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# Effect of Extraction Solvent on Tannin-Formaldehyde Adhesives for Plywood Production

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**Abstract**
Pine bark is a good source of natural polyphenolic compounds for wood adhesives. The objective of this study was to obtain the most suitable solvent for extracting pine tannins in the preparation of tannin-formaldehyde plywood adhesives. Aqueous acetone, aqueous ethanol, aqueous NaOH and water as solvents were used to obtain crude tannins from pine bark. The tannin content, sugar content and Stiasny number of the extracts were determined. Using the extracts from the solvent extractions, synthesis of tannin-formaldehyde resin was carried out. Plywood panels were made using the synthesized resins and the quality of the resins in plywood application determined. The quality of tannin-formaldehyde resins produced from the tannins were generally in close agreement with the chemical characteristics of the extracts obtained from the various solvent extractions. The aqueous NaOH extraction although gave very high tannin yield (16.1%), its associated high sugar content (33.8%) and very low Stiasny number (49) resulted in poor quality resin. Similarly, although aqueous extraction gave a very high Stiasny number (91), its low tannin yield (8.7%) might not be of commercial interest. The extraction process that gave a high tannin yield (12.9%) and a very good Stiasny number (81.5) with a corresponding good quality resin (shear strength = 1.9 MPa, 22% delamination) was found for 60% aqueous ethanol extraction.

**Keywords**
*Pinus caribaea* — bond quality — resin synthesis — chemical characteristics — veneer.

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## Contents



## Introduction

Extracts from the bark of various tree species contain polyphenolics which in the form of tannins are able to form condensation products with formaldehyde to produce wood adhesives. Several researchers [1, 2, 3] have studied these condensation products in an attempt to obtain suitable wood adhesives. These bark tannin and wood extracts are well known in the art and may be obtained, for example, by extraction from milled wood and bark in water in which the tannins tend to dissolve. Initial studies on wattle tannin-based adhesives started in the 1950s by Dalton [4, 5]. Subsequent work by Plomley [6, 7] demonstrated that wattle-bark tannins are suitable raw materials for plywood and particleboard adhesives production. Several attempts to partially replace phenol in phenol-formaldehyde resol-type resins with extracts derived from wood have been reported [8, 9, 10, 11, 12]. In a new Japanese approach for partially replacing phenol in phenol-formaldehyde (PF) resins, whole wood substance, instead of isolated fractions is dissolved in phenol and the resulting material is used to prepare PF adhesives [13, 14, 15]. Among suitable raw materials, tannins represent the best substitute for phenol in resin preparation.

Tannins from pine bark, like all the condensed tannins, consist of flavonoid units with varying degrees of condensation [16], which can be used for the preparation of bio-adhesives for bonding wood. In the past, there has been considerable interest worldwide in the development of tannin wood adhesives as substitutes for wood adhesives derived from non- renewable resources, and in particular phenol and resorcinol which are

derivatives from the petrochemical industry. Tannins from two hardwoods: wattle and quebracho, have been produced and used commercially for many years, but production of pine bark tannins has generally not been successful on a commercial scale [17]. Pine bark, however, is a good source of natural polyphenolic compounds for wood adhesives. Many attempts have been made to utilize it as a wood adhesive [18].

Considering the diversity in composition of the natural sources of polyphenols, as well as the structure and physicochemical properties of these compounds, a universal extraction protocol is not conceivable, and specific processes must be designed and optimized for each phenolic source [19,20]. Moreover, co-extraction of undesirable compounds such as sugars, fats, terpenes or pigments, must be avoided and has to be taken into account during the optimization of the process. Many factors contribute to the efficacy of solvent extraction, such as the type of solvent, the pH, the temperature, the number of steps, the liquid-to-solid ratio, and the particle size and shape of the plant matrix [21].

Several solvents have been utilized to extract tannins from several plant species. Darkwa and Jetuah [22] and Jetuah et al. [23] found 1% NaOH the most effective in extracting most phenols from *Rhizophora* spp. Takano et al. [24]used methanol, ethanol and water as extraction solvents; S iminonescu et al. [25] used alkali, while Chavanet et al. [26]used methanol and acetone at different concentrations with and without acidification, and Honget al. [27],used hot water and methanol as solvents in extracting tannin from *A.magium*.

The factors to be considered in solvent selection include; high saturation limit and selectivity for the solute to be extracted, capability to produce extracted material of high quality, chemical stability under process conditions and low viscosity among others. The objective of this study was to ascertain an appropriate extraction solvent for tannin extraction in tannin-formaldehyde plywood adhesives development.

## 1. Materials and Methods

### 1.1 Materials

By debarking pine trees, pine bark was obtained and dried at 40$^o$C for 48 h in an aerated oven. The dried bark was milled to pass a 100 - 250 $\mu$m sieve, sealed in a plastic bag, and stored at room temperature until needed. Rotary-cut *Ceiba pentandra* and *Antiaris toxicaria* veneer were used for plywood preparation. A local plywood mill supplied the industrial grade phenol-formaldehyde and urea-formaldehyde resins. All chemicals used in this study were of analytical grade obtained from commercial suppliers.

### 1.2 Extraction Process

For each extraction process, powdered pine bark was refluxed in an extracting solvent, the extract filtered through a sintered glass filter under vacuum, and the filtrate dried in an aerated oven at 60$^o$C until a constant weight was achieved. The extraction solvents were aqueous ethanol and aqueous acetone each at concentrations of 10, 20, 40, 60 80 and 100%, aqueous NaOH at concentrations of 0.05, 0.1, 0.2, 0.5, 1.5 and 2% and finally water. The time for extraction was maintained at 120 min, and the extraction temperatures were fixed at the boiling points of the solvents. The highest value of tannin yield for each solvent, was used as an indicator for the best solvent concentration. This solvent concentration was then used to extract the tannins for the tannin-formaldehyde resin synthesis. The dried crude extracts were used for tannin yield and Stiasny number determinations as well as sugar content analysis. Duplicate extractions were run for each solvent.

### 1.3 Chemical Analysis

By using the method of Roux [28] tannin content was determined as follows: 800 mg of sample were dissolved in 200 ml distilled water and 6 g of dried slightly chromated hyde powder added. The mixture was stirred for 1 hour at ambient temperature and filtered without vacuum through a sintered glass filter. The tannin content in the sample was obtained as a percentage of the weight gained by the hyde powder to the starting material. For each sample, triplicate determinations were made.

By using the method of Hillis and Urbach [29], Stiasny number (reactive tannin content) was determined as follows: 200 mg sample were dissolved in 20 ml distilled water and 2 ml of 10M HCl and 4 ml of formaldehyde (37%) added. The mixture was heated under reflux for 30 min and the reaction mixture filtered whilst hot through a sintered glass filter. The precipitate was washed and dried over CaCl2. The yield, expressed as a percentage of the starting material was equated as the Stiasny number. All samples were analyzed in triplicate.

With a slight modification to the phenol-sulfuric acid method [30], total sugars in the samples were measured as follows:10 mg extract dissolved in 10 ml of water was transferred to a centrifuge tube, and then 10 ml of 1% lead acetate aqueous solution was added. After 20 min, the tube was centrifuged at 18 000 rpm for 20 min. To 2 ml of the supernatant transferred to a new centrifuge tube were added 0.05 ml of 80% aqueous phenol solution and 5 ml of concentrated sulfuric acid. After 35 min, the tube was centrifuged at 3500 rpm for 5 min, and the absorptivity of the supernatant was read at 490 nm. Total sugar content was reported as per cent of oven-dried bark meal (w/w) and the experiment was carried out in duplicate. The calibration curve was determined using glucose as the standard sample.

### 1.4 Resin Synthesis and Quality

Synthesis of tannin-formaldehyde resin was carried out in a 2-L glass reactor according to a procedure similar to that described by Pizzi[16]. Fifty five percent aqueous tannin solution was left overnight for complete hydration of the tannin. 2.5 parts of 50-percent aqueous sodium hydroxide, 10 parts of paraformaldehyde, and 17 parts of water were added to 100 parts of tannin solution. The solution was refluxed for an hour and allowed to equilibrate to room temperature. The pH was adjusted to 7.6 by adding 3 parts glacial acetic acid to obtain a resol resin. Each adhesive was made by adding 20 parts

cassava flour, 4 parts urea formaldehyde (as a modifier) and 60 parts water to 100 parts of the resin and agitated using a speed regulated stirrer. To the homogenous solution obtained, was added 1 part hexamine as hardener and agitated. Industrial grade phenol-formaldehyde adhesive was used as the standard. The quality of the resins were determined by their viscosity, pot life and plywood bond strength. Each experiment was done in triplicate.

American Society for Testing and Materials (ASTM) standards [31] were used to measure the viscosities of all the resins and the pot life of the blends using a Brookfield Digital Viscometer Model LVTD (Brookfield Engineering Laboratory, Inc.) withLV-1, LV-2, and LV-3 spindles at various speeds of rotation.

### 1.5 Preparation and Adhesive Bond Evaluation

Three-ply plywood panels were made in an industrial plywood mill as follows: veneer sheets from *Antiaris toxicaria* (Kyenkyen) was used as face and back and *Ceiba pentandra* (Ceiba) as core. Dimensions of 25 cm x 40 cm were made on the veneers, and to each area was applied a separate adhesive using a laboratory roller at a spread rate of 2g/cm$^2$ of single glue-line. The panels were then pressed at 120$^o$C and a pressure of 1.0 MPa at pressing time of 8 minutes to obtain a 9 mm plywood. For each adhesive, three plywood panels were manufactured. To test the strength of the plywood bond, eighteen specimens were cut from each panel and tested in shear under wet and dry conditions [32]. For the dry testing, six specimens were conditioned to equilibrium at 23$^o$C $\pm$ 1$^o$C and 50 $\pm$ 2 percent relative humidity. Wet testing involved soaking another six test samples in water for 24 hours before testing. In the cyclic boil resistance (CBR) test, the last six samples were submerged in boiling water for 4 hours, dried at 60$^o$C for 20 hours in an oven and the cycle repeated before testing. Both dry and wet specimens were tested under shear with an Instron Model 1000 testing machine (Instron Corporation). Bond quality was evaluated from the shear strength of each specimen. For the CBR treatment, delaminations of plywood specimens were also recorded. Figures 1 and 2 respectively depict the plywood preparation stage and the plywood test pieces for adhesive bond evaluation.

**Figure 1.** Plywood panel preparation.

**Figure 2.** Plywood test pieces for bond evaluation

### 1.6 Data Analysis

All data were subjected to analysis of variance (ANOVA) at the 95% level of significance using SPSS 20 statistical software. For each data, significantly different groupings were obtained using LSD (least significant difference).

## 2. Results

The effect of extraction solvent concentration on tannin yield is found in Figure 3. This was used to select the appropriate solvent concentration for each solvent in the extraction of tannins for tannin-formaldehyde resin synthesis. The maximum tannin content for both aqueous acetone extraction and aqueous ethanol extraction was obtained at 60% solvent concentration, whilst the maximum tannin content for the aqueous NaOH extraction was obtained at 0.2% solvent concentration. In Table

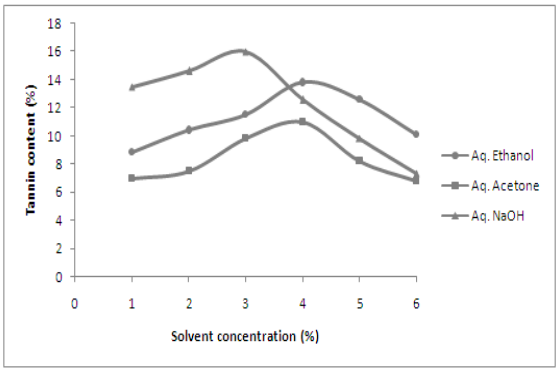


**Figure 3.** Effect of extraction solvent concentration on tannin yield.

1 is found the chemical characteristics of the extracts obtained from Pinus caribaea bark using different extraction solvents. Aq. NaOH extracted the highest amount of tannins (16.1%) and was significantly different from the rest, whilst aqueous extraction gave 10.6 % as the least amount of tannins extracted which was also significantly different from the rest (Table 1). Similarly, aq. NaOH extracted the highest amount of sugars (33%) and was significantly different from the rest, whilst aq. acetone gave the least amount of sugars (2.6%) which was also significantly different from the rest. There was no significant

difference between the sugar content of aqueous acetone and aqueous ethanol extracts. The Stiasny numbers of all the extracts were significantly different with the Stiasny number of aq. NaOH extract (49) being the least, and the aqueous extract having the maximum Stiasny number (91.1). The viscosities and pot lives of the adhesives formulated from tannins obtained from different extraction solvents are presented in Figure 4. The viscosities of aqueous acetone and aqueous ethanol were not significantly different. The extract from aqueous NaOH had the highest viscosity and was significantly different from all the other extracts. The control had the least viscosity and was also significantly different from all the other extracts. Similarly, the pot-life of aqueous acetone (50.5 min) and aqueous ethanol (49.3 min) extracts were not significantly different. The extract from aqueous NaOH had the least pot-life (15.2 min) and was significantly different from all the other extracts. The control had the highest pot-life (105.3) and was also significantly different from all the other extracts. The behavior of dry

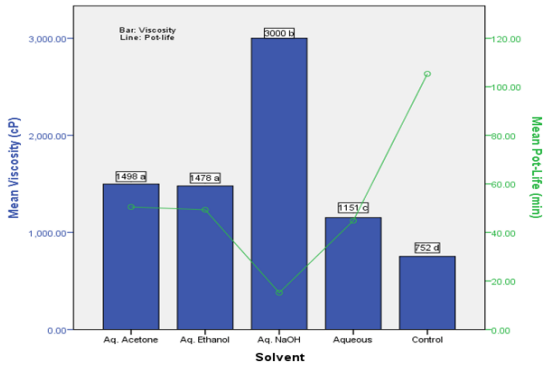


**Figure 4.** Effect of extraction solvent on viscosity and pot-life of resin.

and wet plywood bond strengths and plywood delaminations as a result of using tannins obtained from different solvents used in extracting pine bark tannins are shown in Figures 5 and 6 respectively. The dry bond strength of aqueous acetone (1.8 MPa), aqueous ethanol (1.9 MPa) and aqueous NaOH (1.8 MPa) extracts were not significantly different, but were significantly different from aqueous extract (2.1 MPa) and the control (2.5 MPa) which was the highest and was significantly different from all the other extracts. The wet bond strength of aqueous acetone (1.2 MPa), aqueous ethanol (1.1 MPa) and aqueous (1.2 MPa) extracts were not significantly different, but were significantly different from both aqueous NaOH extract (0.4 MPa) and the control (1.5 MPa). The control which had the highest wet bond strength was significantly different from all the other resins, whilst aqueous NaOH extract which had the least wet bond strength was also significantly different from all the other resins. In general, the dry bond strengths were higher than their wet bond strength counterparts. The percentage pass of plywood delamination of aqueous acetone (75 %), aqueous ethanol (78 %) and aqueous (78 %) extracts were not significantly different, but were significantly different from both aqueous NaOH extract (22 %) and the control (100 %). The control which had the highest percentage pass was significantly different from all the other resins, whilst aqueous NaOH extract which had the least percentage pass was also significantly different from all the other resins.

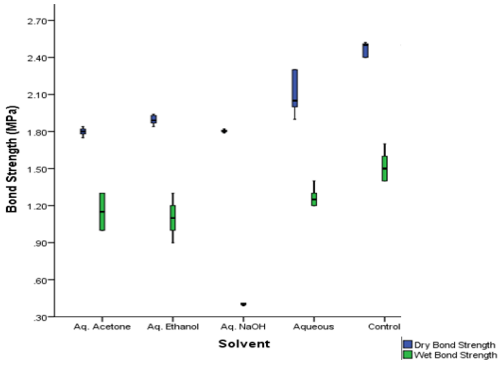


**Figure 5.** Effect of extraction solvent on viscosity and pot-life of resin.

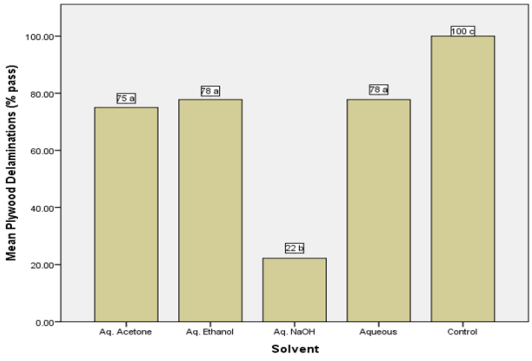


**Figure 6.** Effect of extraction solvent on on dry and wet shear strength of plywood
Values bearing the same letter are not significantly different at the 5% level by LSD.

## 3. Discussion

A suitable extraction solvent must be able to solubilize the target analytes while leaving the sample matrix intact for an efficient extraction to occur. The polarity of an extraction solvent is important as it should closely match that of the target compounds. A range of organic compound scan be obtained by use of mixed solvents of different polarities. In this work, the tannins in the extracts increased with increasing concentration of organic solvent (solute, in the case of aq. NaOH) in water. The tannin content reached a maximum when the acetone and ethanol solvent concentrations were each 60% (Fig. 3). In the case of aq. NaOH, concentration of 0.2% yielded the highest amounts of tannins (Fig. 3).The increased solvent concentration that increased the tannin yield might

be attributed to the fact that this factor perhaps soften the tissues of the bark samples and weaken the phenol-protein and phenol-polysaccharide linkage, resulting in migration of more polyphenols into the extraction solvent. This reason was most likely the explanation to the increased yield of tannin content as also observed by Mane et al.[33] and Wang et al.[34].

In the study of Derkyi et al. [35] on aqueous acetone extraction of tannin from *Pinus caribaea* bark, 60% aqueousacet one extraction with liquid–solid ratio of 29.8:1, resulted in a maximum tannin yield of 14.6%, total sugars of 4.25% and Stiasny number of 90.2% at 58.1$^o$C and 78.5min extraction condition. The low tannin yield obtained in this study is as a result of different extraction conditions employed.

Makino et al. [36],have studied the total sugar content of some tree bark and have observed that they are in the range of 0.4–2.6%. This is in agreement with the observation made in this work in which the minimum sugar content of 2.6% was obtained for aqueous extraction but then the sugar content for the aqueous acetone, aqueous ethanol and aqueous NaOH extractions were 3.7%, 3.6% and 33.8% respectively.

The Stiasny number is an indication of reactive tannins towards formaldehyde and that the higher the value the more formaldehyde-condensable tannins extracted and the more effective the adhesive bonding will be [16]. The Stiasny number of 49% obtained for aqueous NaOH extraction in this study was close to 50-60% quoted for pine bark by Pizzi [16] but rather different from the 75% obtained by Vazquez et al. [37]. The difference might be due to the extraction conditions adopted which might have either suppressed the tannin yield or enhanced the extraction of impurities or both.

Most of the bark extractions using 70% (v/v) aqueous acetone or ethanol have been demonstrated to be efficient for phenolics recovery as reported by several workers [36, 38, 39]. Alkaline solutions are also used extensively to extract tannin from bark. Aqueous alkaline extractionisable to remove extractives including flavonoid oligomers and polymers, waxes, polysaccharides and lignin and tends to lower stability, thus making the total extract less suitable for adhesive manufacture [37]. Using aqueous NaOH gives a higher sugar yield which decreases tannin reactivity toward formal dehyde [40, 41, 42] and would thus reduce the strength and water resistance of adhesives formulated with the tannin extracts [43]. This could explain the very low wet bond strength and very high delamination resulting from the aqueous NaOH extract.

Condensation of tannins with small amounts of urea formaldehyde resins can prevent the water deterioration normally experienced by the latter resins. Conversely, urea-formaldehyde resins improve cross linking and strength of wood tannin-formaldehyde networks [44]. In this study, urea-formaldehyde was used in the tannin-formaldehyde resins formulation. Urea formaldehyde is not water resistant and this could explain the low water resistance of the tannin resins compared with the industrial phenol-formaldehyde control. The viscosities of the tannin resins and shear strengths of plywood reported in this study are comparable to the work done by Santana et al.[45] and Sellers and Miller [46].

It is important to understand the rheological behavior of thermosetting resins in their processing. According to Hu et al.[47], rheological properties such as viscosity can be directly linked to the evolving adhesive properties during resin cure. The different solvents used in this study gave variable effects on the quality of the resins produced. This is due to the fact that the different solvents extracted different quantities of the extractives (Table 1). It may also be due to the fact that the different solvents extracted different organic compounds into solution that affected the adhesive properties.

According to Pizzi [16, 48], tannin-formaldehyde resin tends to perform like a phenol–formaldehyde resin due to the phenolic groups they contain. Also, according to several studies, pine tannin reacts very fast with formaldehyde and has a short pot life [48]. This could explain why the tannin-formaldehyde adhesives in this study had comparatively higher viscosity and lower pot-life than the control. High viscosity and short pot life are disadvantageous to most tannin-formaldehyde resins and tannin-formaldehyde resins fortified with urea-formaldehyde and phenol-formaldehyde resins [45].

## 4. Conclusion

In extracting tannins, the presence of sugar molecules co-extracted impact negatively on the resin produced subsequently. Less sugar is thus desirable in a tannin-containing extract for plywood applications. The quality of tannin-formaldehyde resins produced from the tannins were generally in close agreement with the chemical characteristics of the extracts obtained from the various solvent extractions. The aqueous NaOH extraction although gave very high tannin yield (16.1%), its associated high sugar content (33.8%) and very low Stiasny number (49) resulted in poor quality resin. Similarly, although aqueous extraction gave a very high Stiasny number (91), its low tannin yield (8.7%) might not be of commercial interest. The extraction process that gave a high tannin yield (12.9%) and a very good Stiasny number (81.5) with a corresponding good quality resin (shear strength = 1.9 MPa, 22% delamination) was found for aqueous ethanol extraction under the specified extraction conditions.

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