FORMALDEHYDE BASED RESINS PREPARED USING TANNIN OBTAINED FROM BARK OF *Terminalia arjuna* (Roxb.)

By

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The work described in this thesis was carried out by the undersigned at the University of Sri Jayewardenepura and Eastern University under the supervision of Dr.Laleen Karunanayaka, Senior Lecturer, Department of Chemistry, University of Sri Jayewardenepura and Co-supervision of Dr. M. Printhan, Senior Lecturer, Department of Botany, Faculty of Science, Eastern University, and a report on this has not been submitted to any University for another degree. Also, I certify that this thesis does not include, without acknowledgement, any material previously submitted for a Degree in any University and to best of my knowledge and belief it does not contain any material previously published, written or orally communicated by another person except where due reference is made in the text.

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We certify that the above statement made by the candidate is true and that this thesis is suitable for submission to the University for the purpose of evaluation.

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UNIVERSITY OF SRI JAYAWARDENEPURA, SRI LANKA

FACULTY OF GRADUATE STUDIES

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Submitted for the Degree of

M.Sc IN POLYMER SCIENCE AND TECHNOLOGY

Selladurai Arasaretnam

ABSTRACT

Terminalia arjuna (Roxb.)(Tamil name: Marutha tree, Sinhalese name: Kumbuk tree) is one of the major tannin yielding trees. Five protocols were developed to isolate the tannin from the bark of *Terminalia arjuna*. Extraction with water was an effective protocol (9.01% w/w) to extract the tannin from the bark of *Terminalia arjuna* than acetone (4.01% w/w) and ethanol extraction (4.34% w/w) in order to extract high yield. Tannin and bark from the *Terminalia arjuna* was liquefied with phenol in the presence of an acid catalyst (H_2SO_4). In the case of liquefaction of tannin using 2.8% and 5% addition of H_2SO_4, the amount of residue was remained near 10% and 5% respectively after 90 minutes reaction time. Thus the condition was selected to liquefy tannin for resin preparation. Similarly liquefaction of bark with 7.5% H_2SO_4, the amount of residue was stabilized near 10% thus the condition selected to liquefy bark for resin preparation.

Study on Chemical structure of phenolation of tannin, liquefaction of bark and prepared resins were identified with Fourier Transform Infra Red (FTIR). Liquefaction of tannin, bark with phenol was confirmed by significant absorption differences in FTIR spectrum

from the tannin alone. These absorption signals were useful as a tool to confirm whether phenol is bonded to the tannin structure.

Pine bonded plywood bonded with the liquefied tannin and bark resins had poor shear strength that was comparable to commercial phenol formaldehyde.

CHAPTER 1

INTRODUCTION

Terminalia arjuna(Roxb.) is a large hard wooded trees belonging to family combretaceae. It is almost common in every part of Sri Lanka and grows well along bank of streams, rivers, ravines, and dry watercourses, reaching very large sizes on fertile alluvial loam. It is one of the major tannin yielding trees. The percentage tannin contents of bark, leaves and fruits are (22–24 %), (10–11 %) and (7–20 %), respectively.[31]

Vegetable tannins are natural products of relatively high molecular weight, which have the ability to complex strongly with carbohydrates and proteins. They are most important natural products used industrially, specifically in leather tanning processes and in the synthesis of wood adhesives to replace phenol in phenol-formaldehyde adhesives with tannins [(1), and (2)]. One of the main concerns of the 21st century is the environment. The environment has become a subject of constant attention, and it has become a focal point of our life and welfare. [(3) (4) and (5)]

Formaldehyde has been a subject of concern in the formaldehyde resin-bonded wood-based panel industry for a number of years. Virtually all wood panel products, such as plywood, wood particleboard and Medium Density Fiberboard (MDF) are manufactured using either Urea Formaldehyde or Phenol Formaldehyde adhesive. Formaldehyde is gaseous at room temperature, but it can polymerize forming para-formaldehyde, and it readily dissolves in water forming methylene glycol. [(3) (4) and (5)]

Many consumer products containing formaldehyde based resins release formaldehyde vapour, leading to consumer dissatisfaction and health-related complaints. (3) (4) and (5) These emissions have resulted in various symptoms, the most common of which are irritation of the eyes and of the upper respiratory tract. Formaldehyde has also been found to produce nasal carcinomas in mice and rats after exposure to 14.1 and 5.6 *ppm* of formaldehyde, respectively, over a long period of time.(3) (4) and (5)

These findings have led to an intensified interest in the indoor environment. Consumer products, specifically construction materials, are a major source of formaldehyde in the indoor environment. (3) (4) and (5)

To reduce formaldehyde emission, the possibility of using replacement materials for UF (Urea Formaldehyde) and PF (Phenol Formaldehyde) adhesives have been studied for a long time. Tannin Formaldehyde (TF) adhesives are obtained by the hardening of polymeric flavonoids of natural origin, especially of condensed tannin by poly condensation with formaldehyde.[6] In the last decade several approaches to the problem of producing low formaldehyde emission wood panels using these wood adhesives have been developed. However, hardeners cause formaldehyde emission even when tannin adhesive is used.[7]

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 resources. Principal among these efforts is the development of adhesives from tannin.[8, 9]

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[8-12]. In Nigeria, where mangrove forests abound on the south coast, Ohunyon and Ebewele attempted to develop mangrove tannin based plywood adhesive.[13,and14] 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 *inte alia* include the following.[8, 9, 13, and 14]

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.[10,12-14]

Chemistry of Condensed Tannin

The tannin polyflavonoid molecule essentially consists of five to eleven mono flavanoid units. In the mono flavanoid unit, two phenolic rings (A and B) are joined by a heterocyclic ring (Fig.1.1). Tannin, being phenolic, reacts with formaldehyde in a manner similar to that of 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 there activity of the A ring, are most probably responsible for the poor adhesive properties. In addition, the presence of non-tannin compounds such as gums, which are highly branched polysaccharides, affects the properties of tannin-based adhesive.

Hydrolysis of Tannin

Caustic hydrolysis of resorcinol tannin has been reported to cleave the inter flavonoid bond and open the etherocyclic ring joining the A and B ring of the flavonoid unit[15]. The mechanism proposed by Pizzi [15] based on his study is shown in the Figure 1.1.

Acid hydrolysis has been shown to easily open the etherocyclic ring of poly flavonoids with the formation of carbonation, which is capable of reacting with another nucleophile present [12]. This is represented by Figure1.1.

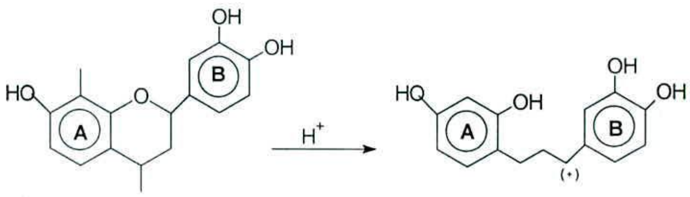

Figure1.1: Acid hydrolysis of the polyflavonoid

Pizzi and Stephanou[16] reported an improvement in the performance of a non-fortified mimosa tannin- based adhesive developed by subjecting tannin extracts to anhydride and subsequent alkaline treatment. The following have been suggested as probable reasons for the improved adhesive performance.[16]

1. Cleaving of the tannin interflavonoid bond: This result 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[10].

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 (low molecular weight) don't 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.

Objectives of this Study

1. Development of economically feasible protocols for extraction of tannin from the bark of *Terminalia arjuna*

2. Study on chemical structure of phenolation of tannin, liquefaction of bark and prepared resins using Fourier Transform Infra Red spectra (FTIR).

3. Study on liquefaction of tannin, bark from the bark of *Terminalia arjuna*

4. Preparation of Formaldehyde based resins with liquefied tannin, liquefied bark of *Terminalia arjuna*.