Industrial Crops and Products 30 (2009) 416–421

Contents lists available at ScienceDirect

Industrial Crops and Products

journal homepage: www.elsevier.com/locate/indcrop

# Fortification of sulfited tannin from the bark of *Acacia mangium* with phenol–formaldehyde for use as plywood adhesive

Y.B. Hoong[a,*], M.T. Paridah[a], C.A. Luqman[b], M.P. Koh[c], Y.F. Loh[d]

[a] Faculty of Forestry, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia
[b] Faculty Engineering, Universiti Putra Malaysia, Malaysia
[c] Forest Research Institute Malaysia, Malaysia
[d] Malaysian Timber Industry Board, Malaysia

ARTICLE INFO

*Article history:*
Received 19 May 2009
Received in revised form 22 July 2009
Accepted 24 July 2009

*Keywords:*
Tannin
*Acacia mangium*
Sulfite tannin
Plywood
Phenol–formaldehyde
Shear strength

ABSTRACT

The *Acacia mangium* tree contains 10% bark (v/v), of which about 20% are extractives. Extraction of this bark using a combination of water and sulfite medium can produce between 15% and 25% tannin materials (dry weight). In this work, several extraction conditions such as bark size, plantation site, extraction time and extraction medium were studied. The results showed that by using either hot water or a sulfite medium, a reasonable amount of tannin yield can be obtained. Bark size of less than 1-mm mesh size gave relatively high tannin yield irrespectively of the extraction medium used. Using a 600:100:2:0.5 (w/w) ratio of water:bark:sodium sulfite:sodium carbonate, and reacted at 75 °C for 3 h improved the tannin yield by at least 30%. The extracts were reasonably reactive towards formaldehyde as shown by their high Stiasny number; water extract, 60–70% and aqueous sulfite–carbonate extracts, 85–90%. The gluing results showed that the shear strength of the plywood can meet the requirements of the European Standards EN 314-1 and EN 314-2:1993. Incorporation of low molecular weight PF resin (10 parts) and PF (10 parts) improved the shear strength from 0.96 MPa to 1.43 MPa after a 72 h boiling test. This study showed that *A. mangium* tannin blended with commercial plywood phenol–formaldehyde resin, low molecular weight PF and paraformaldehyde as a cross-linker can be used to bond Kedondong (*Canarium* spp.) wood veneers suitable for both interior and exterior grade plywood.



## 1. Introduction

### 1.1. Acacia mangium

*Acacia mangium* is one of the most popular fast-growing tree species not only in Malaysia, but also in the rest of Asia. *A. mangium* trees have been planted under the forest plantation program both in Malaysia and Indonesia. Usually, this fast-growing tree is utilized as raw material for pulp and paper production due to small log diameter characteristics as well as for glulam production because of its high bond strength (Alamsyah et al., 2007) and good mechanical properties (Matsumoto, 2003). According to the commercial *A. mangium* chip mill (Melewar Integrated Engineering S/B) in Sabah, Malaysia (Personal communication, 2008), the plants were generating approximately 250,000 mt/annum of *A. mangium* bark. The huge amount of trees would generate a substantial amount of tree barks which can be extracted for tannin.

### 1.2. Sulfited tannin

Sulfitation of tannins is the oldest method and most useful reaction in flavonoid chemistry to increase tannin extraction yield from tree barks. According to Pizzi (1979), the advantages of sulfitation in tannin adhesive application were lower viscosity, enhanced solubility, higher moisture retention by the tannin resin and allowing slower adhesive film dry-out. He reported that modification of tannin on the polyflavonoid A-rings (resorcinol or phloroglucinol) during sulfitation makes it more reactive towards formaldehyde due to the opening of the etherocyclic ring from the methoxyphenol to a hydroxyphenol (Fig. 1).

Reaction of condensed tannins with sulfite ions has long been discovered to increase yield as well as to lower the molecular weight of the tannins. New Zealand Forest Products Ltd. used sulfite extraction of these barks in the production of their tannin-based adhesives, but recently Kreibich and Hemingway (1989) mentioned that this method was discontinued. Kreibich and Hemingway (1987) successfully used sulfonated extracts of southern pine barks as a cold-setting wood-laminating adhesive to replace at least 50% of the existing PRF. Paridah et al. (1999) also successfully replaced PRF up to 30% (w/w) with sulfited mangrove

* Corresponding author. Tel.: +60 124565631; fax: +60 389472180.
*E-mail address:* frence_yeoh@yahoo.com (Y.B. Hoong).

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doi:10.1016/j.indcrop.2009.07.012

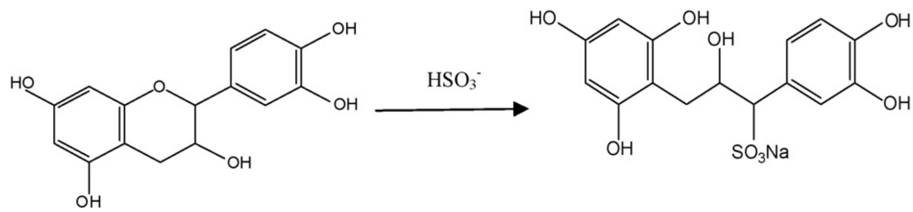


**Fig. 1.** A typical opening of pyran ring during sulfitation of bark extracts.

tannin for bonding kempas (*Koompasia melacencis*) glued laminated board.

Pizzi (1983), successfully used water-extracted tannin to partially replace urea formaldehyde resin in the manufacture of both particleboard and plywood. According to Pizzi, water is the most suitable extraction medium for this type of wood species. Nevertheless, Hoong et al. (2007) found that the yield of water extracts tannin from *A. mangium* bark was relatively low (11%). Thus sulfitation may provide a better extraction medium to improve the tannin yield.

### 1.3. Fortified tannin adhesive

Fortication has been shown to improve the strength and durability of a resin adhesive. However, the fortification of tannin adhesives with other synthetic resins has yet to gain commercial acceptance since the resulting adhesive costs more and often has serious technical drawbacks. *A. mearnsii* tannin adhesive without fortification used in the manufacture of plywood has been studied by Zhao et al. (1994, 1996). Generally, most tannin-based adhesives are fortified with a synthetic polymer system such as commercial PF (Vazquez et al., 2002, 2003); commercial UF (Pizzi, 1983; Bisanda et al., 2003); resorcinol–formaldehyde (Pizzi, 1983; Wen and Wei, 2006); phenol–resorcinol–formaldehyde (Pizzi and Cameron, 1989) and isocyanates (Batubenga et al., 1995).

This paper reports the extraction of tannin from *A. mangium* bark and the preparation of various adhesive formulations by incorporating commercial PF, low molecular weight PF (LPF) and paraformaldehyde for bonding plywood. The addition of LPF was to provide additional cross-linking through methylol groups from the LPF resin.

## 2. Experimental

### 2.1. Collection of tree barks

Fresh barks from 7–8 years old *A. mangium* trees were obtained from processing mills located at four different sites in Malaysia namely Mentakab, Lembah Beringin, Telaga and Tawau. The bark consisted of a mixture of inner bark, outer bark and some woody materials. The barks were chipped to 2–3 cm size and further flaked to sizes less than 1 mm. The barks were stored in an open area (was protected from rain) for at least 2 weeks and then oven dried to 12% moisture content. The 2-week storage period was done to simulate actual conditions in wood processing mills.

### 2.2. Preparation of sulfited tannin

The preparation of bark extracts followed that of Paridah et al. (1999). Hot water extract was prepared by heating a mixture of water and bark (6:1 (w/w) based on the oven-dried weight (OD) of the bark) at 75 °C in a water bath. The sulfited tannin extract was prepared by boiling a mixture of bark, water, sodium sulfite and sodium carbonate at 100:600:2:0.5 (w/w) for 3 h. The solution was first screened through a fine filter (140 mesh) and further filtered on a sintered glass (porosity 2). Both types of extracts were concentrated to 40–50% solids under reduced pressure using a Buchi Rotavapor rotary evaporator at 50–55 °C. The resulting solid was further dried in an oven maintained at 50 °C until the weight was constant. The yield of tannin was calculated as follows:

$$\text{yield}(\%) = (totalweightofsolidsintheextract - totalweightODsodiumsaltsused) \times 100/oven\text{-}driedweightofbark \quad (1)$$

Different concentrations of sulfite–carbonate were used in the extraction process: (1) water (control), (2) $Na_2SO_3$ (1%)/$Na_2CO_3$ (0.25%), and (3) $Na_2SO_3$ (2%)/$Na_2CO_3$ (0.5%).

### 2.3. Determination of gel time

The tannin solution (40% (w/w) solid content; 10 g) was placed in a test tube and paraformaldehyde powder (0.3 g of 96% (w/w)) was added into the test tube. The mixture was heated in a water bath at 90 ± 2 °C and stirred with a glass rod until it had formed a gel (until the product had solidified sufficiently easy removed from the side of the beaker). Then a soft spiral wire was inserted into tannin solution (test tube) to examine the gel state. The gel time required for this to take place is the gelation or gel time. The test was duplicated for each treatment.

### 2.4. Determination of tannin content (reactive tannin)

The Stiasny number reaction was used to determine the polyphenol content of extracts. Fifty milliliters of (0.4%, w/w) tannin solution was pipetted into a 150 ml flask. Aqueous formaldehyde (37%; 5 ml) and hydrochloric acid solution (10 M; 5 ml) were then added and the mixture was heated under reflux for 30 min. The reaction mixture was filtered through a sintered glass filter (porosity 2) whilst it was still hot. The precipitate was then dried in an oven at 105 °C to constant weight. The Stiasny number is the ratio of the oven-dried weight of the precipitate to the total dissolved solid content of the tannin extract expressed as a percentage.

### 2.5. Resin formulation

Four different adhesive formulations were prepared where two were tannin-based adhesives. For adhesive formulation, a tannin solution (40% solids) was prepared and added to PF (40% solids) resin. Both wheat flour and paraformaldehyde were added to the mixture. For the second formulation, a small amount (10 parts) of LPF (40% solids) was first added to the tannin solution before being added to the PF resin. Then the wheat flour and paraformaldehyde were added. The third and fourth adhesive formulations were controls which contained 100 parts of PF (40% solids) and LPF (40% solids) respectively. The adhesive formulations used in the study are given in Table 1.