as due possibly to the polymerization and/or crosslinking of the components of the extracts. The fact that joints prepared from extracts obtained with this binary solvent mixture consistently had the lowest bond strengths reaffirms this explanation. Obviously, the existence of high molecular weight polymers and/or gelled fractions in this extract would affect its utility as an adhesive. In terms of both the quantity of extract and their tannin contents, water-ethanol solvent mixtures were not as effective as water-acetone in the extraction of mangrove bark. However, the bond strengths of joints derived from water-ethanol extract adhesives were consistently superior to those from water-acetone extract adhesives. It is recalled that glycerol was a component of the adhesives used in the preparation of these joints and that the binary solvent mixtures constituted the adhesive media. Glycerol, a polyhydric alcohol, would certainly be more compatible with water-ethanol adhesive medium than water-acetone medium.

Adhesive properties, such as initial viscosity and reactivity, which are strong functions of the adhesive formulation, have a profound influence on wetability

and, consequently, determine such properties as the bond strength and durability of adhesive joints. The influence of the chemistry of adhesives obtained from the binary solvent mixture extracts on adhesive properties is currently receiving attention and will be the subject of a future report.

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