



Synthesis of Urea Formaldehyde Resin through Eco-friendly Route and its Characterization

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ABSTRACT

Urea formaldehyde (UF) resins, the most important formaldehyde resin adhesives. It is obtained by condensation polymerization reaction of formaldehyde with urea and is widely used for the manufacture of wood-based composite panels such as plywood, particle board, fiber board, etc. In spite of its benefits of fast curing, good performance in the panels, colorless and lower cost; the formaldehyde emission (FE) occurred from either UF resin itself or composite products bonded by UF resin is considered a critical drawback as it affects the human health particularly in indoor environment. In order to reduce the FE, lower formaldehyde (F) and urea (U) mole ratio was used for the synthesis of UF resin. In this study, synthesis of UF resin was carried out through eco-friendly modified acid medium route. From the results of basic technological test, there has a greater influence of initial F/U molar ratios on the performance of UF resin. The three types of synthesized UF resins were analyzed for their specifications and characterized with TGA-DTA technique in dynamic heating condition and FTIR measurements.

Key words: Urea Formaldehyde synthesis, Acid modified method, Free Formaldehyde content, Basic tests, FTIR, TGA

INTRODUCTION

Urea formaldehyde resin is an end-stage thermosetting resin in which urea and formaldehyde are polycondensed into an initial urea formaldehyde resin under the action of alkaline or acidic catalyst and then an insoluble and non-fusible resin is formed under the action of curing agent or additives [1]. Formaldehyde-based resins are still being used as adhesive for the manufacture of wood-based composite panels such as particle board, oriented strand board, plywood, medium-density fiber board [2] etc. Formaldehyde is a key material to prepare various kinds of resins such as Phenol Formaldehyde (PF), urea formaldehyde, polymeric Methylene Diphenyl-di-isocyanate (pMDI), Melamine Urea Formaldehyde (MUF) resins [3-4] etc. UF is considered as one of the most important wood adhesive among MUF resin, MF resin and PF resin [5-7]. The use of UF resin as a major adhesive by the forest products industry is due to low cost, low cure temperature, water solubility and ease of use under a wide variety of curing conditions [8]. Initially, wood based industry used this resin and in the development, wood based panels industry has been mainly used this resin up to date [1] for manufacturing wood-based composite panels such as plywood, particleboard and fiberboard. At present, urea formaldehyde resin is the largest adhesive used in wood industry, especially in the manufacture of various wood-based panels in wood processing industry; urea formaldehyde resin and its modified products account for about 90 % of the total amount of adhesive [2]. Although UF resins are widely used in the manufacture of wood composite and their usage is always combined with release of formaldehyde characterized to be hazardous to health during and after the manufacture of the products [9]. In other words, the wood panel industry is a major consumer of UF resin adhesive. In spite of its benefits such as good appearance, good performance, fast curing and economical; formaldehyde emission originated from either UF resin itself or panel products bonded by UF resins is considered a

critical drawback as it affects human health particularly in indoor environment [10-13]. The emission of formaldehyde decreases as the mole ratio falls but unfortunately, the other physical and mechanical properties were influenced negatively at the same time [14]. 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 [15] and particle board [16-17], the effect of resin molar ratio from about 2.0-1.2 have been examined. Modification of the resin with several modifiers has also been studied [18]. Md Nazrul Islam *et al.* showed in their study that the rice bran based adhesive might be a promising adhesive to reduce the formaldehyde emission from the wood-based industries [19]. Although the UF resin is synthesized only from urea and aqueous solution of formaldehyde, the variation of reactions in synthesis, storage and curing make them quite an attractive object for research. Changing of resin synthesis conditions provide relatively good possibilities of designing the structure and technical properties of resin. Several approaches for the production of UF resin can be found in the literature. The most common method of UF resin synthesis is the alkaline-acidic-alkaline process following three steps. First the hydroxymethylation reaction is conducted under mild alkaline conditions followed by the polycondensation reaction under mild acidic conditions and finally the neutralization and addition of the last urea [20-21]. However, under alkaline conditions monomethylol, dimethylol and tri-methylol urea are formed. During the condensation under acidic condition, methylene bridges instead of methylene ether bridges are preferentially formed. Different types of UF structural groups are present in the resin. Thus, methylene linkages, ether linkages, hydroxymethyl group, amide group, uronic acid group and their derivatives are formed during the reaction of urea and formaldehyde and a number of possible side reactions can have a bearing on the resin rate of curing, its structure, the panel strength properties and consequently also on formaldehyde emission [22-24]. Theoretical and experimental results reveal that temperature and molar feed ratio of formaldehyde to urea are significant factors influence the product viscosity. Various characterization methods have been applied for the detection of their thermal behavior, targeting to the location of the critical parameters during its synthesis procedure like pH, mole ratio and the sequence of the various production steps which could be proved effective for the improvement of the resin's performance.

In this study, urea formaldehyde resin of low formaldehyde to urea mole ratio were produced through eco-friendly route and investigated with the application of Fourier Transform Infrared spectroscopy (FTIR) and Thermogravimetric (TGA, DTA and DTG) measurements. The effect of F/U molar ratio on the resin solids content, viscosity, pH, gel time and free formaldehyde content was also examined.

MATERIALS AND METHODS

The commercial grade urea was purchased from Jamuna Fertilizer Co. Ltd., Jamalpur, Bangladesh and aqueous solution (industrial grade, 37 %) formaldehyde was purchased from Merck, Germany. The aqueous solution of formic acid (10 wt %) and NaOH (20 wt %) were used to adjust the pH level during the UF resin synthesis. Ammonium chloride (NH₄Cl) was used as hardening agent.

Synthesis of UF Resin

All UF resins used in this study were prepared in the laboratory, following acid modified method through eco-friendly route. The experimental set up for the synthesis of UF resin is a glass reactor with a capacity of 2.5 litre volume and diameter of 4.5 inches has been used for this purpose. As raw materials, aqueous solution of industrial grade (37 %) formaldehyde and urea were used. Formaldehyde was poured into the glass reactor followed by urea. The initial ratio of F/U was 2.1 and pH was adjusted to 3.0 using a 50 % H₂SO₄ solution and the temperature was raised to 50°C. The urea was added in small portion during 15 minutes, bringing the temperature to 60°C. The mixture was a white-colored solution. The milky white color of the resin is due to ageing or further advancement of the resin by condensation reaction. The viscosity built-up was monitored at regular intervals of three minutes using brookfield viscometer. At the end of the 30-40 minutes, the F/U ratio was 1.05 and the pH of the reaction mixture was adjusted with a 20 % NaOH solution and 100 % tri-ethanolamine. The rest portion of urea was added to the reaction mixture which was further refluxed for about 15 minutes to ensure the completion of the reaction between urea and formaldehyde to form UF resin. After that, the dry solids content of the resin was set to 46-55 % by vacuum drying the resin at a temperature below 40°C. The same experiment was repeated for pH 1.0 and pH 5.0 respectively with the F/U mole ratio 0.95 and 1.15. Analysis of three types of resins (F/U=0.95, 1.05 and 1.15) heat treated at 65-75°C was also carried out after storage during one month.

Curing Reaction of UF Resin

During the curing process a more or less three-dimensional network is built-up. This yield is an insoluble resin that is no longer thermo-formable. The hardening reaction was the continuation of the acid condensation step. The acid conditions was adjusted by the addition of hardener ammonium chloride. Ammonium chloride reacts with the free formaldehyde in the resin to generate sulfuric acid which decreases the pH. This low pH and the ensuing acidic conditions enable resumption of the condensation reaction and finally the gelling and hardening of the resin. The rate

of decreasing of the pH depends on the amounts of available free formaldehyde and hardener and is greatly accelerated by heat.

CHARACTERIZATION TECHNIQUES

The characterization of UF resin has undergone great progress within the last two decades. It is now possible to analyse the polydisperse structure of the resin and the individual structural elements in the resin, even in a partly quantitative way. The curing reaction can also be monitored by means of adequate methods.

Basic Tests of UF Resin

Some basic properties such as solid content, viscosity, pH, gelation time and free formaldehyde are measured of the synthesized resin. These tests are generally easy to perform but nevertheless they yield important information about the quality and performance of the resins.

Solid Content Measurement

In order to calculate the dry weight (solid content) of the resin sample, a series of weight measurements had to be made. First, the sample disks were weighed and then the sample was placed on each disk. The disks with the samples were then placed in an oven at 120°C. After 2 hours, the disks were removed from the oven and placed in a desiccator for 30 minutes to cool off without adsorbing any moisture. The weight of the disk with the dry sample were weighed and by subtracting the weight of the disk from that measured value the mass of the solid content could be calculated. The relative amount of solid content in the resin sample can then be calculated by dividing the dry weight with the mass of the whole sample.

Viscosity and pH Measurement

The viscosity of resin sample was measured by a Brookfield viscometer. The sample was cooled down to 25°C and placed in the viscometer. In this test, spindle 3 was used at a speed of 12 rpm and the viscosity was noted after three turns of the spindle. The pH of different resin samples were measured using a digital pH meter at 25°C.

Gelation Time Measurement

For the calculation of gelation time of UF resin, the test method was performed in boiling water at 100°C. 10 gm of a 20 % aqueous solution of ammonium sulphate was added as a hardener to 100 gm of liquid resin and then the mixture was poured into a sampling tube that was placed in a water bath. The mixture was continuously stirred with a spatula and the time was measured. The sample was stirred until it had cured.

Determination of Free Formaldehyde

Free formaldehyde content of synthesized UF resin was determined by using modified Na₂SO₃ method. A mixture of 25 ml solution of Na₂SO₃ (1mole) and 10 ml 1N HCl was added to solution of 2-3 gm sample of UF resin in 100 ml distilled water were placed in 250 ml Erlenmeyer flask. The mixed solution including about 5 drops of 0.1 % thymolphthalein indicator solution was neutralized with 1N NaOH. The percent of free formaldehyde was determined by the equivalent of the amount of the consumed NaOH titration.

Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The FTIR spectra of the UF resin sample was recorded using Shimadzu FTIR 8400, Japan in the range of 500-4000 cm⁻¹ with a resolution of 4 cm⁻¹. The liquid UF resin was covered on the surface of KBr pellets. The sample pellets were prepared by mixing approximately 0.5 ml of liquid UF resin and 100 mg of dry KBr in small agate mortar pestle. For better resolution 5 times scans were taken.

Thermo-gravimetric Analysis (TGA, DTA and DTG)

For thermal analysis, thermo-gravimetric analyzer (DTA6300) was used to illustrate the thermal performance of the UF resin sample. Just about 2 mg of each sample was heated from 30 to 600°C at a heating rate of 10°C/min and whole of the measurements were implemented under a nitrogen atmosphere with a gas flow of 20 ml/min in order to avoid any thermoxidative degradation.

RESULTS AND DISCUSSION

In this study, the synthesis of UF resin with different ratio (F/U), *i.e.* 0.95, 1.05 and 1.15 was carried out. It was not possible to synthesize UF resin below the mole ratio 0.95. Even though Pizzi *et al.* [25] stated that theoretically F/U mole ratio of 0.70 can give adequate balance between strength and emission but practically only F/U mole ratio in

between 0.90 and 1.0 was effective for industrial application. Therefore, in this study, the synthesized UF resin was provided some basic characteristic results which are shown in Table-1 and Fig. 1. There is a great influence of initial formaldehyde/urea (F/U) molar ratio on the performance of low molar ratio (1.0) urea-formaldehyde resin adhesives [26]. Reducing the F/U mole ratio resulted in increasing of solid content of the resin due to the addition of the second urea; the UF resin with lower F/U mole ratio had more urea than that of higher F/U mole ratio. As expected, the viscosity of UF resin increased with increasing F/U mole ratio. This result may be due to the production of higher molecular weight UF resin with high F/U mole ratio. A lower viscosity indicates a low molecular weight of UF resin because the viscosity of liquid UF resin is proportional to their molecular weight [27]. Roman R. et al. showed that, the addition of filler in UF adhesive increased the viscosity and reactivity of the formed UF resin [28]. The change in pH of UF resin depends on F/U mole ratio. The pH of UF resin slightly increases as the F/U mole ratio decreases due to the F/U mole ratio of UF resin was manipulated by adjusting the amount of the second step addition of urea during its synthesis. Since urea granules are inherently alkaline, the more the amount of second step added urea, the more the alkaline of UF resin obtained after its synthesis. Gel formation and curing time of the UF resin decreases with the increasing F/U molar ratio as shown in Fig. 1(c). The gelation time is also proportion to the pH [29] of the solution. It is shortened when the F/U mole ratio increased from 0.95 to 1.15. By contrast, these results confirm that the curing reactivity of a UF resin decreases by decreasing the F/U mole ratio. This is possibly explained by a decrease the availability of formaldehyde at lower F/U mole ratio. Formaldehyde molecules are released during condensation reaction as well as the reverse hydrolysis reaction with water or atmospheric moisture. The later can take part of the degradation process of the UF resin [30].

Table-1 Characteristics of synthesized UF resin

Name of sample	Mole Ratio, F/U	pH	Colour
UF1	0.95	1.0	Dispersed, milky white
UF2	1.05	3.0	Opaque, milky white
UF3	1.15	5.0	Milky white

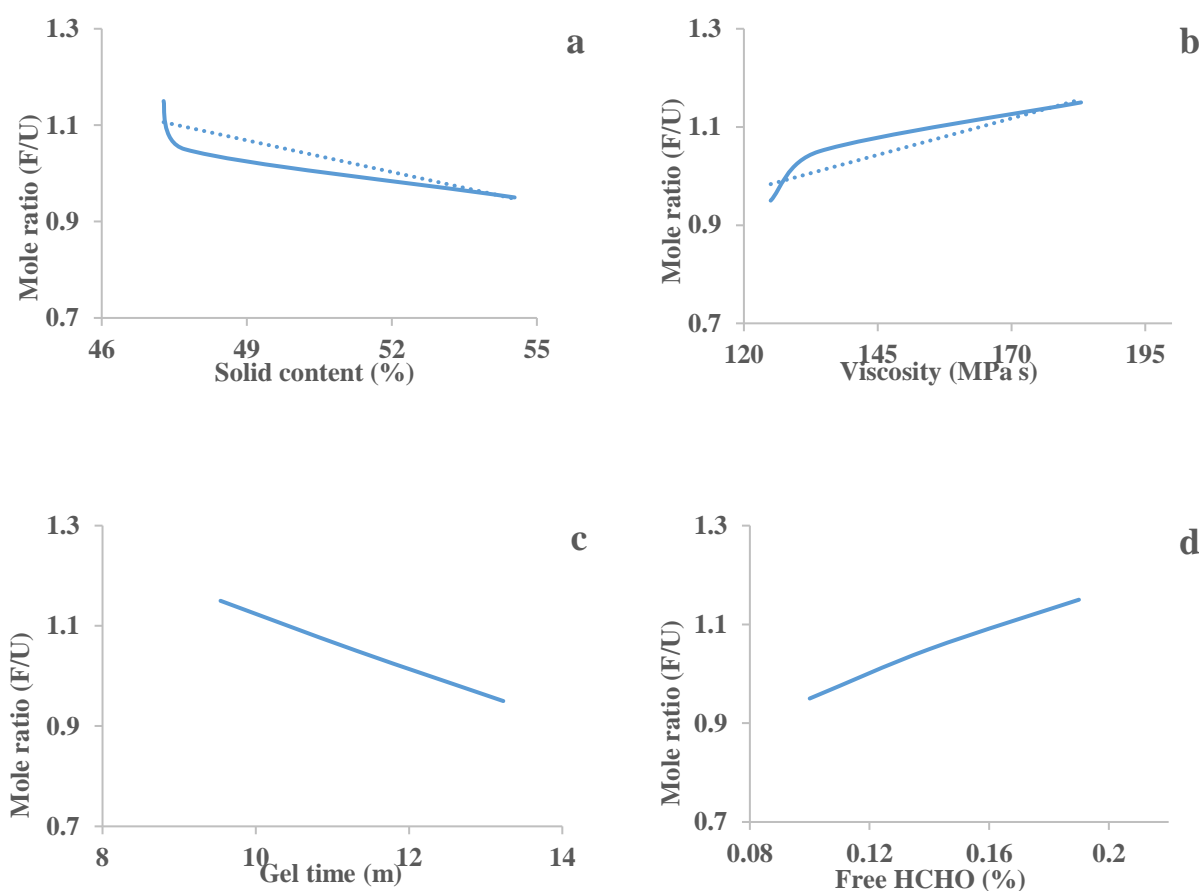


Fig. 1 Characteristics of synthesized resins; (a) Solid content, (b) Viscosity, (c) Gelation time and (d) Free HCHO content against mole ratio of UF (F/U)

The amount of free formaldehyde in prepared UF resin decreased with decreasing F/U mole ratio. These results showed that the formation of UF resin strongly depend on the amount of free formaldehyde molecule. This result could be explained by the role of free formaldehyde and hardener in the curing of UF resin. The free formaldehyde content in UF resin is also affected by the incorporation of catalyst to the synthesis of UF resin. Hui Zhao et al. showed in their study, the free formaldehyde content of the UF resin incorporating 3% copper (II) sulfate was 0.13 wt.%, around 71% lower than that of the untreated control UF adhesive [31]. In summary, the higher free formaldehyde content as well as the higher content of hydroxymethyl groups are present in UF2 and UF3 compared to UF1, confirming and explaining the shortest gelation time in UF2 and UF3.

The infrared spectra and band assignments to the chemical structures involved giving useful information on the structure of synthesized resins. The comparison of the FTIR absorption band assignments of UF1, UF2 and UF3 resin samples spectra in the range of 500-4000 cm^{-1} are shown in Fig. 2 and Table-2. The spectra for the three resins are nearly similar. The peak at 3300-3400 cm^{-1} , is attributed to the -NH groups. The C=O stretching of primary amides was the most dominant absorption band and occurs at 1650 cm^{-1} . The band from 1030 to 1050 cm^{-1} can be assigned to the C-N stretching from the C-N or C-N₂ amide groups in the resins [32-33].

Table-2 Absorption band assignment of FTIR spectra of UF1, UF2 and UF3

Range of absorption band (cm^{-1})	Chemical structure assignment	Observed band (cm^{-1})		
		UF1	UF2	UF3
3340–3355	-NH stretching of primary aliphatic amines	3354	3350	3353
2960–2963	-O-CH ₃ , aliphatic ethers	2961	2962	2962
1646–1664	C=O stretching of primary amide -NH ₂ (urea)	1660	1662	1654
1545–1560	C-N stretching of secondary amines	1546	1548	1547
1440–1465	C-H bending in NCH ₂ N, CH ₂ O, -OCH ₃	1453	1456	1455
1380–1400	C-H mode in =CH ₂ and -CH ₃	1383	1385	1384
1330–1380	CON stretching of CH ₂ ON	1341	1352	1350
1250–1260	C-N and N-H stretching of tertiary amides	1251	1252	1252
1130–1150	C-O stretching of aliphatic ether	1134	1136	1133
1030–1050	=C-N or NCN stretching of methylene linkages (NCH ₂ N)	–	–	–
1000–1020	-COO stretching of methylol group	1025	1023	1024
650–900	=N-H bending of primary aliphatic amines	770	772	775

The most characteristic difference between three types of resins are at the spectral area 3600-3000 cm^{-1} . The broadening of the band of resin sample UF2 and UF3 at ~3400 cm^{-1} could be attributed to pre-polymers by products such as water and excess formaldehyde which allow hydrogen bonding with the reactive functional groups such as -CH₂OH, -NH₂ and =NH [33]. The sharpening and the shifting at 3350 cm^{-1} of this band after curing indicate the formation of bonded =NH group.

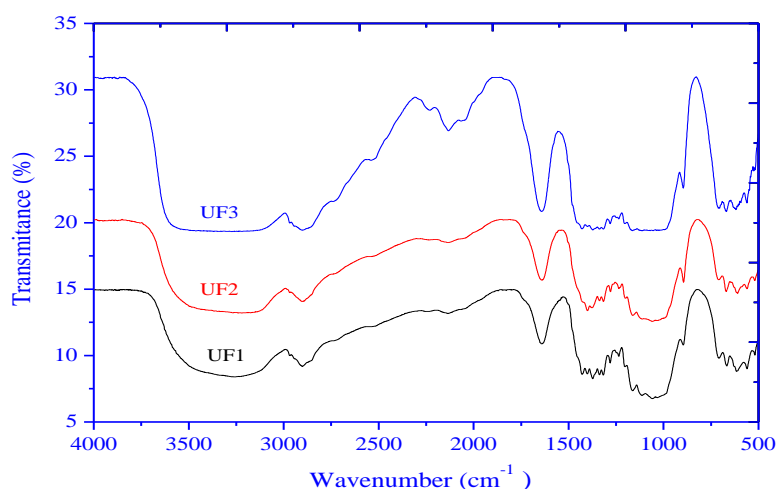


Fig. 2 FTIR spectra of UF1, UF2 and UF3 resins

More sophisticated methods follow the thermal behavior of the resin during curing. The method of differential thermal analysis (DTA) [34-35] measures the difference in temperature between two cells, both heated up according to a certain temperature program, whereby the one of the two cells contains the sample under investigation. TGA thermogram of different UF (UF1, UF2 and UF3) resins (Fig. 3) showed three distinct regions of UF pyrolysis. Generally, each TGA spectra starts with an exothermic peak and is followed by an endothermic peak. The exothermic peak appears before 100°C belongs to the polycondensation reaction between primary amide linkages of unreacted urea and the hydroxymethyl groups (-CH₂OH). The crosslinking reaction, in all three cases takes place at a similar temperature range (80-85°C) and the evolved heat of reaction are similar. Small mass loss between 150-200°C is attributed to slow release of free formaldehyde from UF resin and that between 220-250°C is attributed to degradation of methylene ether bridges in the resins network. Szesztay M. et al. [36] stated that the endothermic heat of reaction vary widely within the temperature range of 100-150°C as they are certainly related to the evaporation of condensed water, free formaldehyde and decomposition of the methylene-ether linkages. The major pyrolysis process of UF takes place between 270-350°C, maximum being at 292°C. The last stage that occurs above 350°C is the further pyrolysis process of a thermally stable residues formed in the former stage with slight weight loss leading to about 15 % of final residual mass. The UF2 resin resulted in the lowest peak temperature and the smallest heat of the exothermic reaction. The thermal stability of UF resins is also affected by the incorporation of modifier. Xiaoteng Li et al. described in their research, incorporation of rice straw greatly improved the thermal stability of UF in the main pyrolysis [37].

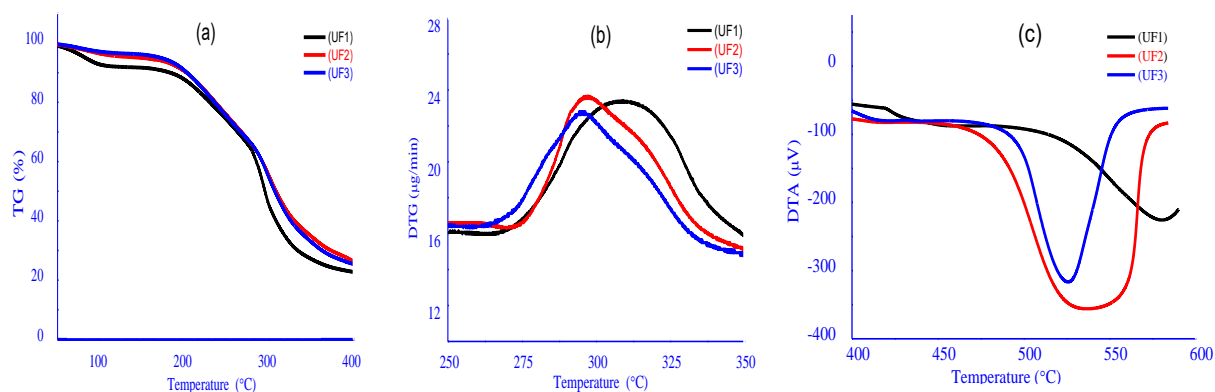


Fig. 3 (a) TGA, (b) DTG and (c) DTA curves of UF1, UF2 and UF3 resins

Fig. 1(d) shows the percentages of free formaldehyde content in UF resin samples obtained from the three different UF resins synthesized by modified acid medium method. The amount of free formaldehyde content in UF1, UF2 and UF3 resins are 0.10, 0.14 and 0.19 % respectively which is minor in amount and goes to approximately zero (0). Edoga M. O. [38] showed in his study that in conventional method, the percentage of free formaldehyde content at the end of the reaction is 17 % for the reaction time of 45-50 minutes. On the other hand, the amount of free formaldehyde is 5 % for the reaction time of 21 hours and the percentage of free formaldehyde content is approximately zero (0) for the acid modified synthesis method at the end of the reaction (35-50 minutes). It is clearly seen that in the acid modified method, had formaldehyde content is approximately zero implies that bonding with UF resins of the type would therefore emit no free formaldehyde. As a consequence, indoor air pollution by formaldehyde issuing from commercial products containing urea formaldehyde resins would be drastically reduced and that makes UF resins environmentally friendly. Overall, the resins produced by modified acid synthesis procedure with zero percent free formaldehyde content cum increased formaldehyde substitution of the hydrogen atom attached to urea to form either tri or tetra-methylol urea. This is a good indication that the resin would produce a three dimensional network cured UF resin and invariably possess greater hydrophobicity. By extrapolation, it would increase the cured resin strength and hence improved stability as well as durability.

CONCLUSION

Due to increasing demand, UF resin will be the most important adhesive for wood-based panels as a consequence of the advantages of the resin, even keeping in mind their limitations. The overall conclusion emerging from the synthesis of UF resins using acid modified synthesized method is more beneficial as compare to conventionally synthesized method as well as neutral modified synthesized method. As F/U mole ratio was lowered, solid content, pH and gelation time increased while free formaldehyde content and viscosity were decreased. These results indicated that lowering F/U mole ratio of UF resin is a way of formaldehyde emission from UF bonded particle. Infrared spectra of UF1 resin showed differences in the chemical structure from the UF2 and UF3 resins. For acid modified synthesis method, a

resin characteristic of tri-and/or tetra-methylol urea was obtained which invariably possessed approximately zero percent free formaldehyde content. Consequently, the zero formaldehyde content makes the final wood products bonded with the resin environmentally friendly. So, all the UF resins produced can be applied as adhesive for making commercial particle board products.

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