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MELAMINE-UREA-FORMALDEHYDE (MUF) RESIN: THE EFFECT OF THE NUMBER OF REACTION STAGES AND MOLE RATIO ON RESIN PROPERTIES

AWANG BONO[1], YEO KIAM BENG[2] & NANCY JULIUS SIAMBUN[1]

Abstract. MUF resin is widely used as an adhesive in wood industries, coating technology, paper industries and as a main material in kitchenware production. In different applications, various MUF resin properties are required. The MUF resin properties are affected by several factors such as the mole ratio of formaldehyde to melamine/urea at each reaction stage and number of reaction stages in which the amino compounds are reacted. Previous researches have developed MUF resin with the desired properties. However, the formulation lack sufficient amount of melamine or urea to balance the cost and performance. Furthermore, shorter curing period could only be obtained with the help of external heat. In this research, the effects of formula variation on resin properties such as resin storage stability, solubility in water and curing period at room temperature are investigated. The results showed that in a 3-stage reaction of MUF resin process, the ratio of formaldehyde to urea/melamine in each reaction stage had caused significant increase in MUF resin curing period, solubility in water and resin storage stability. These formulations, which contain sufficient amount of melamine and urea, are cheaper and capable of maintaining good performance as compared to melamine-formaldehyde (MF) resin.

Key words: Melamine-urea-formaldehyde (MUF), urea, melamine, formaldehyde

Abstrak. Resin MUF yang boleh larut dalam air digunakan dengan meluas sebagai bahan pelekat dalam industri kayu, teknologi salutan, industri kertas dan merupakan bahan utama dalam penghasilan barangan dapur plastik. Sifat resin yang berbeza diperlukan dalam aplikasi yang berlainan. Sifat-sifat resin ini dipengaruhi oleh beberapa faktor iaitu nisbah mol antara formaldehid dengan melamina/urea pada setiap peringkat tindak balas dan bilangan peringkat tindak balas di mana sebatian amino ditindak balaskan. Sifat-sifat resin yang penting ialah kestabilan resin, kelarutan dalam air yang tinggi dan tempoh pengerasan yang pendek. Kajian lepas telah menghasilkan resin MUF dengan sifat-sifat ini yang diperlukan. Walau bagaimanapun, ia tidak mempunyai kandungan melamina dan urea yang mencukupi, untuk menseimbangkan kos dan prestasi. Selain itu haba juga diperlukan untuk membantu memendekkan tempoh pengerasan resin. Dalam kajian ini, kesan perubahan formula ke atas sifat-sifat resin seperti kestabilan resin, kelarutan dalam dan tempoh pengerasan pada suhu bilik dikaji. keputusan menunjukkan bahawa kestabilan resin meningkat apabila bilangan peringkat tindak balas dan kandungan melamina meningkat. Walau bagaimanapun, tempoh pengerasan turut dipanjangkan. Formula ini mempunyai kandungan melamina dan urea yang mencukupi, dengan kos yang lebih rendah berbanding resin melamina-formaldehid (MF) di samping menunjukkan prestasi yang lebih baik.

Kata kunci: Melamina-urea-formaldehid (MUF), urea, melamina, formaldehid

[1] Chemical Engineering, [2]Mechanical Engineering, School of Engineering & Information Technology, 88999 Universiti Malaysia Sabah. E-mail: awang@pc.jaring.my

1.0 INTRODUCTION

Melamine formaldehyde (MF) resin is widely used in the manufacture of moulding compositions, laminating, adhesives, surface coating and other industrial applications. Melamine-formaldehyde resin has a much higher resistance to water attack, which is the main characteristic of urea-formaldehyde (UF) resin (Pizzi, 1994, Sandler, 1994). However, MF resin is expensive as compared to UF resin. For this reason, nowadays MF resin has been made cheaper by introducing urea into melamine to form melamine-urea-formaldehyde (MUF) resin. The MUF resin produced has unique characteristics and properties, which in many ways are very different from the properties of MF or UF resin (Pizzi 1994). Various MUF resin formulations have different properties, performance and durability. The important properties of MUF resin include the shelf life, solubility in water and curing period are formulated according to its applications.

MUF resin formulations are built up from a combination of several factors. Among the important factors are the reaction period for each stage, the efficiency of controlling the pH and the temperature throughout the process, the mole ratio of formaldehyde to urea/melamine and the number of stages in which amino compound is reacted. The combination and variation of these factors produce different resin shelf life, degrees of solubility in water and curing periods (Sandler *et al*, 1994). However, balancing all of these factors to obtain satisfactory properties for specific applications is rather difficult due to the interactions among the factors. For example, improving resin solubility may increase the curing period (Vaughn *et al.*, 1999). On the other hand, shortening the resin-curing period may produce an unstable resin (Tutin 1998).

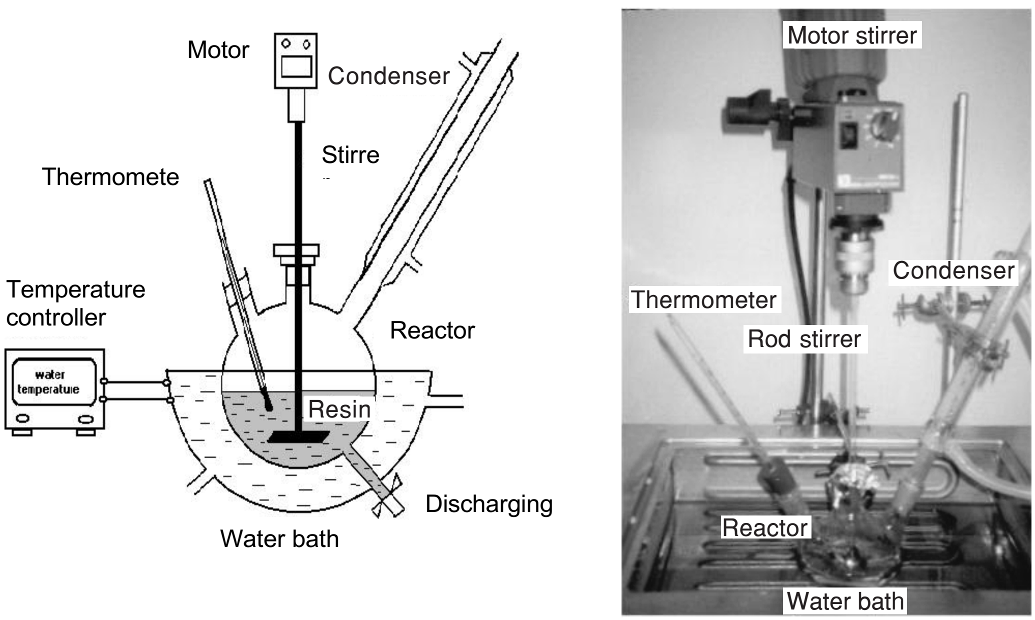
In enhancing unbaked tile properties (Noraini 2001, Hirdawati 2001 and Hartini 2001), thermoset resin with good shelf life, high solubility in water and shorter curing period at room temperature are desirable. MUF resin has the potential to be used in unbaked tiles since it also a thermoset resin with high solubility in water and good physical properties such as being resistance to scratch, heat, stain, water and chemicals.

Previous research to produce MUF resin with good stability and higher solubility in water have been reported. Nevertheless, the resulting formulation does not have a satisfactory amount of melamine or urea. For example, in Breyer *et al*. 1997 and Shieu *et al*. 1985, the amount of melamine is between 2-10%. This percentage is too low for any visible chemical, scratch and stain resistant properties from the melamine. In Heger 1982, the melamine content reaches 40% of the total resin weight, while urea comprises of only a more 3% of total resin weight. Addition of urea is used only as a means to reduce the free formaldehyde emission. Hence, the percentage of urea present is too low for the resin to be economical. Since all of these formulations also require considerable curing period, thus, higher temperature is needed to help enhance the curing process.

Therefore, in this research, MUF resin with sufficient amount of melamine and urea has been developed and modified to obtain resin with good shelf life, higher solubility in water and shorter curing period at room temperature. The research also concentrates on investigating the effects of formula variation as a result of the different number of reaction stages and different mole ratio of formaldehyde to urea/melamine in each reaction stage.

2.0 MATERIALS AND METHODOLOGY

The experimental setup for the MUF resin production is shown in Fig. 1. In the first stage of the process, formaldehyde was poured into the flask followed by urea and melamine raw materials. The mixture was blended homogeneously using a stirrer connected to a motor (Ika Labortechnik model RW20.n), which was set to speed 5. The mixture was a white-colored solution. The solution pH and temperature were recorded simultaniously. In order to prevent the solution from polymerizing too quickly, the pH was adjusted to between 8.8 - 9.0 (Pizzi, 1994) by adding a few drops of sodium hydroxide at 48% concentration.



(i) (ii)

Figure 1 Schematic (i) and actual (ii) equipment set up for resin production

Within 50–60 minutes, the temperature was gradually increased until it reached 80°C. During this period, the pH dropped naturally to below 7.5. At a temperature range of between 58°C– 60°C, the mixture turned clear. As the temperature reached 80°C and the pH dropped to below 7.5, polymerization process proceeded to a second stage where optimum polymerization for MF resin occurred (Pizzi, 1994). Refluxing was continued until the end point (E.P) is reached. The E.P could be determined by dropping the solution mixture into a beaker of water at 50°C for every 5 – 10 minutes. If there is no whitish steak when the droplet is diluted in water, this means that the end point has not been reached (Pizzi, 1994). For a lower degree of polymerization (DP), the end point can be detected by using a lower water temperature.

In stage 3 of the process, the pH was adjusted to between 8.8 – 9.5 when the end point was reached. The resin was then allowed to cool down to the ambient temperature. Additional urea was poured into the mixture when the temperature dropped to 65°C. Finally, the pH was adjusted to a range between 9.5 – 9.8. The cooled resin was transferred to a plastic container for further testing. In this research, resin was produced at different number of reaction stages and different mole ratio for each reaction stage as shown in Table 1.

Table 1 Different formulations for MUF resin

Type of MUF Formulation	**F1**	**F2**	**F3**	**F4**
Number of reaction stage	3	2	3	3
In 1st & 2nd Stage of Resin Processing				
F:U_1	8.00	3.38	8.50	9.00
F:M_1	3.00	3.03	2.97	2.91
F:(U_1+M_1) (total mole ratio)	2.20	1.6	2.20	2.20
In 3rd Stage of Resin Processing				
F:U_3	3.38	–	3.47	3.55
F:(U+M) (total/final mole ratio)	1.60	1.60	1.60	1.60
Mel % (of total resin weight)	29.56	29.56	30.16	30.62
Urea % (of total resin weight)	12.67	12.65	12.27	11.97

Note: Subscripts 1 and 3 refer to stage-1 and stage 3-reaction respectively.

2.1 Determination of Degree of Acidity of MUF Resin

The degree of acidity test was carried out on the resin by conditioning its temperature to 30°C in water bath. An electrode was rinsed thoroughly with water and then cleaned with tissue paper. The electrode was then dipped into the resin and gently swirled around. Care must be taken to allow the pH value to stabilize before the reading was recorded. The pH of the resin was expressed to the nearest 0.05 units.

2.2 Determination of Degree of Rheological Properties of MUF Resin

A rheological property of MUF resin is an evaluation of the viscosity behaviour. A volume of 250 ml resin was poured into a beaker. Resin temperature was adjusted to 30°C by placing it into a water bath at 30°C. Viscosity was checked using Cole-Parmer viscometer (model 98936-15), using R2 spindle and viscometer speed set to 100 r.p.m (rotation per minutes). The process was allowed to proceed for about 15 - 20 seconds before reading was taken.

2.3 Determination of MUF Resin Storage Life

The storage life is a test of the shelf life of the MUF resin under the ambient conditions. Resin was first stored at ambient room temperature. Viscosity of the resin was checked every three to four days according to the procedure in section 2.2. During this period the graph of Days versus Viscosity (cp) was plotted.

2.4 Determination of Resin Curing Period

The curing period of a resin is defined as the period taken for the resin to harden after application of hardener. A mass of 150 g of resin was poured into a plastic beaker. This is followed by addition of NH_4Cl powder to the resin (as hardener) at 1% of the total resin weight. Plastic beaker containing resin and hardener was then placed in a 30°C water bath, where it was stirred for every 10 minutes using a straw or a wooden stick. The resin hardened when it cannot flow or when it begins to crack when lifted using a stick. The time needed for the resin to harden was then recorded.

2.5 Determination of Resin Solubility

A mass of 10 g of resin was weighed into a conical flask. The balance was tared and then distilled water was added slowly into the flask. The flask was shaked and observed for the precipitation of white particles or sediment. Weight of distilled water was recorded when the percipites was formed observed. The water tolerance of resin is expressed as the ratio of part of water (W1) to one part of resin (W2) or W1/W2.

3.0 RESULTS AND DISCUSSION

3.1 Effect of Different Number of Reaction Stages

Generally, most amino-formaldehyde resin formulation consists of different number of reaction stages which affects the properties of the MUF resin produced. In the first stage, resin synthesis undergoes addition process between formaldehyde and amino compound under alkaline condition and at lower temperature, within certain period. In the second stage, propagation of polymer chain takes place under neutral to acidic condition, while the temperature increased gradually within certain period. In this stage, formation of methylene and etherification process occurred. Whereas, in the third stage, additional melamine or urea or formaldehyde is added at a certain mole ratio in the alkaline condition to modify resin properties (Sandler *et al.*, 1994), as shown in Table 1.

The MUF resin with three-reaction stages (F1) is compared with resin produced in two-reaction stages (F2). For MUF resin with three-reaction stages, melamine and part of urea were added in stage-1, and then excess urea was added in stage-3. Whereas, in the resin process using two reaction stages, all melamine and urea were added only in the first stage. Nevertheless, the percentage of urea and melamine to the total resin weight for each formulation is the same. The simplified formulations of the resin process are both shown in Figure 2a and Figure 2b.

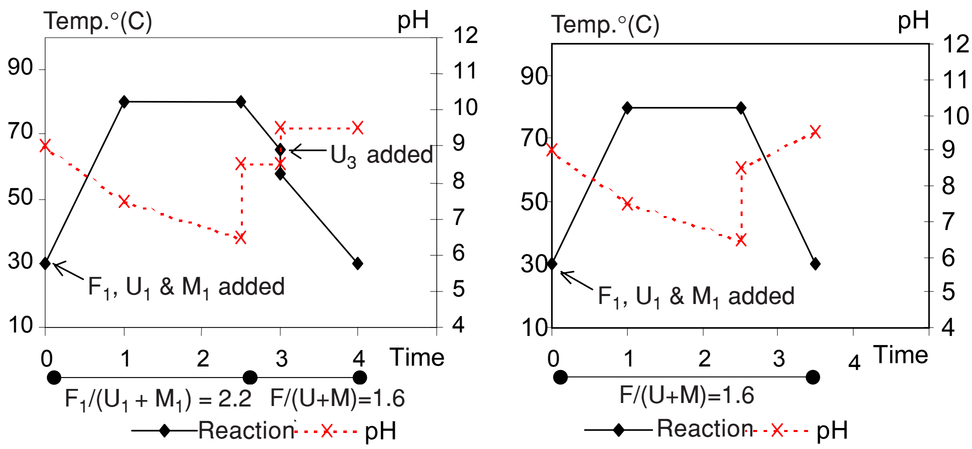


Figure 2 Simplified formulation of MUF resin process using (a) a three reaction stages and (b) a two reaction stages

From the results shown in Table 2, note that MUF resin produced with three reaction stages (F1) has a longer curing period, but has a higher solubility compared to MUF resin produced with two reaction stages (F2). This is due to the propagation of polymer chain that occurs in stage two. Since the reaction period in stage two is the same in both formulations, propagation of polymer chain can only be affected by the concentration of raw material. Since F2 has less raw material compare to F1, therefore, F2 tends to produce shorter polymer chains as compared to F1. With respect to this, F1 can reach a given level of crosslink density faster than F2, which has the same structure with F1 but a shorter polymer chain (Berge *et al.* 1970). However, F2 resin solubility is higher because the resin solubility is affected by the polymer chain length. Resin with shorter polymer chain give higher solubility (Vale *et al.* 1964).

Viscosity characteristic in Figure 3 has also demonstrated that the storage-life for MUF resin with three-reaction stages produce a better storage stability as compared to MUF resin with two-reaction stage. This is also consistent with the findings reported by Pizzi, 1994 who states that increased number of reaction stages can increase resin storage stability. When the amino compound is reacted in many stages, the reaction

Table 2 Effect of different formulation of MUF resin on its properties

Type of MUF Formulation	F1	F2
Number of reaction stage	3	2
In 1st & 2nd Stages of Resin Processing F:(U_1+M_1) (total mole ratio)	2.20	1.6
In 3_{rd} Stage of Resin Processing F:(U+M) (total/final mole ratio) Mel % (of total resin weight) Urea % (of total resin weight) Curing period at 30°C (min) Solubility in water (Water : Resin)	 1.60 29.56 12.67 170 3.5	 1.60 29.56 12.65 95 1.5

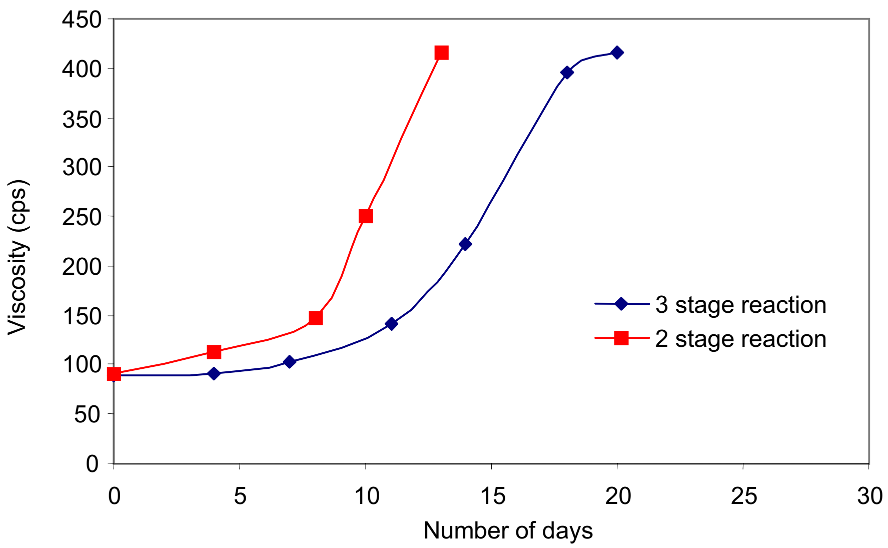


Figure 3 Storage life for MUF resins with different number of reaction stages

between formaldehyde to amino compound is easier to control, thereby enabling stable resin to be obtained.

3.2 Effect of Different Mole Ratio for Each Reaction Stage for MUF Resin

In this study, F1, F3 & F4 types of MUF are produced with three-reaction stages at different U1, M1 and U3 amounts. The amount of U1 reduces while M1 increase. The amount of U3 is reduces from F1 to F3 to F4 MUF types. Nevertheless, the total mole ratio in first and second stages and the total/final mole ratio for F1, F3 and F4 are the

Table 3 Characteristic differences in mole ratio for 3-stage reaction MUF resin

Type of MUF Formulation	**F1**	**F3**	**F4**
In 1st & 2nd Stages of Resin Processing			
$F:U_1$	8.00	8.50	9.00
$F:M_1$	3.00	2.97	2.91
$F:(U_1+M_1)$ (total mole ratio)	2.20	2.20	2.20
In 3rd Stage of Resin Processing			
$F:U_3$	3.38	3.47	3.55
F:(U+M) (total/final mole ratio)	1.60	1.60	1.60
Mel % (of total resin weight)	29.56	30.16	30.62
Urea % (of total resin weight)	12.67	12.27	11.97
Curing period at 30°C (min)	170	180	188
Solubility in water (Water : Resin)	3.5	4.0	4.0

same (as shown in Table 3).

As shown in Table 3 and Figure 4, when the amount of melamine is increased, the MUF resin shelf life improves and the curing period increases. This is because in MUF resin, partially polymerized MF and UF resin are also formed. MF resin has good shelf life and longer curing period compared to UF resin. Therefore, when melamine amount increases, more MF resin is formed in the MUF resin, resulting in a better shelf life and longer curing period.

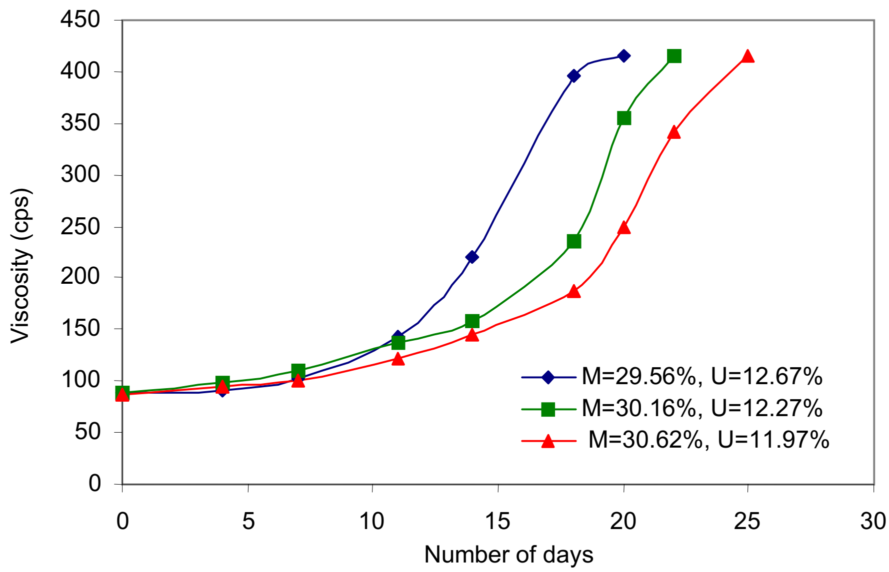


Figure 4 Storage life of MUF resin with different mole ratio at each reaction stages

Nevertheless, there is only slight increment in MUF resin solubility when melamine content increases. This is due to the methylol-group in the MUF resin. The methylol-group is very soluble in water and can from either methylol-melamine or methylol-urea. At the same time, a molecule of melamine can form more methylol as compared to a molecule of urea. Therefore, when melamine amount is increased, more methylol-melamine is formed in the MUF resin resulting in an increment in the resin solubility (Sandler, 1994 and Okana *et al*., 1952).

4.0 CONCLUSIONS

In this investigation, the amount of melamine used is between 28.0 – 31.0% whereas the amount of urea is between 11.0-13.0%. This amount is found sufficient for balancing the cost and performance, compared to MUF resin produced by Breyer *et al*. 1997, Shieu *et al*. 1985 and Heger 1982.

Shelf life for MUF resin produced with three-reaction stages is 10 days longer then that of MUF resin produced with two-reaction stage. The solubility of MUF resin is also higher for water to resin ratio of 3.5 as compared to MUF resin with two-reaction stages, which has only water to resin ratio of 1.5. The curing period is approximately 85 minutes apart; MUF resin with three-reaction stages requires 170 minutes while the one with two-reaction stages requires 95minutes.

In the investigation of the 3-stage reaction process, when the amount of melamine is increased, the amount of urea is reduced to maintain the final mole ratio to F:(U+M) = 1.6. Increment of melamine content between 0.4 – 0.6% has extended MUF resin shelf life to 2 – 3 days. However, only a slow increment is observed in the resin solubility in water, which eventually stabilizes. The curing period increases from 8 – 10 minutes with each group of the melamine content as shown in Table 3.

Finally, these results obtained from the research investigation can served as a useful guideline for the selection and development of MUF resin formulations to achieve the required properties.

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