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MELAMINE-UREA-FORMALDEHYDE RESIN: CHANGES IN PHYSICAL PROPERTIES AND STRENGTH WITH COMPOSITION MOLAR RATIO ALTERATION

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ABSTRACT. *Melamine-urea-formaldehyde (MUF) resin is one of the most used adhesive for exterior and semi exterior wood panels. However the MUF resin can be further developed into a more water soluble without excessive free formaldehyde. A water-soluble resin is useful for many applications such as co-binder for tiles, bricks and other materials that contains water during production. This study is the first step towards providing future research to a safe and water-soluble resin. The formulation for this MUF resin was not based on any previous published formulation. The formula was developed through trials and collective thoughts from literature. The study involved altering the MUF resin's formaldehyde to urea (F/U) molar ratio. A set of MUF resin sample produced with F/U molar ratio ranging from 2 to 9 was tested for their physical properties. The shear strength was also analysed by using D-2339 standard, a test that had been developed and adopted by American Society for Testing and Materials (ASTM). Characteristics of the physical properties, ultimate shear strength versus F/U molar ratio, was obtained and compared. Finally, this research focused on three main properties, which are solubility, free formaldehyde and shear strength. Melamine-urea-formaldehyde resin found to produce solubility that increased with increasing free formaldehyde, F/U molar ratio and the adhesive shear strength.*

KEYWORDS: Melamine-Urea-Formaldehyde Resin, MUF resin, Solubility, Shear Strength.

INTRODUCTION

Resins can be classified into two types, natural and synthetic resin. Natural resins are extracts of the vegetable or animal origin. These include rosin (gum, wood or tall oil rosins from tree and plant exudates; wood extracts; or by-products from paper manufacturing), fossil resins such as amber; mined resins such as asphaltite; shellac as secretion product from an insect; and their main derivatives. On the other hand, synthetic resins are defined as resulting sources from controlled chemical reactions such as polyaddition or polycondensation between well-defined reactants that do not themselves have the characteristics of resins. Synthetic resins are also obtained by polymerisation of unsaturated monomers (Diem & Mantthias, 1976).

Melamine-urea-formaldehyde is a synthetic resin belonging to the amino resin family. Amino resins are thermosetting polymers made by combining an aldehyde with a compound containing an amino ($-NH_2$) group (Amit Mukherjee & Subrata Ghosh, 1996). Besides MUF resin, the most important amino resins are urea-formaldehyde (UF) resin, and melamine formaldehyde (MF) resin. MUF resin has a much higher resistance to water attack, which is a main distinguishing characteristic from UF resin. While MF resin is generally expensive. For this reason, MUF resins, which are cheaper by the addition of a greater or lesser amount of urea, are also often used. MUF resins are intermediate between MF and UF resins with durability proportional to MF content (Pizzi, 1994a & b). Although MUF resin may be cheaper than MF resin, but MUF resin has shown aspects of poorer physical properties.

Melamine-urea-formaldehyde (MUF) resins are among the most used adhesives for exterior and semi exterior wood panels. It is also used for the preparation and bonding of low and high-pressure paper laminates and overlays.

Production of MUF resin consists of copolymerisation, via model compounds and polycondensates. MUF resins obtained by copolymerisation during the resin preparation stage are superior in performance to MUF resins prepared by mixing pre-formed UF and MF resins due to difficulties in the mixing process (Pizzi, 1994a & b). The relative mass proportions of melamine to urea used in these MUF resins is generally in the melamine/urea range of 50:50 to 40:60 (Pizzi, 1994a & b).

The downside of amino resins is its short shelf life. There are no records of MUF resin shelf life in literature. However, through observation and comparison with the UF resin (3 to 6 months) and MF resin (3 months) (Kosh, Klariech, & Exstrum, 1987), MUF resin could have a shelf life of 3 to 6 months. The curing time of MUF resin at room temperature ranges from 3 to 10 hours. This process is slow, and the adhesive strength set at room temperature is lower than pressurized hot press setting. Additional setback in MUF resins is the adhesive strength that has a direct link to the amount of formaldehyde used in the MUF resin. Higher formaldehyde content provides a stronger adhesion in MUF resin. However, the adhesive strength can also be improved through other approaches without increasing the formaldehyde (Conner, 1996).

Other workers on MUF resin includes Pizzi, who has developed formulation of melamine-urea-formaldehyde resin using urea-melamine-second urea method. Kamoun and Pizzi (2000) have also worked on particleboard internal bonding forecast by thermomechanical analysis in MUF adhesive curing. Zhao and Pizzi (2000) also investigated on hot post curing improvement of MUF-bonded particleboard and its temperature forecasting method. Demirata (2000) has also worked on the speciation of Cr(III) and Cr(IV) by means of melamine-urea-formaldehyde resin.

Our research is a unique contribution to the fundamental research work to produce soluble MUF resin. The research is aimed at producing a Melamine-Urea Formaldehyde that has strong adhesion, great solubility and an acceptable free formaldehyde percentage.

MATERIALS AND METHODS

Melamine-Urea-Formaldehyde Resin Formulation

Starting with the molar ratio of formaldehyde to urea (F/U) of 6.278. The raw materials used are shown in Table 3.1.

Table 1.1. Weight of each raw material

Raw material	Weight (g)	wt%
Formalin (37%)	300.00	67.85
Urea	35.36	8.00
Polyvinyl alcohol	1.90	0.43
Melamine	94.25	21.32
Water	10.62	2.40
Total	**442.13**	**100.00**

The total weight for this MUF sample at F/U ratio of 6.278 was 442.13 g. The weight was just right to fill a 500 ml three neck round flask. Firstly, formaldehyde was pour into the flask, and thereafter adding the raw materials of urea, polyvinyl alcohol, melamine, and water. Mixture in the flask was blended with a rotator. The rotator speed was set at medium (number 5 for Ika Labortechnik model RW 20.n rotator). The mixture had a white coloured solution. By using the pH meter, the temperature and the pH value were recorded. The mixture temperature decreases and falls in between 20 to 25 °C. The mixture pH was below 7 (ranging from 6.3 – 6.7). Using sodium hydroxide and acetic acid the pH of the mixture was adjusted to 7.5 – 8.0. This step was to prevent the mixture from polymerising too quickly (Pizzi, 1994). The mixture was slowly heated to reflux until the mixture's temperature reaches 80°C. A water bath had been most suitable for this purpose.

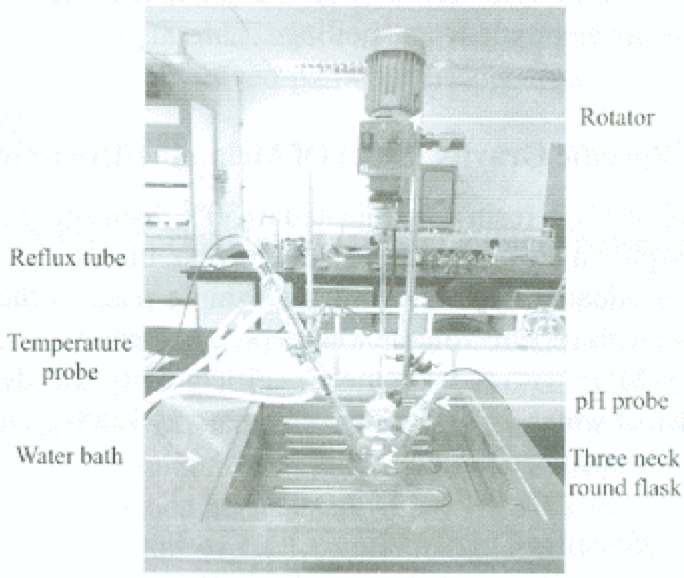

Figure 1. Equipment set-up for resin synthesis.

The equipment set-up in Fig. 2.1 had an aluminium foil to cover the centre neck of the flask (which was used to insert the glass stirrer), thus, preventing formaldehyde fumes and heat from escaping. A pH probe was inserted to the right neck of flask to deduce the pH of the mixture. A reflux tube was attached to the left neck to produce the reflux effect. Through the reflux tube, a temperature probe was also inserted to determine the mixture's temperature. The increment in the mixture temperature must be controlled. Initial setting temperature of the water bath was selected at 30°C. The temperature increment was set at 5°C every 5 minutes until the temperature reaches 60°C. Over a period of 5 minutes, the temperature was set to 70°C. Normally, the white coloured liquid mixture will turn clear when the mixture had reached a temperature in between 60°C to 70°C. Finally, after another 5 minutes, again raise the setting of temperature to 80°C. The temperature of the mixture may slowly increase to 80°C. The mixture was held at this temperature until the endpoint had been reached. The endpoint could be determined by sampling the mixture by using dropper every 5 minutes. A drop of mixture was introduced into a beaker of water with a temperature of 50°C. If the mixture dilutes in the water without a trace it means that the endpoint had not yet achieved. Whereas, when the droplet forms a whitish streak (polymerised), then it had reached an endpoint (turbidity point). The pH of the mixture was again adjusted to 8.8-9.5 using sodium hydroxide and acetic acid. After that, cooling can begin. The resin synthesis was completed and could be stored for further test. The steps were repeated for other F/U molar ratio ranging from 2 to 9.

Determination Of Concentration Of H^+ In Melamine-Urea-Formaldehyde Resin

The pH meter was calibrated according to the manual using buffer solutions of pH 4.0 and pH 7.0. MUF sample was then kept at a temperature of 30°C. Therefore, the pH of the sample was not immediately taken after the MUF had been produced. It was allowed to cool to 30°C before pH reading was taken. The electrode was rinsed thoroughly with distilled water and water gently wiped off using tissue paper. After which, the electrode was dipped into the resin sample and swirl gently around in the beaker containing the MUF resin. The pH value on the display was allowed to stabilize. The final pH reading was recorded to the nearest 0.05 units. Subsequently, remove the electrode from the resin and wash thoroughly with distilled water again. Finally store the electrode in KCl solution when the testing was complete; KCl protects the electrode from spoiling.

Determination Of Specific Gravity (S.G.) Of Melamine-Urea-Formaldehyde Resin

Firstly, the temperature of MUF resin was adjusted to 30°C by heating or cooling. An empty graduated cylinder was put on the analytical balance. Next, the balance was tare and the MUF resin poured into the graduated cylinder until the sample reaches the $100cm^2$ mark. The weight of the MUF resin with $100cm^2$ volume was recorded. Density of resin could be calculated by dividing the mass of MUF with the volume. Specific gravity was defined as the density of resin divided by density of water. The density of water was 1.000 g/cm^2 at 1 atmosphere and 4°C. Therefore, the SG had been defined as:

$$\text{Specific Gravity} = \frac{Density}{1.000 g / cm^2}$$

The S.G. should be accurate to 3 decimals places.

Determination Of Rheology Of Melamine-Urea-Formaldehyde Resin

The viscometer used was a Cole-Parmer (model 98936-15) viscometer with R2 spindle. 250ml of MUF was poured into a beaker, which was then placed in the water bath. When the MUF resin reaches a temperature of 30°C, the R2 spindle was inserted into the resin. The resin must only cover the spindle up to the groove mark. The viscometer's speed was set at 100r.p.m. (rotation per minute). The viscosity was switched on and about 15 – 20 seconds was allowed for equilibration before recording the viscosity as shown on the display.

Determination Of Gelation Time Of Melamine-Urea-Formaldehyde Resin

The first part of this test involved the preparation of the hardener solution. Firstly, 66.67 grams of ammonium chloride was weighted accurately into the container of 1 litre volume. Then, distilled water was added to the ammonium chloride until the weight reached 1000 grams. The container was tightly closed and the contents thoroughly mixed until a homogenous solution was formed. The solution for the determination of gelation of resin was set aside. The second part of this test was the gelation time determination. About 125 grams of resin was weighed into the beaker. 15 grams of the above hardener solution was added into the MUF resin. The mixture was stirred for 3 minutes. Immediately after, 6 grams of the mixture was weighed into each of the two test tubes. A steel stirrer was then put into the test tube, and the test tube was held in the boiling water bath. The stopwatch was immediately started as the content of the test tube was stirred vigorously. The hardening of the resin was stirred and tested by lifting up and down the stirring rod. When the resin started to stick firmly to the steel rod, the stopwatch was stopped and the time taken for the resin to gel was recorded. The gelation time of the resin is expressed in seconds and as an average of two parallel determinations.

Determination Of Solubility Of Melamine-Urea-Formaldehyde Resin

The apparatuses needed for this test were a conical flask, spatula, balance and distilled water. Firstly, 6 grams of resin sample (W1) was weighed into the conical flask. The balance was tared. Distilled water was added slowly into the flask. Then, the flask was shaken and observed for undissolved particles that stuck on the inner wall of the flask. The distilled water was continually added until undissolved particles disappeared. The weight of the distilled water is then recorded.

Determination Of Free Formaldehyde In Melamine-Urea-Formaldehyde Resin

The apparatuses and materials used in this test were 2 pieces of conical flask (250 ml), balance, burette 50 ml, thermometer, distilled water, methyl red methyl blue indicator, 0.1M HCl solution, 0.1M NaOH solution, 10 wt % NH_4Cl solution, 1M HCl solution and 1M NaOH solution. To begin with, weight 15 grams of MUF resin was weighted into the conical flask and then 50 ml of distilled water added. The mixture was stirred. Later, 2 drops of methyl red methyl blue was added. The mixture was then neutralized with 0.1M HCl and 0.1M NaOH. Next, 10ml of 1M NaOH solution and 10ml of HCl solution was added. A stopper was put on the mouthpiece of the conical flask. The flask was shaken and allowed to stand for 30 mins. at

25°C with occasional shaking. Then the mixture was titrated with 1M HCl. The end point was achieved when the colour of the solution changed from green to greyish blue. Since the colour of the indicator changed from green to greyish blue and then to reddish purple, a blank test was obtain from the free formaldehyde formula:

$$H = \frac{0.045(B - A)F}{S} \times 100\%$$

where,

H = the free formaldehyde

B = 1M HCl consumed in blank test

A = the amount of 1M HCl consumed by the sample

F = the factor of 1M HCl which is 1

S = the weight of the sample

Determination Of Solid Content Of Melamine-Urea-Formaldehyde Resin

First of all, an aluminium dish was weighed on the balance. The reading was taken as M3. Then, the balance was tared and about 1.5-2 grams of sample added into the aluminium dish. The weight of the resin is taken as M1. The resin sample is evenly spread throughout the dish. Then, the dish of resin was put into the oven set at 105°C and was allowed to dry for 3 hours. After which, the sample was transferred into the desiccators to cool down to room temperature. The aluminium dish with dried resin was weigh as M2. The solid content of the resin was expressed as the percentage of wet resin.

$$\text{Solid content} = \frac{M_2 - M_3}{M_1} \times 100\%$$

where, M_1 = weight of resin in aluminium dish

M_2 = weight of dried resin + aluminium dish

M_3 = weight of aluminium dish

D-2339: Test Method For Strength Properties Of Adhesives In Two-Ply Wood

This test method by tension loading in shear had been especially useful for laminations of veneers or other relatively thin woods. The veneers used in this test were Nyatuh veneers (a type of local tree species). The veneers were spread with MUF resin on the gauge area and cut into the specific geometry and dimension according to D-2339 standard, shown in Fig. 2.2.

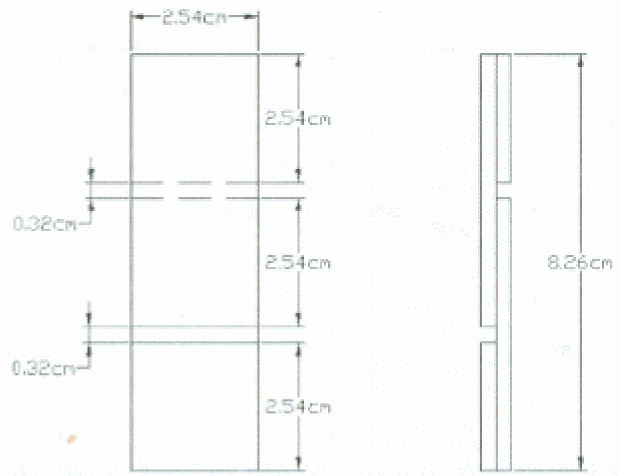

Figure 2. Basic wood lap shear specimen (D-2339)

The specimen was tested for its shear strength via tension loading. The machine used was the Instron Universal Testing Machine Model 8801 as shown in the Fig. 2.3.

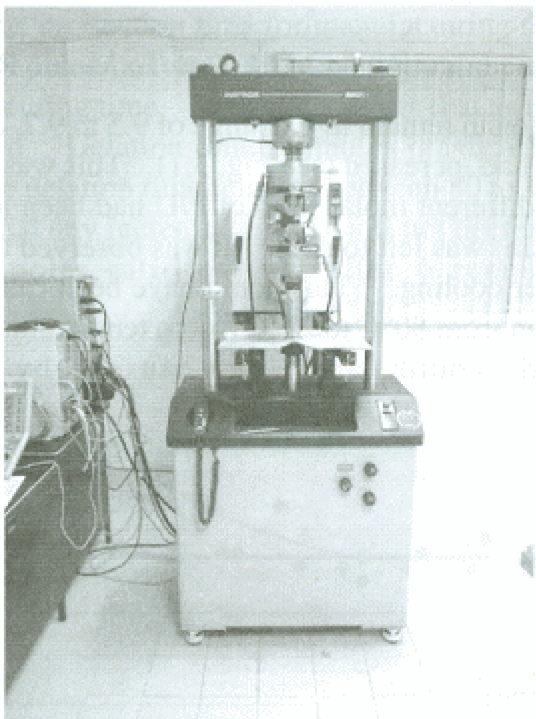

Figure 3. Instron Universal Testing Machine Model 8801.

Test Method For Strength Properties Of Adhesives In Denim Material

This test in shear by tension loading was similar to the D-2339 test discussed above. Instead, the wood adherend was replaced with denim material. In addition, the orientation of the fibre direction was set at 55 degrees (see Fig. 2.4). Denim material had the ability to withstand larger load than veneer. In this case, more adhesive failure was expected to take place in the denim specimen compared to the previous veneer lap shear specimen. The specimens were again tested using Instron Universal Testing Machine Model 8801.

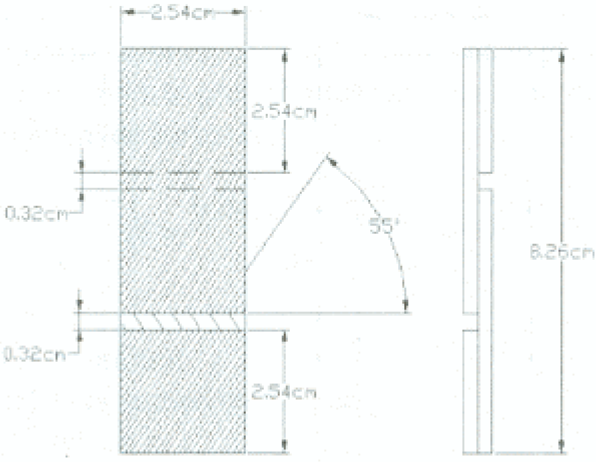

Figure 4. Fibre direction of denim lap shear specimen

RESULTS AND DISCUSSION

Effects Of H⁺ Concentration In MUF Due To Molar Ratio Alteration

Apparently, the pH for each resin remain in the range of 9.5 to 9.7, although the molar ratio of formaldehyde to urea (F/U) had increased (see Fig. 3.1). This was due to the fact that the pH of all the MUF resins with different molar ratio of F/U had been adjusted to from 8.8 to 9.5 before the final product (resin) was left to cool. It was observed that there was an increased in the pH of MUF resin after cooling. This could have been caused by the decrease in the temperature of the MUF resin from 80°C to 25°C (room temperature). The fluctuation of pH as the F/U increased could also be caused by unclean pH probe.

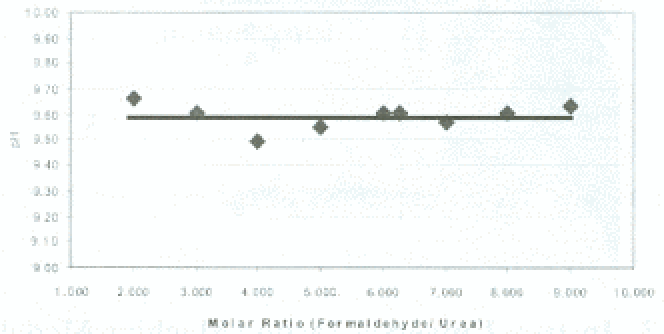

Figure 5. pH of melamine-urea-formaldehyde remains in the range of 9.5 to 9.7.

Effects On Specific Gravity Due To Molar Ratio Alteration

The experimental results in Fig. 3.2, indicated that as the molar ratio F/U of MUF resin increases the specific gravity decreases. This implies that as F/U increase the density of the MUF resin decrease. Basically, the Figure 3.2 demonstrates a sharp drop in the specific gravity, then moves into a constant region and eventually rapidly decreases as the molar ration approaches the value of 9.

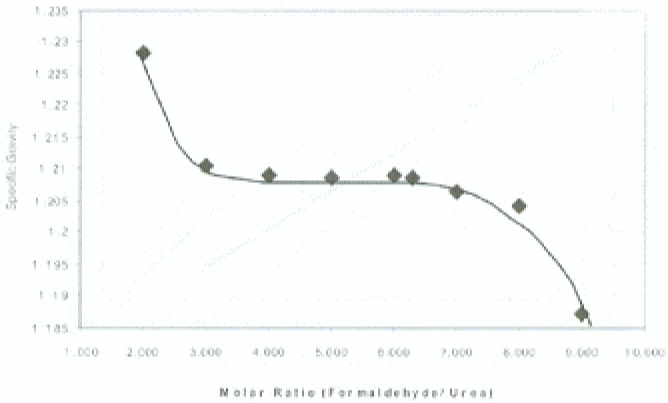

Figure 6. Specific gravity decreased as molar ratio of formaldehyde to urea increased.

Effects On Gelation Time Due To Molar Ratio Alteration

Gelation time is an important property of melamine-urea-formaldehyde resin. The gelation time gives an approximation for the resin curing time in the presence of ammonium chloride. Fast curing time reduces the production time for manufacturing that requires the adhesives to cure completely. For example in the wood industry, plywood production will be increased if MUF resin used has a fast curing time. Figure 3.3 shows that as molar ratio of F/U increased, the gelation time decreased. Gelation time decreases drastically at the beginning as molar ratio of F/U increased. The gelation time remains between 80 to 100 seconds after molar ratio F/U reaches 6. It shows that any increased in F/U will not decrease the gelation time further. Further increment of molar ratio of F/U after 6 remains practically constant.

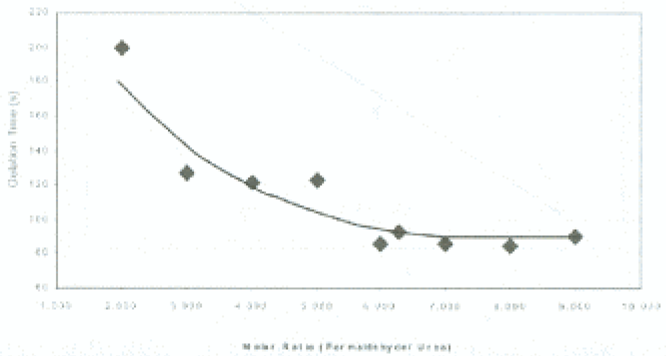

Figure 7. Characteristic of Gelation time and Molar Ratio.

Effects On Viscosity And Solid Content Due To Molar Ratio Alteration

Essentially, viscosity and solid content govern the application of the resin produced. MUF resin with low viscosity can be spread on wood surfaces (adherend) by using a brush. Low viscosity and low solid content MUF resin also can be used in tiles and bricks production, because only with this characteristic can the resin and the other components (cement, concrete, clay) mix easily to produce strong bricks and tiles. In this research, viscosity and solid content demonstrated a relationship. Both the viscosity and solid content decreased linearly with increment of F/U molar ratio (see Fig. 3.4).

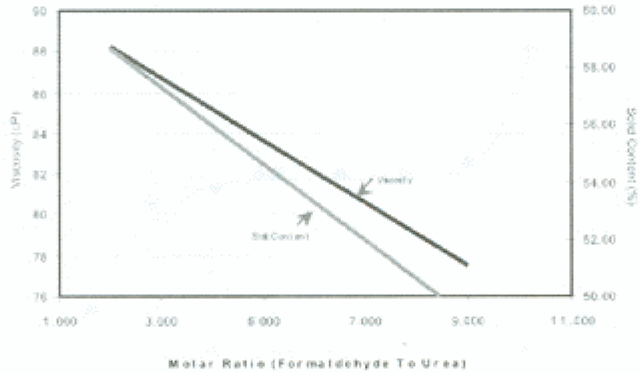

Figure 8. Viscosity and solid content decreases linearly with increment of F/U molar *ratio*.

3.2 Effects On Solubility And Free Formaldehyde Due To Molar Ratio Alteration

Another benefit that comes with increment of F/U molar ratio is the solubility or water tolerance. As F/U increases, the solubility increases linearly. This is good sign because the higher the solubility the more water can be dissolved in the MUF resin. But a downside also comes with this benefit. As the solubility and F/U increases, the free formaldehyde also increases. This behaviour is demonstrated in Fig. 3.5.

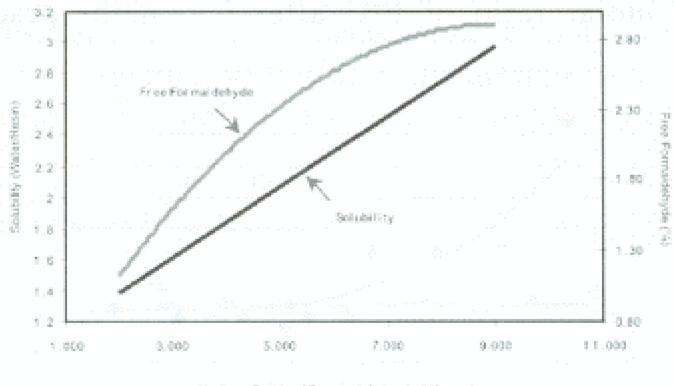

Figure 9. Solubility and free formaldehyde increases with increment of F/U molar ratio.

Changes In Ultimate Shear Strength Using MUF Resin With Different F/U Molar Ratio

Figure 3.6 shows that ultimate shear strength increase (from Veneer Lap Shear samples) is obtained with increasing F/U molar ratio. Strength increase is good, but there is the disadvantage of free formaldehyde increment (see Fig. 3.6). The lowest ultimate strength, which is about 1.31 MPa for veneer specimen occurs for MUF resin with an F/U ratio of 2.00.

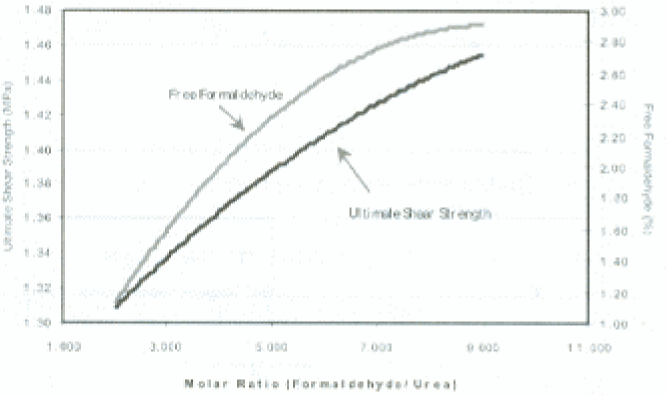

Figure 10. Ultimate shear strength and free formaldehyde increases with increment of F/U molar ratio.

Qualitative evaluation upon the performance of the joint can be established from Fig. 3.7. It indicates that at F/U molar ratio of 2.00, the percentage of adhesive failure is at a highest 3.20 %. In comparison to the rest of F/U molar ratio formulation it is the weakest. As the F/U molar ratio increased the percentage of adhesive failure decreased. From the F/U molar ratio of 6.00 to 9.00, the percentage of adhesive failure observed is 0 % (failure is located in the wood); local adhesive failure is not investigated.

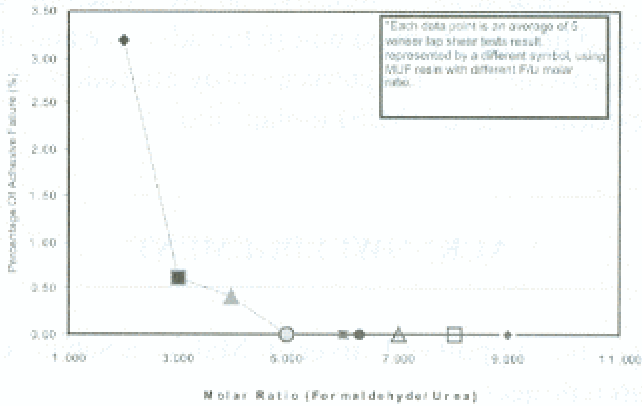

Figure 11. Percentage adhesive failure with formaldehyde to urea molar ratio increment by veneer lap shear test.

Changes In Ultimate Shear Strength In Denim Lap Shear Specimen Using MUF Resin With Different F/U Molar Ratio

In Fig. 3.8, the denim lap-shear specimen using MUF resin with F/U molar ratio of 2.00 has an ultimate shear strength lower than 1.2 MPa. While all other specimen with F/U molar ratio 3.00 to 9.00 has ultimate shear strength of about 1.25 MPa. Adhesive failure does not occurred in denim specimens for F/U molar ratio above 3.00. In the specimen with F/U molar ratio of 2.00, 44% adhesive failure occurs, which is extremely high compared to the rest, that is, MUF resin with F/U of 2.00 is weak for denim application. This correlation proves that lower F/U molar ratio MUF resin is weaker than the higher ones.

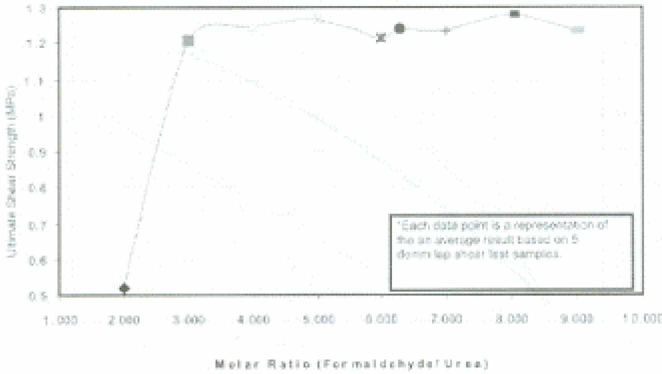

Figure 12. Characteristic of ultimate shear strength of MUF resins with different F/U molar ratio.

CONCLUSION

The melamine-urea-formaldehyde resin produced has a solubility that increases with increasing formaldehyde in the resin mixture. Results showed that free formaldehyde increases with increasing F/U molar ratio. Finally the adhesive shear strength of melamine-urea-formaldehyde resin has shown to have enhanced with increasing formaldehyde constant; through both veneer and denim lap-shear tests. Adhesive failure in denim specimen can be further researched on the bonds and linkages formed within the adhesive and also between adhesive to adherend via electron microscopy. Characterisation by alteration of MUF resin can also be made against melamine-formaldehyde (M/F) molar ratio.

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