

## Urea-formaldehyde Resins Synthesis, Modification and Characterization

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**Abstract:** Urea-formaldehyde resins (UF resins) were prepared by a two-stage reaction. The comparative analysis were made of the resulting laboratory samples with some commercial samples. Some of the drawbacks of UF resins, such as poor adhesive strength, especially in moisture or humid environments and high free formaldehyde emission (FE). In order to reduce the FE, lowering urea/formaldehyde (U/F) mole ratio in the synthesis of the UF resin was done. In this study, synthesis of UF resins was carried out following the conventional alkaline-acid two-step reaction with a second addition of urea, resulting in the following U/F mole ratio: 1:2.60, 1:2.70, 1:2.30, 1:2.04, 1:1.97, 1:2.13 and 1:2.90. Remarkably, the free formaldehyde was found to decrease with increased mole U/F mole ratio, solid content and ash content. The key parameter in the decrease of formaldehyde emission is lowering the urea/formaldehyde (U/F) ratio in the synthesis of UF resins. This leads to a reduction in the content of crosslinking groups in cured UF resins, lowering the strength and water resistance of adhesive joints in boards. The laboratory synthesized UF resins samples were modified using different types of alcohols. N-butyl alcohol modified UF resins samples were found to possess better properties generally.

**Keywords** Ash content Drawbacks, emission, solid content, resin, synthesis

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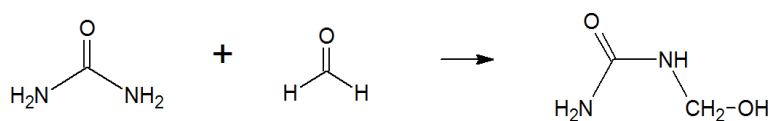
### I. Introduction

Urea-formaldehyde (UF) products (also called aminoplasts) are highly crosslinked, semi-crystalline thermosetting plastics; which is the product of a condensation reaction between urea and formaldehyde<sup>[1]</sup>. The UF resins are noted for their high strength, rigidity, cost effectiveness, and fast cure. UF resins are among the fastest curing resins available. At elevated temperatures, they can be cured in as little as two seconds<sup>[2]</sup>.

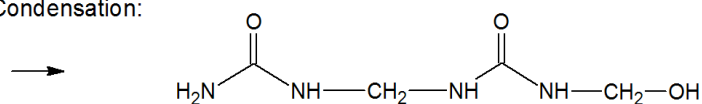
A large portion of UF resins are consumed by the wood products industry; most especially, it serves as adhesives for particleboards<sup>[2]</sup>. The popularity of urea-formaldehyde resins as the main adhesive for wood products has several reasons, including low cost, ease of use under a variety of curing conditions, versatility, low cure temperature, resistance to mold formation, excellent thermal properties, lack of color of the cured product, and excellent water solubility of the (uncured) resin<sup>[3]</sup>. A major drawback of urea-formaldehyde adhesives compared with other thermosetting wood adhesives, such as phenol-formaldehyde and polymeric diisocyanates, is the lack of moisture resistance especially at elevated temperatures. Furthermore, the reversal bond-forming reactions can lead to the release of formaldehyde<sup>[2, 3]</sup>.

Urea formaldehyde (UF) resins are primarily made up of urea and formaldehyde with formaldehyde acting as the cross linker. The UF resins are formed in water at a pH above 7 at the start of the reaction, because the methylol derivatives that form in the first steps condense rapidly at acidic conditions, as illustrated in scheme (1):

Initial Step:

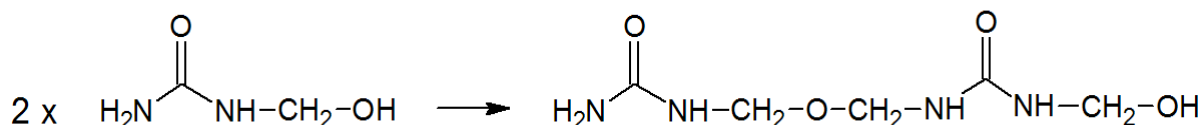


Condensation:



**Scheme 1: Reaction Urea with formaldehyde and condensation reaction of the methylol group formed**

Under alkaline conditions, on the other hand, in scheme (2), the condensation is much slower and better to control. Instead of methylene linkages, dimethylene ether groups form:



**Scheme 2: Formation of dimethylene ether groups.**

The condensed oligomers are water soluble and contain hemiformal groups<sup>[4]</sup>. This mixture is further reacted under acidic conditions (usually at about pH 5) and by heating, which leads to the desired degree of condensation.

In the case of surface coatings, the UF resins are often modified to improve their solubility in solvent, for example, by reacting them with n-butyl alcohol (etherification) prior to condensation (resin formation).

Urea-formaldehyde resins find applications in adhesives, coatings, laminating, and moulding compositions. More than 1 million metric tons of urea-formaldehyde (UF) resin is produced annually<sup>[5]</sup>. This comprises about 80% of all amino resins produced worldwide. More than 70% of it is consumed by the wood industry for bonding particleboards (61%), medium-density fiberboard (27%), and hardwood plywood (5%). It is also used as an adhesive for decorative laminate applications (7%). Other applications include wet laid fiberglass mats, air filtration, coated and bonded abrasives.

Due to the lack of moisture resistance, UF wood adhesives are mainly used for the manufacture of wood products intended for interior use only.

The principal petrochemical adhesives often used in furniture industries are formaldehyde - condensation plastics. They are urea - formaldehyde (UF), phenol - formaldehyde (PF), phenol - resorcinol - formaldehyde (PRF), and melamine - formaldehyde (MF), plastics. It is interestingly of note that bonding with UF adhesive is cheaper than bonding with PF adhesive, and it permits the formation of strong bonds under a wider variety of conditions. Moreover, since the manufacturing costs of urea - formaldehyde resins is relatively the least expensive synthetic organic resin as well as the most versatile in wood - adhesive bonding worldwide. However, the poor durability and stability of UF bonded products limit their use to interior, non - structural applications. These limitations are evidenced for example, in strength losses of UF bonded joints; irreversible swelling of UF bonded composite panels and formaldehyde release<sup>[6, 7]</sup>. A significant improvement in the durability - stability of UF bonded wood products and drastic reduction in the formaldehyde emission would broaden the applications and markets for the products and thereby allow substitution of the UF - resin for more expensive, less versatile and more supply - dependent PF - system.

Several attempts have been made to develop hydrolytically stable and durable UF systems. For example, since formaldehyde - to - urea molar ratio (F/U) governs to some extents the stability and durability of wood joints<sup>[8]</sup> and particle board<sup>[9]</sup>, the effects of resin molar ratio from about 2.10 - 1.21, have been examined. Modification of the resins with alcohols and other modifiers has also been studied<sup>[10]</sup>. The effectiveness of the cross - links induced in the UF resins has also been studied. A remarkable improvement in stability - durability has been made by modifying the UF resins with alcohols.

The objective of this research is to improve the hydrolytic stability of the UF resins and equally reduce its free formaldehyde content. In order to achieve a product with wide range of end uses.

## II. Experimental Procedure

### 2.10 Materials and Apparatus

Urea (M&B), 40 % formaldehyde (BDH), formic acid (BDH), sodium hydroxide (M&B), sodium sulphite (MJ&B), sulphuric acid (M&B), copper II sulphate-pentahydrate (BDH), boric acid (M&B), Ethanol (BDH), phosphoric acid (M&B), ferrous sulphate (M&B), lead acetate (M&B), silver nitrate (BDH), nitric acid (M&B), ammonia solution (M&B), sodium metal (BDH), methanol (M&B), isobutyl alcohol (BDH), tert-butyl alcohol (M&B), local gin (Nigeria), xylene (Eagle scientific Ltd), hydrochloric acid (HAIG), potassium sulphate (M&B), Torsion viscometer (Gallenkamp), Abbe Refractometer, Instron Testing Machine.

### 2.2.0 Methods

#### 2.2.1 Synthesis of Urea – formaldehyde Resins

123g of 40 % aqueous solution of formaldehyde was accurately measured and poured into a 500 ml – 3- neck round bottom water jacketed glass reactor and neutralized with 2M sodium hydroxide solution. 82g of Urea was added and the pH adjusted in the range of 7.5 – 8.0 using the 2M sodium hydroxide. The flask was connected to a reflux unit and the mixture slowly heated to reflux for 2 h at 98 °C with vigorous agitation,

stirring was initiated using a mechanical stirrer. After 10 minutes interval of refluxing, a sample was removed and cooled to 25 °C, for pH and viscosity analysis. The pH was then adjusted to between 4.5 and 5.0 with the lactic acid. The mixture was refluxed again until the aliquots gave rise to a precipitate on addition to a large volume of water after which the pH was adjusted back to 7.5 – 8.0 with 2M sodium hydroxide solution. The viscosity of the mixture was regularly checked using the Gallenkamp Torsion viscometer. The final solution (UF resin liquor) was concentrated at a temperature below 50 °C and subjected to vacuum distillation until it attained a syrup like consistency; with viscosity of about 225 centipoise. The batch was dried using the oven pre-set at a temperature below 50 °C, and then cooled to room temperature and weighed. 7 different samples were prepared by repeating the above procedure.

### **2.2.2 Determination of Free formaldehyde**

3.0 g of the resin sample was weighed and placed in a 250 ml conical flask. 75 ml of distilled water which had been cooled to 8 °C was added. 10 drops of 0.1 % ethanolicthymolphthalein indicator solution was added and then neutralized with 0.5 N sodium hydroxide to the blue end point. Exactly 20 ml of 0.5 N sulphuric acid was added. Then 25 ml of 1M sodium sulphite which had been neutralized to the colourless thymolphthalein end point with two drops of 0.5 N sulphuric acid was added. The whole content in the flask was titrated immediately with 0.5 N sodium hydroxide to the blue point. The above procedure was repeated for all the prepared UF resins, including the commercial sample. The same procedure was used in the determination of free formaldehyde in all the alcohol – modified UF resins.

### **2.2.3 Determination of Nitrogen and Urea Content**

8 g of potassium sulphate and 1 g of copper II sulphate were accurately weighed and placed in a 1000ml distillation flask. 35 ml of concentrated sulphuric acid was added followed by the addition of 1 g of the urea – formaldehyde resin sample to be analyzed. The flask and its contents was placed in a hood over a low flame. The hood blower was turned on and the contents in the flask digested until the solution became clear green in colour. The solution was then cooled and carefully diluted with 190 ml of distilled water, while cooling the flask under running tap water. A distillation unit with a receiving flask was set – up. A 250 ml conical flask containing 50 ml of 0.6M boric acid solution and 5 drops of methyl red indicator solution was used as the receiving flask. While cooling under the tap water, 110 ml of 12 N sodium hydroxide was added to the distilling flask, pouring it down the side to prevent mixing. The distilling flask was then quickly connected to a distillation unit and about 100 ml distilled over. The flask generally started to bump at this point, indicating that the distillation was complete. The solution in the receiving flask was titrated immediately with standardized 0.25 N hydrochloric acid to the red end point. The titration was continued until the end point colour was comparable to the colour obtained with 50 ml of boric acid solution diluted with 100 ml of water and 5 drops of methyl red indicator solution. The above procedure was repeated for each of the eight resin samples and the modified resin samples.

More test and experiments were carried out for the characterization of the synthesized UF resins alongside the commercial samples and the alcohol modified samples, which include: determination of solid content, determination of ash content, measurement of specific gravity, sodium – fusion test, Nitrogen (Prussian blue test), Sulphur (Lead sulphide test), test for halogens, test for borates, determination of Rate constants for acid catalysis to form network polymer, dilute solution viscosity, Determination of the concentration of alcohol modified resins, measurement of the refractive index of modified resins and the tensile strength test of the UF resins including synthesized, modified and commercial samples.

## **III. Results and Discussion**

TABLE 3.1 Show the detail results of some of the quantitative elemental analysis carried out. The reaction between urea and formaldehyde is a condensation reaction. Whether the forward or the backward reaction is favoured depends largely on the reaction conditions, among which; pH, molar ratio (Urea: formaldehyde), and reaction time are the most critical.

These factors largely affect the kinetics of the reaction and hence efficiency. This is why it is difficult to achieve 100 % efficiency, which is only a measure of the extent of reaction. This accounts for the presence of free formaldehyde in the resin. Within the limit of experimental errors, the molar F/U ratio of the commercial UF resins and the laboratory synthesized resins are 1: 1.94 and 1: 1.97 respectively. These values are within the literature values. 1: 1.5-2.0<sup>[11]</sup>.

The slight variation in mole ratio and free formaldehyde of the laboratory resins samples could be attributed to difficult and non- uniform temperature control during synthesis, which in combination with other reaction parameters determine to a large extent the nature and properties of the resins.

From the results in TABLES 3.1, it was observed that the solids content of the resins increased as the free formaldehyde decreased. This trend was expected, being that the solid content is a measure of molecular growth. The higher the solids content, the larger the molecular growth and the smaller the free formaldehyde. It was equally noticed that the free formaldehyde and solids content of the laboratory UF resins samples compared favourably with those of the commercial resins samples. The free formaldehyde of the laboratory sample is only slightly higher than those of commercial resins by 0.1 %, while the solids content is slightly lower by 1.6 %.

Ash content is a measure of non-volatile substances in the UF resins. By forming complexes, these substances may block reactive sites and hence reduce reactivity and molecular growth. Thus the higher the ash content, the smaller the molecular growth and the more the free formaldehyde. This explains why a linear relationship is obtained between free formaldehyde and the ash content as shown in TABLES 3.1. It was equally observed that the commercial resins samples have least ash content and free formaldehyde, these values are only slightly lower than of the laboratory samples by 0.5 % and 0.1 % respectively.

The borates and sodium – fusion test results of the laboratory and commercial UF resins agree. The specific gravity values, nitrogen and urea contents of the resins also agree very closely as shown in TABLE 3.1.

The kinetics of the crosslinking reaction of the local and commercial prepolymers was investigated. The order of the reaction and rate constant,  $K_2$  for each to form network polymers were determined. From the reaction rate equation, a linear curve was achieved; this proves that the crosslinking reactions were of first order.

Laboratory synthesized UF resins were not soluble in common organic solvents; hence the need to modify the resins using alcohols. The modified resins were analyzed and the results were presented as shown in TABLE 3.2. From the results, the mole ratio of the modified UF resins decreased in the order: n-butyl alcohol modified resins > isobutyl alcohol modified resins > tert butyl alcohol modified resins > local gin modified resins > ethyl alcohol modified resins. Reactivity also decreased in the same order. The greater the steric effect the less the reactivity and hence the higher the free formaldehyde. Steric hindrance is most pronounced in tert butyl alcohol modified resins, more in isobutyl alcohol modified resins and least in n-butyl alcohol modified resins. This explains the decrease in the reactivity and mole ratio.

**Table 3.1 Results of Quantitative and Qualitative Analysis of Urea – formaldehyde Resins**

Sample no.	% Free HCHO	% Nitrogen	% Urea	Mole ratio (Urea:HC HO)	% Mole ratio (Urea: HCHO)	% Solids content	% Ash content	Specific Gravity	Sodium Fusion			Borate Test
									N	HAL	S	
1	4.04	34.51	73.99	1:2.60	38.46	79.80	16.20	1.46	+ve	-ve	-ve	-ve
2	4.52	33.60	72.04	1:2.70	37.04	60.10	21.50	1.43	..	..	..	..
3	4.10	38.50	82.50	1:2.30	43.48	68.00	17.50	1.46	..	..	..	..
4	4.47	43.75	93.80	1:2.04	49.02	62.40	20.50	1.46	..	..	..	..
5	3.98	45.50	97.60	1:1.97	50.76	77.20	15.50	1.46	..	..	..	..
6	4.08	42.00	90.00	1:2.13	46.95	71.20	16.70	1.46	..	..	..	..
7	4.22	30.80	66.03	1:2.90	34.48	65.30	18.60	1.43	..	..	..	..
Commercial 8	3.88	46.20	99.05	1:1.94	51.55	78.80	15.00	1.46	..	..	..	..

Following modification of the laboratory samples of the UF resins with different types of alcohols; the results showed a decrease in free formaldehyde in the order of the strength of the alcohols as follows: ethyl alcohol > local gin > tert butyl alcohol > isobutyl alcohol > n-butyl alcohol. Whereas, it was observed that there was a decrease in the solids content of the resins modified with alcohol and hence reactivity followed a reverse order. This is expected for n-butyl alcohol, isobutyl alcohol and tert butyl alcohol due to increase in steric effect in that order. Solids content of local gin is greater than that of ethyl alcohol for the same reason earlier stated<sup>[12, 13]</sup>.

It could be deduced from the results of the analysis of the alcohol modified UF resins in TABLE 3.2 that the free formaldehyde and ash content depends on the nature of alcohol used in the resins modification. As mentioned before, Ash content is a measure of non-volatile substances and hence purity level of the resins. The non-volatile substances may singly or in combination block reactive sites and reduce reactivity. Free formaldehyde decreases as reactivity increases. This explains the trend in the decrease in free formaldehyde as the ash content decreases. The least values of ash content and free formaldehyde are obtained with n-butyl alcohol which shows that n-butyl alcohol modified UF resins contains the least amount of non-volatile substances.

**Table 3.2 Results of Quantitative Analysis of Alcohol – Modified UF Resins**

Type of Alcohol Used	% Free HCHO	% Nitrogen	% Urea	Mole ratio (Urea:HCHO)	% Mole ratio (Urea:HCHO)	% Solid content	% Ash content	Ref. Index at (30 °C)
Isobutyl Alcohol treated Resins	4.61	39.11	83.85	1:2.07	48.31	57.30	18.30	1.4503
Tert butyl Alcohol treated Resins	4.92	34.10	73.11	1:2.22	45.05	55.80	19.60	1.4508
Ethyl Alcohol treated Resins	5.21	28.13	60.31	1:2.33	42.95	53.80	23.30	1.4534
Local Gin treated Resins	5.08	29.42	63.07	1:2.31	43.29	53.90	20.10	1.4723
n-Butyl Alcohol treated Resins	4.10	43.10	94.50	1:1.88	53.19	62.40	14.40	1.4512

TABLE 3.3 shows the values of the solubility parameters of the different alcohols used in the modification of the UF resins, alongside values of the Huggins constant  $K^1$  and intrinsic viscosity  $[\eta]$  obtained from the results of the dilute solution viscosity tests. It was observed that n-butyl alcohol modified resins has the highest intrinsic viscosity, followed by resins modified with isobutyl alcohol and then tert butyl alcohol. Intrinsic viscosity is a measure of the molecular size in solution. Reactivity and molecular size is largely affected by steric effect<sup>[14, 15]</sup>. Steric hindrance is least pronounced in n-butyl alcohol, more in isobutyl alcohol and most in tert butyl alcohol. Reactivity and hence molecular size therefore decrease in the order: n-butyl alcohol treated resins > isobutyl alcohol treated resins > tert butyl alcohol treated resins, which explains the decrease in intrinsic viscosity in that order. The slightly higher value of intrinsic viscosity obtained with local gin compared to ethyl alcohol may be due to the small amount of methanol and propyl alcohol present in local gin which increased the reactivity of the local gin. The Huggins constant was determined from the plot reduced viscosity ( $\eta_{sp}/C$ ) versus concentration, C of the alcohol-modified resins using equation (1), Huggins equation:

$$(\eta_{sp}/C) = [\eta] + K^1[\eta]^2C \tag{1}$$

Also the slope of the graph is obtained from equation (2), as follows:

$$\text{Slope} = K^1[\eta]^2 \tag{2}$$

The Huggins constants  $K^1$  obtained for the n-butylalcohol,tert butyl alcohol, isobutyl alcohol, local gin and ethyl alcohol modified resins are: 0.49, 0.85, 4.97, 93.83 and31.02 respectively; whereas, for polymers dissolved in good solvents, the  $K^1$  value is given as  $0.41 \pm 0.1$ . This agrees more closely with the  $K^1$  value of the n-butyl alcohol modified resins<sup>[16]</sup>. This suggests that n-butyl alcohol is a good solvent for the n-butyl alcohol resins; while the  $K^1$  value of isobutyl alcohol suggests that isobutyl alcohol is a fairly good solvent. The very high  $K^1$  values obtained with local gin and ethyl alcohol, proved that these alcohols are not good solvents for the resins.

**Table 3.3 Values of Huggins constant  $K^1$ , Intrinsic Viscosity  $[\eta]$ , of Alcohol-modified UF Resins and Solubility Parameters of the Corresponding Alcohols**

Modified UF Resins	Solubility Parameter Values of Alcohol	Huggins Constant ( $K^1$ Value)	Intrinsic Viscosity Value ( $[\eta]$ )
Isobutyl Alcohol Modified UF Resins	(Isobutyl Alcohol) - 10.5	0.85	$2.80 \times 10^{-1}$
Tert butyl Alcohol modified UF Resins	(Tert butyl Alcohol) – 11.4	4.97	$2.40 \times 10^{-1}$
Ethyl Alcohol Modified UF Resins	(Ethyl Alcohol) – 10	31.02	$1.40 \times 10^{-1}$
Local Gin Modified UF Resins	(Local Gin) – Nil	93.83	$1.80 \times 10^{-1}$
n-butyl Alcohol Modified Resins	(n-butyl Alcohol) – 18.6	0.49	$3.80 \times 10^{-1}$

Fig. 3.1, 3.2 and TABLES 3.4 summarize the results of the mechanical behaviour of the alcohol modified UF resins using different types of alcohol. The results show that mechanical behaviour of the UF resins modified with alcohol depends on the type of alcohol used. The mechanical strength of the C<sub>4</sub> alcohol-resins decrease in the order: n-butyl alcohol > isobutyl alcohol > tert butyl alcohol, as evidenced by the values of the initial modulus, elongation at break, ultimate tensile strength (UTS) and toughness (TABLE3.4). It was also observed that the Initial

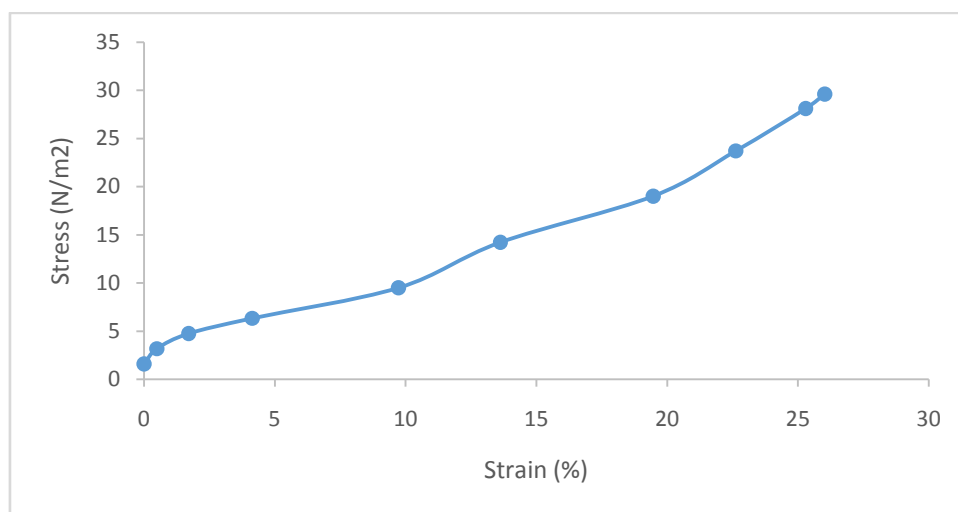


Figure 3.1 Variation of Stress with Strain of UF resins modified with Isobutyl Alcohol

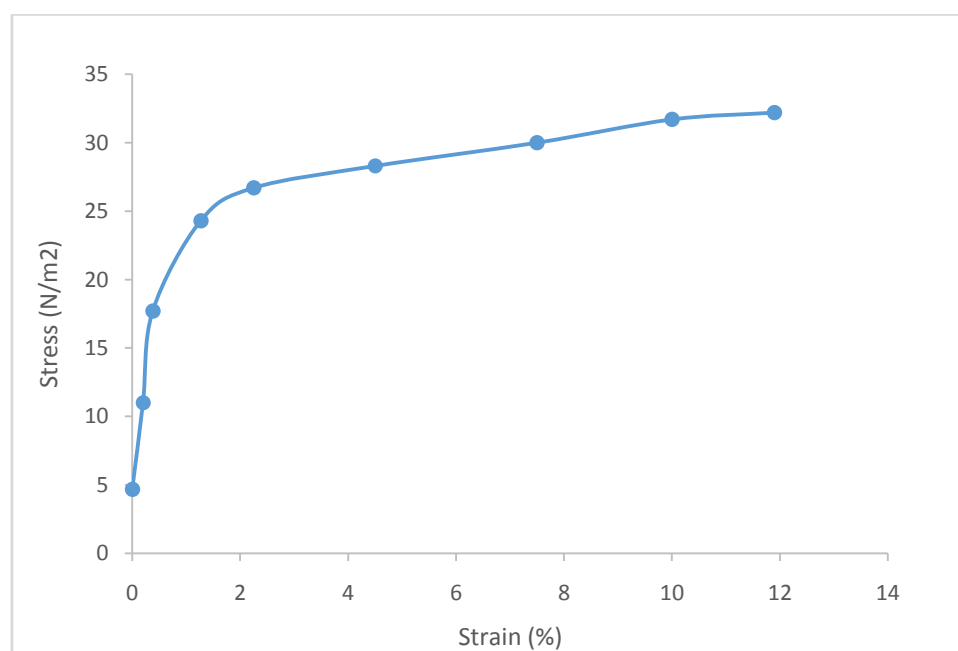


Figure 3.2 Variation of Stress with Strain of UF resins modified with n-butyl Alcohol

Table 3.4 Dependence of Initial Modulus, Ultimate Tensile Strength Elongation at Break and Toughness of Alcohol-Modified UF Resins on Type of Alcohol

Sample	Initial Modulus (N/m <sup>2</sup> )	Ultimate Tensile Strength (N/m <sup>2</sup> )	Elongation at break (%)	Toughness (N/m <sup>2</sup> )
Isobutyl alcohol Modified UF Resins	2.67 x 10 <sup>4</sup>	2.92 x 10 <sup>5</sup>	0.85	4.14 x 10 <sup>6</sup>
Tert butyl Alcohol Modified UF Resins	2.40 x 10 <sup>4</sup>	1.45 x 10 <sup>5</sup>	4.97	2.55 x 10 <sup>6</sup>
Ethyl Alcohol Modified UF Resins	1.40 x 10 <sup>4</sup>	1.54 x 10 <sup>5</sup>	31.02	2.13 x 10 <sup>6</sup>
Local Gin Modified UF Resins	1.50 x 10 <sup>4</sup>	2.05 x 10 <sup>5</sup>	93.83	2.38 x 10 <sup>6</sup>
n-butyl Alcohol Modified	3.45 x 10 <sup>4</sup>	3.22 x 10 <sup>5</sup>	0.49	4.98 x 10 <sup>6</sup>

UF Resins			
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modulus being a measure of the strength of the material, increased with increase in intrinsic viscosity (a measure of the molecular weight). This explains why n-butyl alcohol modified resins with the highest value of intrinsic viscosity gave the highest initial modulus. Also, toughness is the total energy absorbed by a material under test at or before failure. This absorbed energy is expected to increase as the molecular weight of the material increases. This also explains why the n-butyl alcohol treated UF resins samples recorded the highest value of toughness as well as intrinsic viscosity. The results of the mechanical properties of the local gin modified UF resins were slightly better than those of the ethyl alcohol modified resins.

#### IV. Conclusion

Free formaldehyde decreased as the solid content and mole ratio (urea: formaldehyde) increased; and increased with increasing ash content. The least value of free formaldehyde comparable to the commercial resins sample was obtained with mole ratio of, 1: 1.97.

Intrinsic viscosity and mechanical properties of the alcohol-modified UF resins depend on the type of alcohol. Values of intrinsic viscosity, initial modulus, toughness and ultimate tensile strength obtained with local gin modified UF resins agree closely with those of the C<sub>4</sub> alcohols, and was even better than what obtains with ethyl alcohols.

From the results of the rate constants, the UF resins synthesized in the laboratory during this study is expected to cure faster than the commercial samples. Besides, the free formaldehyde present in the laboratory samples was comparable with that of the commercial grade; the formulation used in this study is therefore recommended for use in the commercial scale production of Urea-formaldehyde resins.

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