THE EFFECTS OF AMORHOUS FORTIFIERS ON THE THERMOMECHANICAL PROPERTIES OF UREA-FORMALDEHYDE RESINS

A THESIS

Presented To

The Post Graduate School,

Federal University Of Technology,

Minna

BY

Olanrewaju Sule Arogundade

(M. ENG/SEET/97/ 98/80)

In Partial Fulfillment Of The Requirements For

The Award Of Master Of Engineering (M. Eng) Degree

(Chemical Engineering)

Department Of Chemical Engineering,

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DECLARATION

I, Olanrewaju Sule Arogundade, hereby declare that this thesis 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 reference.

9-10-09

O. S. Arogundade

Date.

CERTIFICATION

This thesis entitled THE EFFECTS OF AMORPHOUS FORTIFIERS ON THE THERMOMECHANICAL PROPERTIES OF UREA – FORMALDEHYDE RESINS by OLANREWAJU SULE AROGUNDADE meets the regulation governing the award of the degree of Master of engineering (Chemical engineering) of Federal University of Technology, Minna, and is approved for its contribution to knowledge and literary presentation

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DEDICATION

This is dedicated to the following people for the role they played in the successful completion of the project

(i) My Wife, Mrs. Arogundade

For giving me both financial and moral assistance despite all difficulties.

(ii) Dr. M. O. Edoga,

Under whose supervision the Project was carried out.

ACKNOWLEDGEMENTS

I am grateful to God for making it possible for me to conclude the programme successfully despite all hurdles on the way.

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NOTATION

M_1 = Neat Urea- Formaldehyde

M_2 = Urea -Formaldehyde modified with maize cob during synthesis.

M_3 = Urea- formaldehyde modified with Rice husk after synthesis

M_4 = Urea -formaldehyde modified with Onion during synthesis

M_5 = Urea- formaldehyde modified with rice husk during synthesis

UF = Urea -formaldehyde

ρ_1 = Density

μ_1 = Viscosity

V = Volume

W = Weight of sample

√ = Kinematic Viscosity

M = Molecular weight

Risk = Rice husk

CHAPTER ONE

1.0 INTRODUCTION

An adhesive is defined as a synthetic polymeric material or precursor which at least initially must be a liquid or a tacky semisolid, and can be used in a relatively thin layer that capable of transmitting stresses between two substrate[18]. Adhesive are capable of holding materials together so that they act as a single piece [19].Example of such adhesives include formaldehyde condensation polymers, namely urea – formaldehyde, phenol – formaldehyde, resorcinol- formaldehyde, melamin- formaldehyde, just to mention a few.

Urea-formaldehyde resins are prepared by heating urea and formaldehyde in the presence of mild alkaline such s pyridine or ammonia. The initial products, which are water-soluble, are used to formulate adhesive and coating agents or are mixed with wood fibre, pigments, and other substances to produce powders that can be moulded into solid objects. Under the influence of heat and pressure, further reactions occur that convert the resin into an insoluble infusible form. The molecular structure of the final product is that of a three-dimensional network resembling those of resin made by the reaction of formaldehyde with phenol or with melamine.

Different members of the class of urea-formaldehyde resins are used in making moulded articles such as buttons, tableware, and housings for apparatus, and in adhesives, lacquers and agents that renders textile resistant to creasing or crushing.

Since mostly all UF resins bounded products have poor heat resistance, poor water resistance and slow release of formaldehyde during curing and in some cases after curing, their applications are therefore resisted to interior use.

1.1 Aims and Objective

The aim of this project, therefore is to develop urea-formaldehyde resins that are both hydrolytically and thermally stable as well as posses no free formaldehyde by incorporating different extracts from red onion skin, maize cob and rice husk into the structure of urea-formaldehyde resins.

Approach

The scope of this research would include: (a) development of neat urea-formaldehyde resin as well as (b) modification of the neat UF resins by incorporating amorphous fortifiers. Subsequently, the various adhesive samples will be applied in bonding some wood panels so as to ascertain their performance. Some instrumental analyses namely infrared (IR) and nuclear magnetic resonance (NMR) would be performed on the adhesive samples so as to ascertain the effect of the modifiers on the adhesives.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Urea-formaldehyde Resins:

Urea-Formaldehyde resins (UF) are polycondensation products of reacting urea with formaldehyde in alkaline, neutral or acid environment. They are amino-plastics and are in the finished product, cross-linked (thermo set), insoluble, infusible. Material [19] Compared to other amino plastics, UF resins are by far the most important commercially [19].

Polycondensation is a reversible reaction[4]. It involves two processes taking place simultaneously, namely: formation of the condensation product and their degradation. Degradation may be caused by the functional group of the initial monomers or be due to the interaction of the condensation product with the by-product. Owing to the reversibility of the polycondensation process, equilibrium is reached at certain condition corresponding to the formation of polymer product of definite molecular mass [4]. It has been found from research and therefore established as a rule that polycondensation product have lower molecular mass (20,000 – 50,000) than polimerisation product[4]. In order to obtain polymer of higher molecular mass, it is therefore necessary to remove the by-product from the system as well as, use strictly the equivalent ratio of the functional group[4]. This is because an excess of one reactant always result in the formation of low molecular mass product[4].

The intensive study of urea - formaldehyde resin started early 1908. The first useful commercial product, a moulding resin was invented in England by Edmond C. Rossister and it did not arrive until 20 years later. Similar products were subsequently produced in other countries[10]. The new products had a hard, stain resistant surface, no objectionable phenolic odour and were supplied in translucent colours[10].

Although, the use of thiourea gave the moulding with a better gloss and improved water resistance, it had the disadvantage of staining the steel mould. As the technology advanced, it was found that the amount of thiourea could be reduced and finally eliminated. Today's Urea-Formaldehyde moulding compounds contain no thiourea[10].

The Commercial Development of UF was delayed until it was able compete with other amino plastic on a cost basis despite the fact that the use of U-F resin as an adhesive was suggested by U. John in 1918[10]. U-F adhesives are used in bonding plywood, chipboard, foams, firelighter and solid wood joints. With the several advantages of the Urea-formaldehyde, its poor water and thermal resistance as well as slow release of formaldehyde from UF-bonded product limits its use to the interior non –structural application[10].

2.2 Raw Materials

The major raw materials for preparing urea-formaldehyde resins include:

(a.) Urea

(b.) Formaldehyde.

2.2.1 **Urea**

Rouelle discovered urea in Urine in 1775[10]. Wohler first synthesized it in the laboratory in 1828 by Isomerization of ammonium cyanate through intermolecular rearrangement[10].

$NH_4OCN \longrightarrow NH_2CONH_2$ - (1)

This was one of the most famous and important chemical discoveries. Until that time it was believed that man could synthesize only inorganic substances. Organic substances according to the then prevailing theory demanded the presence of a hypothetical "life Force" for their formation[10].

For inexpensive, commercial production, however, the process used by I.G. Farbenindustic A. G. became the really significant method[10]. In this process, carbon dioxide reacts with ammonia at 140 – 160°C and 700 – 1400 Psi leading to an equilibrium mixture containing about 10 – 50% Urea and ammonium carbonate[10]. This reaction as simple as it is [15]given in (2).

$CO_2 + 2NH_3 \rightarrow NH_2CONH_2 + H_2O \longrightarrow H_4NCONH_4$

There are also various other processes for the production of urea but none has been able to compete with the above process. One of those other processes was the "Lidholm process" of Union Carbide Co[10]. In this process, Calcium carbide is treated with Nitrogen to form calcium Cyanamide, which is converted to Cyanamid in weekly acid solution[10] This in turn is hydrolyzed in dilute acidic solution, producing Urea.

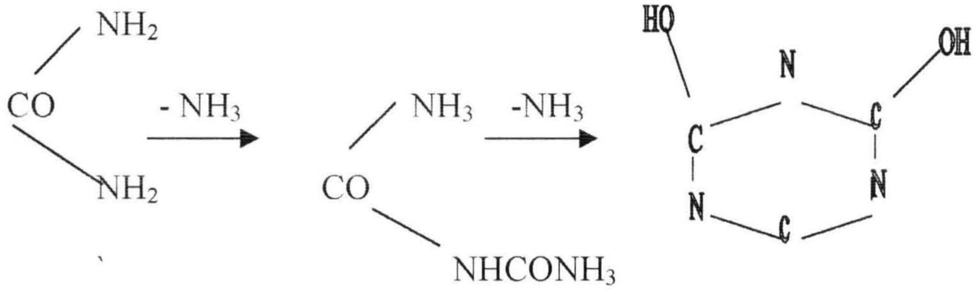
$CaC_2 + N_2 \rightarrow CaNCN + C$ .... (3)

$CaNCN + CO_2 + H_2O \rightarrow H_2NCN + CaCO_3$ .... (4)

$H_2NCN + H_2O \longrightarrow H_2NCONH_2$ ....(5)

Urea has a melting point of 132.7°C[10]. Urea is soluble in water (100ml of water dissolves 78g of urea at 5 ^{0}C) alcohol to the extent of 15.8g in 100ml of alcohol at 20°C, slightly soluble in ether, and insoluble in chloroform. Urea when heated to 130°C, it evolves ammonia and gives rise to a series of deamination products, for example, biuret and cyanuric acid, as shown below in: (6) [10].

Treatment of urea with water above 100°C or boiling with alkalis or acids hydrolyses Urea into its original component, carbon dioxide and ammonia[10].



(6)

Biuret Cyanuric Acid

2.2.2 **Formaldehyde**

Formaldehyde has a molecular formula CH_2O and molecular weight of 30g and is produced in large quantity (ties) from methanol by partial oxidation with air[10]. A mixture of air and Methanol vapor is passed over a heated platinum wire catalyst and the crude product containing water, formaldehyde and methanol is purified by fractional distillation[10].

$$CH_2OH \xrightarrow[O_2]{\text{Air}} HCHO + H_2O \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

Another important source of formaldehyde is partial combustion of methane in the same way as above[10]

For amino resin production, the aqueous formaldehyde solutions are nearly always used since formaldehyde dissolves very easily in water by forming a hydrate called methylene glycol[10].

$CH_2O + H_2O \longrightarrow HOCH_4OH$ ……………………………… 8)

Usually such aqueous formaldehyde solutions called “formalin” contain 30 to 40 by weight formaldehyde[10]. However, since formaldehyde polymerizes easily even in aqueous solution, particularly at higher concentrations, the 36% commercial solution is stabilized with 6-10% methanol[10]. Other concentration such as 50% are also being stabilized by small amount of melamine.

Pure Formaldehyde is a gas at room temperature, which turns into a colorless liquid at – 21°C. Its density at – 20°C is 0.8153[10].

2.3 Chemistry of reactions

The Chemistry of reaction of Urea with formaldehyde involves both polyaddition and condensation reactions, depending on the medium of reaction[10]. Urea has four replaceable hydrogen atoms, and thus a functionality of four, so there are various possibilities of reaction with formaldehyde[4]. Formaldehyde in turn has a functionality of two[4]. Urea therefore has the capacity of building up a three-dimensional space lattice[4].

The reaction of Urea and formaldehyde was studied many years ago, by, among others, Goldschmidst in 1808[10]. This investigator used various amount of Urea and formaldehyde in acid solution of various strengths[10]. He obtained insoluble, white, granular deposits, which were analyzed and found to correspond to the empirical formular $C_5 H_{10} N_4O_3$[10]. He found no use for the compound then[10]. However, this so called "Goldschmidt's compound" was latter made with varying amounts of formaldehyde and was therefore somewhat different from its original composition[10]. Its formula was given as:

$[CH_2 - NOCHNCH_2 NHCONHCH_2OH]_2$ ....(9)

It was believed that the $N=CII_2$ group was polymerized to form a higher molecular weight substance[10]. Einhorn and Hamburger in 1908 made it a point in their experiments to use only mild reaction conditions[10]. They condensed Urea with formaldehyde in alkaline solution; by neutralization and drying they isolated various white crystalline, easily soluble products[10]. The UF products melt at 126°C, and subsequently formed amorphous substances on further heating at 137°C, and finally decomposed at 260°C[10]. These substances were given the formulas:

- $NH_2CONHCH_2OH$..(10)

  Melthylolurea

- $CO\ (NHCH_2OH)_2$..(11)

  N, N- dimethylolurea

Other investigators (scheiber et al., 1928) then found that in acid solution these methylolureas are converted into insoluble substances, similar to Goldschmidt's Compound[10]. From monomethylolurea in glacial acetic acid, they isolated low-molecular weight polymethyleneurea and polymethylene urea acetate[10].

$[CH_2 = NCONH_2]_{11}\ H_2O$…………………………….(12)

Polymethylene Urea

$[CH_2 = NCONH_2]_{12}\ CH_2\ COOH$……………………… …(13)

Polmethyleneurea acetate.

All researches now indicate that further increase of molecular size is very probably caused by the following reactions, all of which occur with the simultaneous evolution of water and in some cases of formaldehyde[10].

(i) The formation of unsaturated azomethine groups e.g. from monomethylolurea. This unsaturated group supposedly polymerizes easily to polymethylene urea[10].

$X[NH_2CONHCH_2OH] \longrightarrow [NH_2CON = CH_2]_X + XH_2O$………. (14)

(ii) The formation of methylene bridges as in the following equation, between methylol and amino groups of neighbouring molecules[10].

$R\ NHCH_2OH + NH_2R^1 \longrightarrow RNHCH_2NHR^1 + H_2O$……………(15)

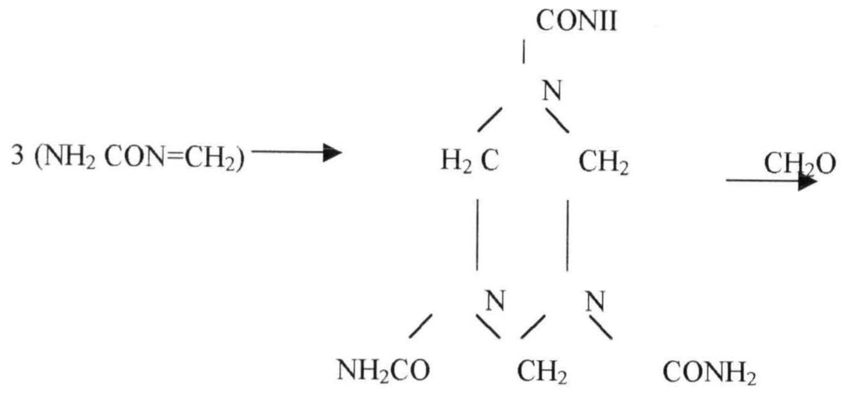
(iii) The formation of ether bridges between two methylol groups of two neigbouring molecules[10].

$RNHCH_2OH + HOCH_2NHR^1 \rightarrow RNHCH_2OCH_2NHR^1 + H_2O$…… (16)

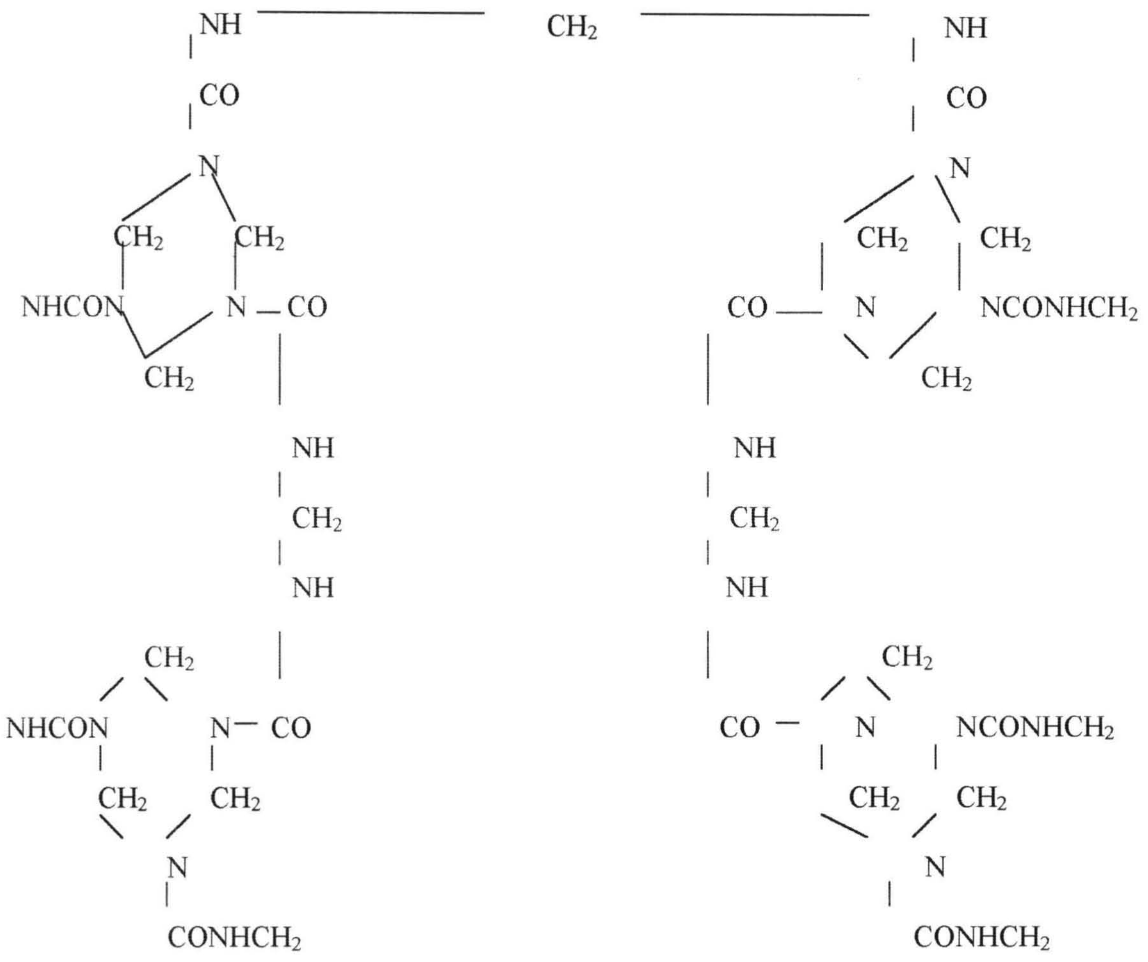
(iv) The formation of methylene bridges between two methylol groups by the splitting off of water and formaldehyde[10].

$RNHCH_2OH + OHCH_2NHR^1 \longrightarrow RNHCH_2NHR^1 + H_2O + CH_2O$……(17)

Marvel et al held that the primary reaction product of urea and formaldehyde leads to the formation of methylene urea ($NH_2\,CON = CH_2$), which polymerizes instantly to its trimer, forming a ring of the trimethylenetriamine type[10]. In a second stage, by the formation of methylenebisamides, this ring would produce the polymeric urea – formaldehyde resin[10] (see Equation 18). The formula for this cured resin is given in Equation 19.



(18)



(19)

The probability of a rather irregular constitution in such cured urea-formaldehyde resin is suggested by the fact that well cured urea-formaldehyde resins do not give a well-defined x-rays diffraction pattern. This indicates the absence of a regular-space lattice[10].

De Jong and De Jonge have conducted a very interesting series of investigations of the Kinetics and Mechanism of the Urea-formaldehyde reaction (equation 18) [10]. Their investigation have rendered additional evidence that the condensation products of urea and formaldehyde are formed by a stepwise polymerization that leads finally to methylene bond between urea fragments which stands in contradiction to the polymerization scheme of Marvel[10].

De Jong and De Jonge (1920) started by first examining the Kinetics of the reaction of Urea and formaldehyde in O.1M aqueous solution within a pH range of 2 to 11 in an attempt to elucidate the production of mono, and di-methylolurea[10]. (See Figure 1). They found that the reactions producing both substances showed a close resemblance to each other[10]. In both cases, equilibrium is reached from both sides that is independent of the pH of the solution[10]. Although the formation of both substances appears to be a bimolecular reaction, the decomposition of dimethylolurea proved to be a monomolecular reaction. The reaction rates of both were found to be directly proportional to the proportional to the concentration of the hydroxyl and hydrogen ions, which have a catalytic influence[10]

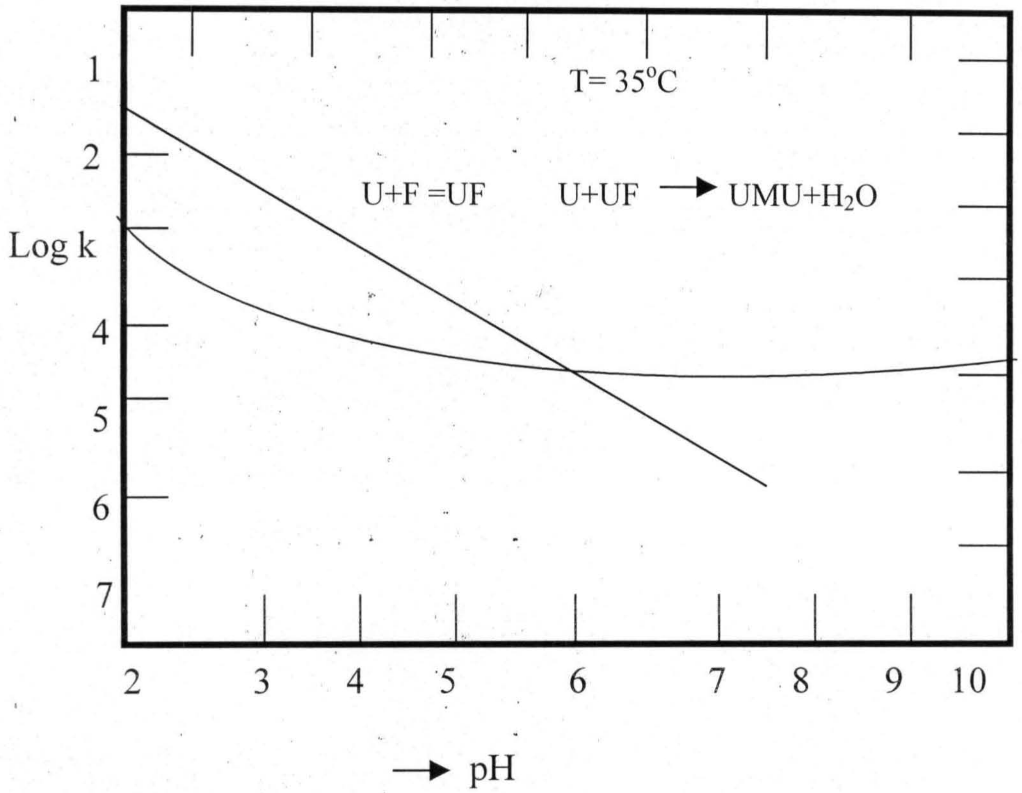


Figure 1: Influence of pH on the Addition and Condensation Reactions of Urea and Formaldehyde.

Further investigation by the same authors referring to the "Kinetics of the formation of methylene linkages in solutions of urea and formaldehyde" as applied to 1.3M aqueous solutions with a pH of 4.1 to 4.4, strongly indicated that the reaction involved were all of one type, namely bimolecular, hydrogen ion catalysed reactions between an amino group and aminomethylol group, leading to the formation of methylene linkages between urea fragments[10].

$$-NHCH_2OH + -NH_2 \rightarrow NHCH_2NH + H_2O \;\ldots\ldots\ldots\ldots\ldots\ldots (20)$$

These findings seem to confirm the validity of equations 15, 16, 17

2.4 Factors affecting properties of urea – formaldehyde resin

The following are the factors that affect the kind and quality of the condensation products of urea-formaldehyde resins[10].

(1) Molecular proportion of Urea to formaldehyde: This is an important factor as the relative amount of the reactants determine, to a large extent the property of the product.

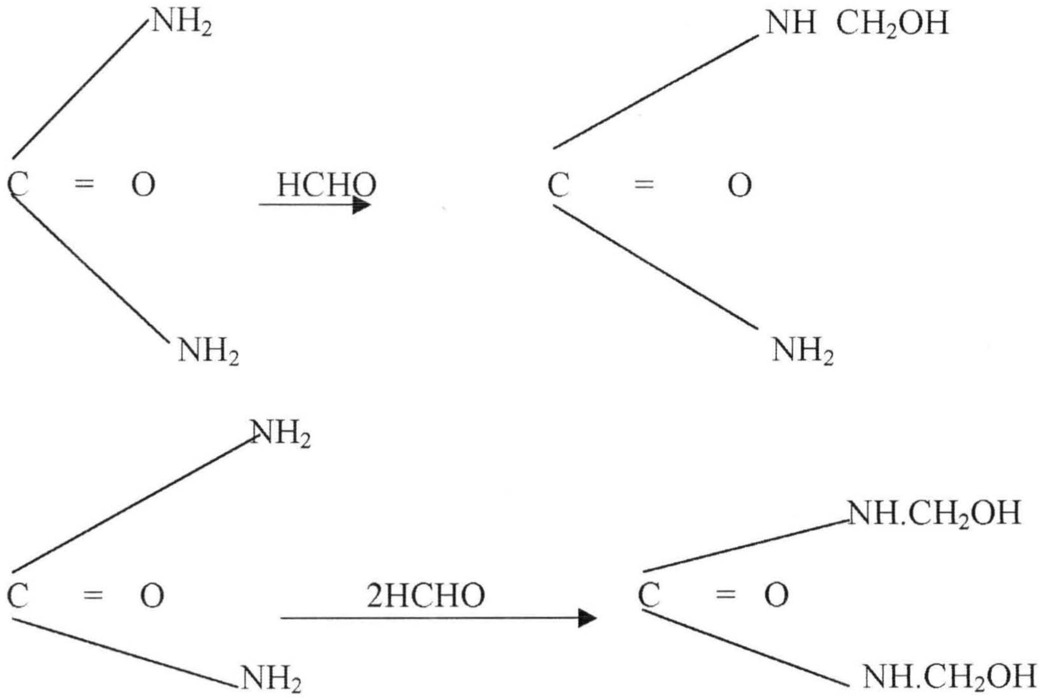
(2) Reaction Temperature: The reaction temperature like, ambient, medium or high temperature produces resins with different properties.

(3) The reaction products also differ very much when lower or higher condensation stages are compared, especially with respect to solubility and viscosity, both of which depend on molecular weight.

(4) The pH value of the reacting medium is also another important factor that affects the quality of the urea-formaldehyde: When investigating a new reaction, one of the first factors to consider is the pH, and one looks immediately for the optimum pH range to obtain best result.

2.5 Theories of Resinification

Urea – formaldehyde resins are usually prepared by a two – stage reaction. The first stage involves the reaction of urea and formaldehyde under neutral or mildly alkaline condition leading to the production of mono and di-methylolurea ureas[19].



(21)

The ratio of mono to dimethylol compound will depend on the urea – to-formaldehyde ratio and it is important that there should be enough formaldehyde to allow some dimethylol urea formation. If the product of the first stage, which in practice usually also contains unreacted urea and formaldehyde is then subjected to acidic condition at elevated temperatures the following sequence of events is observed during the second stage[19].

i. A solution is produced from which if cooled, a white precipitate would be produced.

ii As heating proceeds, the temperature at which precipitation occurs drops progressively until a stage is reached when the condensation products remain in solution at room temperature.

iii. With further heating, there is an increase in viscosity and the syrup sets to an Insoluble and irreversible gel, which eventually converts, with the evolution of water and formaldehyde to a hard, colourless, transparent and infusible mass.

For technical purposes, it is often convenient to arrest the reaction prior to gelation by changing to a slightly alkaline pH and to remove some if not all of the water [19.]

. The first hardening reaction may then be carried out when desired by changing once again to an acidic pH. Based on the literature, it appears that in the first part of the second stage methylol ureas condense with each other by reaction of an – CH_2OH group of one molecule with an – NH_2 group of another [Equation 22] 19.

$H_2NCO\ NHCH_2\ [OH]\ +\ H_2N\ CO\ NH\ CH_2\ [OH]$

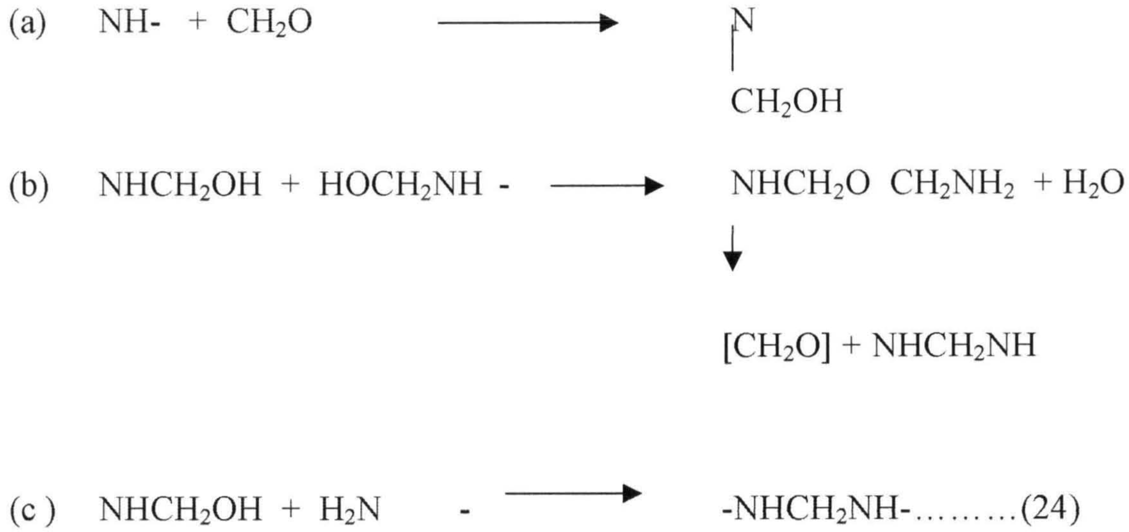
$\rightarrow$ HN.CO . NH . CH_2 . NH. CO. NH. CH_2-............................(22)

Since – NH – groups in dimethylol urea are presently less reactive, the initial reaction products appear to be based on linear polymer of the form;

$HO\,(CH_2\ NH\ CO\ NH)_n\ CH_2\,OH$..(23)

These probably form the basis of the amorphous precipitates formed on cooling[19]. The more soluble resins produced on continuation of the reaction probably contain pendant methylol groups formed by reactions of the –NH- groups with free formaldehyde (Equation 23)[19].

These methylol groups and the methylol groups found on the chains ends of the initial reaction product can then react with other methylol groups to give ether linkages or with amino groups to give methylene linkages[19]. Furthermore, the ether linkages on heating may break down to methylene linkages with the evolution of formaldehyde, (Equation 24 (a) & (b)).



(a) $NH- + CH_2O \longrightarrow \begin{array}{c}N\\ |\\ CH_2OH\end{array}$

(b) $NHCH_2OH + HOCH_2NH- \longrightarrow NHCH_2O\ CH_2NH_2 + H_2O$

$\downarrow$

$[CH_2O] + NHCH_2NH$

(c) $NHCH_2OH + H_2N\ - \longrightarrow -NHCH_2NH-$.........(24)

When reaction (b) and (c) occur on average more than twice per molecule the resins gels and cross-linking may be considered to have occurred[19].

2.5.1 Urea - formaldehyde-moulding materials

Thermosetting compositions based on urea-formaldehyde resins are widely employed because of their low cost, wide colour range, rigidity and good electrical properties[19].

2.6 Manufacturing of Urea-Formaldehyde Resins

A moulding powder based on urea formaldehyde resin contains a number of ingredients[19].

Those most commonly present include the following[19]:

i. Resins
ii. Filler
iii. Pigments
iv. Hardener (more commonly referred to as an accelerator)
v. Stabilizer
vi. Plasticiser
vii. Lubricant.

The first stage of resin preparation is to dissolve urea into the 36% w/w formalin, which has been adjusted to a pH of 8 with caustic soda. Since formaldehyde interferes with the normal functioning of universal indicators a pH meter is used when making pH adjustments[19]. The blending may be carried out without heating in a glass-lined of stainless steel reactors for about 90 minutes[19]. In an alternative process, the blending is carried out at about 40°c for 30 minutes. In some cases, the pH, which may drop during reaction, is adjusted by addition of small quantities of hexamine[19].

The urea to formaldehyde ratios normally employed are in the range 1:1.3 to 1:1.5. Only a small amount of reaction occurs in the first stage so that the solution at the end of this process contain urea, formaldehyde, mono and dimethylol urea, the latter in insufficient concentration at this stage to separate out[19]

Only a limited range of fillers is used commercially with (UF) resins. Bleached wood pulp is employed for the best range of bright colours and in slightly translucent mouldings[19]. Wood flour, which is significantly cheaper may also be used for mouldings of enhanced translucency, chopped regenerated cellulose (Cellophane) film which is free from voids and has a refractive index (1.56) close to that of the resin (1.55-1.56) can be incorporated[19]. Fabric fillers and mineral fillers are not commonly employed with (UF) resin[19].

A wide variety of pigments is now used in UF moulding compositions. Their principal requirements are that they should not affect the stability or moulding characteristics of the powder, that they should be stable to processing condition, be unaffected by condition of service including insolubility in any solvents with which the mouldings might come into contact, should be light fast, and should not interfere with the electrical properties[19].

Hardener (accelerator) of about 0.2 – 2.0% is sometime added to UF resin to obtain a sufficient rate of cure at moulding temperature. This functions by decomposing at moulding temperatures to give an acidic body that will accelerate the cure rate[19].

Some of the prominent hardeners are ammonium sulphate, ammonium phenoxyacetate, ethylene sulphite and trimethyl phosphate[19].

Urea –formaldehyde powders have a limited shelf life, which has been improved by incorporating a stabilizer such as hexamine into the moulding powder[19].

Plasticisers are used in special grades of moulding powders[19]. Their main virtue is that they enable more highly condensed resins to be used and thus reduce curing shrinkage whilst maintaining good flow properties[19]. Glyceryl $\propto$ tolyl ether (monocresyl glycidyl ether) is often used for this purpose[19]. Plasticisers may also be used in small quantities to improve the flow of other grades[19].

Metal stearates such as Zinc, Magnesium or aluminium stearates are commonly used as lubricants at about 1% concentration[19]. Other materials that have been used successfully include oxidized paraffin wax and sulphonated castol oil[19].

2.6.1 Processing

Urea – Formaldehyde-moulding powders may be moulded without difficulty on conventional compression and transfer moulding equipment[19]. The powders however have a limited storage life[19]. They should thus be stored in a cool place and, where possible, used within a few months of manufacture[19]. Moulding temperatures in the range of 125 – 160°C are employed[19]. The low temperatures are used with thick sections and the high temperatures for thin sections[19]. Mouldings may easily be over-cured by moulding for too long and/or at too high a temperature and this is made manifest by blistering, bleaching and a distinct fleshy smell[19]. Compression moulding pressures recommended range from 15-60 MN/m^2, the higher pressures being usually employed for deep draw articles[19]. The cure time will depend on the thickness of the moulding and on the mould temperature[19]. The amount of cure carried out should depend on the properties required of the moulding and the economics of the process[19]. It has been discovered that for the best balance of mechanical and electrical properties the degree of cure required coincides with that giving the best water resistance[19].

Thus in practice a moulding is deemed properly cured if, sawn through its thickest section, it is unaffected in appearance, or cannot be scratched with a fingernail, after 10 minutes immersion in boiling water[19].

Pre-heating techniques are commonly employed since these lead to shorter cure, easier flow and generally better products[19]. The high power factor of the material enables high efficiency preheaters to be used successfully[19].

2.6.2 Properties and Application

The major desirable features of U-F mouldings are[19]:

1. Low Cost: The cheaper grades are sometimes lower in weight & cost than the general-purpose phenolics.
2. Wide colour range
3. Do not impart taste and odour to foodstuffs and beverages with which they come in contact.
4. Good electrical insulation properties with particularly good resistance to tracking.
5. Resistance to continuous heat up to a temperature of 70°C.

The bulk of U-F moulding compositions are used in two applications, bottle caps and electrical fittings[19]. However, UF moulding is the preferred material for such application as coloured toilet seats, hair drier housings and vacuum flask cups and jugs. Other uses include meat trays, toys, knobs, switches and lampshades[19].

2.7 Preparation of UF Adhesive

To prepare a suitable UF resin for adhesive formulation, formalin is first neutralized to a pH of 7.5 and urea then dissolved into it at U/F molar ratio 1 to 2[19.] Sodium formate may be added as a buffer to regulate the pH. The mixture is boiled under reflux, for about 15 minutes to give dimethylolurea and other low molecular weight products[19]. The resin is then acidified to pH 4, conveniently with formic acid and reacted for a further 5-20 minutes. The resulting resin is then stabilized by neutralizing to a pH 7.5 with alkali to give a water-soluble resin with an approximately 50% solids content[19].

When the resin is to be used in aqueous solution, as it is normally the case, it is then partially dehydrated to give 70% solid content by vacuum distillation[19]. For some uses, for example for application in tropical countries, the resin is spray dried to ensure greater stability[19]. The finished product is checked for viscosity, solids content, pH value (which must be in the range of 7.3-7.5 and for its reactivity with a standard hardener.

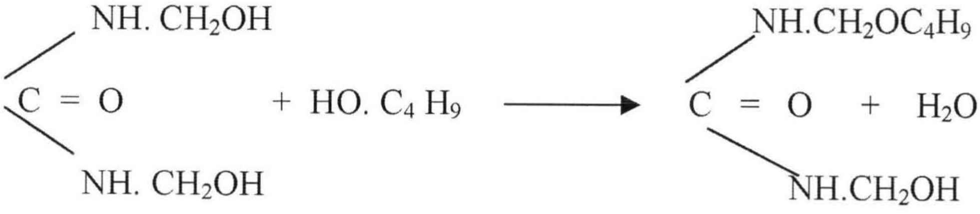
Resins are commonly available with UF molar ratio ranging from 1:1.4 to 1:2.2. [19] The lower the UF ratio, the better the quality of product and the higher the price because formalin is much more expensive than Urea.[19]

The resins are hardened by acidic conditions; Phosphoric acid, or more commonly ammonium chloride, an acid donor, is employed. The ammonium chloride functions by reaction with formaldehyde to give hydrochloric aci Hexamine is also formed during this reaction[19].

$4NH_4Cl + 6CH_2O \longrightarrow N_4(CH_2)6 + 6H_2O + 4HCl$............(25)

about 1.5 parts ammonium chloride per 100 parts of the resin solution ar generally used. the hardner is added as an aqueous solution[19]. U-F resins present, find extensive application in the manufacture of chipboard[19]. U- resin can also be used in other general wood assembly work, for exampl resin – hardner mixture is applied to the surfaces to be joined and the clamped under pressure while hardening occurs[19].

Modification of Urea-Formaldehyde resins with reagents gives rise to number of useful materials. For example, condensation of UF and monohydric alcohol in the presence of small quantities of an acidic catalys will involve simultaneous etherification and resinification. Propanol, n butanol and Iso-butanol are commonly used for this purpose. As an exampl n-butanol will react with the methylolurea as shown in Equation 25.



$$\begin{matrix} NH.\ CH_2OH \\ C = O \\ NH.\ CH_2OH \end{matrix} + HO.\ C_4H_9 \longrightarrow \begin{matrix} NH.CH_2OC_4H_9 \\ C = O \\ NH.CH_2OH \end{matrix} + H_2O \quad (26)$$

By varying reaction conditions and reactant proportions, different product may be obtained. Many of the alkoxy groups are retained during cure and th resin have degree of thermoplasticity. These materials being soluble in organic solvents are used in conjunction with plasticising alkyd resins to form useful storing lacquers. Air drying lacquers suitable as wood finishes may be obtained by addition of acid hardeners[19].

Whereas the butylated resins have enhanced solubility in organic solvents, enhanced solubility in water (which is rather limited in resins of high molecular weight) is required for some purposes and this may be achieved in a number of ways. For example, in an acidic condensation of urea with formaldehyde in the presence of sodium bisulphate the following reaction takes place[19]

$$\mathrm{NH\ CH_2OH} - \mathrm{NaHSO_3} \longrightarrow \mathrm{NH.CH_2.SO_3Na} + \mathrm{H_2O} \ldots\ldots\ldots \text{(27)}$$

Ionization occurs in aqueous solution to give a resin of negative charge, an example of a number of anionic ‘resins’[19]: -

$$\mathrm{NH.CH_2SO_3Na} \longrightarrow \mathrm{NH.CH_2}\overset{(-)}{\mathrm{SO_3}} + \overset{(+)}{\mathrm{Na}} \ldots\ldots\ldots\ldots\ldots\ldots \text{(28)}$$

Modification of urea resins with certain organic bases e.g. triethylene tetramine, will give resins with basic groups which form ionisable salts in the presence of acids[19].

$$\mathrm{CNRR^1} + \mathrm{HCl} \longrightarrow \mathrm{CNHR}\overset{(+)}{\mathrm{R}} + \overset{(-)}{\mathrm{Cl}} \ldots\ldots\ldots\ldots\ldots\ldots \text{(29)}$$

CHAPTER THREE

3.0 MATERIALS AND METHOD

3.1 Materials

In this research work, the following materials were used:

Table 3.1: Experimental materials

S/no	Materials
1.	Urea
2.	Formalin (37% Conc 2)
3.	Sulphuric Acid 50% Conc (aq)
4.	Sodium Hydroxide 50% Conc (aq)
5.	Monosodium dihydrogen Phosphate(s)
6.	Red Onion Skin
7.	Maize Cob
8.	Rice Husk
9.	Ammonium Sulphate
10.	Veneer and Co-veneers

Also find below, the list of the apparatus/equipment used in this research work:

Table 3.2: Equipment used for the experiment

S/no	Equipment
1.	Tray
2.	Sieve
3.	Weighing balance
4.	pH Meter/electrode
5.	U - tube Viscometer
6.	Electric Oven (Vaccum)
7.	Refractometer
8.	Soxhlet Extractor
9.	Water bath Regulator
10.	Desicator
11.	Thermometer
12.	Aluminium Dish
13.	Stop Watch
14.	Conical flasks
15.	Retort Stand
16.	Specific Gravity Bottle

17. Beakers
18. Magnetic stirrer
19. Specific gravity bottle
20. IR spectrometer
21. NMR spectrometr
22. Reactor
23. Hydraulic press
24. Autoclave

3.2 Experimental Procedure

3.2.1 Gathering of the agricultural By-products

Agricultural by-products such as rice husk, red onion-skins and maize cubs were gathered from farm, cleaned, oven dried at temperature of 45°C until a constant weight was attained. They were sieved to remove the foreign bodies and subsequently ground to fine particles of 0.05μm.

3.2.2 Extraction of Amorphous Fortifiers from the Agricultural By-products

The extraction was carried out by two methods namely soxhlet and leaching extraction.

(a) Soxhlet Extraction

The extraction by this method, involved two stages. The first stage involved the extraction of oil content of the ground agricultural by-product using nhexane as the solvent. The second stage involved extraction of the (amorphous fortifier) phenolic matter from the agricultural by-products using ethanol as the solvent.

50g of each sample of the agricultural by-products were weighed into thimbles. Subsequently, each thimble was put into different soxhlet extractors. Each of the samples was extracted using 300ml of n-Hexene for six hours for the first stage and then using 300ml of ethanol as solvent for the second stage for another nine hours. The apparatus is as shown in the figure below.

Fig. 2 Soxlet Extraction.

(b) Extraction By Direct Leaching

20g of each of the agricultural by product was weighed into different beakers and about 100ml of benzyl alcohol was added. The mixture was heated using a heating mantle at temperature of 50^{oC} for 2 hours. The filtrate was separated from the mixture using a separating medium. The filtrates were later heated on heating mantle until all the solvent (Benzyl alcohol) was distilled off. The essence of using this process was to compare the extractive efficiency of the two processes.

3.2.3 Preparation of urea - formaldehyde resin (neat)

One mole (30.03g) of formalin was measured and charged into a water-jacketed glass reactor. The pH of the formalin was adjusted to 8.0-8.5 by adding 50% NaoH into the formalin in the reactor and stir vigorously. The pH was latter adjusted to 3 using 50% conc. H_2SO_4 and stirred vigorously. Monosodium dihydrogen phosphate (buffer) was also charged so that a constant pH medium was ensured.

21.06g of urea (.35mole) were charged slowly into the reacting mixture over a 15 minutes time interval. The rate of addition of urea was regulated and at the end of the 15-30 minutes, the F/U ratio was 2.8.

The reacting mixture was neutralized with 50% NaoH and $1.5cm^3$ of 100% triethanol amine to bring the pH to 6.5 and later 7.5 respectively.

39.039g of urea (.65 mole) were added to the reaction mixture to bring the mole ratio of formaldehyde to urea (F/U) to 1.0.

Finally, the reacting mixture was refluxed for about 15minutes in order to ensure that all the urea has reacted with the formaldehyde.

Figure 3 Reactor set-up.

3.2.4 Preparation of urea-formaldehyde resin fortified with red onion skin powder extract.

Two grams of red onions skin powder extract was added to 0.5mole of formalin measured into a beaker. The solution was vigorously stirred and the pH adjusted to 8.0-8.5. The solution was transferred into a reactor and the reacting temperature was maintained at 50°C.

0.5 mole of urea (30.03g) was measured and slowly added to the reacting mixture in the reactor and stirred to dissolve. The mixture was then heated for 4 hours at 50°C after which the reaction mixture was adjusted to pH3 using 50% conc. H_2SO_4 and subsequently heated at reflux for 40minutes. The resulting resin's pH was adjusted to 8.0-8.5 using 50% conc. NaoH and then buffered with monosodiumdi hydrogen phosphate.

3.2.5 Preparation of urea -formaldehyde resin fortified with maize-cob extract

A 0.5 mole (30.015g) of Formalin and 2g of maize powder cob Power extract, respectively were weighed into a water-jacketed glass reactor. The reaction mixture was well stirred and the pH was adjusted to 8.0-8.5 with adding 50% conc. NaoH.

A 0.5 mole of urea was weighed and slowly charge into the reacting mixture in the reactor and was stirred thoroughly. The mixture was heated for one and half hours at temperature of 50°C after which the reaction mixture was adjusted to pH 3 using 50% conc. H_2SO_4 and later was heated at reflux for 20 minutes. The resulting adhesive was adjusted to pH8-8.5 using 50% conc. NaoH and then stabilized by adding monosodiumd sulphate.

The same method was repeated using other fortifiers, namely rice husk extract and red onion extract. Moreover, the above was also repeated by varying the medium first from pH 4.5 and then pH 1.0.

Finally, the neat urea-formaldehyde was further divided into four equal parts and each was mixed with each of the fortifier (extract), i.e. after the resin synthesis.

3.3 Characterisation of urea- formaldehyde adhesive

3.3.1 pH Measurement

The pH of any compound or solution is the measure of its acidity and alkalinity. The pH of the resin prepared was measured by pH meter. 50ml of the sample was poured into a beaker and the pH value was determined by inserting the meter's electrode into it and the pH value was read from the meter.

3.5.2 Viscosity Measurement

The standard method of determining the viscosity of UF resin samples was by using the viscometer bath and the U-tube viscometer with capillary tube inserted into the viscometer bath.

A known quantity of the sample was taken and poured into the U-tube viscometer with capillary tube and then corked. The U-tube was suspended into the viscometer bath containing water and the temperature of the bath was adjusted to 32°C. The cork was then removed and the time taken for the content to run up to the middle mark starting from the top mark was noted using a stopwatch. By so doing, the viscosity of the sample was calculated.

3.3.3 Specific Gravity Measurement

The specific gravity of any compound is the ratio of density of the compound at ambient temperature to that of water at 4^0C. The common instrument normally used for measurement is the specific gravity bottle.

The empty specific gravity bottle was weighed and its weight was recorded. The same specific gravity bottle was filled with urea formaldehyde samples and the weight was recorded.

The difference in weight between the specific gravity bottle filled with UF samples and that of empty specific gravity bottle gives the specific gravity of the UF sample.

3.3.4 Total Solid Content (TDS) Measurement

Total solid content of any compound is the weight of the solid content of that compound. The total solid content of the resin was determined by weighing 3grams of the resin into a small aluminium dish. The dish was placed in an oven at 100°C for 2hours and allowed to cool in a desicator. The dish was then re-weighed to find the weight of the dry resin remaining.

The result obtained was used to calculate the total solid content.

$$\%TDS = \frac{W_1}{W} \times 100\%$$

3.3.5 Determination Of Refractive Index

Certain quantity of pre-heated resin was introduced into the prism chamber of the refractometer through the appropriate provision made for it and allowed to stabilize for sometime. The refractometer reading was taken by turning the compensation ring of the refractometer until there was a shary division between the dark portions of the sample. The accurate refractometer reading was taken as the whole number and the decimal unit shown on the micrometer screw gauge.

3.3.6 Nuclear Magnetic Resonance (NMR) Measurement

The synthesized neat UF resin, UF modified with red onionskin, UF modified with rice husk (both during and after synthesis) and UF modified with maize cob were subjected to NMR analysis.

The ^{13}C- and ^{1}H-WMR spectra were obtained with a Bruker WM250 spectrometer on the above samples. The resin samples were frozen immediately after the synthesis and analysis. Usually, deuterated dimenthylsulfoxide (DMSO) was used as solvent, but occasionally deuterated chloroform was substituted[13.]

Typical parameters for ^{1}H spectra were 3KHz sweep width, 5 μ (30^{O}) pulse width, 25 pulse delay and 1 or 2 scans[13].

3.3.7 Infrared Spectroscopy

Infrared spectra were obtained on the neat and modified samples of UF in potassium bromide pellet using a Nicolet Model 6000 Fourer transform Infrared Spectrometer.

3.3.8 Plywood Bonding

Table 3.3: Plywood bounding condition

Conditions	Plywood
Glue Spread (g/mm^2)	0.03
Open Assembly time (Min)	8.00
Closed Assembly Time (Min)	2.00
Press Time (Min)	7-10
Bonding Pressure (psi)	100-120
Bounding Temperature (^0C)	115

Neat UF and the modified samples were applied on to the two side of the veneers each assembled with the co-veneer and put in the hydraulic press Under the above condition.

The shear block panels were kept for a period of 5-7 days in laboratory locker under ambient condition during which the samples attained approximately 6% moisture content before testing for shear strength. Four standard shear block specimens were cut from each main block panel. A group of specimens in duplicate were subjected to water boiling at pressure of 2×10^4 N/m^2 and temperature of 115°C in autoclave for 2 hours. After soaking in tap water for 23 hours, the specimens were equilibrated to approximately 6% moisture content. Both dry and steamed specimens were tested in duplicate for failure using tension machine [13].

Figure 4: Auto Clave

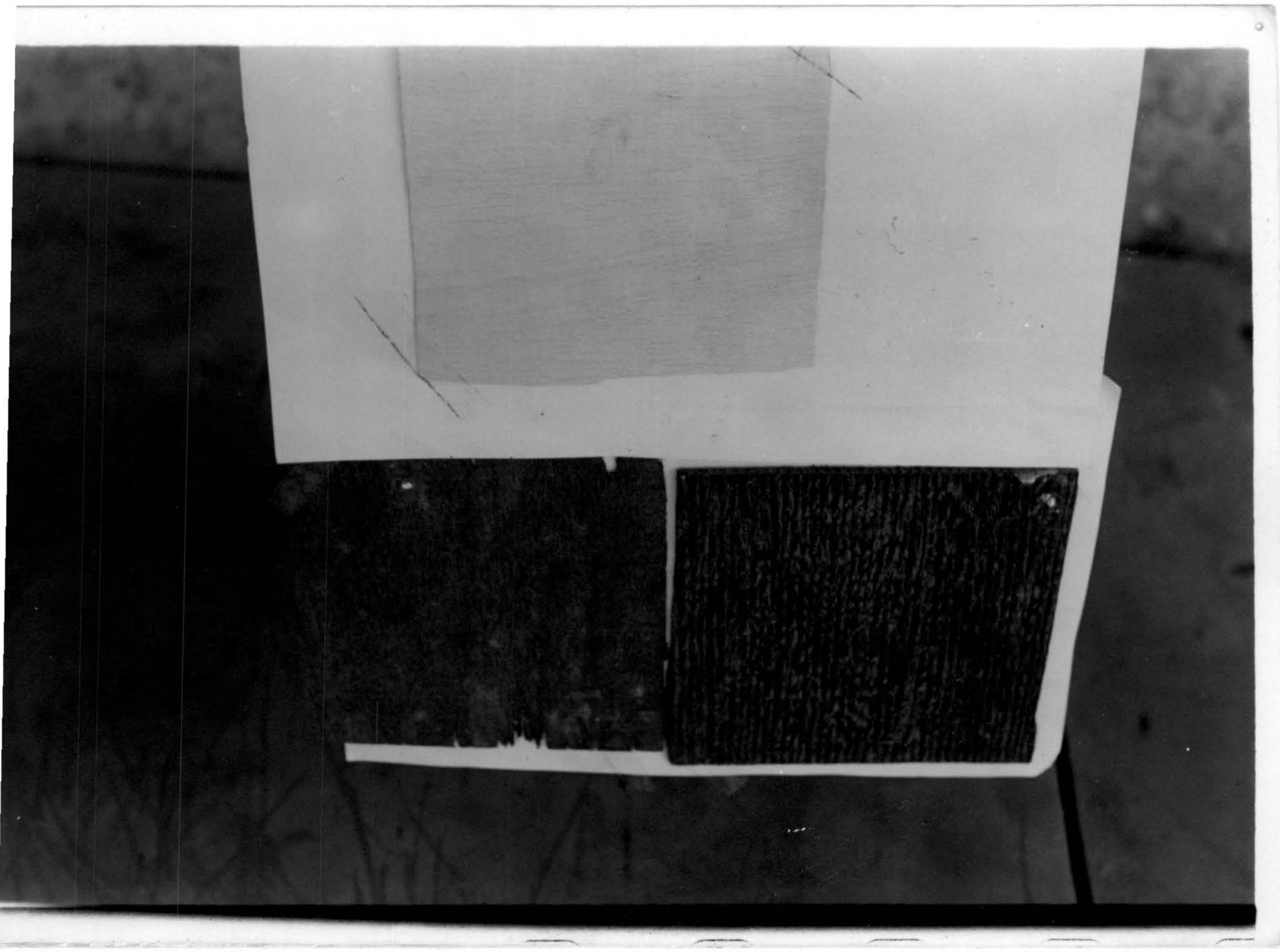


Figure 5: Veneer and Co-Veneer

Figure 6: Hydraulic Press

3.3.9 Formaldehyde liberation from cured resin

Resin samples were cured with 5% curing agent by heating thin films between Teflon coated platens in a press at 0.14 MPa and 115°C for 10 minutes. After cure, the resins were ground and sieved. The materials passing through an 80.mesh sieve were collected, pumped under vacuum for several days, and stored over phosphorous pentoxide.

About 10mg of the powder was weighed into a weighing bottle, a glass cross placed on the bottom, and a small beaker containing 500ml of 27% H_2 SO_4 placed on the cross. After sealing with greased caps, the bottles were stored in cabinet at 27°C. The formaldehyde subsequently liberated from the powder at that temperature and 80% RH was absorbed by the H_2SO_4. At intervals, the H_2SO_4 was removed and analysed for formaldehyde.

CHAPTER FOUR

4.0 RESULTS

The Table 4.1 shows properties of the various samples of urea-formaldehyde resin samples produced.

TABLE 4.1: Properties of Neat, and fortified - UF samples synthesized at pH 3.

Properties and Temperature (^{0}C) at which they were determined	**Sample M_1**	**Sample M_2**	**Sample M_3**	**Sample M_4**	**Sample M_5**	**Literature value**
pH (at 32^{0}C)	8.5	8.8	8.6	8.7	8.9	9.0
Viscocity (cp) (at 32^{0}C)	16	9.33	21.8	10.1799	20.4318	-
Specific gravity (g/cm^3 at 30^{0}C)	1.1063	1.1135	1.1776	1.1542	1.1468	1.1 – 1.18
Refractive (at 30^{0}C) Index	1.4	1.37	1.39	1.32	1.37	37 – 1.39
Total Solid content (TDS X'100%)	65	63	65.5	63	64.5	63 - 65
Molecular Weight (g)	38021	9473	24827	10464	49737	49737
Operating Temperature (^{0}C)	55 – 60	55 – 60	55 – 60	55 – 60	55 – 60	-
Formaldehyde-Urea Ratio	1	1	1	1	1	1.4-2.2
% Free Formaldehyde	3.9	3.6	3.75	3.5	3.8	3.5 - 4.0
Operating Pressure (atm)	1.0	1.0	1.0	1.0	1.0	1.0
Tensile Strength (MN/m^2)	56 60*	79 80*	73 74*	72 79*	75 77*	52 - 80 -
Cross –breaking Strength (MN/m^2)	76 80*	1000 115*	95 96*	96 102*	99 100*	96 - 117 -

Value of the samples with curing agent.

M_1= Neat UF resins, M_2 = UF modified with maize cob(during synthesis), M_3 = UF modified with Rice husk (after synthesis), M_4=UF modified with red onion skin (During synthesis),M_5= UF modified with rice husk (During synthesis), UF = Uria formaldehyde resins

Table 4.2: Properties of Neat, and Fortified UF samples synthesised at pH 4.5.

Properties and Temperature (^{0}C) at which they were determined	**Sample M$_1$**	**Sample M$_2$**	**Sample M$_3$**	**Sample M$_4$**	**Sample M$_5$**	**Literature value**
pH (at 32^{0}C)	8.2	8.5	8.1	8.4	8.7	8 - 9
Viscocity (cp) (at 32^{0}C)	15	8.93	18.57	9.75	18.85	-
Specific gravity (g/cm^3 at 30^{0}C)	1.1	1.105	1.175	1.149	1.142	1.1 – 1.18
Refractive (at 30^{0}C) Index	1.39	1.35	1.38	1.30	1.38	1.37 – 1.39
Solid content (TDS X 100%)	64.9	63 .1	64.95	63.4	64.4	63 - 65
Molecular Weight (g)	37804	9401	24772	10417	49528	-
Operating Temperture (^{0}C)	55 – 60	55 – 60	55 – 60	55 – 60	55 – 60	55 - 60
Formaldehyde-Urea Ratio	1	1	1	1	1	1.4-2.
% Free Formaldehyde	3.85	3.55	3.7	3.6	3.75	3.5 - 40
Operating Pressure (atm)	1.0	1.0	1.0	1.0	1.0	1.0

M$_1$= Neat UF resins, M$_2$ = UF modified with maize cob(during synthesis), M$_3$ = UF modified with Rice husk (after synthesis), M$_4$=UF modified with red onion skin (During synthesis),M$_5$= UF modified with rice husk (During synthesis), UF = Uria formaldehyde resins

4.1Proton NMR Spectra

Figure 7 gives the proton NMR spectra of neat UF resin, risk – fortified UF samples both during and after synthesis. The spectrum of neat UF is given in figure 7a. In the spectrum, there are four peaks showing presence of primary amine groups (RNH_2; 0.6ppm) methylene protons (R^1CH_2R; 2.35ppm), unsaturated carbon ($ROCH = CH_2$; 4.15ppm) and secondary amide group ($RCONH_2$; 5.9ppm). The spectrum of Risk- fortified UF adhesive after synthesis (figure7b) differs from that of neat UF spectrum by the absence of amine group at 0.6ppm, amide group at 5.99ppm, unsaturated carbon at 4.125ppm and the appearance of both methyl proton at 0.838ppm and methylene proton at 1.44ppm-2.45ppm.

The UF structure in figure 7b has therefore been fortified with rice husk extract (after synthesis) to give a new structure that is richer in methylene protons.

Similarly, figure 7c gives the spectrum of risk – fortified UF during synthesis at 55^0C, pH 3 and F/U 1. The spectrum has four peaks as that of neat UF but differs in that there are absence of both amine groups (RNH_2; 0.6ppm) and amide groups ($RCONH_2$; 5.833); and appearance of unsaturated carbon ($RCH = CH_2$; 4.9ppm). This risk – fortified UF during synthesis structure is equally reacher in methylene protons than of the neat UF resin.

When spectra in figure 7b & 7c are compared, they are almost same except in the appearance of unsaturated carbon (RCH = CH_2 4.9ppm) in risk fortified UF during synthesis' spectrum.

Figure 8 gives the spectrum of neat UF resin, red onionskin – fortified UF (during synthesis) and Risk-fortified UF (during synthesis), at 55^0C, F/U .1 & pH3. Figures 8a and 8c give the spectra of neat UF and Risk- fortified UF (during synthesis) respectively while figure 8b gives the spectrum of red onion skin – fortified UF (during synthesis) The difference between the spectrum of neat UF resin (figure 8a) and that of red onion skin – fortified UF (during synthesis)(figure 8b) is in the appearance of OH group (2.57ppm). The OH group must have been introduced by red onion skin fortifier. The red onion skin fortified UF (during synthesis) spectrum differs from that of Risk-fortified UF (during synthesis) by the appearance of unsaturated carbon at ($RCH=CH_{2;}$ 4.9ppm) and ether (ROCH=CH; 6.65ppm).

Figure 9 gives the proton NMR of neat UF resin, maize-cob-fortified UF and Risk-fortified UF, both (during synthesis). The spectra in figures 9a and 9c are that of the neat UF and Risk-fortified UF resins respectively while the spectrum in figure 9b represents that of maize-cob – fortified UF resin (during synthesis). In the spectrum of figure 9b, there are two prominent peaks appearing at (RNH_2; 0.5ppm) showing the presence of amine group and (R^1CH_2R; 2.38ppm) showing the presence of methylene proton. In between these peaks is a diminished one appearing at ($ROCH_3$; 3.2ppm) indicating the presence of ether groups". The differences between the spectra in figures 9a and 9b are in the disappearance of amide group ($RCONH_2$; 5.83ppm); and appearance of other group ($ROCH_3$; 3.2ppm) and unsaturated carbon ($ROCH_3 = CH_2$; 4.16ppm) in figure 9b. The new structure in figure 9b i.e. maize Cob – fortified UF resin is therefore richer in methylene either which must been introduced by the maize – Cob fortifier.

Similarly, the differences between the spectra in figures 9b and 9c are in the appearance of both amine group (RNH_2; 0.5ppm) and ether group ($ROCH_3$; 3.2ppm) in figure 9b, which are absent in figure 9c.

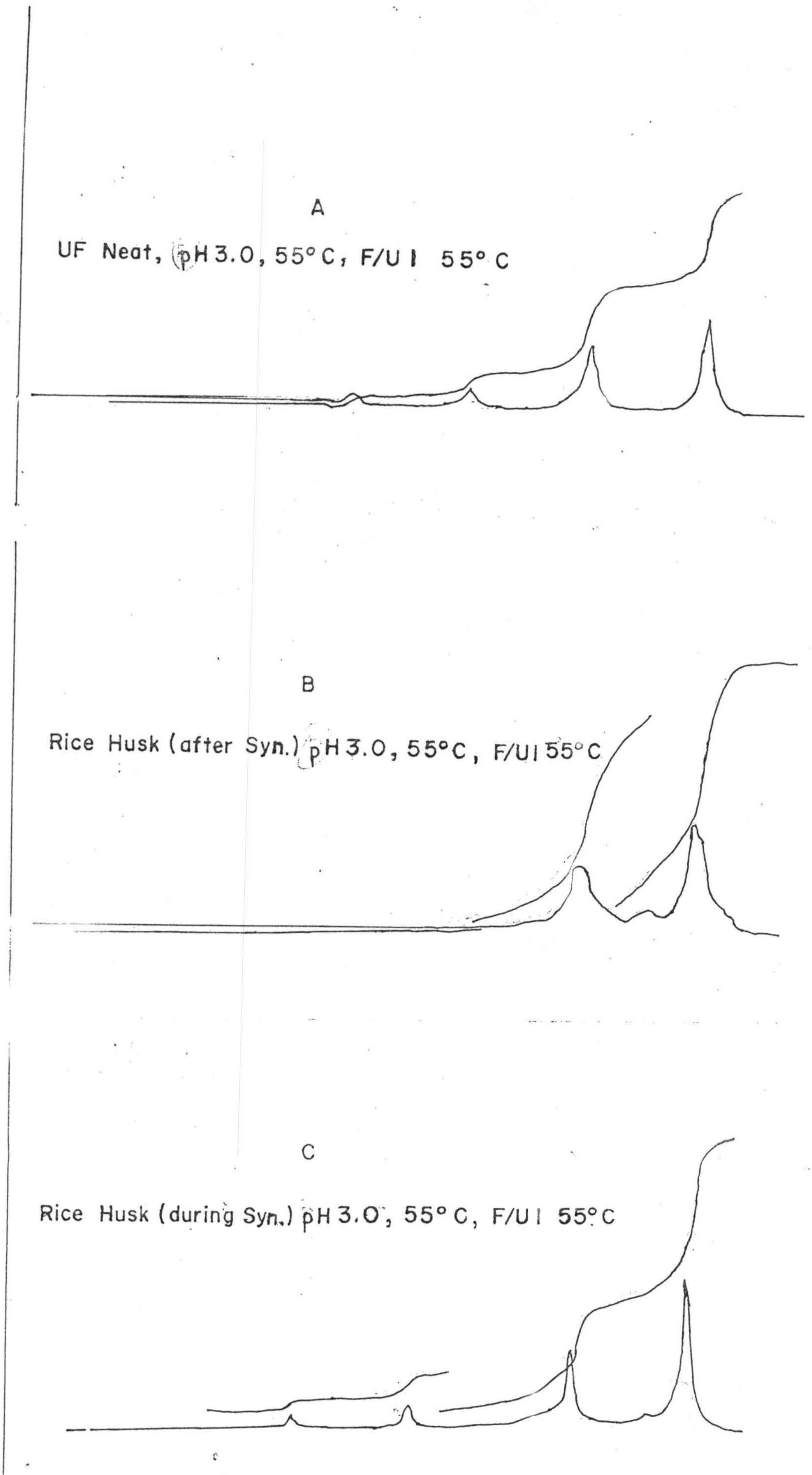


Figure 7: Proton NMR Spectra of Neat UF Resin, Rice husk modified (during Syn.) and Rice husk modified (after Syn.) systhesized at pH 3.0, U/F 1·0 and at Temperature 55° C

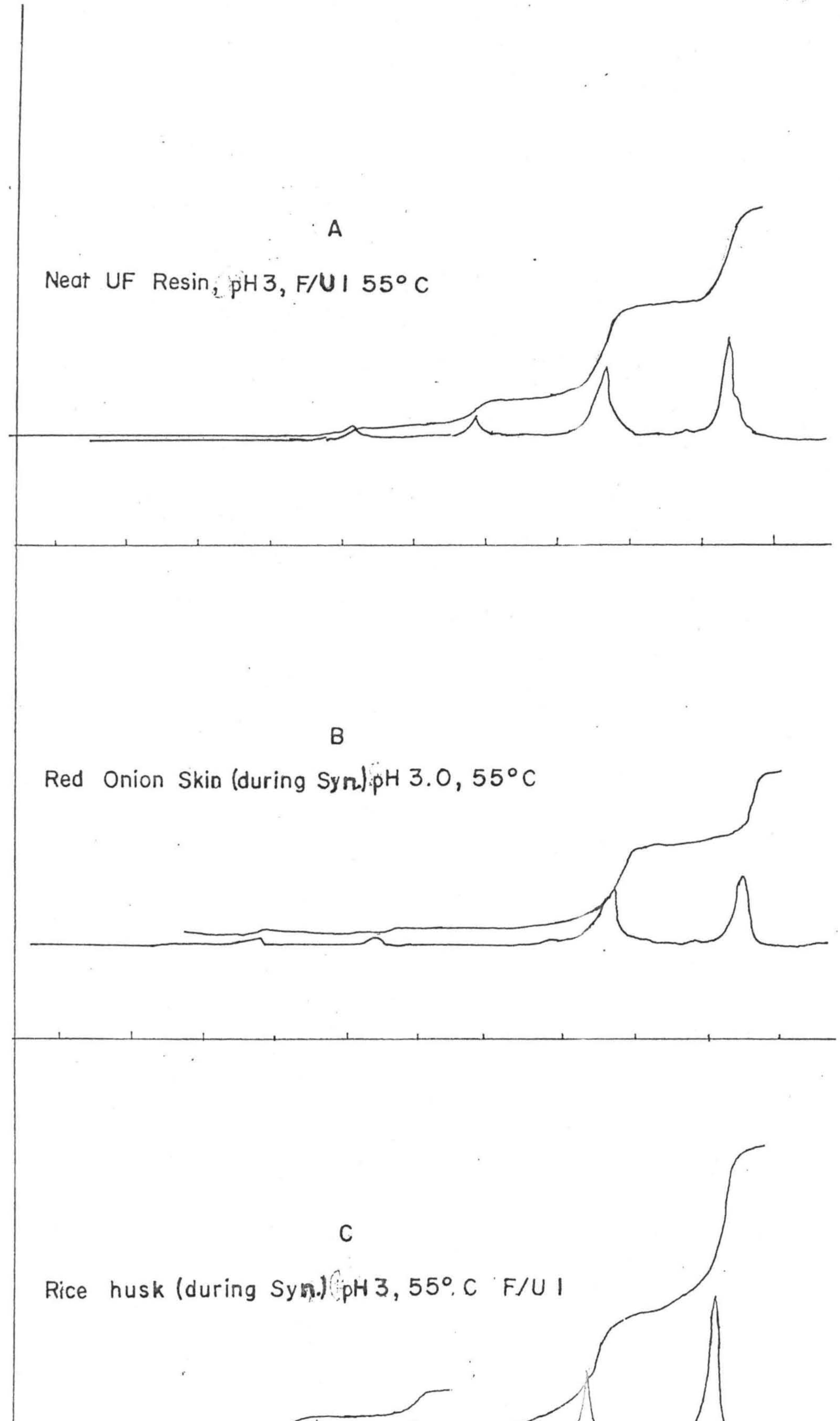


Figure 8: Proton NMR Spectra of Neat UF Resin, Red Onion skin modified (during Syn.) and Rice husk modified (during Syn.) Synthesised at pH 3.0 U/F 1:0 and temp 55° C.

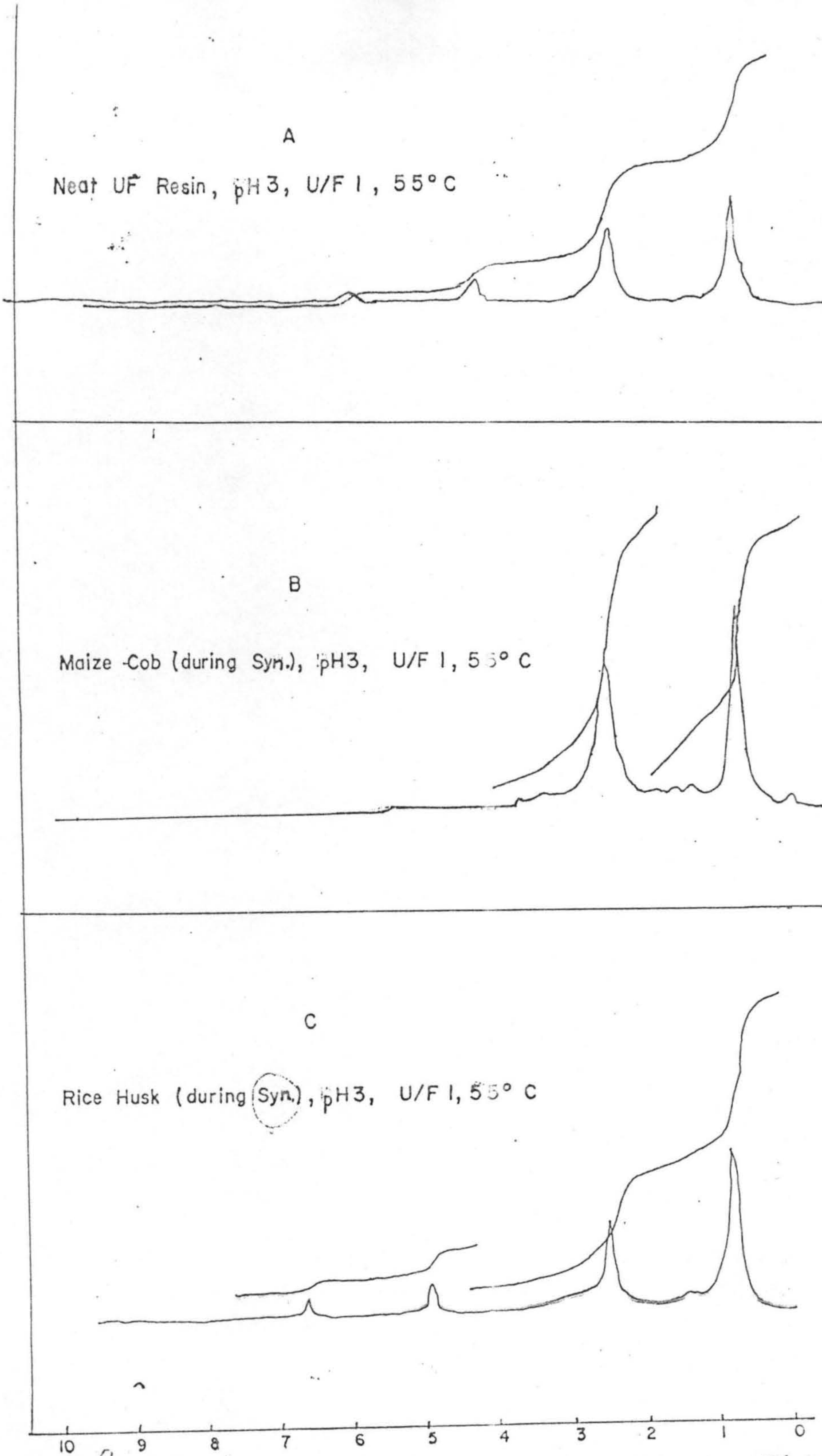


Figure 9 : IR (absorption Spectra) of Neat UF Resin, Maize Cob modified (during Syn.) and Rice Husk modified (during Syn.) Systhesised at Temperature 55° C, pH3, and U/F 1.

4.2 Infrared Spectra

Figures 10 – 12 gives the infrared spectra of the same samples for which NMR spectra were recorded. In figure 10a, which shows the spectrum of neat UF resin sample, there is strong absorption band at region 3400cm^{-1}. This absorption is peculiar of N-H (stretching vibration), which indicates the presence of secondary amine group. Also observed in the spectrum is the amide carbonyl stretching at 1640cm $^{-1}$ region. This shows the presence of $RCONH_2$ group". Furthermore, the absorption at 2100cm $^{-1}$ shows the presence of C =C groups indicating presence of alkynes. Equally observed in the spectrum is the absorption at 1250cm $^{-1}$ representing C – N stretching vibration which indicates the presence of amine group. Also featured in the spectrum is the absorption at 1000cm $^{-1}$ indicating the presence of alkene group ($RCH = CH_2$)". This spectrum confirms the UF structure.

Figures 10b and 10c present the 1R spectra of Risk – fortified UF both after and during synthesis respectively. The spectrum in figure 10b defers from that of 10a by the presence of alkene group (1600cm^{-1}), methyl group (1400cm^{-1}), phenolic group (1200cm^{-1}), aromatic group (1500cm^{-1}), carbonxylic group (2000cm^{-1}); and absence of absorption at 1640cm^{-1} (amide group), and 1250cm^{-1}(C-N stretching vibration)". Also, the absorption at 1000cm $^{-1}$ is sharper and deeper in figure 10a, while the absorption of 3400cm^{-1} are wider and deeper in figure 10b.

The new structure i.e. Risk – fortified UF after synthesis has in addition to UF composition, the phenolic group that fortifies it.

The spectra in both figures 10b and 10c are almost the same except that absorption at the regions 1400cm $^{-1}$,1500 $^{-1}$, 1200cm $^{-1}$ and 1600cm $^{-1}$ are stronger in figure 10b than that of 10c.

Figure 11 shows 1R spectra of neat UF, red onionskin – fortified UF during synthesis and Risk – fortified UF during synthesis. The spectrum of red onion skin – fortified UF(during synthesis) (figure 11b) differs from that of neat UF resin (figure 11a) at 3400cm $^{-1}$ and 1000cm $^{-1}$ where absorptions are broader and deeper, and presence of absorptions at 1200cm $^{-1}$, 1450cm $^{-1}$ and 2450cm $^{-1}$ indicating presence of phenolic (O-H stretch), methylene and carboxylic groups respectively (figure 11b).

Further more, there is no absorption at 1640cm $^{-1}$ (amide group) instead there are absorptions at 1600cm $^{-1}$ (alkene) and 1500cm $^{-1}$ (benzene). The structure in figure 11b therefore has both phenolic and methylene groups that have fortified the UF structure.

The spectra in both figures 11b and 11c represent that of red onionskin – fortified UF and Risk – fortified UF structure both during synthesis respectively. The two spectra are different at regions 1000cm $^{-1}$ and 1200cm $^{-1}$

where absorptions are stronger (figure 11b); and by the appearance of Methylene group (1450cm^{-1}) (figure 11b)".

The structure in figure 11b i.e. red onion skin – fortified UF structure is therefore expected to perform better than that rice husk – fortified UF structure because of the presence of abundant methylene group.

Figure 12 presents the spectra of neat UF; Risk – fortified UF (during synthesis) and maize cob – fortified UF (during synthesis). Figures 12a and 12b represent the spectran of neat UF and maize cob – fortified UF during synthesis respectively.

The spectrum in figure 12b defers from that in figure 12a by the absence of amide group (1640cm^{-1}), and presence of phenolic (1200cm^{-1}) and aromatic (1500cm^{-1}) groups.

The absorptions at regions 2400cm^{-1}, 2100cm^{-1} and 1000cm^{-1} are also stronger.

The amide group that is absent in figure 12b is being modified by phenolic and aromatic groups that make the new structure in figure 12b to withstand hydrolysis.

The spectrum in figure 12b defers from that of figure 12c in that absorptions at 3400cm^{-1}, 1600cm^{-1}, 1500cm^{-1} 1000cm^{-1}, and 1200cm^{-1} are weaker while it is stronger at 2100cm^{-1}, hence Risk–fortified UF during synthesis structure (figure 12c) is expected to perform better than that of maize cob-fortified UF.

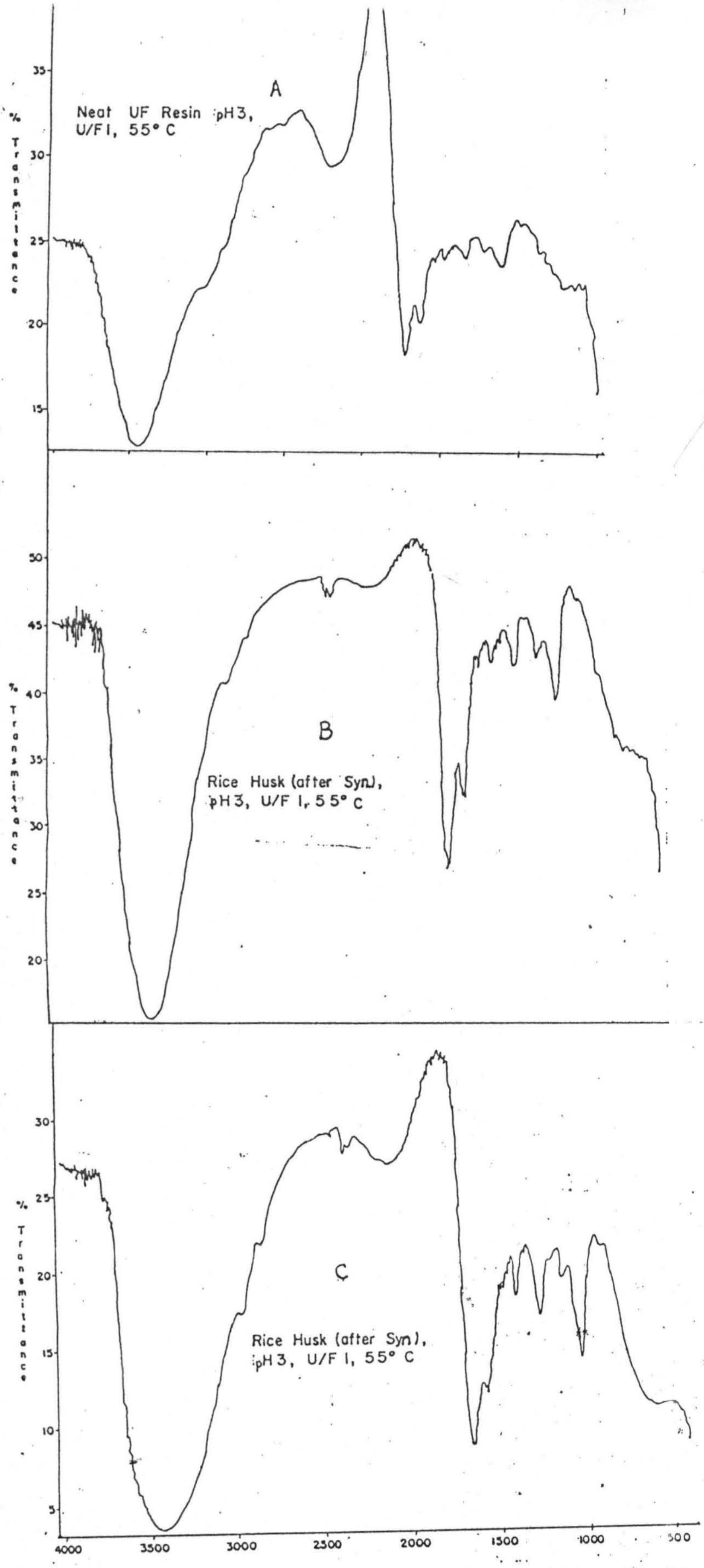
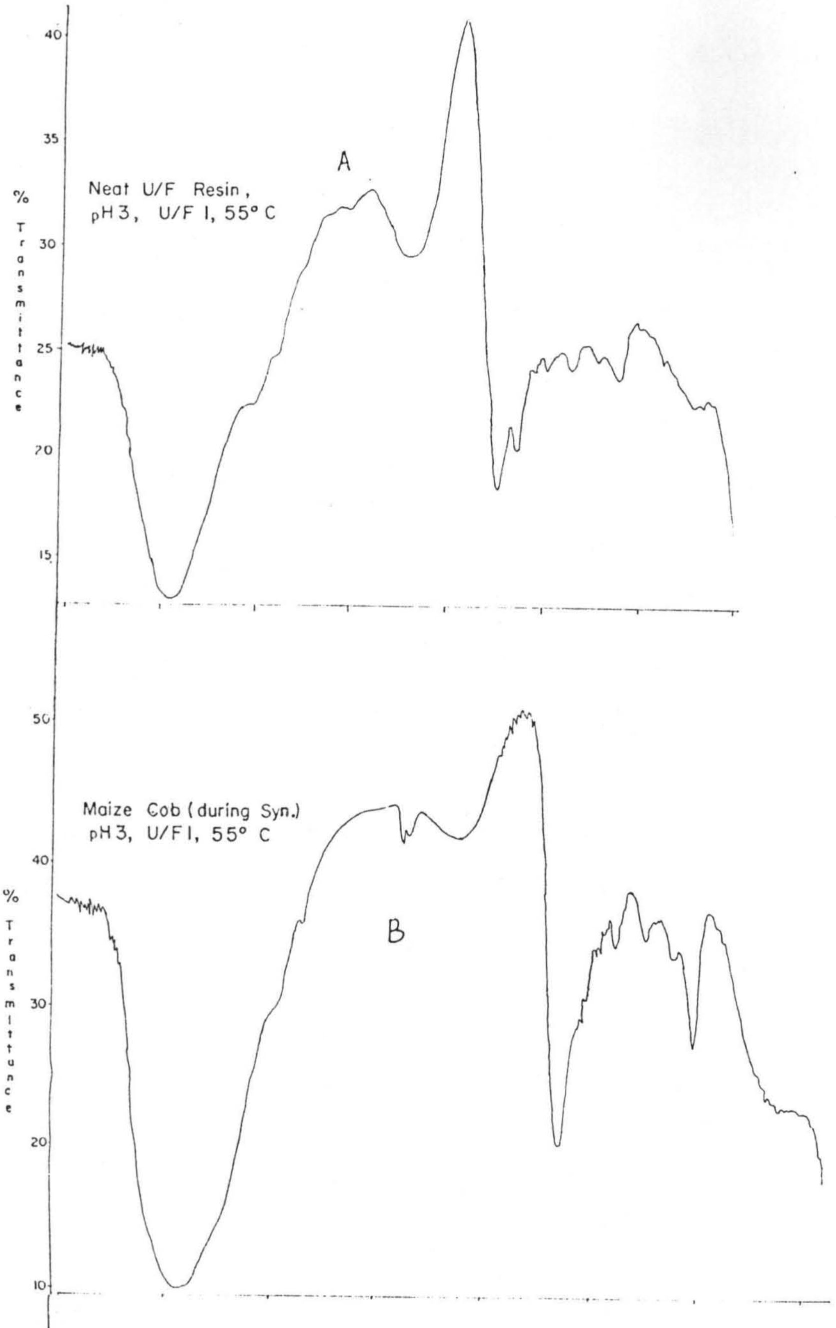


Figure 10: IR (absorption Spectra.); [illegible] of Neat UF Resin, Rice Husk modified (after Syn) and Rice Husk modified (during Syn) Synthensised at pH3, U/F 1, and Temp. 55° C



igure II: IR absorption Spectra of Neat UF Resin, Red Onion Skin modified (during Syn.) and Rice Husk modified (during Syn.) Synthensised at PH3 Temparature 55° and U/F I.

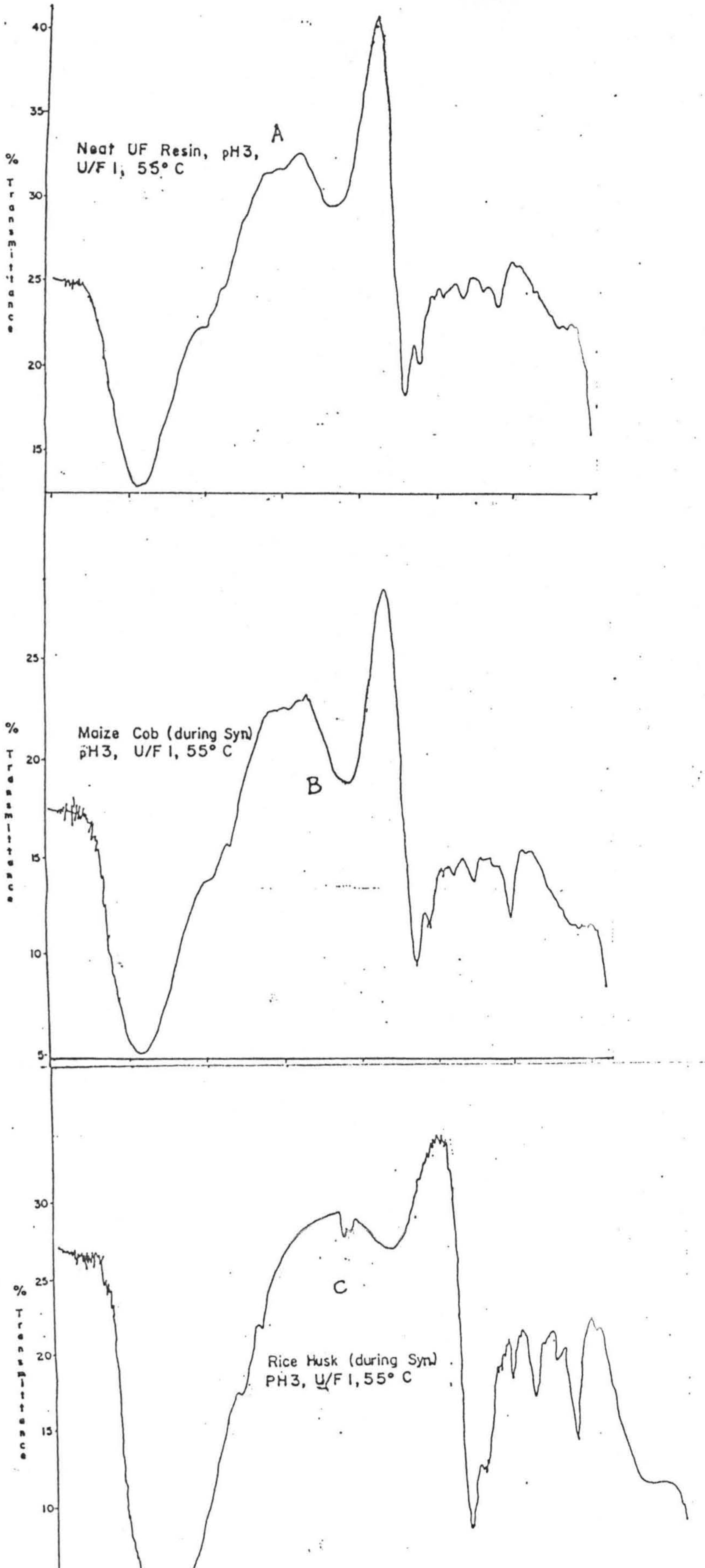


Figure 12 : IR (absorption Spectra) of Neat UF Resin, Maize Cob modified (during Syn) and Rice Husk modified (during Syn) Systhensised at Temperature 55° C pH3 and U/F 1

CHAPTER FIVE

5.0 DISCUSSION OF RESULTS

The values of the properties of the samples as obtained from the analysis of the physico-chemical properties were tabulated as shown in tables 4.1 and 4.2

From table 1, the pH value of sample M_1, M_2, M_3, M_4 and M_5 are 8.5, 8.8, 8.6, 8.7 and 8.9 respectively. These values are considered reasonable as compared to the literature value of 9.0.

The specific gravity of the samples measured at 30°C are 1.1063, 1.1135, 1.1776, 1.1542 and 1.1468 kg/m^3. These values are also within the range 1.1 – 1.18 that is the literature value range.

The molecular weight of the samples M_1, M_2, M_3, M_4 and M_5 are 38021, 9473, 24827, 10464 and 49737 respectively. This result shows that M_5 has the highest value. The marked differences in molecular weight can be considered as a result of the fact that samples had undergone certain extent of polymerization after the termination of reaction with M_5 having highest. M_5 will therefore be expected to have better mechanical properties as compared to the remaining samples[17].

The viscosities of the samples are 16, 9.33, 21.8, 10.1799 and 20.4318cp respectively. The results show that the values of M_2 and M_4 are very close to each other while that of M_3 and M_5 are also close though much higher in value. The simple reason for this is that the viscosities were not determined at the same time; while one is being determined other samples were undergoing polymerization. The one with highest degree of polymerization is expected to have high viscosity and high molecular mass[17].

The refractive indexes of the samples are 1.4, 1.37, 1.39, 1.32 and 1.37 respectively. The literature value is 1.37 – 1.39. The values of M_2, M_3 and M_5 fall within the literature value range. The value of M_1, which is 1.4, is not far from the literature value too. The only value, which is a little bit low, is that of M_4 which is 1.32. This value can be attributed to the error in the reading of the equipment.

The total solid content of the samples as in table 1 agreed with the literature value of 63-65[16]. The only value, which is out of the range, is that of M_3 which is 65.5 and this, can as well be considered closed to the literature range

The percentage free formaldehyde in samples M_1, M_2, M_3, M_4 and M_5 are 3.9, 3.6, 3.75, 3.5 and 3.8 respectively. The literature value is 3.5-4.0[16]. These values are reasonable as they fall within the literature range.

The analysis of the infrared spectra in chapter 4 showed that sample M_1 contains the following functional groups: NH, CO, CH_2 and CH. NMR spectral also confirm the same groups, hence the two spectra confirm the presence of Urea formaldehyde. The other samples, i.e. M_2, M_3, M_4 and M_5 were also analysed to contain other functional groups apart from those found in sample M_1 such as phenol, benzene rings, methylene proton, carbonxylic groups etc. In view of these NMR and infrared spectrum analyses, the samples M_2, M_3, M_4 and M_5 can be said to contain phenol and hence are expected to possess certain degree of water resistance since phenolic compounds are hydrophobic in nature.

The tensile strength of the samples M_1, M_2, M_3, M_4 & M_5 – were 56, 70, 73, 78 and 75 MN/m^2 respectively which lie within the literature value of 52-80 MN/m^2 while the cross breaking strength were 76, 90, 95, 100 and 99 MN/m^2 which also lie within the literature value of 76 – 117 N/m^2.[19]

CHAPTER SIX

6.0 CONCLUSIONS AND RECOMMENDATIONS

The research reported here focused on Urea Formaldehyde that were fortified in three ways:

(a) By incorporating 5% by wt (total UF resin) extracts from rice husk, maize cob and red Onion skin during UF synthesis.

(b) By incorporating into UF resin 5% by wt (total resin) extract from rice husk after synthesis.

(c) By adding 5% by wt (total resin) of curing agent (ammonium sulphate) into (a) and (b).

It was concluded that:

(a) Fortifying UF resins by adding extracts from maize-cob, red onionskin and rice husk directly to UF during synthesis destroys resin cure activity.

(b) Resistance of UF bonded wood to sheer stress was substantially improved by modifying the resins through:

(i) Incorporating extracts from rice husk, maize cob and red Onion skin respectively into the resin during and after synthesis.

(ii) Curing the resin samples with curing agent.

The inadequacies of research work equipment such as differential Scanning Calorimeter (DSC) which would have been used to determine the thermo response of the urea – formaldehyde resin samples, both neat and fortified, limited the research to what was presented here.

However, the equipment I listed here were rented from distanced Universities, which makes the research works more expensive and cumbersome.

I hereby implore the Department to try as much as possible to procure all the necessary equipment for research work so as to assist the students in carrying out their research work.

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APPENDIX

A KINEMATIC VISCOSITY, VISCOSITY, DENSITY AND MOLECULAR WEIGHT

(i) FOR SAMPLE M_1

$t_1 = 165$ seconds

Dilution Ratio = 1:20.

$\sqrt{}_1 = Ct_1 = 0.0882 x 165 = 14.553$ stokes.

$W_1 = 30.9525$gm

$W_2 = 40.6428$gm

$W_3 = 41.6720$gm.

$W_4 = W_2 - W_1 = 40.6428 - 30.9525$gm $= 9.6895$gm

$$W_5 = W_3 - W_1 = 41.6720\text{gm} - 30.9525\text{gm}$$

$$= 10.7195\text{gm}$$

$$\rho_1 = \frac{10.7195\text{gm}}{9.6895\text{gm}} = 1.1063$$

$$= \text{Specific gravity.}$$

The actual density = 1.1003g/cm$_3$ at 32°C.

$$\mu_1 = \sqrt{}_1 \text{ x } \rho_1 = 1.1063 \text{ x } 14.553 = 16.1000 \text{ cp.}$$

$$[\mu]_1 = \frac{\mu_1 - \mu_O}{\mu_{oc}}$$

$$= \frac{16.1000 - .26}{.26 \text{ x } 0.5}$$

$$= 1218.4615.$$

From the relationship of [μ] and molecular weight,

i.e [μ]$_1$ = KM_1^a, where K = $9.2 \text{ x } 10^{-21}9\text{cm}^3/\text{g}$ and a = 0.9.

. . 1218.4615 $= 9.2 \times 10^{-2} \times M^{-9}$

$$M_1 = \sqrt[0.9]{\frac{1218.4615}{9.2 \times 10^{-2}}}$$

Hence M_1 = 38021.27gm= Molecular Weight.

Using the steps outlined above for sample M_1, the results for samples M_2, M_3, M_4 and M_5 are obtained as follows:

ii. **SAMPLE M_2**

t_2 = 95 seconds

Dilution Ratio = 1.10

$\sqrt{}_2$ = 8.399 stokes

W_4 = 9.6895gm

W_5 = 10.7895gm

$$\rho_2 = \frac{10.7895gm}{9.6895gm} = 1.1135$$

= $1.1135gkm^3$ at 32°C

μ_2 $=\surd_2$ x ρ_2 = 1.1135 x 8.379 = 9.3300cp

$$[\mu]_2 = \frac{9.3300 - .26}{.26 \times .1}$$

= 348.846

$$M_2 = \sqrt[0.9]{\frac{348.346}{9.2 \times 10^{-2}}}$$

= 9473.1730.

(iii) **SAMPLE M_3**

T_3 = 210 Second

Dilution Ratio = 1:10

$\surd_{3-}$ = 18.522 stokes

$W_4 \quad = \quad 9.6895\text{gm}$

$W_5 \quad = \quad 11.4105\text{gm}$

$$\rho_3 \quad = \quad \frac{11.4106\text{g/m}}{9.6895\text{g/m}}$$

$$= \quad \frac{11.4106\text{g/m}}{9.6895\text{ g/m}}$$

$= \quad 1.1776 \text{ g/cm}^3$

$\mu_3 \quad = \quad \surd_3 \text{ x } \rho_3 = 18.552 \text{ x } 1.1766$

$= \quad 21.8473C_P$

$$[\mu]_3 \quad = \quad \frac{21.8473 - .26}{.26 \text{ x } .1} \quad = 830.2809$$

$$M_3 \quad = \quad \sqrt[0.9]{\frac{830.2809}{9.2 \text{ x } 10^{-2}}}$$

= 24827.3436gm

(iv) **SAMPLE M_4**

t_4 = 100 Seconds

Dilution Ratio = 1:10

$\surd_4$ = 8.82 Stokes

W_4 = 9.6895 gm

W_5 = 11.1835gm

$$\rho_4 = \frac{11.1835g/m}{9.6895g/m}$$

= 1.1542 g/cm^3 at 32°C.

μ_4 = 1.1542 x 8.82

= 10.1799CP

$$[\mu]_4 = \frac{10.1799 - .26}{.26 \times .1}$$

= 381.5359

$$\sqrt[0.9]{\frac{381.5359}{9.2 \times 10^{-2}}}$$

= 10464.525gm

(V) **SAMPLE M_5**

$t_5 = 202$ seconds

Dilution Ratio = 1:20

$\surd_5 = 17.8164$ stokes

$W_4 = 9.6895$gm

$W_5 = 11.1118$gm

$$\rho_5 = \frac{11.1118\text{gm}}{9.6895\text{gm}}$$

$$= 1.1468\text{g/cm}^3$$

$$\mu_5 = 1.1468 \times 17.8164$$

$$= 20.4318\text{CP}$$

$$[\ \mu\ ]_5 = \frac{20.4318 - .26}{.26 \times .05}$$

$$= 1551.6806$$

$$M_5 = \sqrt[0.9]{\frac{155.6806}{9.2 \times 10^{-2}}}$$

$$= 49737.3651\text{gm}$$

B TOTAL SOLID (TDS) CALCULATION AT TEMPERATURE T=100°C

(i) W_1 = 45.946g

W_3 = 48.499g

W_2 = 47.605g

Therefore % TDS = $\frac{W_2 - W_1}{W_3 - W_1}$ x100%

$= \frac{47.605g - 45.94g}{48.499g - 45.946g}$

$= \frac{1.659}{2.553}$ x 100%

= 64.982%

Above steps are similarly used for sample M_2, M_3, M_4 and M_5

SAMPLE M_2

W_1 = 46.409g

W_2 = 47.984g

W_3 = 48.109g

% TDS = $\frac{47.984 - 46.409g}{48.909g - 46.409g}$ x 100%

$= \frac{1.575}{2.5}$ x 100%

= 63%

SAMPLE M_3

W_1 = 45.585g

W_3 = 48.085g

W_2 = 47.2225g

$$\% \text{TDS} = \frac{47.2225 - 45.585}{48.085 - 45.585} \times 100\%$$

$$= \frac{1.6375}{2.5} \times 100\%$$

$$= 65.50\%$$

SAMPLE M_4

W_1 = 29.347g

W_3 = 31897g

W_2 = 30.922g

$$\% \text{TDS} = \frac{30.922g - 29.347g}{31.897g - 29.347g} \times 100\%$$

$$= \frac{1.575}{2.5} \times 100\%$$

$$= 63\%$$

V. **SAMPLE M_5**

W_1 = 30.046g

W_2 = 31.6585g

W_3 = 32.546g

$$\% \text{ TDS} = \frac{31.6585g - 30.046g}{32.546g - 30.046g} \times 100\%$$

$$= \frac{1.6125}{2.5} \times 100\%$$

$$= 64.5\%$$

C. FREE FORMALDEHYDE

(i) **SAMPLE M_1**

X = 18ml.

Y = 5ml.

W = 10gm.

$$\% \text{ Free Formaldehyde} = \frac{(X - Y) \times 3}{W}$$

$$= \frac{(18 - 5) \times 3}{10g}$$

$$= 3.9\%$$

(ii) **SAMPLE M_2**

$X = 22ml$

$Y = 10ml$

$W = 10g$

$$\% \text{ Free Formaldehyde} = \frac{(X - Y) \times 3}{W}$$

$$= \frac{(22 - 10) \times 3}{10}$$

$$= 3.6\%$$

(III) **SAMPLE M_3**

$X = 22\text{-}5ml$

$Y = 10ml$

$W = 10g$

$$\% \text{ Free Formaldehyde} = \frac{(X - Y) \times 3}{W}$$

$$= \frac{(22.5 - 10) \times 3}{10}$$

$$= 3.75\%$$

(IV) **SAMPLE M_4**

$X = 16.67ml$

$Y = 5ml$

$W = 10g$

$$\% \text{ Free Formaldehyde} = \frac{(x-y)\,x3}{W}$$

$$= \frac{(16.67 - 5) \times 3}{10}$$

$$= 3.5\%$$

(V) **SAMPLE M_5**

X = 19.67ml

Y = 7ml

W = 10g.

$$\% \text{ Free Formaldehyde} = \frac{(X - Y) \times 3}{W}$$

$$= \frac{(19.67 - 7) \times 3}{10}$$

$$= 3.8$$

D **Formulas Used**

(i) $\sqrt{i} = Cti$

(ii) $\mu i = \sqrt{i} \times \rho i$

(iii) $[\mu]i = \frac{\mu i - \mu_O}{\mu_{oc}}$

(iv) $[\mu]I = KM^a$

(v) $\text{Free Formaldehyde} = \frac{[\text{Blank} - \text{Titre}] \times 3}{\text{wt of resin.}}$