

RING OPENING POLYMERIZATION OF TANNIN

EXTRACT

BY

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NIGER STATE, NIGERIA.**

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**A RESEARCH PROJECT REPORT SUBMITTED TO THE
DEPARTMENT OF CHEMICAL ENGINEERING SCHOOL
OF ENGINEERING AND ENGINEERING TECHNOLOGY,
FEDERAL UNIVERSITY OF TECHNOLOGY, MINNA,
NIGER STATE.**

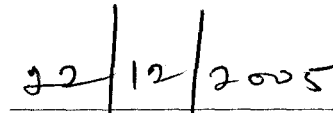
**IN PARTIAL FULFILLMENT OF THE REQUIREMENT
FOR THE AWARD OF BACHELOR OF ENGINEERING
(B.ENG.) DEGREE IN CHEMICAL ENGINEERING**

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DECLARATION

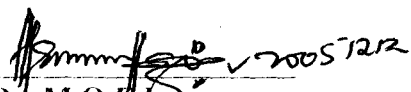
I, **ALATE WAHEED OLATUNJI** with registration number **99/8083EH** wrote and carried out this project. Information obtained from published and unpublished works have been duly acknowledged by means of references and to the best of my knowledge it has never been presented for any degree programme elsewhere.


Signature


Date

CERTIFICATION

This is to certify that this thesis "Ring Opening Polymerization of Tannin Extract" is the original work of Alate Waheed Olatunji, carried out wholly by him under the supervision of Dr. M.O. Edoga and submitted to the Department of Chemical Engineering, School of Engineering and Engineering Technology, F.U.T Minna, Nigeria.


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Date

External Examiner

Date

DEDICATION

This project work is dedicated to my parents, Alh. Alate Abdulrouf and Mrs. Alate Rabiati, and also, to the family of Alh. Alabi Amuda for their encouragement, support and understanding.

ACKNOWLEDGEMENT

My existence till date is as a result of God's infinite mercies, to whom otherwise, a successful completion of this degree programme would not have been accomplished. I say, "Al-hamdu-lillah".

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ABSTRACT

The aim of this present study is to produce tannin-formaldehyde adhesive. This was achieved by a consecutive acid and alkaline hydrolysis of tannin extract to open up the tannin ring before polymerizing with formaldehyde.

The tannin used was extracted from mangrove bark at a temperature of 85°C for 2hrs using ethanol as the solvent. This gives a tannin yield of 20.54%.

The physicochemical properties such as viscosity, pH, density of the tannin and tannin-formaldehyde adhesive were determined and found to be in the standard range for phenolic resins.

The infrared analysis of the tannin-formaldehyde adhesive showed that the peaks were in the frequency range typical of phenol, aldehydes, aromatics, with less CH₂ bonds that are responsible for methylene bridges.

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NOMENCLATURE

W_a = Weight of empty density bottle

W_b = Weight of tannin extract + W_a

W_c = Weight of tannin adhesive + W_a

W_d = Weight of tannin extract

W_e = Weight of tannin adhesive

V = Volume of water displaced by sample

t = Time taken for sample to flow through the capillary of the viscometer

C = Viscometer constant

K = Kinematic Viscosity

μ = Viscosity of sample

ρ = Density

cP = Centipoise

Subscript 1 = Tannin extract

Subscript 2 = Tannin adhesive

CHAPTER ONE

1.0

INTRODUCTION

Adhesives constitute an important component in the manufacture of a wide array of composite products produced by the forest products industry and used by the consumers. Phenol, a finite and petrochemical product is a primary feedstock in the production of wood adhesives. About 57% of all phenolics are used for the production of wood adhesives and binders through polymerization reaction (Anthony, 2000).

Polymerization reaction therefore, is a chemical reaction in which small molecules (monomers) combine to form larger molecules (polymers) of linear chains or a three dimensional network of polymer chains that contain repeating structural units of the original molecules. In ring-opening polymerization, the monomer is a cyclic compound and reaction starts with the cleavage of the cyclic compound and subsequently, its polymerization into linear polymers.

From time to time during recent decades, the inevitable decline in petroleum reserves couple with the economic and political instability in the Middle East has led to recognition of the importance of research on alternative sources of starting materials for the production of adhesives. There had been several attempts to partially replace phenol in phenol-formaldehyde resol-type resins with renewable agricultural products such as carbohydrates, lignin and tannins. Among these suitable substitutes, tannins represent the best substitute for phenol in resin preparation (M.A.E Santana et al, 1995).

In this present study, the tannin used was extracted from mangrove bark, which was found in abundant in Sapele, Delta State, Nigeria. The tannin extract was hydrolyzed using an alkaline (caustic) and acid to open up its cyclic ring (ring opening) before its polymerization with formaldehyde.

1.1

Aim and Objective

The aim of this study is to produce tannin-formaldehyde adhesive.

1.2

Approach

- (i) Ring-opening polymerization of tannin extract.
- (ii) Alkaline hydrolysis using caustic.
- (iii) Acidolysis using acetic anhydride.

CHAPTER TWO

2.0

LITERATURE REVIEW

The reactions of phenolic compounds with formaldehyde to form polymeric systems can be either acid or base catalysed. Resins made using an acid catalyst and a phenol-to-formaldehyde ratio greater than one are referred to as novolaks. Novolaks require the addition of another reactive component to effect cure. Resins made using a basic catalyst and a phenol-to-formaldehyde ratio less than one are referred to as resoles. Resoles contain reactive hydroxymethyl end-groups that can further react to form the cured state. Almost all phenolic adhesives systems used to bond wood are based-catalysed resole resins (Anthony, 2000).

In resole resins, polymer formation occurs in two steps; firstly, an addition reaction in which formaldehyde reacts with the phenolic compound to form hydroxymethyl derivatives, and secondly, a condensation reaction in which the hydroxymethyl derivatives react to form oligomers and eventually cross-linked polymers.

2.1

Adhesives

Adhesives can be regarded as materials or substances that are capable of joining bodies together by surface attachment. It can generally be classified into natural and synthetic adhesives.

Natural adhesives are those derived majorly from animal parts (skin, bone, albumen, fish, casein), while synthetic adhesives are mainly from the petrochemical (vinyl acetate, formaldehyde etc). The synthetic adhesives are further classified into thermoplastic and thermosetting adhesives. Table 2.1 shows a basic classification of adhesives (Gana, 2000).

Table 2.1: Basic Classification of Adhesives

Origin	Basic Type	Adhesive Material
Natural	Animal	Albumen, Animal glue, Casein, etc
Natural	Vegetable	Natural resins (i.e. gum Arabic oils and waxes), protein (soya bean)
Natural/ Synthetic	Elastomers	Carbohydrates (dextrin, starch), natural rubber (and derivatives), latex cyclised rubber, chlorinated rubber, butadiene/acrylonitrile rubbers.
Synthetic	Thermoplastic	Cellulose derivatives, vinyl polymers, copolymers, polyethers.
Synthetic	Thermosetting	Amino plastics, epoxies and modifications, phenolic resins and modifications, polyesters, etc.
Synthetic	Minerals	Inorganic materials (e.g. silicates), mineral waxes (paraffin), mineral resin (copal, amber), bitumen.

2.2

Early Works on Tannin-Formaldehyde Adhesive

Teck et al. (1993) evaluated mangrove bark tannin in particleboard made of rubber wood (*Heava* spp.) and compared it to board made with three synthetic resins (UF, PF, and polymeric diphenylmethane diisocyanate [pMDI]) as well as with blends of tannin and synthetic resins. The test results were compared to the requirements of British Standard BS 5669-1979, Type I Bond. The particle-boards containing 14 percent tannin binder solids (dry fiber weight basis) passed the standard for modulus of rupture (MOR), internal bond (IB), screw withdrawal, and thickness swell (TS). Panels bonded with all synthetic resins passed the standard, as did the tannin blended with 10 percent UF resin and tannin blended with 8 to

10 percent pMDI, tannin solids basis. Panels bonded with the tannin/10 percent PF blend did not pass the standard (low MOR, high TS, and borderline IB).

In Nigeria, where mangrove forests abound on the south coast, Ohunyon and Ebewele attempted to develop mangrove tannin based-plywood adhesive. Their efforts were concentrated on using metal acetate to induce participation of the "B" (phenyl) ring of the tannin flavonoid molecule in the tannin formaldehyde condensation reaction. This B is normally inert except at $\text{pH} > 8$, at which the reactivity of the "A" ring becomes very high. These problems were addressed by treating tannin extract with acetic anhydride and then sodium hydroxide followed by modification with 20% resole-type PF resin (Sowunmi, 1996).

2.3 Uses of Tannin-formaldehyde Adhesive

Tannin based adhesives are mostly used in forestry industries and other vital areas as discussed below:

(a) Bonding wood products

Tannin based adhesives are mostly used in binding plywood and particleboards. This is due to the fact that it is one of the closest substitutes to phenolic resins. Its source is renewable in nature and the by-products are less hazardous to the environment.

(b) Production of ion exchange resin

Synthetic zeolites for the purification of water and other solutions of non-ionic materials can be generated from variety of phenols, tannin etc. Ion exchange resins from tannin are particularly useful for the removal of calcium, magnesium and other cations.

2.4 Adhesive Composition

In order to formulate adhesive, a number of general components are commonly incorporated for various purposes. The components are highlighted below:

2.4.1

Binders

This is the component of the adhesive, which primarily acts as the adhesion forces that hold the two binders together. These binders used for adhesives are primarily polymers having optimal strength properties. The binder is generally the component from which the name of adhesive is derived using a classification based on composition.

2.4.2

Catalysts and hardeners

These are curing agents for adhesive systems. Hardeners effect curing by chemically combining with the binder materials. The ratio of the hardener to the binder determines the physical properties of the adhesives. Catalysts are used as curing agents for thermosetting resins to reduce curing time and increase the cross-linking of the synthetic polymer.

2.4.3

Extenders

Extenders are substances that have some adhesive action. They are usually added to an adhesive to reduce the amount of primary binder required per unit area and thus reduce the cost of the action joint. An example of extenders is wheat flour commonly added on the ratio of 1:1 on a solid basis by physical mixing and additional dilution with water to a desired viscosity.

2.4.4

Fillers

These are relatively non-adhesive substances added to an adhesive to improve its working properties, permanence, strength or other qualities. Some of these fillers like walnut shell; flour is added to improve the spreading properties into certain porous wood. They can also alter thermal expansion coefficient of the cured adhesive film in order to reduce stresses between the adherend and film due to excessively different thermal expansion and contraction characteristics

2.4.5

Fortifiers

The durability of an adhesive can be improved by addition of some materials to the adhesive binder. The material may be binders or may have some distinct adhesive value. An example is the addition of formaldehyde to improve the resistance of the resultant joint. The resultant adhesive has a greater durability than the initial one.

2.4.6

Preservatives

Preservatives are agents added to adhesives to prevent micro-organisms' decompositions or action either while the adhesive is being stored or applied or during service of the completed bond. These agents are usually most important in formulations containing carbohydrates or proteins that are readily attacked by mould, fungi or bacteria. Preservatives include inorganic materials such as copper or mercury salts, and newer organic compounds such as organic mercury components and the various chlorinated phenols.

2.5

Tannin

The word 'tannin' is owed to 'sequin' who introduced the terminology to describe extractable matter in certain plant tissues capable of turning hide into leather (Gana, 2000). Tannins are one of the many types of secondary compounds found in plants and occurred in varying degree in nearly all forms of plants. One of the most satisfactory definitions of tannin was given by Horvath (1981): "any phenolic compound of sufficiently high molecular weight containing sufficient hydrolysis and other suitable groups (i.e. carboxyls) to form effectively strong complexes with protein and other macro-molecules under the particular environmental conditions being studied" (www.ansci.cornell.edu).

Tannin therefore, is a large, astringent molecule found in plants that bonds readily with proteins. They are generally yellow-white to brown, deepen in colour when exposed to light. Their ability to transform proteins into insoluble products

that are resistant to decomposition makes them to be used as tanning agent for leather (www.braintan.com).

Other characteristics of tannin are given below:

- (i) They are oligomeric compounds with multiple structure units with free phenolic groups.
- (ii) They have molecular weight ranging from 500 to >20,000.
- (iii) They are soluble in water, with exception of some high molecular weight structure.
- (iv) They bind proteins and form insoluble or soluble tannin-protein complexes.
- (v) They have a pI of 3.5-6.0 and they decompose at temperature 210-215⁰C

2.6

Common sources of tannin

Tannins occur in nearly every plant from all over the world, in all climates. It is found in almost any part of the plant, from root to leaves, bark to unripe fruit. Algae, fungi and mosses do not contain much tannin. Most trees contain plenty of tannin, concentrated in the bark layer where it forms a barrier against micro-organisms such as fungi and bacteria. Average compositions of tannin from different sources are given in Table 2.2 below (www.braintan.com).

Table 2.2: Sources and Composition of Tannin

Sources	Average Composition (%)	Types of Leather formed
Oak bark	10	Mellow and tight, with a yellow brown colour.
Oak wood	6	As in Oak bark
Fir bark	11	Yellow/brown
Birch bark	12	Fragile leather gives a light red- brown colour.
Hemlock bark	10	Good for both heavy sole as well as lighter fancy leather.

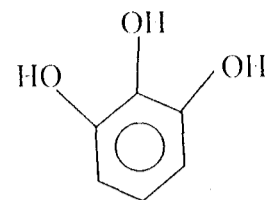
2.7 Types of Tannin

Tannins are usually subdivided into two groups

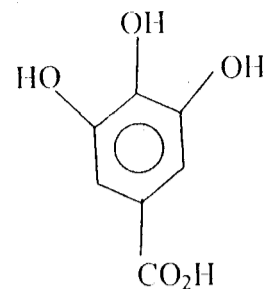
- (i) Hydrolysable tannins
- (ii) Proanthocyanidins (often called condensed tannins)

2.7.1 Hydrolysable tannins

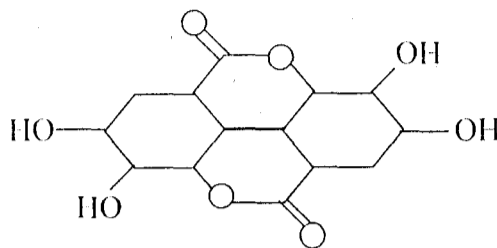
Hydrolysable tannins are molecules with a polyol (generally D-glucose) as a central core. The hydroxyl groups of these carbohydrates are partially or totally esterified with phenolic groups like pyrogallol, gallic acid (gallotannins) or ellagic acid (ellagitannins). Hydrolysable tannins are usually present in low amounts in plants. They are hydrolyzed by mild acids or mild bases to yield carbohydrate and phenolic acids. They are equally hydrolyzed by hot water or enzymes (i.e. tannase):



(i) Pyrogallol



(ii) Gallic acid



(iii) Ellagic acid

Fig. 2.1: Hydrolysable Tannins

They have been used successfully as partial substitution of phenol in producing phenol-formaldehyde resins. Their chemical behaviour is analogue to that of simple phenols of low reactivity toward formaldehyde and their moderate use as phenol substitute in the above mentioned resins does not present difficulties. Their lack of macromolecular structure in their natural state, the low level of phenol substitution they allow, their low nucleophilicity and limited worldwide production somewhat decrease their chemical and economic interest (Evwierhurma, 2000)

2.7.2

Proanthocyanidins

Proanthocyanidins are more widely distributed than hydrolysable tannins. They are oligomers or polymers of flavonoid units (i.e. flavan-3-ol) linked by carbon-carbon bonds not susceptible to cleavage by hydrolysis. They constitute more than 90% of the total world production of commercial tannins (350,000 tons/yr), and are both economically and commercially more interesting for the preparation of adhesive and resin. Among the important proanthocyanidins are the extract from the wood or bark of wattle, schnopsis (quebracho) and mangrove (Ogunmola, 2000).

Mangrove bark, which is the major raw materials for this research work, has proanthocyanidins as the major constituents. Proanthocyanidins consist of flavonoid analogs, carbohydrates and traces of amino and imino acids. Mono flavonoids and nitrogen containing acids are present in concentrations, which are too low to influence the chemical and physical characteristics of the extract as a whole. However, the simple carbohydrates (hexoses, pentoses, and disaccharides) present in sufficient quantities to decrease and increase viscosity respectively and excessive variations in their percentages would alter the physical properties of the natural extract independently of contributions related to the degree of condensation of tannins. Among the groups of mono-flavonoids noted above, only flavon-3,4-diols and certain flavon-3-ols do appear to participate in tannin formation. The main polyphenolic pattern is represented by flavonoid analogs based on resorcinolic A-rings and pyrogallol B-rings. These constitute about 70% of tannin.

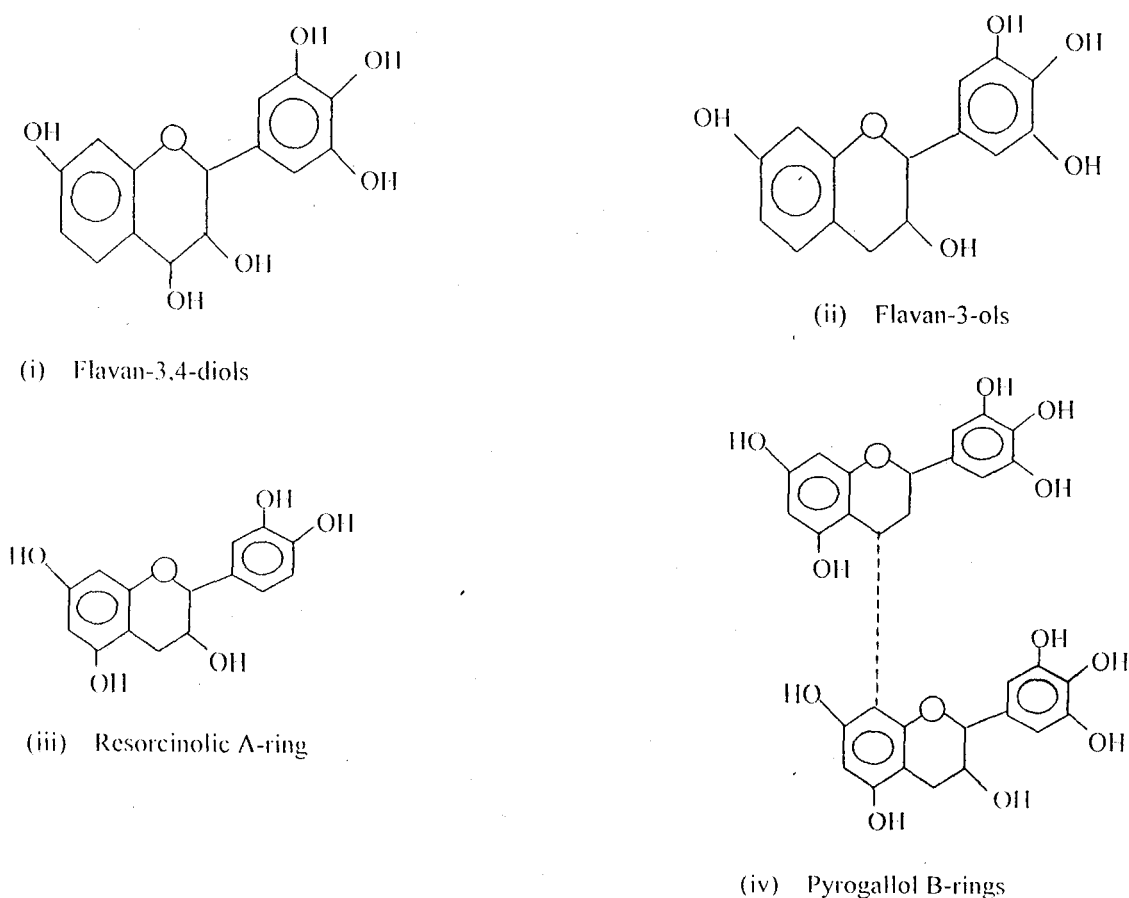


Fig. 2.2: Condensed Tannins

The phenolic hydroxyl groups are highly reactive and they induce reactive centers in the ortho and para positions of the benzenoid nuclei as shown in Fig. 2.3

X = highly reactive centre
 x = reactive centre

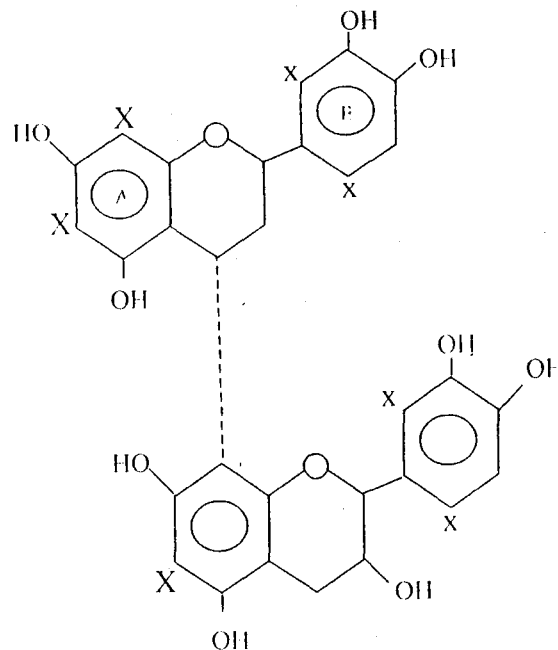


Fig. 2.3: Reaction centres in the ortho and para positions of benzenoid nuclei.

The nucleophilic centres on the A-ring of a flavonoid unit tend to be more reactive than those of the B-ring. This is due to the vicinal hydroxyl substitutes, which merely cause general activation in the B-ring without any localized effect as those found in the A-ring.

In their reactions with formaldehyde, tannins behave as typical phenols. The reactivity of wattle bark tannins is somewhat closer to that of resorcinol than phenol. Formaldehyde reacts with tannin to produce polymers through methylo bridge linkages of reactive positions on the flavonoid molecules. Some of the nuclei in proanthocyanidins have the ability to form crosslink with aldehydes. The high molecular is required for crosslinking the molecules.

Because of their size and shape, the tannin molecules become immobile at a low level of condensation with formaldehyde so that the available reaction sites are too far apart for further methylene bridge formation. The result is incomplete polymerization and therefore weakness. Bridging agents with longer molecules such as resorcinol formaldehyde, phenol-formaldehyde condensates have been shown capable of bridging the distances that are too large for methylene bridges.

2.8

Tannin Hydrolyses

Caustic hydrolysis of resorcinolic tannin has been reported to cleave the interflavonoid bond and open the heterocyclic ring joining the A and B ring of the flavonoid unit. A proposed mechanism based on this study is shown in Figure 2.4 below.

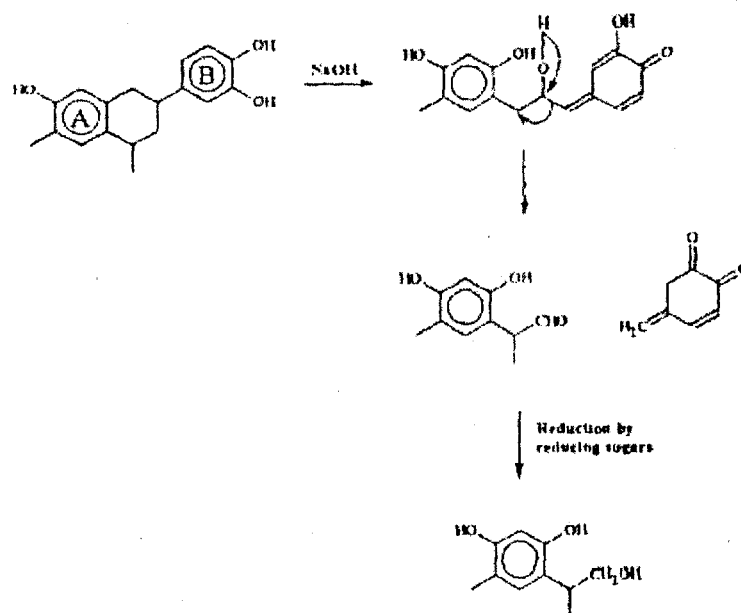


Figure 2.4: Proposed caustic hydrolysis reaction.

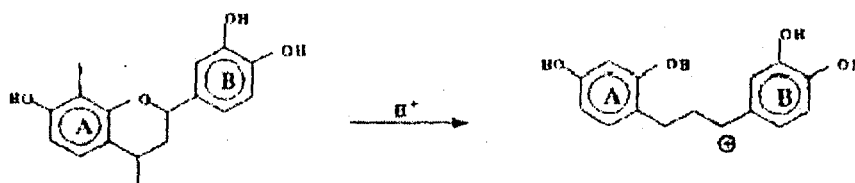


Figure 2.6: Acid hydrolysis of the polyflavonoid.

Acid hydrolysis has been shown to easily open the heterocyclic of polyflavonoids with the formation of carbonation, which is capable of reacting with another nucleophile present. Figure 2.5 represents this.

Pizzi and Stephanou 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 were suggested as probable reasons for the improved adhesive performance.

- i. Cleaving of the tannin interflavonoid bond: This results in smaller, more mobile tannin flavonoid compounds. Therefore, the level of condensation is enhanced with formaldehyde.
- ii. Opening of the heterocyclic ring joining the A and B rings of the tannin flavonoid compounds leads to a more flexible compound and 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 the tannin-based adhesive. On the other hand, their corresponding sugars (of low molecular weight) do not 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 (Sowunmi, 1996).

2.9

Uses of Tannin

The usefulness of tannin cannot be over-emphasized. It has found a wide range of applications in the under-mentioned areas:

- (i) Manufacture of adhesives: Phenol is now being replaced with tannin in the production of phenol-based adhesives. Tannin can react with formaldehyde to give a polycondensation product of tannin-

formaldehyde adhesive, which can be used for wood, and wood products.

- (ii) Leather tannin: This is one of the traditional uses of tannin. Tannin has the property of converting the gelatin of hides into insoluble non-putrefying material, thus changing the hide into leather.
- (iii) Tannin is used in compounding ink.
- (iv) It is used as a mordant in dyeing.
- (v) It is as well used in the clarification of wine and beer.
- (vi) Due to its styptic and astringent properties, tannin has been used to treat tonsillitis, pharyngitis, hemorrhoids and skin eruptions. It has been administered internally to check diarrhoea and intestinal bleeding.
- (vii) It is used in oil drilling to reduce viscosity of drilling mud oil wells without reducing the specific gravity.
- (viii) Used in boilers water to prevent scale formation.

2.10 Phenol

Phenol (formerly called carbolic acid) is found naturally in decaying dead organic matter like rotting vegetables and in coal. It was first isolated in 1834 from coal tar this remained the main source of phenol until the First World War. The first synthetic method was then devised and all of the phenol today is man-made. The prolonged sulphonation of benzene produces a benzene sulphonic acid, which, when fused with caustic alkalis, form a phenol (www.3dchem.com).

Phenol is the simplest member of a family of compounds in which OH-functional group is directly attached to a benzene ring.

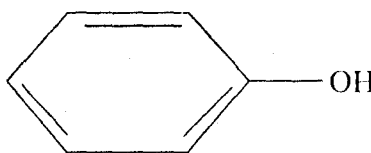


Fig 2.6: Phenol Structure

2.10.1 Properties of phenol

- (i) Pure phenol is a white crystalline solid, smelling of disinfectant.
- (ii) It has a chemical formula of C_6H_5OH .
- (iii) It boils at $182^{\circ}C$ and melts at $40-43^{\circ}C$.
- (iv) It is moderately soluble in water. About 8g of phenol will dissolve in 100g of water. Dissolving more than this quantity of phenol in water forms two layers of liquid. The top layer is a solution of phenol in water, and the bottom one a solution of water in phenol (www.chemguide.co.uk).

2.10.2 Uses of phenol

- (i) The primary use of phenol is in the production of phenolic resins, which are used in the plywood, construction, automotive, and appliance industries.
- (ii) Phenol is also used in the production of caprolactam and bisphenol A, which are intermediates in the manufacture of nylon and epoxy resins, respectively.
- (iii) Other uses of phenol include as a slimicide, as a disinfectant, and in medicinal products such as ear and nose drops, throat lozenges, and mouthwashes (www.lakes-environmental.com)

2.11 Formaldehyde

Formaldehyde is a colourless with a strong, pungent, irritating odour. For laboratory use, it is typically sold as formalin, a methanol-stabilized water solution that contains 37%, 44% or 50% formaldehyde. It is one of the most commonly produced chemicals in the United State, ranking 24th overall in chemical production.

Formaldehyde is used primarily in the production of resins, as a intermediate in the production of industrial chemicals (such as ethylene glycol) and as a bactericide or fungicide. It can also be used in urea-formaldehyde foam

insulation, production of cosmetics, paints, adhesives, and fabrics. It is as well used in the funeral service industry, by pharmaceuticals as an antibacterial agent, and by the oil industry in the preservation of oil well drilling and production fluids.

CHAPTER THREE

3.0 MATERIALS AND METHODOLOGY

3.1 Equipment and Materials

3.1.1 Equipment

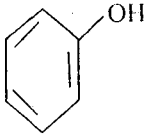
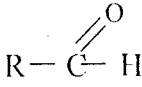
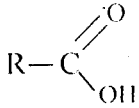
Some common laboratory equipment like beaker, measuring cylinder, spatula and thermometer were used in the present work. Table 3.1 shows the list of new equipment that were equally used.

Table 3.1: List of New Equipment Used in the Experiment

Equipment	Source	Comment
50 ml Double Jacketed Glass Reactor	BDH, Pool, England.	Used for high pressure reaction.
Water Bath	Chemical Eng'g lab FUT, Minna	Supplied hot water at a regulated temperature to the reactor.
pH Meter	Kent Ind. Ltd, England.	Determined the pH of the system
Magnetic stirrer	Chem. Eng'g lab FUT, Minna	Maintained product homogeneity through constant stirring.
Pump	Chem. Eng'g lab FUT, Minna	Used to pump hot water from water bath to the reactor
Viscometer	Pyrex, England	U-tube glass apparatus

Materials used to carry out the present work are given in table 3.2

Table 3.2: Materials Used in the Experiment

Materials	Research Code	Structure	Source	Comments
Mangrove bark extract	Rhizophoraceae	Flakes	Mangrove bark, bank of Ethiopian river, Sapele, Delta State	An acidic solution with deep brownish colour.
Phenol	-		Avondale Lab. England	Pure white solid crystals that melts at temperature less than 43 ⁰ C
Sodium hydroxide	Caustic	NaOH	Avondale Lab. England	White crystalline solid
Formaldehyde	Formalin		Aldrich Chem. Gillingham	Colourless liquid
Acetic anhydride	-	(CH ₃ CO) ₂ O	Aldrich Chem. Gillingham	Pure, colourless liquid with 98% assay.
Acetic acid	-		Aldrich Chem. Gillingham	Pure, colourless liquid with 99.8% assay

3.2

Experimental Procedure

The procedure employed in this work involved three processes viz; tannin extraction from mangrove bark, tannin hydrolysis and tannin-formaldehyde polymerization.

3.2.1

Tannin extraction

60g of mangrove bark was accurately weighed into the porous thimble that was inserted into the extraction unit (soxhlet apparatus). Extraction was done by heating the solvent (ethanol) for 2hours at 85⁰C. The solvent was later recovered to concentrate the tannin.

3.2.2

Acid and subsequent alkaline hydrolysis of tannin

10 parts of mangrove tannin extract were charged into the double-jacketed glass reactor with 19 parts of distilled water, 0.5 parts of acetic anhydride and 0.5 parts of (3:5) phenol: acetic acid mixture was later added to the mixture. The reaction mixture was constantly stirred and held under reflux at 90⁰C for 1hr. After that, the pH of the reaction mixture was brought to 8 by adding 4.5 part of 33% NaOH solution. The reaction was then allowed to go on for 3hrs after which it was allowed to cool.

3.2.3

Tannin-formaldehyde Polymerization

10 parts of the hydrolysed tannin were combined with 9.9 parts of formaldehyde, the mixture was heated to 75⁰C and held for 1hr. This was followed by adding 0.9 parts of 33% NaOH_(aq). The reaction was again held at 75⁰C for another 1hr, after which 1.33 parts of (33%) NaOH_(aq) were finally added. The reaction was then heated for 3hrs at 75⁰C before cooling to room temperature.

3.3 Characterization of Tannin and Tannin-formaldehyde Adhesive

3.3.1 Viscosity

The standard method of viscosity determination was employed using viscometer bath and U-tube viscometer with capillary inserted into the viscometer bath.

A known quantity of the sample was poured into U-tube viscometer with capillary and then corked. The U-tube was suspended into the viscometer bath containing water and the temperature of the bath was 32⁰C. The cork was removed and then time taken for the content to run up, starting from the top mark to the middle mark was noted using a stopwatch.

The viscosity of the sample was then calculated from this procedure.

3.3.2 Density

An empty, clean and dry density bottle was accurately weighed and its weight was recorded. The density bottle was then filled with the sample and weighed again. The weight was also recorded. The difference between the two weights was taken and recorded.

The density bottle already filled with the sample was immersed in a calibrated bath of water and the volume of water displaced, which represents the volume of the sample, was noted and recorded. The ratio of the difference in weights and the displaced volume gives the density.

3.3.3 pH

The pH of the sample was measured using a pH meter. A certain quantity of the sample was poured into a beaker and the pH electrode was dipped into it. The value displayed by the pH meter was recorded.

3.3.4

Infrared (IR)

The adhesive sample was smeared on a cell and placed on a light path of the spectrophotometer. The absorption of radiation was immediately detected as presented in Figure 4.1.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Results

The results of the extraction and physicochemical properties carried out on tannin and tannin-formaldehyde adhesive are presented in the tables below. Figure 4.1 shows the infra red analysis of the tannin adhesive.

Table 4.1: Percentage Yield of Tannin Extract

Mass of sample before extraction(g)	Mass of sample after extraction (g)	Mass of tannin extracted (g)	Yield (%)
60	47.676	12.324	20.54

Table 4.2: Physicochemical Properties of Tannin

Properties	Values obtained	Standard Values
Viscosity (cP)	28.3	-
Density (g/cm ³)	1.021	1.4-1.5
Refractive Index	1.46	-
pH	5.7	3.5-6.0

Table 4.3: Physicochemical Properties of Tannin-formaldehyde Adhesive

Properties	Values obtained	Standard Values
Viscosity (cP)	34.4	-
Density (g/cm ³)	1.22	1.4-1.5
pH	6.0	6.5-7.1

4.2

Discussion of Results

The extraction process of 60g mangrove bark for 2hours at 85°C, using ethanol as solvent, gives a tannin yield of 20.54%. Extraction of tannin using other solvents (water, acetone) was not considered, but solvent like acetone gives a higher tannin yield than the ethanol used (Ogunmola, 2000). Because of its readily availability and cost, ethanol was used in this present study.

The physicochemical properties of tannin and tannin adhesives were obtained. The pH of tannin and tannin adhesives are 5.7 and 6.1 respectively, which fall within the standard range value. Similarly, the values of their respective densities fall slightly below the standard range. The density of tannin extract is 1.02g/cm³ while that for tannin adhesive is 1.22g/cm³. This could be due to environmental influence on the set-up, and the likely presence of impurities in the tannin extract.

From the infrared analysis (Fig: 4.1), the tannin-formaldehyde adhesive shows frequency range of 3600-3800cm⁻¹, which indicate the presence of phenol, a characteristic property of tannin flavonoid molecules (polyphenols). The trough at frequency 3500cm⁻¹ indicates absence of amine groups, while at a broad frequency stretch of 3000-2500cm⁻¹, indicating aldehydes presence. This confirms the presence of formaldehyde used. At frequency range of 1900-1600cm⁻¹, acids are present, which confirms the hydrolysis of tannin in ring opening polymerization.

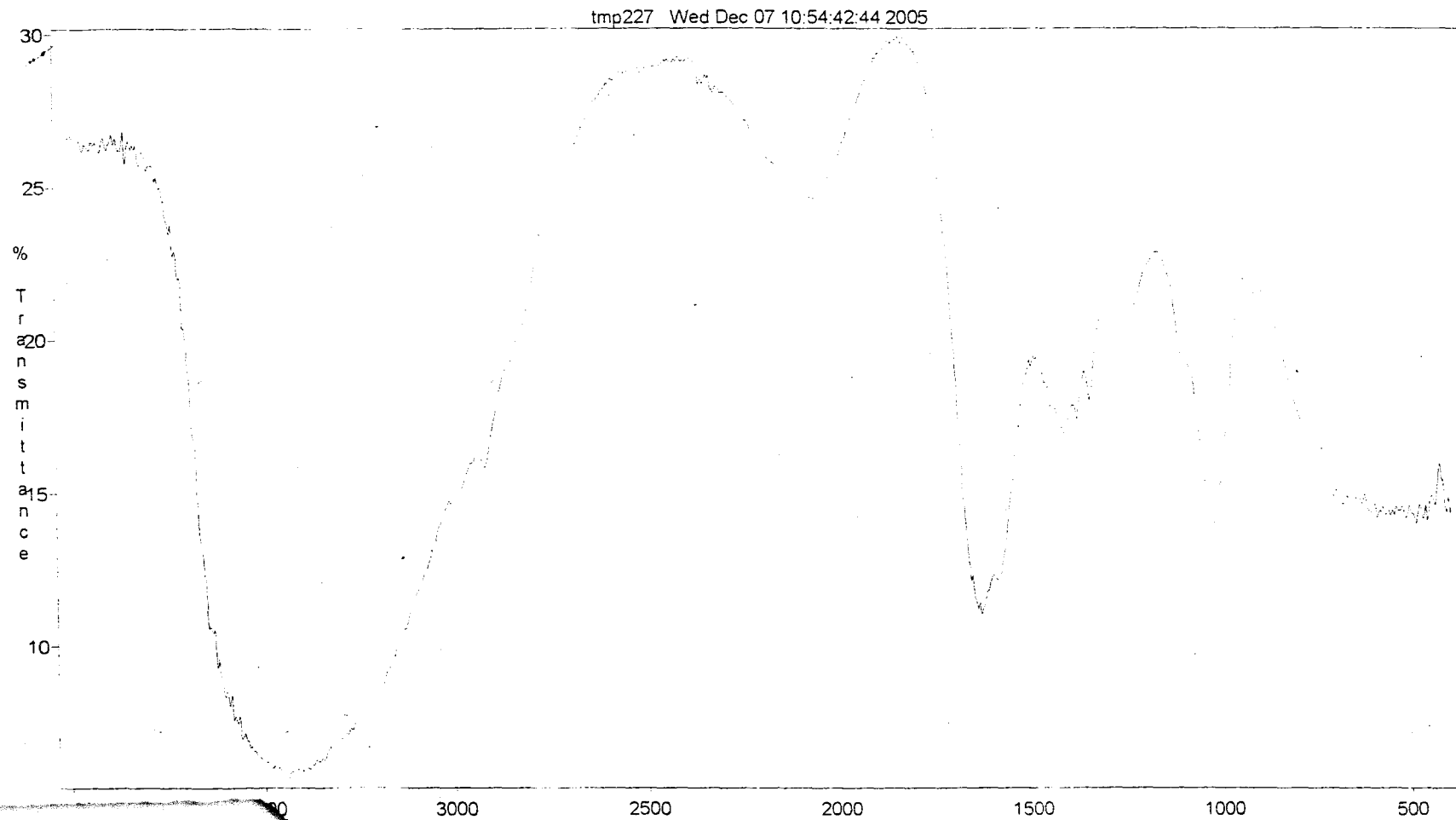
WinFIRST Report

Name: Alate Waheed

Date:

Sample: TanninFormaldehyde

Comments: Neat



Alkenes are present at a low transmittance (<12%) at frequency range of 1600-1500 cm^{-1} . This shows that the characteristic methylene bridge in tannin-formaldehyde polymerization has been improved upon through tannin hydrolysis. The frequency range of 1000-1500 cm^{-1} shows the presence of OH group, which confirms polycondensation reaction of flavonoid molecules (tannin) with formaldehyde.

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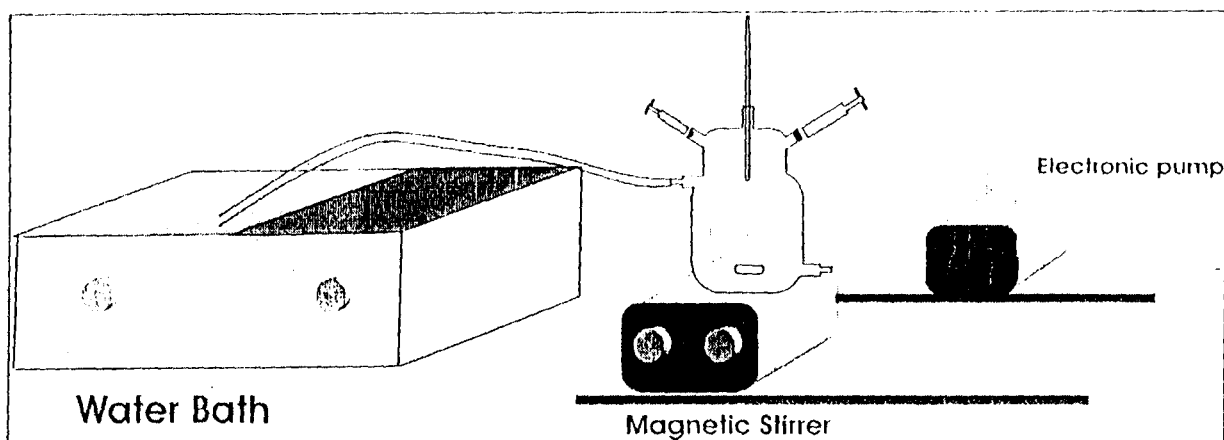


Fig 3.1: Experimental set-up

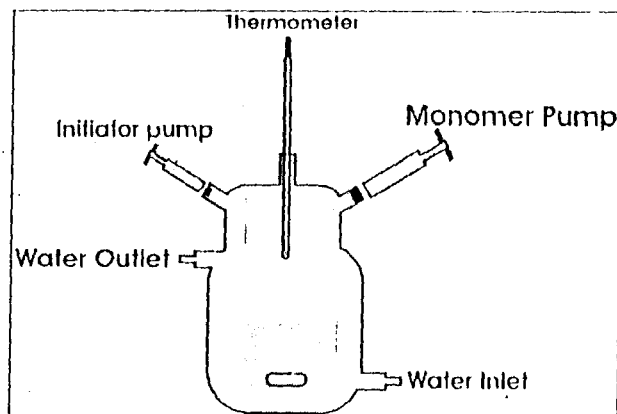


Fig 3.2: Semi batch reactor

APPENDIX

Calculations

$$\% \text{ Yield} = \frac{\text{Total weight of tannin extracted}}{\text{Initial weight of mangrove bark}}$$

$$= \frac{12.324}{60} \times \frac{100}{1} = 20.54\%$$

$$W_a = 26.13\text{g}$$

$$W_b = 36.34\text{g}$$

$$W_c = 64.27\text{g}$$

$$W_d = W_b - W_a = 10.21\text{g}$$

$$W_e = W_c - W_a = 34.14\text{g}$$

$$V_1 = 10\text{cm}^3$$

$$V_2 = 28\text{cm}^3$$

$$t_1 = 314.2$$

$$t_2 = 320$$

$$C = 0.0882$$

$$\rho_1 = \frac{W_d}{V_1} = 1.021\text{g/cm}^3$$

$$\rho_2 = \frac{W_e}{V_2} = 1.22\text{g/cm}^3$$

$$\text{But } K = C \times t$$

$$K_1 = C \times t_1 = 27.71$$

$$K_2 = C \times t_2 = 28.22$$

$$\mu = K \times \rho$$

$$\mu_1 = 28.3\text{cP}$$

$$\mu_2 = 34.4\text{cP}$$