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Properties of Urea-Formaldehyde Resin Adhesives with Different Formaldehyde to Urea Mole Ratios*1

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ABSTRACT

As a part of abating the formaldehyde emission of urea-formaldehyde (UF) resin adhesive by lowering formaldehyde to urea (F/U) mole ratio, this study was conducted to investigate properties of UF resin adhesive with different F/U mole ratios. UF resin adhesives were synthesized at different F/U mole ratios of 1.6, 1.4, 1.2, and 1.0. Properties of UF resin adhesives measured were non-volatile solids content, pH level, viscosity, water tolerance, specific gravity, gel time and free formaldehyde content. In addition, a linear relationship between non-volatile solids content and sucrose concentration measured by a refractometer was established for a faster determination of the non-volatile solids content of UF resin. As F/U mole ratio was lowered, non-volatile solids content, pH, specific gravity, water tolerance, and gel time increased while free formaldehyde content and viscosity were decreased. These results suggested that the amount of free formaldehyde strongly affected the reactivity of UF resin. Lowering F/U mole ratio of UF resin as a way of abating formaldehyde emission consequently requires improving its reactivity.

Keywords : urea-formaldehyde resin, formaldehyde to urea mole ratio, resin properties, resin reactivity

1. INTRODUCTION

Urea-formaldehyde (UF) resin adhesive is a thermosetting polymer obtained by addition and condensation reaction between urea and formaldehyde, and is recognized as the most common type of adhesives in use for the production of wood-based composite panels (Graves, 1999). For example, the production of formaldehyde-based resin in 2002 was about 470,000 tons, of which 37% of the total production of adhesives in Republic of Korea. The production of UF resin was about 74% (i.e. about 170,000 tons) of the formaldehyde-based resin.

Compared to other wood adhesives, such as phenol-formaldehyde (PF) resins and diphenylmethane diisocyanate (MDI), UF resin adhesive possesses some advantages such as fast curing, good performance in the panel, water solubility and lower price. In spite of these advantages, disadvantages of using the UF resin are formaldehyde emission (FE) from the panels and lower resistance to water. However, the FE from the panels used for interior applications

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was one of the factors, affecting sick building syndrome in indoor environment. Free formaldehyde present in UF resin and hydrolytic degradation of UF resin under moisture condition has been known as responsible for the FE from wood-based panels (Myers, 1983). In other words, un-reacted formaldehyde in UF resin after its synthesis could be emitted from wood panels even after hot-pressing at high temperature. In addition, the reversibility of the aminomethylene link and its susceptibility to hydrolysis also explains lower resistance against the influences of water and moisture, and subsequently formaldehyde emission (Dunky, 1998). Therefore, the FE issue has been one of the most important aspects of UF resin in last few decades (Myers and Koutsky, 1987; Myers 1986; Pizzi *et al.*, 1994; Marutzky, 1986; Hse *et al.*, 1994; Gu *et al.*, 1995).

Much attention has been paid to reduce or control the FE from UF resin-bonded panels through resin technologies. Lowering the formaldehyde to urea (F/U) mole ratio for the synthesis of UF resin was adopted as one of the approaches to reduce the FE of UF resin-bonded panels (Marutzky, 1986). An excellent literature review on the influence of F/U mole ratio on the FE as well as panel properties has been reported (Myers, 1984). In general, lower F/U mole ratios cause less FE form the panel with a loss of panel properties, particularly internal bond (IB) strength as well as thickness swelling after water immersion for 24 hours (Marutzky, 1986; Que *et al.*, 2007).

Even though many authors investigated the influence of F/U mole ratio on the FE of wood-based panel products, there is limited data available for the properties of UF resin adhesives prepared under different F/U mole ratios. Therefore, this study was conducted to investigate the properties of UF resin with different F/U mole ratios as a part of abating the FE of UF resin adhesives.

2. MATERIALS and METHODS

2.1. Resin Synthesis

All UF resins used for this study were prepared in the laboratory, following traditional alkaline-acid two-step reaction. Formaldehyde (37 %) was placed in the reactor and heated to 60°C and then adjusted the reaction pH to 7.5 with sodium hydroxide (20 wt%). Subsequently, urea was added in equal parts at 1-min intervals, and the mixture was heated to 90°C for 1 hour. Then, the reaction pH was adjusted to 4.5 with formic acid (20 wt%) for the condensation. The second urea was again placed in the reactor at 40°C before rapid cooling to 25°C terminated the reaction. Different amounts of the second urea were added for the synthesis in order to obtain F/U mole ratios of 1.6, 1.4, 1.2, and 1.0.

2.2. Properties of UF Resin

2.2.1. Non-volatile Solids Content and pH

About 1 g of UF resin was poured into a disposable aluminum dish, and then dried in a convective oven at 105°C for 3 hours. Non-volatile solids content was determined by measuring the weight of UF resin before and after drying. An average of three replications was presented.

A Brix refractometer (N-3E, Atago, Japan) with the Brix range from 58% to 90% was also used to measure the non-volatile solids content of UF resin adhesives. 1 or 2 drops of the sample resin was placed on the prism, and closed the daylight plate over the sample. And then the sucrose concentration was read by looking through the eyepiece. In order to establish a relationship between two methods (i.e., refractometer and gravimetric method), UF resin with the F/U mole ratio of 1.2 was distilled to obtain a UF resin with the non-volatile solids content of 70%. And then the UF resin distilled was diluted with water to obtain various non-volatile solids contents of 58, 61, 64, and 67%.

The pH of UF resin after synthesis was measured with an electronic pH meter at 25°C.

2.2.2. Viscosity

The viscosity of UF resin adhesives at 25°C were measured using a cone-plate viscometer (DV-II+, BROOKFIELD, USA) with no. 2 spindle at 60 rpm.

2.2.3. Water Tolerance

5 g of UF resin in 250 mℓ beaker was placed in water at 25°C, and then increasingly added distilled water (25°C) into the beaker while stirring the resin with a magnetic bar. The amount of water was determined when insoluble precipitates occurred in the resin. The water tolerance was obtained by measuring the amount of water divided by the weight of the sample resin (KS M 3701, 1997).

2.2.4. Specific Gravity

50 mℓ of UF resin in mass cylinder weighed to obtain its density at 25°C. The specific gravity of UF resin was determined by dividing the UF resin density with the density of water at 25°C. An average of three replications was presented.

2.2.5. Gel Time Measurement

The gel time was measured by adding 3 wt% ammonium chloride (NH_4Cl) (20 %wt solution) as hardener at 100°C, using a gel time meter. The measurements were done using a gel time meter (Sunshine, USA) with three replications for each UF resin with different F/U mole ratios.

2.2.6. Determination of Free Formaldehyde

Free formaldehyde in the prepared UF resins was determined by a slightly modified sodium sulfite method (McCaffery, 1970). The solution of 25 mℓ 1 *M* sodium sulfite mixed with 10 mℓ HCl was added to 2~3 gram of UF resin sample dissolved in 100 mℓ distilled water. The mixed solution containing about 10 drops of 0.1% thymolphthalein was neutralized with 1 *N* sodium hydroxide. The percent of free formaldehyde was determined by the equivalent of the amount of the consumed sodium hydroxide in titration.

3. RESULTS and DISCUSSION

Fig. 1 shows the non-volatile solids content of UF resin adhesives with different F/U mole ratios. The non-volatile solids contents was ranged from about 53 to 58%, and increased with decreasing F/U mole ratio. This result could be attributed to the amount of water produced by the condensation reaction of UF resin (Pizzi, 1983; Saunder, 1988). In other words, UF resin with a greater F/U mole ratio went through a condensation reaction to produce a greater amount of water as by-product. Another reason could be due to the synthesis procedure of UF resin. Since the F/U mole ratio was manipulated by adjusting the amount of second urea, the UF resin with lower F/U mole ratio had more urea than that of higher F/U mole ratios, which resulted in greater non-volatile solids content.

In industrial practice of synthesizing UF resin, a Brix refractometer is often used to predict the non-volatile solids content of UF resin during its distillation. However, the relationship between the sucrose concentration and non-vol-

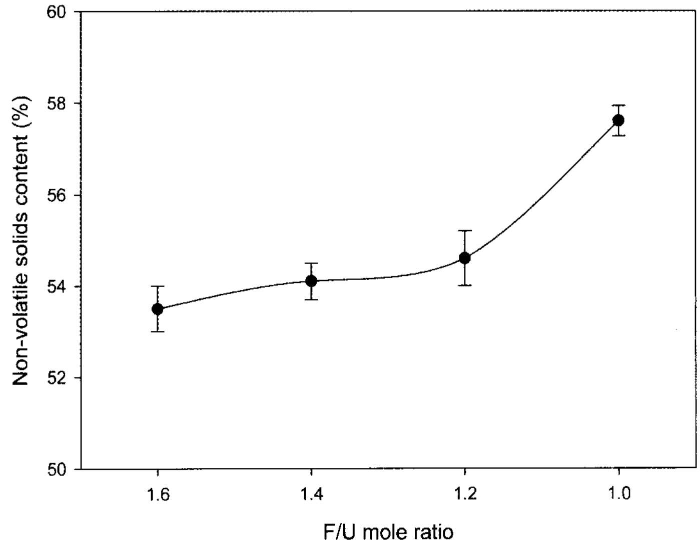

Fig. 1. Non-volatile solids content of UF resins with different F/U mole ratios.

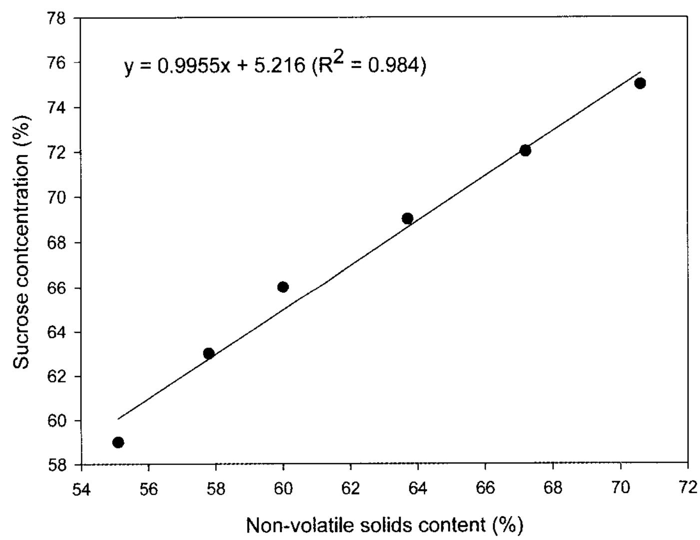

Fig. 2. Relationship between the sucrose concentration measured by the refractometer and non-volatile solids content of UF resin measured by the gravimetric method.

atile solids content of the UF resin was not reported yet. Fig. 2 shows a relationship between the sucrose concentration and non-volatile solids content of UF resins. The sucrose concentration measured by a Brix refractometer had a quite linear relationship with the non-volatile solids content measured by gravimetric method. The regression coefficient was 0.996. The linear regression equation shows that the non-volatile solids content obtained with the refractometer is 5% greater than the one of the counterpart. This relationship established makes it possible to

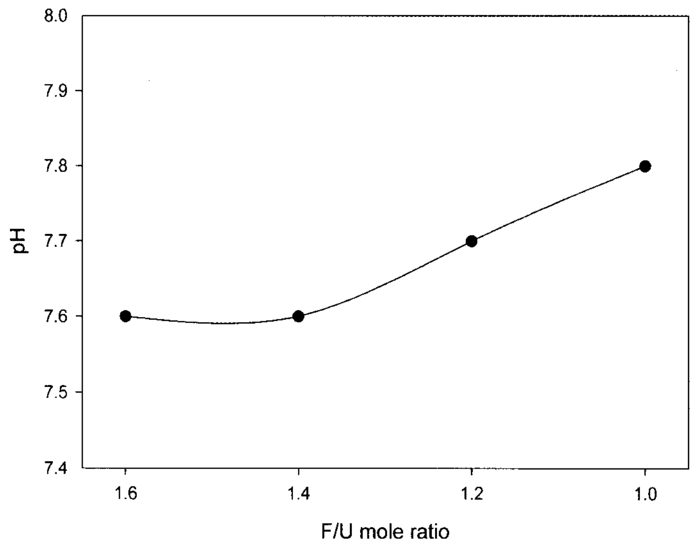

Fig. 3. pH of UF resins with different F/U mole ratios.

predict non-volatile solids content of UF resin using the sucrose concentration measured with the refractometer. This result could be applied for UF resin synthesis in industrial practice.

Fig. 3 shows the change of pH of UF resin, depending on F/U mole ratio. As expected, the pH of UF resin slightly increased as the F/U mole ratio decreased. This could be due to the synthesis procedure of UF resin used in this study. In other words, F/U mole ratio of UF resin was manipulated by adjusting the amount of the second urea during its synthesis. Since urea granules are inherently alkaline, the more the amount of the second urea, the more alkaline of UF resin after its synthesis.

Fig. 4 shows the specific gravity of UF resins, depending on F/U mole ratio. The specific gravity of UF resin ranged from 1.17 to 1.18, and increased with decreasing F/U mole ratio. This result was quite compatible with those of non-volatile solids contents of UF resins with different F/U mole ratios. This result was quite similar to other results reported (Que *et al.*, 2007). An increase of the specific gravity at lower F/U mole ratio could be attributed to less amount of water produced by the condensation reaction under acidic condition.

Fig. 5 shows the viscosity of UF resin adhesives at different F/U mole ratios. As expected, the viscosity of UF resin adhesives decreased with decreasing F/U mole ratio. This result could be due to the production of greater molecular weight of UF resin adhesive with high F/U mole ratio. In general, the viscosity of polymer has relationship with its molecular weight as expressed the Mark-Houwink equation (Young, 1986).

$$[\mu] = KM^{\alpha} \tag{1}$$

This is a semi-empirical equation between the intrinsic viscosity, $[\mu]$ and the molar mass of polymer, M. And α is the Mark-Houwink constant, ranging from 0.5 to 1.0. And another reason might be due to less amount of the second urea for high F/U mole ratio during the resin synthesis. The addition of the second urea dissolved at later stage of UF resin synthesis could reduce the viscosity of UF resin.

Fig. 6 shows water tolerance of UF resins at

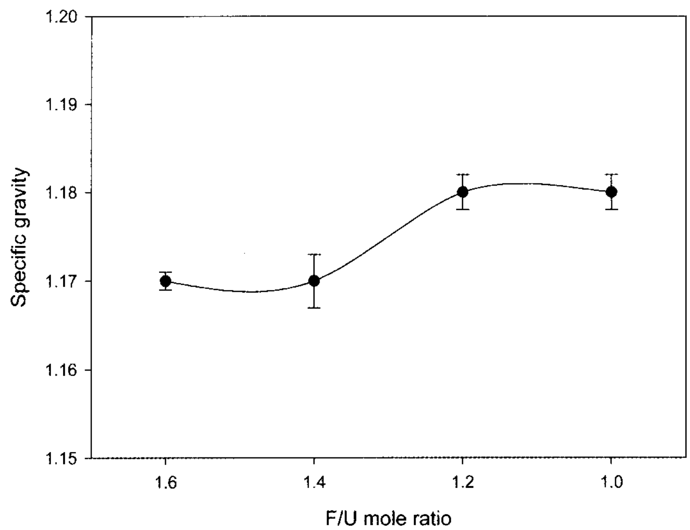

Fig. 4. Specific gravity of UF resins with different F/U mole ratios.

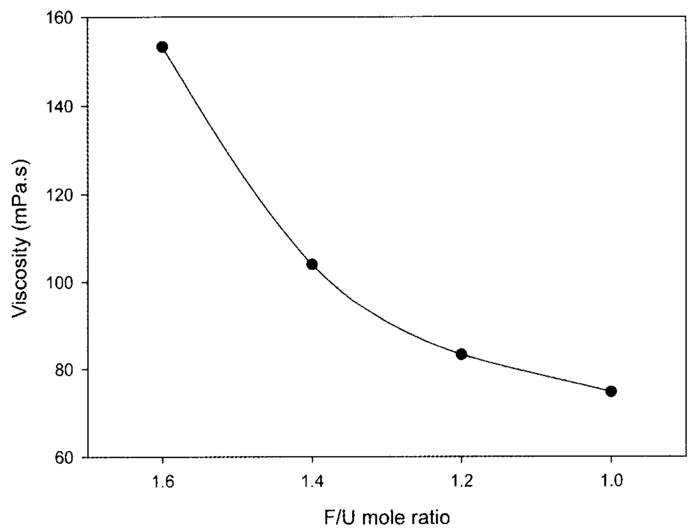

Fig. 5. Viscosity of UF resins with different F/U mole ratios.

different F/U mole ratios. The water tolerance is an important parameter when a glue mix of UF resin is prepared with various additives. For example, lower water tolerance of UF resin adhesive could cause a phase separation of the resin adhesive into water and resin solids, and furthermore retard the resin flow for the production of particleboard. The water tolerance of UF resin increased with decreasing F/U mole ratio, but it was stable at the F/U mole ratio of 1.0. Lower water tolerance of UF resin at high F/U mole ratio could be due to the production of large amount of meytholated urea since UF resin of high F/U mole ratio usually resulted in more branched polymer structure (Park *et al.*, 2006).

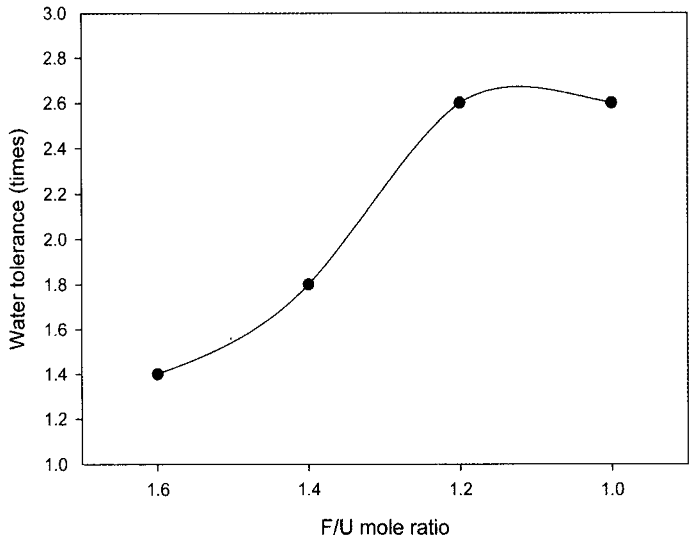

Fig. 6. Water tolerance of UF resins with different F/U mole ratios.

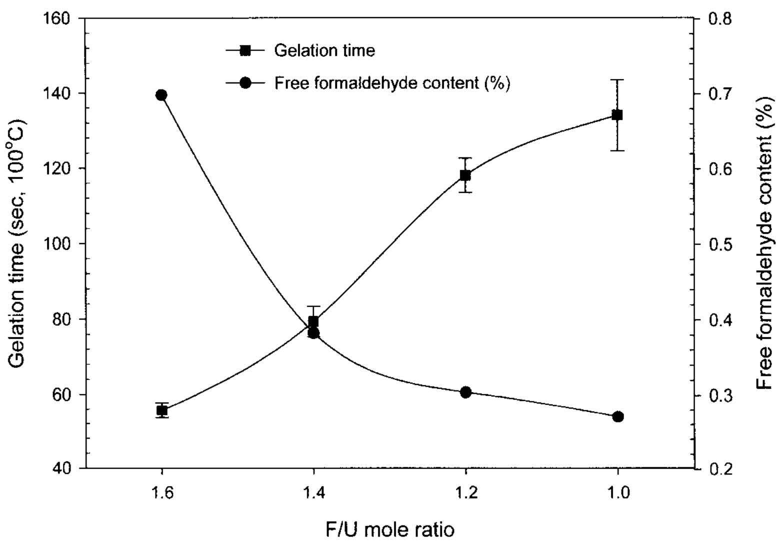

Fig. 7. Gel time and free formaldehyde content of UF resins with different F/U mole ratios.

The gelation time and free formaldehyde content of UF resin adhesives depending on F/U mole ratio were shown in Fig. 7. As the F/U mole ratio decreased, the gelation time steadily increased, indicating that the reactivity of UF resin decreased with decreasing F/U mole ratio. This is quite similar to the result reported (Park *et al.*, 2006). By contrast, the amount of free formaldehyde in UF resin decreased with decreasing F/U mole ratio. These results shows that the reactivity of UF resins strongly depend on the amount of free formaldehyde. In other words, the amount of free formaldehyde strongly affected the reactivity of UF resin. This result could be explained by the role of free formaldehyde and hardener in the cure of UF resin.

In general, UF resin cures under acidic condition created by the reaction of hardener with free formaldehyde present in the resin. When ammonium chloride was used as hardener, the following reaction occurred to provide acidic condition. In other words, the chloride reacts with free formaldehyde to form hydrochloric acid and hexamethylenetetramine as shown below:

$$6NH_4Cl + 6HCHO \rightarrow 4HCl + (CH_2)_6N_4 + 6H_2O \qquad (2)$$

4. CONCLUSIONS

This study was conducted to investigate properties of UF resin adhesive with different F/U mole ratios for the reduction of the formaldehyde emission by lowering formaldehyde to urea (F/U) mole ratio. The properties of UF resin adhesives synthesized at different F/U mole ratios of 1.6, 1.4, 1.2, and 1.0 were presented. As F/U mole ratio was lowered, non-volatile solids content, pH, specific gravity, water tolerance, and gel time increased while free formaldehyde content and viscosity were decreased. In addition, a linear relationship between non-volatile solids content and sucrose content measured by a refractometer was established for a faster determination of the non-volatile solids content of UF resin. These results indicated that lowering F/U mole ratio of UF resin as a way of abating formaldehyde emission consequently required improving its reactivity.

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