

**PRODUCTION AND CHARACTERISATION OF TANNIN  
ADHESIVE FROM MANGROVE BARK**

*BY*

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**NOVEMBER, 2004**

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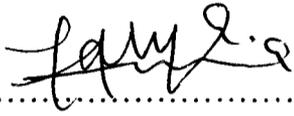
**In partial fulfilment of the requirement for the Degree of Bachelor of  
Engineering (Chemical Engineering)**

**Department of Chemical Engineering , School of Engineering and  
Engineering Technology, Federal University of Technology,  
Minna, Nigeria**

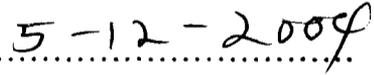
**NOVEMBER, 2004**

**DECLARATION**

I, Mohammed Yahaya Aruna, declare that this project is solely the result of my work and has never been submitted anywhere for any degree. All literature cited have been duly acknowledged in the references.



Mr. M·Y. Aruna



Date

## CERTIFICATION

This project titled PRODUCTION AND CHARACTERISATION OF TANNIN ADHESIVE FROM MANGROVE BARK by Mohammed Yahaya Aruna meets the regulations governing the award of degree of Bachelor of Engineering (Chemical Engineering) of Federal University of Technology Minna, and is approved for its scientific contribution to the knowledge and literary presentation.



.....  
Dr M.O. Edoga  
Supervisor

2004-11-29

.....  
Date

.....  
Dr. F. Aberuagba  
Head of Department

.....  
Date

.....  
External Examiner

.....  
Date

## DEDICATION

This work is dedicated to Almighty Allah. It is also dedicated to all that affected my life positively in the pursuance of Bachelor of Engineering Programme.

## ACKNOWLEDGEMENT

Glory and adoration to Almighty Allah, the controller of the Universe, the beneficent, in his mercy I dwelled upon throughout this Bachelor of Engineering Programme.

My profound gratitude goes to my project supervisor, Dr M.O. Edoga, for his advice and useful suggestions towards the accomplishment of this project.

Special thanks go to the whole academic and non-academic staff in chemical Engineering Department for their attention and co-operation given to me throughout my years of study.

I owe an appreciation to my brothers and sisters for their splendid contribution towards my success in life.

The brotherly advice of my friends: Mr. Areo Oluseye, Mr. Dadi Afolayan, Mr Balogun Deji is not left unacknowledged. My appreciation goes to Miss B Akinyemi, Mr. Olaniyi Hori for their support towards the completion of this programme. Special appreciation is also due to those that are not mentioned in this acknowledgement but God knows you better.

Finally, my gratitude goes to Almighty Allah once again for all things belong to Him, and for his unending mercy showering on me every second, minute, hour, day, week, months, year and for keeps on this earth.

## ABSTRACT

This work was based on the production and characterisation of tannin adhesive from the bark of mangrove. In attempt to extract tannin, about 8.70kg of fresh Mangrove bark was gathered from Federal Ministry of Forestry, Minna, Nigeria. The fresh bark was oven dried at 40<sup>0</sup>C until constant weight was attained before crushing it into smaller particle size of 250µm. About 25.00g each of the crushed Mangrove bark was soaked in 200.00ml of ethanol and distilled water using direct and indirect (soxhlet extraction) methods to leach out the tannin. The operation was performed repeatedly until substantial amount of tannin was recovered. 40.00g of tannin was reacted with 5g paraformaldehyde to produce tannin adhesive as a result of polycondensation reaction at a pH range of 6.5-7 and operating temperature of 40<sup>0</sup>C at atmospheric pressure.

The formulated adhesive was subjected to various tests and analysis such as viscosity, density, refractive index (RI), pH and molecular weight measurement as well as infrared analysis (IR).

The results of the tests show that the tannin adhesive has a viscosity of 28.59cp, density of 1.013g/cm<sup>3</sup>, refractive index of 1.34, pH 6.52 and molecular weight 2254.06, respectively. Also, the results of the IR analysis show that there was strong absorption at 3500-3600cm<sup>-1</sup> and 1300cm<sup>-1</sup> indicating the presence of phenol and methylene linkages due to the presence of C-H bond, respectively.

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## NOMENCLATURE

**C** = Viscometer constant

**t** = time for a fixed volume of liquid to flow

**v** = kinematic viscosity

**$\mu$**  = viscosity of liquid

**$\rho$**  = density

**$M_1$**  = mass of density bottle

**$M_2$**  = mass of tannin adhesive

**$M_3 = M_1 + M_2$**  = mass of density bottle + adhesive sample

**V** = Volume of sample

**$\mu_i$**  = Viscosity of the polymer solution

**$\mu_0$**  = Viscosity of solvent

**$[\mu_i]$**  = Limiting viscosity number

**k and a** = parameters that depend on solvent and polymer

**T.A** = Tannin adhesive fortified with Para formaldehyde

## CHAPTER ONE

### INTRODUCTION

#### 1.0 Background

An adhesive is a non-metallic material that is capable of joining bodies together by surface tension and internal strength (adhesion and Cohesion) without the structure of the bodies undergoing significant changes. It could be regarded as a social material in that it is capable of bringing two bodies together. Adhesive is a generic term and covers other terms like glue, paste, gums and binding agents.

The origin of adhesive could be traced back to ancient Egypt. The advancement in modern technology necessitated the use of adhesive in construction works, automotive, manufacturing plants, paints medical and laboratory equipment, pharmaceuticals, furniture, shoes and book binding industries, textile products and general industries.

The most prominent wood adhesives used for the past forty and fifty years have been amino plastics types. Polyhenolic adhesive continue to be the most used for weather resistant wood products. These adhesives are largely derived from petroleum however/petroleum and its by products) a finite natural resources whose supply and price are subject to international political climate as witnessed by sudden price upsurge after 1973 oil crisis is of increasing demand in a variety of ways such as in petrochemical, processing, pharmaceutical, manufacturing and a host of all other allied industries.

Therefore, the need for forest product industry to look for alternative sources of raw materials from non-petroleum based and renewable resources for its production cannot be overemphasised. There have been several attempts to replace part of petroleum derived phenolic compounds in wood adhesive with phenolic type compound obtained from renewable resources. Principal among these efforts

is the development of adhesive from tannin which represents such potential substitute and or supplement for synthetic adhesives.

Tannin adhesive is a resinous product of poly condensation reaction of tannin extract with formaldehyde. The use of tannin- formaldehyde resin as an adhesive was suggested after the Second World War due to the energy crisis and high cost of petroleum derivatives. Various sources of tannin are mangrove bark, Mangrove bark; Oak bark etc. Tannin is polyphenolic in nature and renewable resources as compared to phenol from petroleum derivative which is a finite resource. This makes Tannin- formaldehyde adhesive a favourable substitute to phenol-formaldehyde.

### **1.1 Aims and Objectives**

The main objective of this thesis is to produce tannin adhesive from Mangrove bark using both direct and soxhlet extraction for wood based products and there after determine the properties of the adhesive.

### **1.2 Scope of Work**

The scope of this project includes the following.

- (i) Extraction of Tannin from Mangrove bark.
- (ii) Production of Tannin adhesive.
- (iii) Analysis of the Tannin adhesive.

## CHAPTER TWO

### LITERATURE REVIEW

#### 2.1 Historical Background

An appropriate chronology of early adhesive has been compiled, in which the use of natural resins and bitumen went back 4000BC when the Egyptians used starch and casein during the reign of the pharaohs. A glued cedar-wood chest and other glued objects were also found in the tomb of Tutankhamen in 1365BC.

In another development, a partly synthetic adhesive was developed from cellulose nitrate at the end of the 19<sup>th</sup> century that provides a plastic with an adhesive use. Thus the first wholly synthetic adhesive was accepted to phenol-formaldehyde resin resulting from the work of Baekeland in the U.S.A. during 1905 to 1910. Similarly, another adhesive known as "Urea formaldehyde" resin was developed at the end of 1920, in Germany. It came into use as a wood adhesive in the early 1930s. Another outstanding landmark in the adhesive Technology was the development of epoxy in 1946 by CIBA in Switzerland and also by Shell in U.S.A. This was found to be versatile in all applications. For the past twenty-five years, another pressure adhesive tape was developed to meet the needs of variety of applications, which have their origin in surgical plaster.

The most prominent wood adhesive used in the past 40 to 50 years have been aminoplastic and. Polyphenolic types. Polyphenolic adhesive continue to be the most used for weather resistant wood products. These adhesives are derived largely from petroleum. Apart from the disruptive influence of international politics in the supply and price of this commodity, as demonstrated in 1937 following the Arab-Israeli war, and also during the Gulf war, it is also a finite

natural resource. Therefore the need for the forest products industry to look for alternative sources of raw materials for its production processes cannot be over emphasised. In the past, some research efforts were made into obtaining substitute phenolics of equal quantity and performance, but based on cheaper raw materials from natural and renewable resources, such as tannins, lignin and furans. However, it was the energy crisis of the 70s and the consequent high cost of phenolics that forced wood product industry to look inward for phenol-type adhesives.

Tannins extracted from wood bark and other natural resources represent potential substitutes and/ or supplement for phenolics derived from petroleum. Attempts are being made world wide to utilize these tannins as major components in wood adhesives (Pizzi and his group, 1977) have successfully developed tannin- formaldehyde adhesive for use in plywood and particles board using tannins from wattle (*Acacia mearnsii*).

## 2.2 Adhesive

Adhesive can be defined as a substance capable of holding materials together by surface attachment, that is to say any thin layer of liquid that completely wets two flat solids, can serve as an adhesive. The first adhesive was found to be resinous exudates from a tree or coagulated blood of which the use is known to date back to ancient times. If the contact angle of a liquid adhesive with each adherent is not large a prompt adhesive action is obtained upon pressing them together, even though imperfectly fitted, until they are separated by only a thin liquid layer.

Adhesives are generally furnished to the job in liquid or paste form. Some physical or chemical changes are necessary to convert the adhesive to a solid. One of these changes may be hydration, as in a paste of Portland cement and

water, it may be polymerisation, as with the epoxy and polyester resins; or it may be simple evaporation of volatile materials, as in the solvent-based rubber adhesives. Other method of curing, such as vulcanization, oxidation, gelation, and pressure reduction, are also used in various applications. Since curing method vary so widely, some understanding of the properties of adhesives is necessary to ensure that proper curing method will be used on the job.

In essence, an adhesive should have the following requirement.

- Wetting
- Solidification
- Sufficient deformability to reduce the build-up of elastic stresses in the formation of the joint.

The typical adhesive joint consists of two pieces to be bonded (substrate and adherents), a layer of adhesive, and two interface where the adhesive comes in contact with the substrate. Because of the nature of specific adhesion, many substances have a natural affinity towards adhesion. If two thin sheets of glass, such as microscope slides were rubbed together, it will require some degree of tensile force to separate them.

It is often helpful to consider an adhesive bonded joint being analogous to a chain of at latest five links. These links include the cohesive strength of one adherent, the interfacial bond strength of the adhesives to this adherent, the cohesive strength of the adhesive layer itself, the interfacial bond strength of the opposite adherent, and finally the cohesive strength of the opposite adherent. In any type of bonded joint, some degree of pressure is usually required to keep the parts in intimate contact until the adhesive has cured. This may vary from simple and hand pressure to that exerted by the large presses used in fabricating glued- laminated wood members. Bonding pressure depends on the flatness of the surface, the type of substrate, the viscosity of the

adhesive and the temperature. Therefore, to obtain the best bond with particular adhesive, it is best to follow the adhesive manufacturer's recommendations.

### 2.2.1 Adhesion and bonding theory

Adhesion is the phenomenon in which surfaces are held together by interfacial forces. The total adhesive force holding two materials together is the sum of two factors namely, specific adhesion and mechanical adhesion. Specific adhesion is chemical, it is the molecular materials between two material. The actual bond may be a chemical union such as sulphur linkages in rubber to metal bonding or the silicon bond to oxygen on the surface of material or it may be simply an electrical attraction between electrons of two substances.

Mechanical adhesion is the bonding force provided by the interlocking action. Specific adhesion can be considered as an active force holding the materials together. It is effective under tensile, shear, and peel-type loadings, whereas mechanical adhesion is passive and not very effective until acted upon by an outside force. Mechanical adhesion is most effective shear-type loading and contributes little to the tensile strength of a joint.

The total force holding two materials together is proportional to the bond area. It is a common misconception that roughening the surface of a joint increases the strength of the bond because it provides mechanical interlocking. Current research indicates that surface roughening increases the bond area for specific adhesion, and that the effect of mechanical interlocking is minimal in many cases. However, a roughened surface is more difficult to wet with the adhesive, and this may result in discontinuities in the adhesive film. Consequently, best results are generally obtained with surfaces that are smooth but not polished.

Most surfaces are contaminated. Even so-called clean surfaces are generally coated with a thin layer of foreign materials, such as an absorbed film of water or a thin oxide film. Clean dry glass may often contain a thin film of water. These films often interfere with specific adhesion and should be removed with a solvent wipe or other chemical wash. Xylene or toluene will remove most greasy or oily films. Acetone will also give good results, but is a little difficult to handle at the construction site since it evaporates so rapidly. For metallic surface such as steel and aluminium, a light sanding with fine sand paper will remove the oxide film, then a quick wipe with a clean rag and acetone will remove the sanding dust, and the surface is ready for bonding. For porous substrates such as wood, a fine sanding and a wipe with a clean dry rag will produce a satisfactory substrate. Therefore, a strong adhesion occur between carefully polished containing surfaces as a results of surface tension effect caused by the presence of a thin layer of liquid between them.

### **2.2.2 Adhesive composition**

Regardless of the basic type of adhesive involved a number of general component are commonly incorporated for various purposes. The components are highlighted below.

- **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. Example of extenders are wheat flour commonly added to urea- formaldehyde wood adhesive to reduce glue- line costs often flour is added on the ration of 1:1 on a solid basis by physical mixing and additional dilution with water to a desired viscosity.

- **Solvents:-** This is needed in most adhesives to disperse the binder to a spread able liquid film- water is the solvent in wood and paper binding adhesives while organic solvents are used for synthetic resins, rubber etc.
- **Stabilizers:-** These are used to increase the adhesive resistance to adverse service conditions such as light, heat radiation etc. stabilizer also promote interfacial contact between adhesive and adherent.
- **Fillers:-** These are relatively non adhesive substances added to an adhesive to improve its working properties, permanence, or other qualities. Some of these fillers like walnut shell, flour are added to improve the spreading properties into certain porous woods. They can also alter the thermal expansion coefficient of the cured adhesive film in other to reduced stresses between the adherent and film due to excessively different thermal expansion and contraction.
- **Binders:-** These are components of adhesive which provide primarily the adhesion forces that holds the two bodies together. They are primarily polymers with optimal strength properties. The binder is generally the component from which the name of the adhesive is derived using a classification based on composition.
- **Catalyst and hardener:-** These are curing agent for adhesive system. Hardeners affect curing by chemically combining with the binders. The ratio of the hardeners to the binder determines the physical properties of the adhesive. Example of hardeners are urea, Para formaldehyde, hexamine (Hexamethylene Tetra amine) etc. Catalysts are used as curing agents for thermosetting resins to reduce curing time and increase the cross linking of the synthetic polymer.
- **Preservatives:-** These are agents added to adhesive in order to prevent micro-organisms growth or decomposition while the adhesive is being

stored or applied. These are usually important in formulation containing carbohydrates or proteins that are readily attacked by mold, fungi or bacteria examples are copper or mercury salts organic mercury and the various chlorinated phenols.

- **Fortifiers:-** These components improve the durability of the adhesive if added to the binder. They may be binders or have some distinct adhesive characteristics. e.g. addition of formaldehyde to improve the resistance of the resultant joints. The adhesive formed as a result is of greater durability than the initial one.

### 2.2.3 Classification of adhesives

Adhesives may be classified on the basis of chemical composition, setting mechanism and adhesion mechanism in pressure sensitive, adhesion and diffusion adhesives. H. Licke (II) proposed a flexible classification in which each adhesive was supposed to be characterized and classified according to various characteristics features, such as chemical basis, form of application, application temperature, thermal behaviour, uses.

The following summarise the classification of adhesive based on the setting mechanism as their uses.

- **Setting without a chemical reaction:-** The high molecular weight bonding substance is present before bonding.
- **Application without volatile solvent:-** The adhesive film is obtained by the action of heat. Example, hot melt adhesives use for paper, fibre board, plastics, textiles, leather (assembly bond).
- **Application of solution, solvent escape before bonding:-** Adhesive layer is heated before or during bonding e.g. heat sealing adhesive and high

frequency welding auxiliaries use in paper, plastic, packaging metal foil lamination etc.

- Application of solution solvent evaporated during bonding:- Solution of polymeric, natural and or synthetic substances in organic solvents e.g. polymeric vinyl compounds, natural rubber, synthetic rubbers of low polarity. Adhesive may be classified based on the principal components into:

- Naturally occurring materials e.g. starch, dextrin, vegetable matter (Tannin), protein from both vegetable and animal sources, asphalt, shellac, natural rubber etc.

- Synthetic Material;

Thermo plastic resin e.g. cellulose, ester, and ether, alkyd and acrylic ester, poly amide, polystyrene, polyvinyl alcohol etc

Thermosetting resins e.g urea formaldehyde, melamine formaldehyde, phenol- formaldehyde etc.

Another classification is based on the main types of uses. According to this adhesives are classified into

a) **Structural Adhesives:** Which primary function is to hold two adherents (bodies held together by adhesive) together and produced high strength in shear and tension. Structural adhesives are commonly used in wood and metal bonding in the fabrication of building components such as trusses and structural sard with panels.

b) **Holding Adhesives:-** Which are intended primarily for mere attaching one adherent to another and holding it in place without significant resistance to external stress.

c) **Sealing adhesives:-** Which primary function is to close a joint between two adherents to provide a seal against moisture, gases or vapours

without necessarily providing any significant strength. Sealing adhesives are used in close packaging for food and drug items in chemical processing industries.

#### **2.2.4 Advantages of adhesives bond**

Adhesive bonding has many advantages to offer the construction industry.

These include.

- 1) It makes optically transparent joints possible.
- 2) It eliminates corrosion due to metal fasteners.
- 3) It makes joints resistant to low temperature.
- 4) It produces joint resistant to high temperature.
- 5) It makes thin films and small particles that could not be joined by other techniques to be readily bonded. Typical of such products are label, abrasive wheels, sand paper and emery cloth.
- 6) Simplifies disassembly where required.
- 7) It makes joints nearly impermeable to liquid and gases.
- 8) Stresses are distributed over wide areas.

#### **2.2.5 Characteristics properties of adhesives**

The following are some of the properties used in characterising adhesives.

- **Shelf life:** This is the period of time an adhesive retains its end use properties under suitable, specific conditions. Appropriate storage generally is underspecified conditions. Appropriate storage generally is understood to mean that adhesives are stored in clean, hermetically sealed containers and cool, dry well-ventilated rooms. Shelf life is largely dependent upon temperature.
- **Bond strength:-** The bond strength is a term synonymous with adherence. It is the force required to break an adhesive assembly with failure occurring

near, or at the interface. Bonds may be stressed in shear, tension or compression, peel, or any combination of these stresses through most adhesives display optimum strength or properties in tension or compression. Tensile strength is measured by pulling a cured adhesive joint apart at right angle to the adhesive line. Shear strength may also be determined by compression loading, peel strength is determined by measuring the pulling force needed to separate adherence when force is applied to the adhesive at an angle of  $180^{\circ}$ , if one adherent is flexible and the other is rigid.

- Tack: Tack is the adhesion that can be felt when an adhesive layer comes into contact with an adherent in the virtual absence of pressure. High tack is particularly important in the case of pressure sensitive adhesive (tapes, labels) where it even measured. Tack is generally difficult to measure in setting adhesives.
- Glass Transition Temperature ( $T_g$ ): All amorphous polymers assume at sufficiently low temperature the characteristic of glasses, including hardness, stiffness and brittleness.  $T_g$  is in fact the temperature of onset of extensive molecular motion.
- Viscosity:- Viscosity is the resistance to the flow of fluids. It is extremely important as characteristic of adhesives and as an expression of their rheological behaviour. Adhesive generally show non-Newtonian behaviour.
- Pot life and application time:- The application time is the maximum time interval that may pass between mixing of the components of a two component system and application of the adhesive mixture. Normally, it is referred to more briefly as the "pot life" which is characterised by a drastic increase in the viscosity of the mixture or by gelation of the mixture.

## 2.3 Tannin

Tannins are large class of amorphous substances present in plants. They are found mostly in the bark of pine, the wattle of mimosa and Hemlock and in the wood of certain trees such as quebracho and summach. They have an astringent taste, give a blue or green colour with iron salts and are precipitated from water solution by proteins and by alkanioids. Tannins are phenolic based natural products i.e condensation products of various phenols.

Table 2.1 below gives the principal sources of tannins

Table 2.1: Principal sources of Tannin

Barks	Woods	Fruits	Leaves	Roots
Wattle	Quebracho	Myobalans	Sumach	Canaigre
Mangrove	Chest nut	Volonia	Gambier	Palmetto
Oak	Oak	Dividivi		
Hemlock	Urunday	Tara		
Eucalyptus				
Pine		Algarrobilo		
Larche				
Willow				

### 2.3.1 Chemistry of tannin

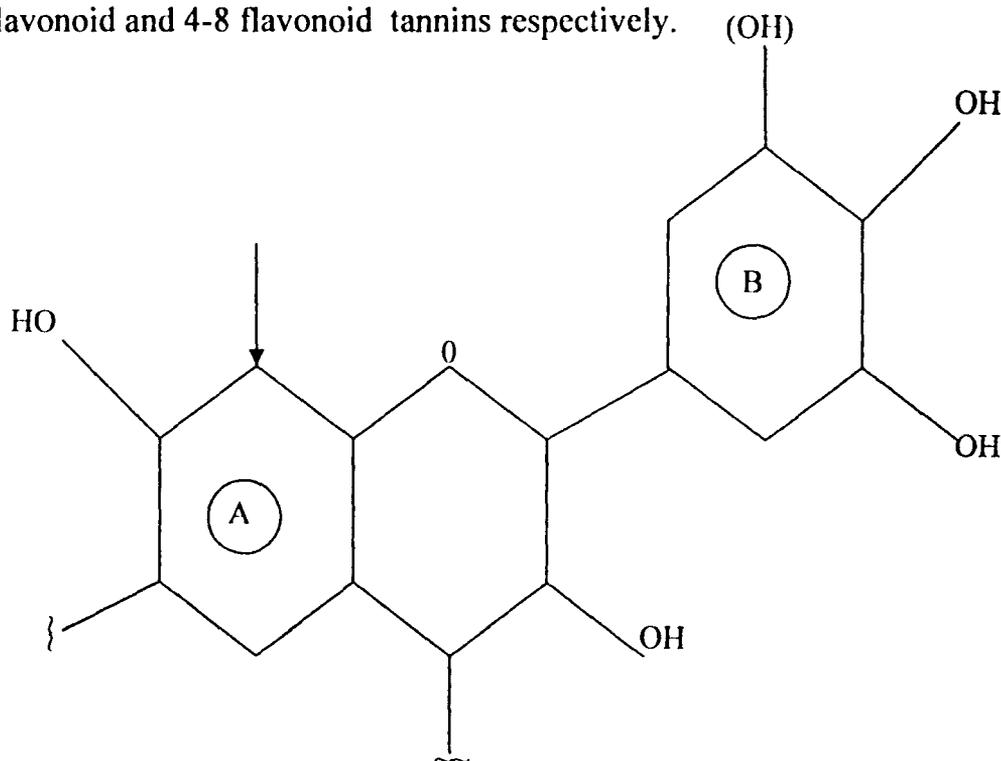
The word "Tannin" has been used loosely to define two different classes of chemical compounds of mainly phenolic nature. These are:

- 1) Hydrolyzable Tannins:- These are yellowish powder with an astringent taste, soluble in water, and alcohol, insoluble in acetone and ether, derived from nut gall, chestnut, myobalans and dividivi. They are mixtures of simple phenol that lacks macro-molecular structure in their natural state, low phenol substitution

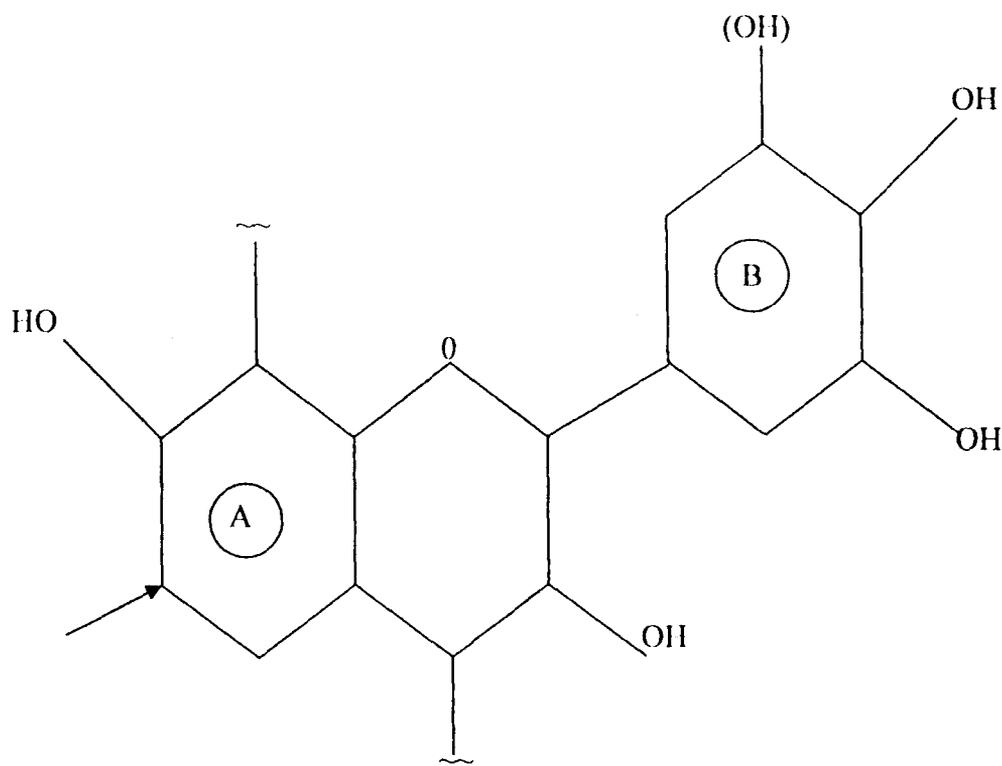
level, they allow their low nucleophilicity and limited world wide production some what decrease their chemical and economic interest. It has molecular formular  $C_{14}H_{10}O_9$  and decomposes at  $210^{\circ}C$ .

2) Condensed Tannins:- These are yellowish- white to light brown amorphous powder or flakes, decomposes at  $210^{\circ} - 215^{\circ}C$ , very soluble in alcohol and acetone, they constitute more than 90 percent of the total worlds production of commercial tannins ( $\pm 350,000$  tons per year), are both chemically and economically more interesting for the preparation of adhesives and resins.

This class of tannins yield in soluble brick red precipitate on treatment with hot dilute mineral acids. The extraction of these substances lead to a mixture of oligo- and poly- flavonoids which are known as condensed tannins, with number average molecular weight ranging from 1000 to 4000 depending on the species which generated them. The poly- flavonoid tannin essentially consists of several mono- flavonoids units ranging from 5 to 11 which includes flavon -3,4- diols, flavon -3- ol, etc. There are two typical structures of flavoniod units from mimosa and pine namely 4-6 flavonoid and 4-8 flavonoid tannins respectively.



Structure of 4-6 flavoniod tannins



### Structure of 4-8 flavonoid tannins

Tannin molecules can also form an oligomeric compound possibly through hydrogen bonding in solution, extensive hydrogen bonding between molecules like tannin-carbohydrates, tannin-tannin and tannin-gums could lead to the formation of insoluble materials (oligomers) which would be precipitated from the solution in the form of particles or gels.

### 2.3.2 Thermal hydrolysis of tannin

Thermal hydrolysis of tannin involves the use of heat to break bonds present in tannin molecules. The term bond dissociation energy is used to describe the energy required to break a specific bond in molecules. For a particular bond, the magnitude of a Standard bond dissociation energy depends on the local environment and the presence or absence of nearby electrophilic groups. Table 2.2 shows the types of bonds present in tannin molecules and their corresponding average bond dissociation energies.

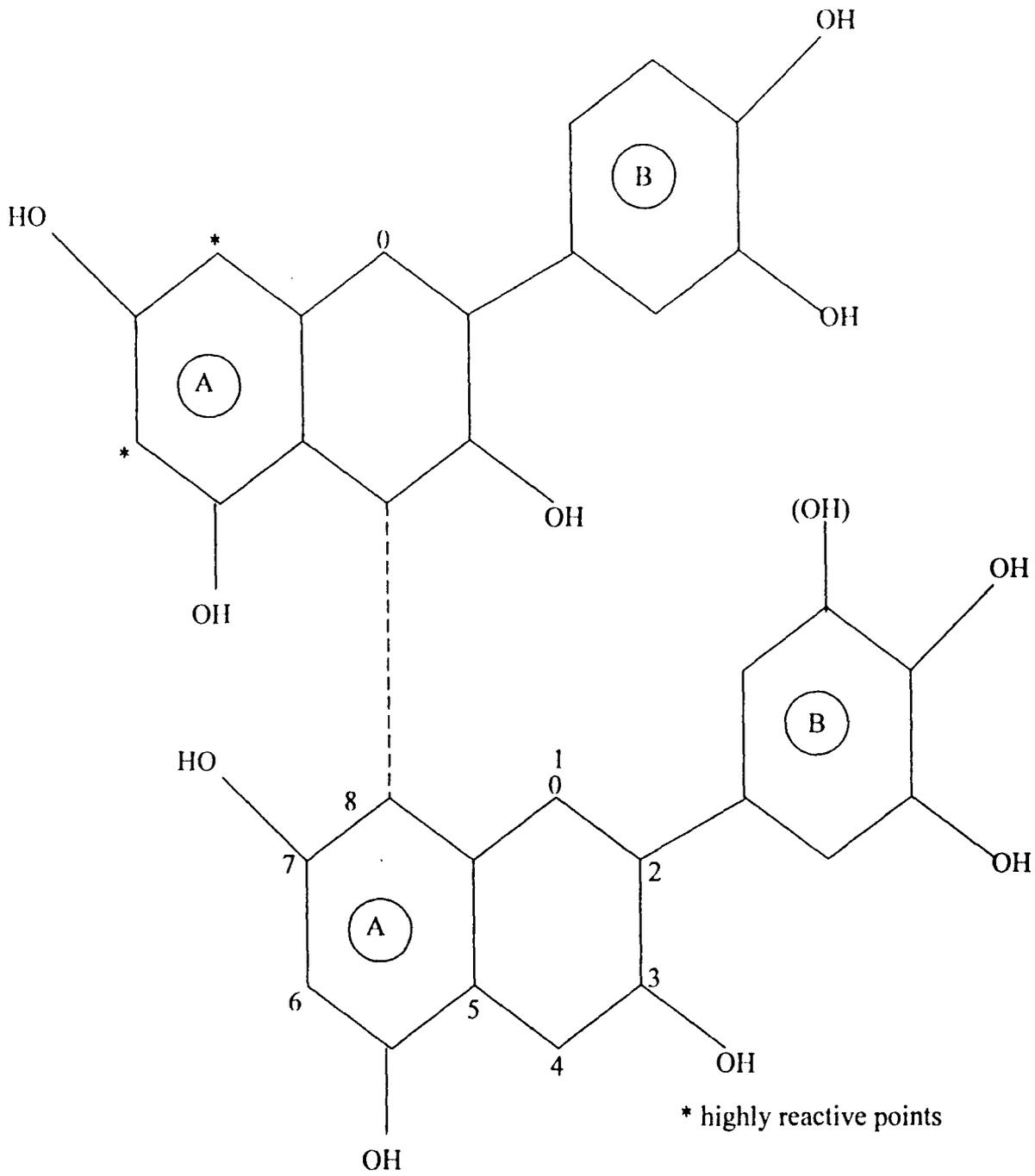
Table 2.2 bond types and their dissociation energies in a tannin molecule

Bond type	Bond strength (KJ/mol)
C-H	413
C-O	351
O-H	463
C-C	348
C=C	682
C-O-C	*
C-O-H	*

\*- not available in the literature used.

### 2.3.3 Reactivity of tannin

Formaldehyde reacts with tannins in a condensation reaction to produce polymerisation through methylene bridge linkage at relative positions on the flavonoid molecules mainly the A- ring of the tannin structure. The relative positions of the A-ring are the position “6” of the terminal flavonoid units and the position 6 and 8 of the upper terminal flavonoid unit

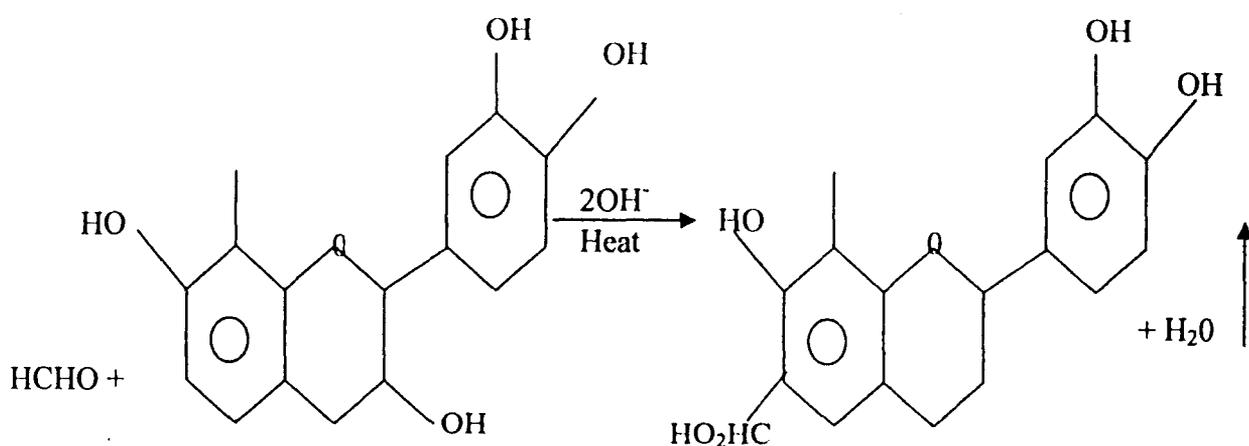


### Relative Positions of Phloroglucinolic A- Ring of Tannin Structure

For Phloroglucinolic tannin, the position 8 is more reactive than 6. This is perhaps due to the steric hindrance as a result of the presence of a hydroxyl group on either side of the '6' position as demonstrated by Pizzi (1977) who, using resorcinol as a simple model compound showed that di-tri-and tetramers formed by the acid or alkaline catalysed reaction of resorcinol with formaldehyde do not favour the position ortho to both hydroxyl group formaldehyde attacks. The catecholic and pyrogalllic 'B'- rings do not take part in the reaction with formaldehyde to any noticeable extent within the pH range for adhesive preparation because of their

low nucleophilic character. At pH 10 and above, at which the 'B'- ring is so high that the tannin formaldehyde adhesive prepared have unacceptably short pot lives metal acetate have been found to induce the 'B'- ring of tannin to participate in tannin formaldehyde reactions at lower pH values. This finding implies that, in the presence of soluble metal acetate, further cross linking of the tannin formaldehyde network could be achieved through 'B'- ring participation in the reaction.

Unlike most synthetic phenol compounds, on heating tannin degrades rather than melts. Therefore, during the condensation reaction of tannin with formaldehyde especially at high temperature, tannin molecules become immobile due to evaporation of water and low level of condensation with formaldehyde so that the reactive sites are too far apart for further methylene bridge formation. This leads to incomplete polymerisation and cross linking and therefore weak adhesive properties. It therefore appears that the size and the non-melting nature of tannin and not just the reactivity of the 'A' -ring are most probably responsible for poor adhesives properties.



Tannin-formaldehyde reaction

When dry strength increases are required from tannin adhesives in the production of interior grade panels, it is definitely possible to increase the strength of the panel by favouring the auto condensation reaction. This enables a decrease in use of formaldehyde emission by the panel. When water resistance of the panel needs to be improved that depends on the level of poly condensation between the tannin and formaldehyde yielding hardeners, other techniques have to be used to decrease formaldehyde emission without losing strength, such options include addition of urea or use of hexamine as hardener. It should be noted that urea gives greater strength than when formaldehyde is used alone, as it also participates in cross linking and hence urea does not only work as a formaldehyde emission reducer

### 2.3.4 Physico-chemical properties of tannin adhesive

Table 2.3 Physico-chemical properties of tannin adhesive

Properties	Value
Molecular weight	1000-4000g/gmol
Density	1.40g/cm <sup>3</sup>
pH	6.5-7
Refractive Index	1.3-1.6

### 2.3.5 Uses of tannin

Tannin has found wide range of application after the second world war when its traditional market (leather tanning) declined progressively coupled with increased prices and decrease availability of synthetic phenolics materials due to the advent of energy crisis. Some of the uses of tannin are as below.

#### Manufacture of Adhesive

Condensed tannins are phenolic raw materials which can be used for the manufacture of synthetic resins, for in contrast to hydrolysable tannin, they readily react with formaldehyde. Among tannins, the ability to undergo with formaldehyde condensation is a reliable diagnostic test for condensed tannins.

### **Protection of Metals**

Recent archaeological excavation have revealed that tannins in the solid preserve iron objects by exerting bacteriostatic action against the sulphate-reducing vibrio, *V. disulfuricans*. Mild oxidation increases the toxicity of tannins toward sulphate-reducing bacteria.

### **Leather Tanning:**

Leather tanning forms the traditional use of tanning in ancient times. It turns the gelation hides into insoluble non-putrefying element.

### **2.3.6 Uses/ application of tannin adhesive**

- It is used in bonding of wood together as in furniture.
- It is also used in the production of ion exchange resin.

## CHAPTER THREE

### METHODOLOGY

#### 3.1 Materials and Equipment

The tables given below show the materials and equipment used in conducting the present experiment.

Table 3.1 List of Materials used for the experiment.

S/No	Materials	Chemical formular
1	Tannin	$C_{76}H_{52}O_{46}$
2	Para formaldehyde	$(HCHO)_n$
3	Distilled water	$H_2O$
4	Ethanol	$C_2H_5OH$
5	Sodium hydroxide	NaOH
6	Monosodium dihydrogen phosphate	$NaH_2PO_4$

Table 3.2 List of Equipment used for the experiment.

S/No	Equipment	Model
1.	Weighing balance	Ohausct 1200
2.	Magnetic stirrer	Jouans 502
3.	Retort stand	Clamp 45
4.	Electric oven .	Prolabo 2k828
5.	Measuring cylinder	Jaytec BS 1792
6.	Thermometer	Jen Way 3071
7.	pH meter/ Electrode	Jen Way 3071
8.	Double jacketed reactor	Corning S- 48
9.	IR Spectrometer	Perkin Elmer 1310

## 3.2 Equipment Set-up

### 3.2.1 Soxhlet extractor

Soxhlet apparatus/ extractor is an equipment that is working based on continuous extraction of soluble components from solids by means of volatile solvents.

The diagram below (Fig 3.1) is a typical Soxhlet apparatus used for extracting tannin from the Mangrove bark. The volatile solvent placed in the round bottom flask upon heating to boiling vaporized, the vapour rose through the vertical tube at the right arm into the condenser at the top. The liquid condensed at the thimble in the centre, which contained the solid sample to be extracted (Mangrove rushed bark). The extracts seeped through the pores of the thimble and eventually filled the siphon tube at the left, where it could flow back down into the round bottom flask. In the Soxhlet, the siphoning was done intermittently. No liquid would flow through the siphon until the liquid in the thimble reached the top of the tubes at the point almost all the liquid in the siphon and the thimble drain out and the cycle of filling and draining started again.

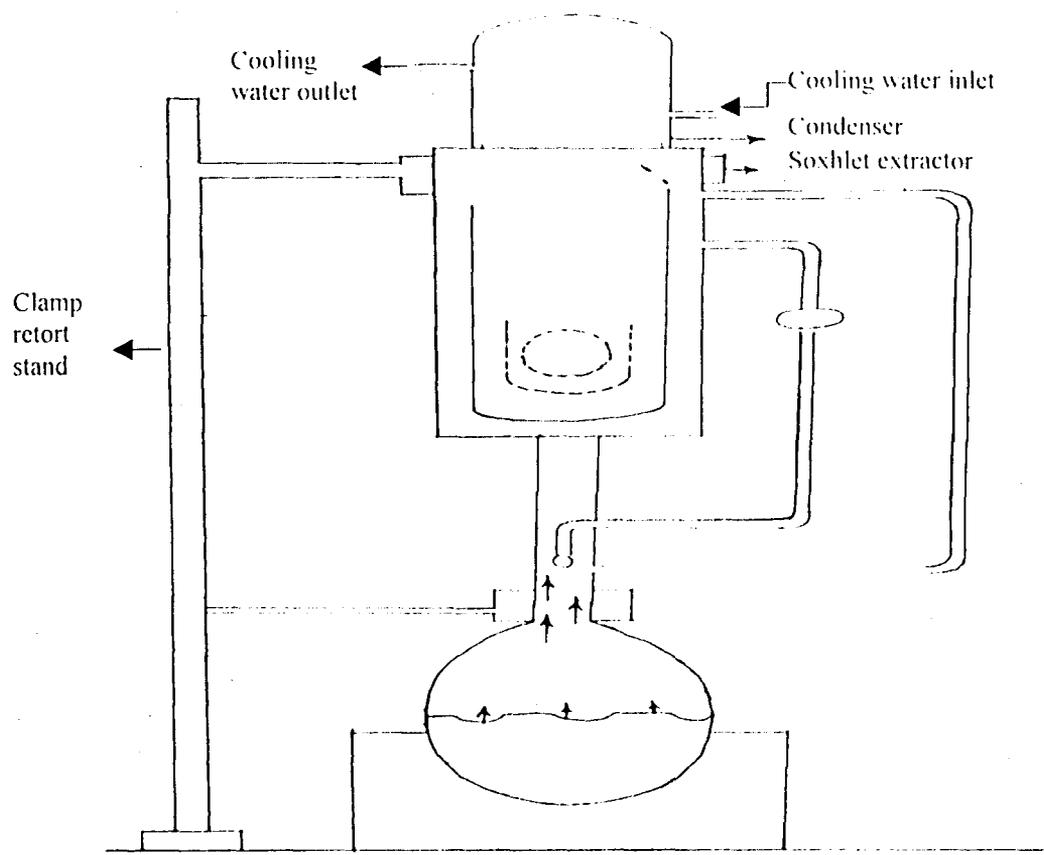


Fig 3.1 Soxhlet Apparatus

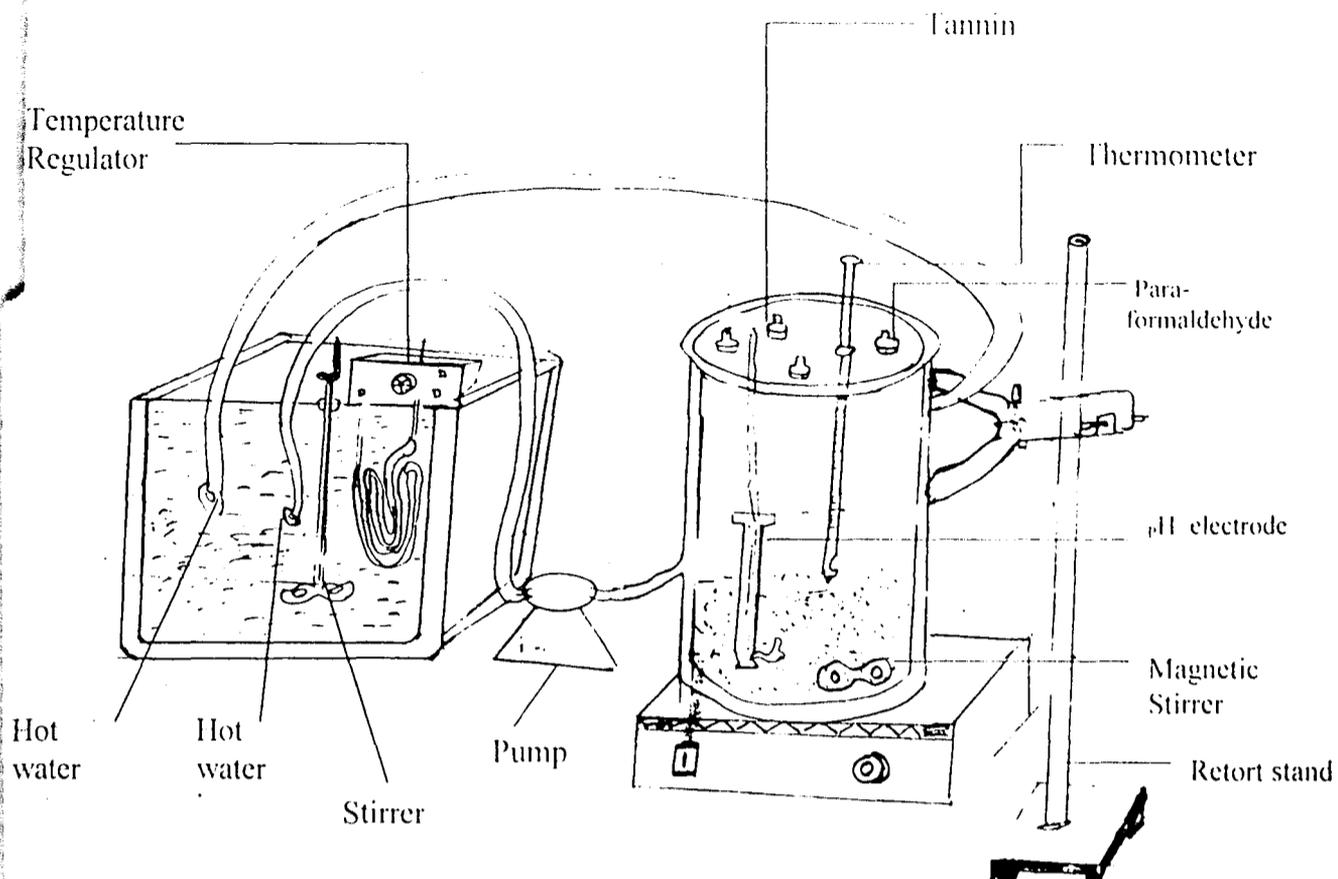


Fig. 3.2 Tannin Adhesive Production Set-up

### 3.2.2 Water bath reactor system

Fig 3.2 shows the system comprising of different apparatus used in the preparation of tannin- paraformaldehyde adhesive. The water bath was used to maintain a constant temperature of the reaction at  $40^{\circ}\text{C}$ . Tannin and para-formaldehyde were charged into the reactor at once. The piece of bar magnet in the reactor aided in mixing through stirring action induced by magnetic field of the magnetic stirrer. The pH meter and thermometer were also inserted into the reactor to monitor the pH and temperature values of reaction mixture, respectively.

### **3.3 Bark Collection**

Mangrove barks (fresh barks) were collected from Federal Ministry of Forestry, Minna Niger state, Nigeria. The barks were obtained from the mangrove tree with the aid of cutlass from the trunk. When cut new, the inner part of the barks was initially yellowish-white, which later turned reddish-brown as the cut surfaces were exposed to air. The samples were packed in a bag and subsequently were transported to the Chemical Engineering laboratory. It was weighed and dried in the electric oven at temperature of 40<sup>0</sup>C-80<sup>0</sup>C. The weight of the sample was taken on a daily basis until it reached a constant weight implying that the sample was moisture free. The weight was taken and recorded and the moisture content was eventually calculated.

### **3.4 Crushing of the Dried Bark**

The bark samples were crushed in a mortar with pestle to 250µm particle size so as to increase the surface area of the dried bark.

### **3.5 Extraction of Tannin from the Bark**

Extraction of tannin from the ground bark was carried out using the following solvents based on direct and indirect methods:

- Ethanol (Anhydrous)
- Distilled water
- Toluene
- Hexane

### 3.5.1 Direct method of extraction

#### **Extraction tannin with ethanol**

25.00g of the crushed bark was weighed on a weighing balance and then poured into 250.00ml conical flask. 200.00ml Ethanol was measured using 1000.00ml measuring cylinder and then poured into the conical flask containing the bark. The mixture was tightly closed and left aside with shaking at interval (5.00 minutes) for 1.00 hr. The conical flask with the content was weighed and recorded. The mixture was then filtered, filtrate which is reddish-brown in colour was weighed and the extract collected was evaporated to remove the ethanol, at 60<sup>0</sup>C-70<sup>0</sup>C. The resulting solution was weighed and the solution is tacky when felt with the finger due to loss of moisture. This resulting solution is tannin extract. The corresponding weight of insoluble was taken and recorded. The experiment was repeated for 5 times with time variation from (2.3.4.5.6 hours) respectively.

#### **Extraction of tannin with distilled water**

25.00g of crushed bark was weighed and poured into 250 ml conical flask. 200ml distilled water was poured into the solid and the mixture was weighed. The mixture was closed, and left for 1 hr. The procedure continues as in the case of ethanol. The product is also tannin extract.

#### **Extraction of tannin with toluene and hexane**

25.00g of the crushed bark each was weighed and each poured into 250ml conical flask (2 flask labelled A and B). 200ml of toluene was taken and poured into conical flask A and 200ml of Hexane was also taken, then poured into flask B. each flask with the contents was weighed and recorded. The mixture were tightly closed and left for 1 hr. with regular interval of shaken (5 minutes). The mixture

were than filtered into two different beakers A and B. The filtrate which is yellowish with hexane and toluene was weighed each and evaporated to remove hexane and toluene at 40<sup>0</sup>- 50<sup>0</sup>C for hexane and 100-110<sup>0</sup>C for toluene. No solution of tannin is obtained in each case. The experiment was repeated for 2, 3,4,5,6 hrs) respectively.

### 3.5.2 Indirect method of extraction (Soxhlet extraction)

25.00g of crushed bark was wrapped in a filter paper which replaced thimble, and placed in the soxhlet apparatus. Ethanol was poured into the round bottom flask and heated to boiling. The vapour in contact with the solid upon condensing leached out the Tannin, a light-brown solution. The experiment was carried out under 1 hr and the resulting solution was weighed and evaporated to give tannin extract, the insoluble was also weighed and both were recorded. The experiment was repeated for (2, 3,4,5,6 hrs) respectively.

The whole experiment was repeated for distilled water, Hexane and Toluene. Hexane and toluene did not yield any Tannin extract, but water yielded some tannin extract.

### 3.6 Adhesive Formulation

In formulating the adhesive (tannin adhesive) about 40 part of tannin extract was charged into the reactor after stabilising the pH at about 8 with monosodium dihydrogen phosphate (NaH<sub>2</sub>PO<sub>4</sub>). The whole system was clamped with a retort stand above a magnetic stirrer. The water bath supplied hot water which heats the reaction mixture to the required temperature of 40<sup>0</sup>C. Para formaldehyde was intermittently charged into the reactor to avoid gelling of the mixture. The reaction was allowed to produce for 30 minutes. The resulting solution is tannin adhesive

hardened Para formaldehyde. The pH was measured with pH meter and the temperature was read from the thermometer.

### **3.7 Characterisation of Tannin Adhesive.**

#### **3.7.1 Viscosity measurement**

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

A known quantity of sample was poured into U-tube viscometer bath containing water, and the temperature of the bath was 32<sup>0</sup>C. The cork was removed and the time taken for the content to run up, starting from the top mark to the middle mark was taken using a stop watch. The result obtained was used to calculate the viscosity of the sample.

#### **3.7.2 Density measurement**

The empty density bottle was weighed and its weight was recorded the same density bottle was filled with adhesive sample and weighed, and its weight was recorded. The difference in weight between the bottle filled with the adhesive and empty density bottle gives the weight of the adhesive added. The density was obtained by dividing the weight of the adhesive with the volume or capacity of the density bottle.

#### **3.7.3 Refractive index measurement**

The surface of the refractometer was cleaned with 95% ethanol and subsequently was dried. The liquid sample was then placed on the lower prism so that the entire width of the prism plate was covered. This was done using dropper to come into direct contact with the prism as this might scratch the prism surface. The upper prism was then brought into contact with the lower prism so that the liquid forms

an unbroken layer between the two. The control was manipulated to bring the light and dark fields into focus with the cross hairs in order to obtain the reading.

#### **3.7.4 pH measurement**

A pH meter/ electrode was used to measure the pH of the resin produced. This was done by inserting the pH meter into a baker containing tannin adhesive. The value of the pH of the resin was then read from the instrument after a couple of minutes.

#### **3.7.5 Infrared (IR) analysis**

0.5ml of the adhesive sample was spread on a cell and placed on a light path of the perkin Elmer-130 infrared spectrophotometer. The absorption of radiation was detected as shown in the Fig 4.3.

## CHAPTER FOUR

### RESULTS AND DISCUSSION

#### 4.1 Results

##### 4.1.1 Drying of Mangrove bark.

The results of drying of the mangrove bark for eight days are presented in Table 4.1

**Table 4.1: Drying Rate of Mangrove Bark in the Oven at 40<sup>0</sup>C**

Day	Time started (a.m)	Time stopped (p.m.)	Duration Hr.	Starting Weight Kg	Stopped Weight kg	Moisture Loss Kg
1.	8.30	4.30	8.00	8.700	8.093	0.607
2.	8.30	4.30	8.00	8.093	7.486	0.607
3.	8.30	4.30	8.00	7.486	6.879	0.607
4.	8.30	4.30	8.00	6.879	6.069	0.810
5.	8.30	4.30	8.00	6.069	5.259	0.810
6.	8.30	4.30	8.00	5.259	4.855	0.405
7.	8.30	4.30	8.00	4.855	4.450	0.405
8.	8.30	4.30	8.00	4.450	4.450	0.00

##### 4.1.2 Extraction of tannin using ethanol (Direct method)

The results of extracting tannin from the mangrove bark using anhydrous ethanol by direct leaching method are presented in Table 4.2.

**Table 4.2: Extraction of Tannin from the Mangrove Bark Using Ethanol (Direct Method)**

Weight of solid (g)	Volume of solvent(ml)	Weight of solution + insoluble g	Filtrate ml	Yield g	% yield	Raffinate g	Insoluble g
25.00	200.00	188.60	108	109	2.7	10.8	22.3
25.00	200.00	188.0	110	112	3.20	12.8	21.8
25.00	200.00	188.40	115	118	3.80	15.2	21.2
25.00	200.00	188.20	118	123	4.70	18.8	20.3
25.00	200.00	188.35	120	125	4.80	19.2	20.2
25.00	200.00	188.35	120	125	5.03	20.12	19.97

#### 4.1.3 Extraction of tannin using distilled water (Direct method)

Table 4.3: Extraction of Tannin from the Mangrove Bark using distilled water (Direct method).

Time hr	Weight of solid (g)	Volume of solvent (ml)	weight of solution + insoluble g	Filtrate ml g		Yield g	% yield	Raffinate g	Insoluble g
25.00	200	225.00	105	107	2.30	9.2	118.0	22.70	
25.00	200	225.00	108	110	2.80	11.2	115.0	22.20	
25.00	200	224.50	106	108	3.50	14.00	116.50	21.50	
25.00	200	225.00	109	112	4.30	17.20	113.0	20.70	
25.00	200	224.00	115	117	4.40	17.60	107.0	20.60	
25.00	200	225.20	116	117	4.60	18.40	108.20	20.40	

#### 4.1.4 Extraction of tannin using ethanol (Indirect method)

Table 4.4: Soxhlet Extraction Using Ethanol

Time Hr	Weight of solid (g)	Volume of solvent (ml)	Filtrate ml g		Yield g	% yield	Raffinate g	insoluble g
1	25	200	110.50	112.20	3.10	12.40	114.5	21.9
2	25	200	112.00	116.00	3.70	14.80	113.0	21.30
3	25	200	117.00	12.70	4.50	18.00	108.00	20.50
4	25	200	118.00	123	6.02	24.08	107.00	18.98
5	25	200	122.00	126.00	6.05	24.20	103.00	18.95
6	25	200	125.00	129.00	6.20	24.80	100.00	18.80

#### 4.1.5 Extraction of tannin using distilled water (Indirect method)

Table 4.5: Soxhlet extraction using distilled water

Time hr	Weight of solid (g)	Volume of solvent(ml)	Filtrate ml	Filtrate g	Yield (g)	% yield	Raffinate g	Insoluble (g)
1	25.00	200	107	110	2.80	11.20	118.00	22.2
2	25.00	200	110	112.00	3.40	13.60	115.00	21.6
3	25.00	200	115	117	4.40	17.60	110.00	20.6
4	25.00	200	117.50	122.90	4.80	19.20	107.50	20.20
5	25.00	200	119.00	124.0	5.10	20.40	106.00	19.90
6	25.00	200	120.00	125.20	5.10	20.40	105.00	19.90

#### 4.1.6 Results of physico-chemical properties

Table 4.6: Results of physico-chemical properties

Properties	Values
pH	6.52
Density	1.013g/cm <sup>3</sup>
Refractive index	1.34
Viscosity	28.59cp
Molecular weight	2254.06

### 4.2 Discussion of Results

#### 4.2.1 Extraction of tannin from mangrove bark

Tables 4.2 and 4.3 are the results obtained from direct extraction (leaching) method using different solvents i.e ethanol and distilled water over a time interval of 1.00 hr.

In Table 4.2, the highest yield obtained was 5.03g at the end of 6.00hr, while in Table 4.3, the highest yield obtained was 4.60g at the end of 6.00 hr. These results show that tannin is more soluble in ethanol than water. This solubility is a function

of time. The plot of % yield versus time of extraction shows an optimum yield of 20.12% at the 6.00 hr of extraction. The results in the tables and the plot show that ethanol is better than distilled water in the extraction of tannin.

Table 4.4, and table 4.5 show the results of indirect method of extraction (soxhlet extraction) using ethanol and distilled water over the time interval of 1 hr.

In table 4.4, the highest yield obtained was 6.20g at the end of 6.00 hr. while in table 4.5 the highest yield was 5.10g at the end of 6.00 hr. the plot of % yield versus time of extraction for ethanol and distilled water show optimum yield of 24.8% and 20.40% respectively at the 6.00 hr of extraction. From this, ethanol is better than distilled water in the soxhlet extraction in the sense that the solvent is not making direct contact with the solid.

The results of the experiment also shows that tannin is not soluble in toluene and Hexane, therefore no yield of tannin is obtained using the two solvents.

#### **4.2.2 Characterization of tannin adhesive**

The characterisation of tannin adhesive carried out shows that the pH of the tannin adhesive produced is 6.52 which is still within the standard, 6.5-7. Also the refractive index of the tannin adhesive was 1.34 which is within the range available in the literature i.e 1.3-1.6. The lower range is for alcohols and ketones while the upper range i.e 1.6 is for heavy hydrocarbon liquid. Therefore, since the refractive index was 1.34 this shows that it falls within the alcohol group. The density of tannin adhesive is found to be  $1.013 \text{ g/cm}^3$ . The viscosity and molecular weight are found to be 28.59cp and 2254.06 respectively.

Infrared spectrum is one of the most important properties of an organic compound that gives information about the compound's structure using the standard characteristic; infrared absorption frequencies, the infrared frequency of tannin adhesive (fig4.3) indicated the presence of phenol at a broad frequency of 3500-

3600cm<sup>-1</sup> and a sharp peak at 2500cm<sup>-1</sup>, a characteristic feature of tannin flavonoid molecules (polyphenols). The presence of aromatics at 1710-690cm<sup>-1</sup> contains polycondensation reaction of flavonoid molecules (tannin) with para formaldehyde by C-H bond at 1300cm<sup>-1</sup> which is a clear indication of methylene linkages (-CH<sub>2</sub>-), a special feature of phenolic resins.

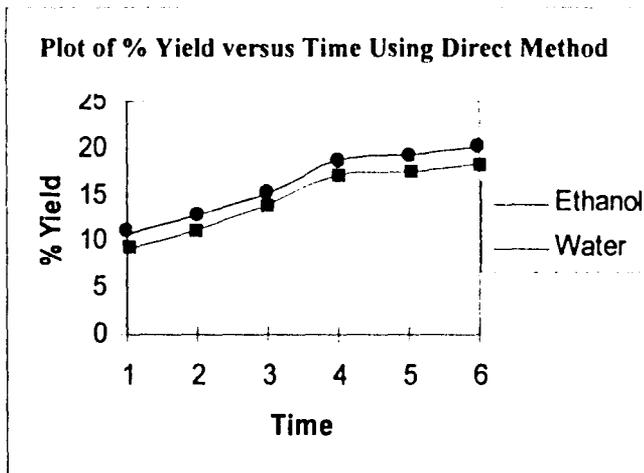


Fig. 4.1 plot of % yield versus Time using direct method

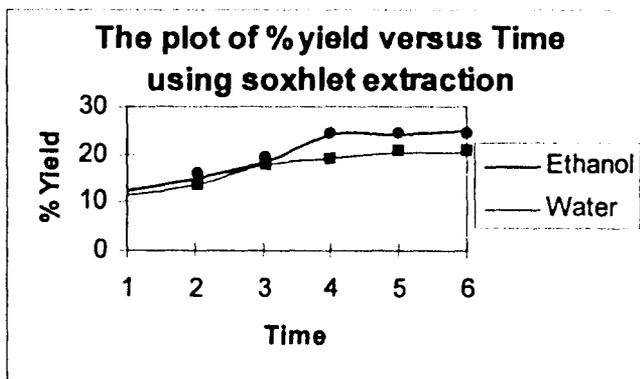
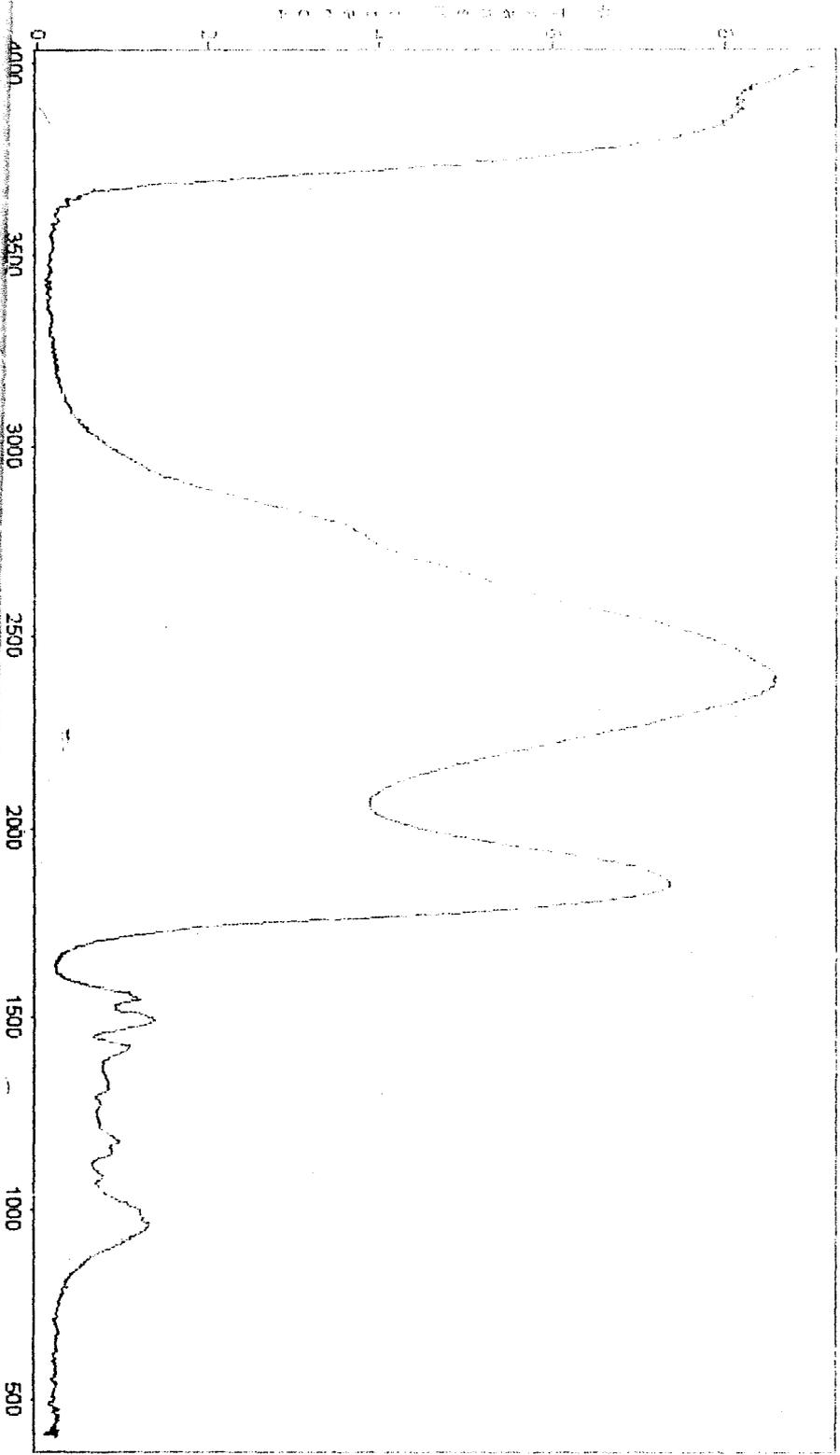


Fig. 4.2 plot of % yield versus Time using Soxhlet Extraction

HAIR FIRST REPORT

NAME: KEVIN NATHAN M.  
DOB: [REDACTED]  
Sample: F.A.  
COFFEEHANS

SMITH ORD NO. 10 23 19 09 41 2004



## CHAPTER FIVE

### CONCLUSIONS AND RECOMMENDATIONS

#### 5.1 Conclusions

The extraction of tannin from Mangrove bark and synthesis/ characterisation of tannin adhesive produced by polycondensation reaction of tannin with para formaldehyde were carried out. Tannin extracted by direct and indirect method from the bark was formulated into adhesives at a pH range of 6.5-7, operating temperature of 40<sup>0</sup>C and at atmospheric pressure over a period of 30 minutes.

The result of the physico-chemical properties and IR analysis depict that tannin adhesive was developed by polycondensation reaction of tannin and para formaldehyde based on the above stated thermodynamic conditions.

The adhesive produced was not subjected to mechano-chemical tests due to time constrain, but the physico chemical properties like pH, RI, molecular weight determined are in conformity with the literature standard, except density that slightly varied. In view of this, tannin from agricultural product can be substituted to phenol in the production of adhesive for ply wood and particle board bonding.

#### 5.2 Recommendations

The source of Mangrove bark tannin adhesive are renewable in nature. This makes them potential substitutes to phenol-formaldehyde (PF) wood bonding adhesives. However, the inherent shortcomings which the adhesive exhibit e.g poor wet strength brittleness and gel formation etc can be physically and chemically solved insitu or during production in industries. The following recommendations are therefore made.

- Standard buffer solution such as borax should be used in place of monosodium dihydrogen phosphate so as to stabilise the mixture to proceed to completion.

- The extraction must be subjected to acid or alkaline hydrolysis prior to synthesis to avoid gel formation even at room temperature. This will open the heterocyclic ring of tannin molecules.
- Tannin adhesive formulation at different temperatures should be investigated.

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## APPENDIX

### CALCULATION OF DRYING RATE OF MANGROVE BARK

Moisture content = Initial weight- final weight.

$$Mc = L_1 - L_2$$

Day 1,

$$Mc = 8.7 - 8.093 = 0.607\text{kg}$$

Day 2,

$$Mc = 8.093 - 7.486 = 0.607\text{kg}$$

Day 3,

$$Mc = 7.486 - 6.879 = 0.607\text{kg}$$

Day 4,

$$Mc = 6.879 - 6.069 = 0.81\text{kg}$$

Day 5,

$$Mc = 6.069 - 5.259 = 0.81\text{kg}$$

Day 6,

$$Mc = 5.259 - 4.855 = 0.404\text{kg}$$

Day 7,

$$Mc = 4.855 - 4.45 = 0.405\text{kg}$$

Day 8,

$$Mc = 4.45 - 4.45 = 0.00\text{kg}$$

### CALCULATION OF % YEILD OF TANNIN [DIRECT METHOD] USING ETHANOL AND DISTILLED WATER.

% yield of tannin using ethanol.

$$\% \text{ yield} = \frac{\text{Extract Weight}}{\text{Total Solid Weight}} \times 100$$

When time (t) = 1hr,

$$\% \text{ yield} = \frac{2.7}{25} \times 100 = 10.80\%$$

when t = 2hr,

$$\% \text{ yield} = \frac{3.2}{25} \times 100 = 12.80\%$$

when t = 3hr,

$$\% \text{ yield} = \frac{3.8}{25} \times 100 = 15.20\%$$

when t = 4hr,

$$\% \text{ yield} = \frac{4.7}{25} \times 100 = 18.80\%$$

when t = 5hr,

$$\% \text{ yield} = \frac{4.8}{25} \times 100 = 19.20\%$$

when t = 6hr,

$$\% \text{ yield} = \frac{5.03}{25} \times 100 = 20.12\%$$

% yield of tannin using distilled water.

$$\% \text{ yield} = \frac{\text{Extract Weight}}{\text{Total Solid Weight}} \times 100$$

When time (t) = 1hr,

$$\% \text{ yield} = \frac{2.3}{25} \times 100 = 9.20\%$$

when t = 2hr,

$$\% \text{ yield} = \frac{2.8}{25} \times 100 = 11.2\%$$

when t = 3hr,

$$\% \text{ yield} = \frac{3.5}{25} \times 100 = 14.0\%$$

when t = 4hr,

$$\% \text{ yield} = \frac{4.3}{25} \times 100 = 17.20\%$$

when t = 5hr,

$$\% \text{ yield} = \frac{4.4}{25} \times 100 = 17.60\%$$

when t = 6hr,

$$\% \text{ yield} = \frac{4.6}{25} \times 100 = 18.4\%$$

### **CALCULATION OF % YEILD OF TANNIN [ SOHLET EXTRACTION] USING ETHANOL AND DISTILLED WATER.**

% yield of tannin using ethanol.

$$\% \text{ yield} = \frac{\text{Extract Weight}}{\text{Total Solid Weight}} \times 100$$

When time (t) = 1hr,

$$\% \text{ yield} = \frac{3.10}{25} \times 100 = 12.40\%$$

when t = 2hr,

$$\% \text{ yield} = \frac{3.7}{25} \times 100 = 14.80\%$$

when t = 3hr,

$$\% \text{ yield} = \frac{4.5}{25} \times 100 = 18.00\%$$

when t = 4hr,

$$\% \text{ yield} = \frac{6.02}{25} \times 100 = 24.08\%$$

when t = 5hr,

$$\% \text{ yield} = \frac{6.05}{25} \times 100 = 24.20\%$$

when t = 6hr,

$$\% \text{ yield} = \frac{6.2}{25} \times 100 = 24.8\%$$

% yield of tannin using distilled water.

$$\% \text{ yield} = \frac{\text{Extract Weight}}{\text{Total Solid Weight}} \times 100$$

When time (t) = 1hr,

$$\% \text{ yield} = \frac{2.8}{25} \times 100 = 11.20\%$$

when t = 2hr,

$$\% \text{ yield} = \frac{3.40}{25} \times 100 = 13.6\%$$

when t = 3hr,

$$\% \text{ yield} = \frac{4.40}{25} \times 100 = 17.60\%$$

when t = 4hr,

$$\% \text{ yield} = \frac{4.8}{25} \times 100 = 19.20\%$$

when t = 5hr,

$$\% \text{ yield} = \frac{5.10}{25} \times 100 = 20.4\%$$

when t = 6hr,

$$\% \text{ yield} = \frac{5.10}{25} \times 100 = 20.4\%$$

## CALCULATION OF DENSITY AND VISCOSITY AND MILECULAR WEIGHT

### DENSITY

Mass of density bottle (M1) = 26.21g

Mass of density bottle (M1) + sample (M2) = 76.86g

Mass of sample (M2) = 76.86-26.21  
= 50.65g

Volume of the density bottle = 50.00cm<sup>3</sup>

Therefore, density of tannin adhesive =  $\frac{\text{mass of sample (M2)}}{\text{Volume of sample}}$   
=  $\frac{50.65\text{g}}{50.00\text{cm}^3} = 1.013\text{g/cm}^3$

### Viscosity

Viscosity = Kinematic viscosity (v) x density (ρ)

$$= v \times \rho$$

but v = C x t

where C = viscosity constant = 0.0882

t = time taken for the sample to flow through the capillary of the viscometer tube.

And t = 320sec.

$$v = 0.0882 \times 320\text{sec}$$

$$= 28.224\text{sec.}$$

therefore,  $\mu_i = 28.22 \times 1.013$

$$= 28.59\text{cp}$$

Hence,  $[\mu] = \frac{\mu_i - \mu_0}{\mu_{oi} \times 0.7} = \frac{28.59 - 0.42}{0.42 \times 0.7}$

$$= \frac{28.17}{0.294} = 95.82$$

$$0.294$$

Molecular weight,

Using the calculation of  $[\mu]$  and molecular weight.

i.e  $[\mu] = KM^a$

where  $K = 9.2 \times 10^{-2}$ ,  $a = 0.9$

therefore  $M = \left[ \mu / K \right]^{1/a}$

$$= \left[ 95.82 / 9.2 \times 10^{-2} \right]^{1/0.9}$$

$$= 2254.06$$