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Effects of Formaldehyde to Urea Mole Ratio on Thermomechanical Curing of Urea-Formaldehyde Resin Adhesives*[1]

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ABSTRACT

This study was conducted to investigate the effects of formaldehyde to urea (F/U) mole ratio on thermomechanical curing of UF resin adhesives with different F/U mole ratios. Thermomechanical curing of these UF resin adhesives was characterized using parameters of dynamic mechanical analysis (DMA) such as the gel temperature, maximum storage modulus, and peak temperatures of storage and loss modulus. As the F/U mole ratio decreased, the gel temperature of UF resin adhesives increased. The maximum storage modulus as an indicator of the rigidity of UF resin adhesives decreased with decreasing F/U mole ratio. The peak temperature of tan δ increased with decreasing F/U mole ratio, indicating that the vitrification occurred faster for high F/U mole ratio of UF resin adhesives than for the one of lower F/U mole ratio. These results partially explained the reason why UF resin adhesives with lower F/U mole ratio resulted in relatively poor adhesion performance when they were applied.

Keywords : formaldehyde to urea mole ratio, urea-formaldehyde resin, thermomechanical cure, dynamic mechanical analysis

1. INTRODUCTION

Urea-formaldehyde (UF) resin adhesive is a polymeric condensation product of the chemical reaction of formaldehyde with urea, and is most widely used for the manufacture of wood-based composite panel, particularly plywood, particleboard or medium density fiberboard. Therefore, UF resin adhesives are considered as one of the most important wood adhesives, and are mainly consumed for the production of wood-based composites in wood panel industry. In fact, the production of formaldehyde-based resin in 2005 was about 207,000 tons, which is 39% of the total production of adhesives in Republic of Korea. The production of UF resin adhesives was about 75% (i.e. about 155,000 tons) of the total production of formaldehyde-based resin

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adhesives.

UF resin adhesive possesses some advantages such as fast curing, good performance in the panel, water solubility and lower price. Disadvantages of using the UF resin are formaldehyde emission (FE) from the panels and lower resistance to water. Lower resistance to water limits the use of wood-based panels bonded with UF resin to interior applications.

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 (Hse *et al.*, 1994; Gu *et al.*, 1995; Myers, 1986; Myers and Koutsky, 1987; Marutzky, 1986; Pizzi *et al.*, 1994).

Much attention has been paid to reduce or control the FE from UF resin-bonded panels through resin technologies. So, 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). In recent years, lower F/U molar ratios from 1.1 to 1.2 started to be used for the resin synthesis (Que *et al.*, 2007).

An excellent literature review on the influence of F/U mole ratio on the FE as well as panel properties has been made (Myers, 1984). According to the review, the gel time used as an indicator of resin reactivity increased with decreasing F/U mole ratio. In general, lower F/U mole ratio of UF resin adhesives reduced the emission of formaldehyde from the panel at the expense of panel properties, particularly internal bond (IB) strength as well as thickness swelling after water immersion for 24 hours (Myers, 1984; Que *et al.*, 2007; Sundin and Hanetho, 1978). Lower F/U molar ratios also reduced modulus of rupture (MOR) (Martutzky, 1986). It was reported that close F/U mole ratio to 1.0 produced quite similar structures and performance in UF resin, leading the conclusion that the most important factor in synthesis of UF resin was the F/U mole ratio (Christjanson *et al.*, 2002). However, the reason why UF resin adhesives with lower F/U mole ratio resulted in deterioration of panel properties at the expense of lower FE was not fully explained.

Different methods of characterizing curing behavior of UF resin have been employed. For example, thermal analysis includes thermogravimetric (TG) analysis (Zeman and Tokarova, 1992), differential thermal analysis (DTA) (Chow and Steiner, 1975; Siimer *et al.*, 2003), differential scanning calorimetry (DSC) (Myers and Koutsky, 1990; Park *et al.*, 2006), and dynamic mechanical analysis (DMA) (Christiansen *et al.*, 1993; Follensbee *et al.*, 1993; Kim *et al.*, 1991; Young, 1986).

DMA measures mechanical response of viscoelastic material exposed to oscillation at varying temperatures. DMA provides mechanical responses of specimen such as storage modulus (E'), loss modulus (E''), and tan δ, the ratio of loss modulus to storage modulus. The E' is a measure of stored energy of material and depends on polymer type, temperature, and frequency of oscillation, while the E'' measures dissipated energy of specimen due to the molecular frictions occurring in the viscous flow.

UF resin adhesive becomes a thermosetting polymer via curing processes such as gelation, vitrification, or devitrification. The gel of UF

Table 1. Properties of UF resins with different F/U mole ratios

F/U Mole ratio	Solids content (%)	pH	Viscosity (mPa · s)	Specific gravity
1.6	53.5	7.6	153.3	1.17
1.4	54.1	7.6	104.0	1.17
1.2	54.6	7.7	83.3	1.18
1.0	57.6	7.8	74.7	1.18

resin is a point of infinite increasing molecular weight of the resin, which drastically reduces resin flow and greatly increases its viscosity. After the gel, UF resin continues to cure to reach a glass transition temperature where the rubbery-elastic state of UF resin changes to glassy state. Thus, DMA could be used to monitor these curing processes of UF resin. DMA as a tool of characterizing thermosetting adhesives has been widely used for phenol-formaldehyde (PF) resin adhesives (Christiansen *et al.*, 1993; Follensbee *et al.*, 1993; Kim *et al.*, 1991; Young, 1986). Earlier work on PF resin showed that the result of DMA could be related to the degree of cure of PF resin adhesive, and to the performance of wood composites (Young, 1986). The use of DMA method also provided a characterization tool of PF resin including cure time, vitrification time, and other useful parameters (Kim *et al.*, 1991). In particular, Kim *et al.* (1991) interpreted the maximum tan δ as the vitrification point of PF resin. It was found that the area under the tan δ curve during isothermal scanning was related to an inverse of measure of precure of PF resin (Follensbee *et al.*, 1993; Christiansen *et al.*, 1993).

By contrast, limited work has been done on thermomechanical curing behavior of UF resin adhesives (Ebewele, 1995; No and Kim, 2005; Onic *et al.*, 1998; Umemura *et al.*, 1996). DMA has been used to investigate curing behavior of amine-modified UF resin (Ebewele, 1995), low level melamine fortification of UF resins (No and Kim, 2005), and thermomechanical curing of different wood adhesives (Onic *et al.*, 1998).

Even though many authors investigated thermomechamical curing of UF resin adhesives, there is limited data available for thermomechanical curing behavior of UF resins prepared under different F/U mole ratios. Therefore, this study was conducted to investigate the influence of F/U mole ratio on thermomechanical curing behavior of UF resins using DMA.

2. MATERIALS and METHODS

2.1. UF Resin Adhesive Preparation

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 first urea were added for the synthesis in order to obtain F/U mole ratios of 1.6, 1.4, 1.2, and 1.0. For all resins prepared, final pH was adjusted to 8.0 after the cooling. Properties of UF resins prepared at different F/U mole ratios were shown in Table 1.

2.2. Methods

2.2.1. Sample Preparation for DMA

Since UF resin adhesive is in aqueous solution state, the use of DMA requires the solidification of the resin adhesives after its impregnation into a substrate. The selection of a substrate for the resin impregnation is important because the substrate should be inert to the resin with no interaction, maintain mechanical properties at high temperature (up to 300°C), not be hygroscopic, and be porous structure (Follensebee *et al.*, 1993). A borosilicate glass microfiber filter (Whatman GF/C) was selected for the UF resin adhesive impregnation in this study.

For the sample preparation, 3% of ammonium chloride (20% solution) was added to samples of UF resin adhesives with different F/U mole ratios based on the non-volatile resin solids content, and then thoroughly mixed. The glass microfiber filter (90 mm wide and 0.3 mm thick) was impregnated with the resin prepared, and then dried at room temperature for 2 hours. Preliminary experiments showed that an optimum resin loading ratio was 1.0 mg/mm^3. Air-dried glass filter was cut to a specimen with a length of 60 mm and width of 13 mm, and then further dried for 48 hours in a desiccator with phosphorous pentoxide (P_2O_5). Shorter or longer drying time than 48 hours caused problems of sticking to the instrument, or easy breaking of specimens. Prepared specimens were put on the grips of DMA (Diamond DMA7, Perkin Elmer, USA).

2.2.2. DMA Measurement

All DMA measurements were made in bending mode using specimen clamped in a horizontal plane between the ends of two parallel arms. A fixed displacement mode with 0.3 mm amplitude and 1 Hz oscillation frequency was used. For a dynamic scan of the DMA, the temperature increased from room temperature to 300°C at a heating rate of 5°C per minute. Nitrogen gas was used to prevent any oxidation of the sample and to purge the DMA chamber at a rate of 200 mℓ per minute. Duplicate scans were made for each UF resin adhesive, which resulted in similar curves without any significant difference. Thermomechanical parameters such as storage modulus (E′), loss modulus (E″) and tan δ, a ratio of E″/E′ were obtained from DMA curves.

3. RESULTS and DISCUSSION

Fig. 1 shows DMA curves of UF resin adhesives with the F/U mole ratio of 1.0. Definitions of thermomechanical parameters were also given in Fig. 1. The storage modulus, E′, decreased to a minimum modulus (E'_{min}), and then increased to a maximum modulus (E'_{max}) as the temperature increased. The difference of storage modulus between the E'_{min} and E'_{max} was defined as $\Delta E'$. The temperature where the E′ reached minimum was defined as the gel temperature (T_{gel}) of UF resin adhesive. Peak temperatures of reaching the maximum storage modulus (E'_{max}) and loss modulus (E''_{max}) were defined as T_1 peak and T_2 peak, respectively.

As shown in Fig. 1, the rigidity represented as the E′ initially decreased to a minimum and then reached a maximum. The initial decrease of E′ could be due to the softening of UF resin adhesives as the temperature increases. After the E'_{min}, the E′ started to increase toward a maximum. This was possibly due to the gelling of UF resin adhesive, where an infinite molecular network began to be formed. Thus, this temperature was defined as the gel temperature. Similar definition of the gel time was already reported for an isothermal scanning of melamine-modified UF resins (No and Kim, 2005).

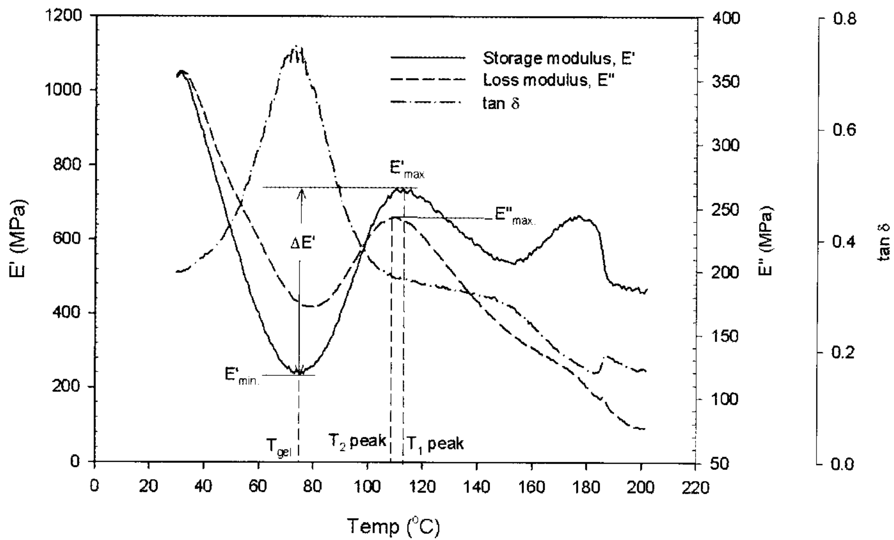

Fig. 1. DMA curves of UF resins with F/U mole ratio of 1.0.

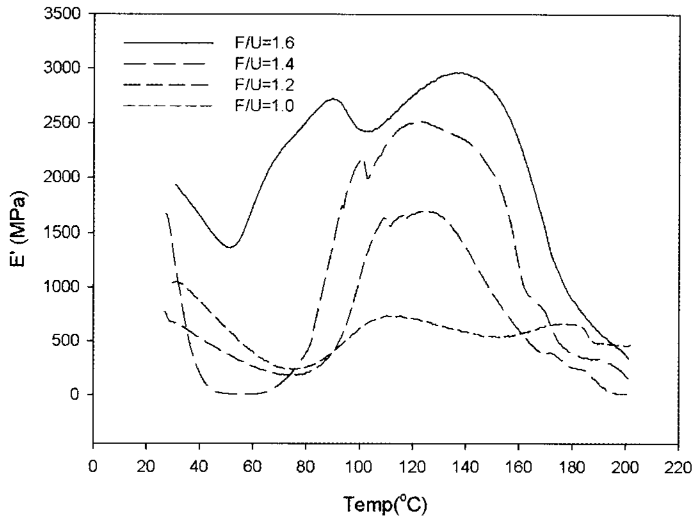

Fig. 2. Storage modulus of UF resins with different F/U mole ratios.

Further discussion on the change of the gel temperature will be followed.

Fig. 1 also showed the presence of two peaks of E'_{max}. This observation could be explained as the curing process of UF resin adhesive underwent vitrification for the first peak and another vitrification followed by devitrification for the second peak. However, the first peaks of F/U mole ratios of both 1.4 and 1.2 were quite different from those of F/U mole ratios of 1.0 and 1.6 as shown in Fig. 2. It colud be due to a crack on the surface of the resin impregnated

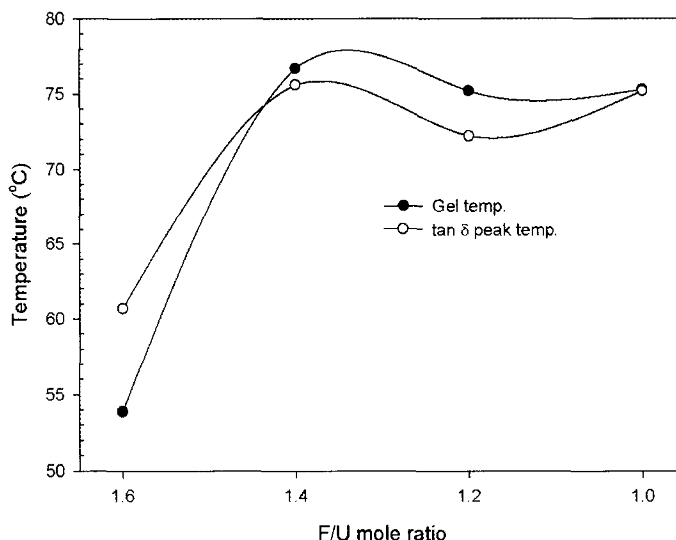

Fig. 3. The gel temperature and peak temperature of tan δ of UF resins with different F/U mole ratios.

glass filter as the resin proceeds curing process. Further work is necessary to understand the presence of these two peaks.

Loss modulus of UF resin adhesive with the F/U mole ratio of 1.0 followed similar change to the E'. Initial decrease of E'' could be due to the softening of UF resin as the rigidity. After reaching the minimum, the E'' started to increase, but followed behind the storage modulus. This result also reflects the gelling of UF resin, where the polymerization reaction started to form the network that resulted in efficient energy dissipation.

Fig. 2 shows the E' curves of UF resin adhesives with different F/U mole ratios. All E' curves had similar pattern as the temperature increased. In other words, the E' initially decreased to a minimum and then reached a maximum followed by a decrease. The increase of E' after the minimum possibly ascribed to the network change of UF resin adhesive from gel state to glassy state where the number of cross-linking increased as it went through curing process. A decrease of the E' after the maximum could be due to combined effects of many factors. One of the factors might be devitrification of UF resin after its glass transition temperature (T_g). Another factor would be hydrolytic or thermal degradation of UF resin as the temperature increased. Thus, as the resin adhesive went through gelation, the E' continuously increased to a maximum where the resin became vitrified. Further increase in temperature resulted in a decrease of the E', which could be resulted from devitrification of UF resin. Fig. 2 also shows that the maximum storage modulus, E'_{max}, of UF resin adhesive decreased with decreasing F/U mole ratio. This result indicated that the rigidity of UF resin decreased with lowering F/U mole ratio. In other words, lower E'_{max} of UF resin with lower F/U mole ratio, particularly, 1.0 could have provided the resin adhesive with lower cohesive adhesion strength. This result partially explains why UF resins with lower F/U mole ratio resulted in a deterioration of particleboard properties.

Fig. 3 shows the gel temperature (T_{gel}) and peak temperature of tan δ of UF resin adhesives depending on F/U mole ratios. In general, the gel temperature of UF resin adhesive

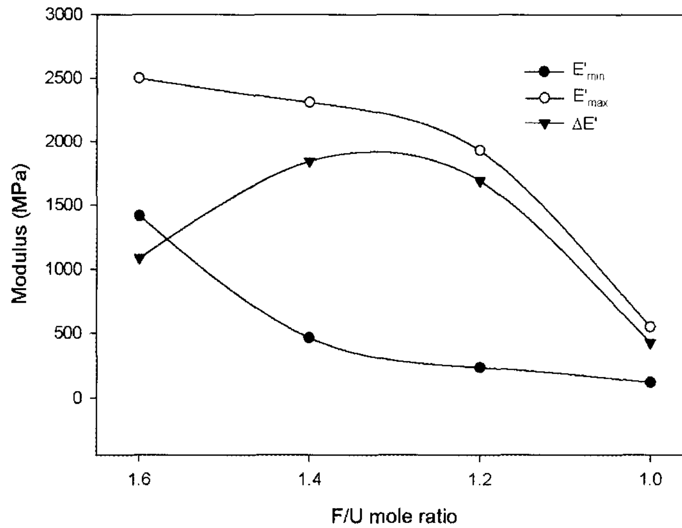

Fig. 4. E'_{min}, E'_{max}, and $\Delta E'$ of UF resins with different F/U mole ratios.

increased with decreasing F/U mole ratio, but they were much different at the F/U mole ratio below 1.4. This result indicated that higher F/U mole ratio resin reached faster gelling than that of lower F/U mole resin, showing a greater reactivity of UF resin at higher F/U mole ratio. This result is quite compatible with the results PF resin adhesives (Kim *et al.*, 1991), and is confirmed by the results of DSC (Park *et al.*, 2006). The peak temperature of tan δ of UF resin also showed a similar pattern to the gel temperature. This could be due to the gelation of UF resin adhesive as the UF resin adhesive start to increase the number of cross-linking.

Fig. 4 shows the E'_{min}, E'_{max} and $\Delta E'$ of UF resin adhesives with different F/U mole ratios. As the F/U mole ratio decreased to the F/U mole ratio of 1.0, the E'_{max} and E'_{min} continuously decreased. But the E'_{min} did not change much below the F/U mole ratio of 1.4. In other words, the influence of F/U mole ratio to the storage modulus was more predominant on the E'_{max} rather than the E'_{min} did. And the decreased E'_{max} of UF resin adhesive with decreasing F/U mole ratio suggested a reduction in the rigidity of UF resin adhesive. As a result, the ΔE, the difference between E'_{min} and E'_{max} increased up to the F/U mole ratio of 1.4 and then decreased. This result also indicated a reduction of the rigidity of UF resin as the F/U mole ratio decreased. Onic *et al.* (1998) reported that the $\Delta E'$ as a stiffening coefficient was more appropriate for the comparison of thermomechanical behaviors of different of adhesive systems.

Fig. 5 shows peak temperatures of both E' and E'' of DMA curves. T_1 peak is the peak temperature of the E'_{max}, and T_2 peak is the peak temperature of the E''_{max}. As the F/U mole ratio decreased, the T_1 peak increased to the F/U mole ratio of 1.4 and then decreased. By contrast, the T_2 peak decreased to the F/U mole ratio of 1.4 and then increased. Lower T_1 peak at the F/U mole ratio of 1.6 could be attributed to a greater reactivity of UF resin adhesives at higher F/U mole ratio. In other words, lower peak temperature of the E' meant that UF resin with the F/U mole ratio of 1.6 reached a maximum rigidity faster than the other UF resins, which resulted in an increased maximum peak

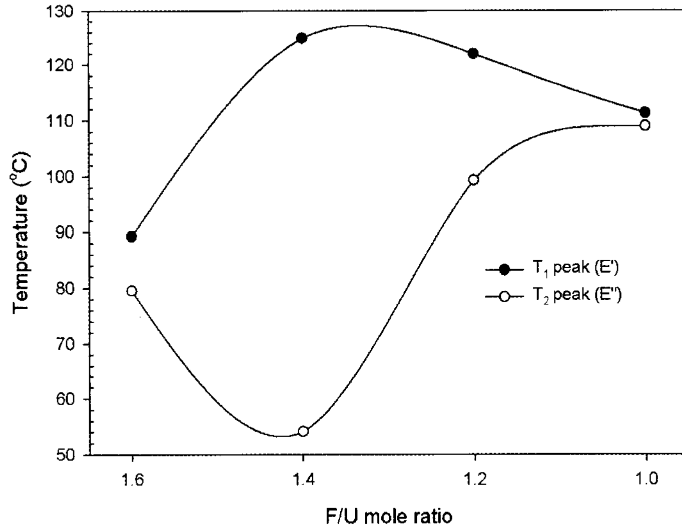

Fig. 5. Peak temperature of storage and loss modulus of UF resins with different F/U mole ratios.

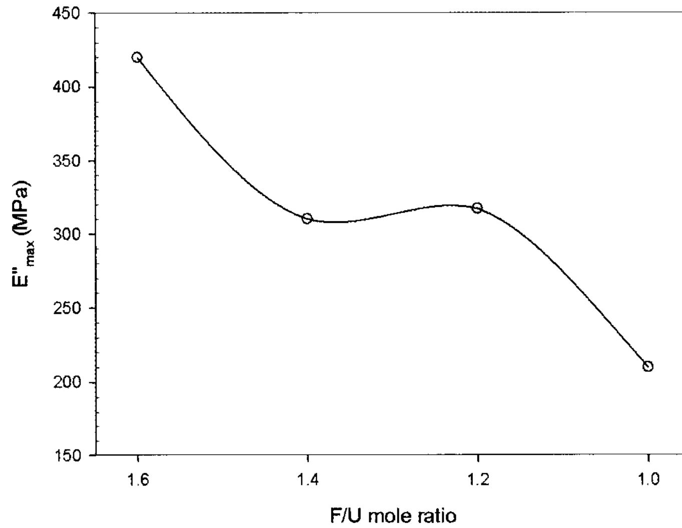

Fig. 6. Maximum loss modulus (E''_{max}) of UF resins with different F/U mole ratios.

temperature of the E''. As the F/U mole ratio decreased below 1.6, the T_1 peak decreased while T_2 peak increased.

Fig. 6 shows the E''_{max}, maximum loss modulus of UF resin adhesives depending on F/U mole ratios. As shown, the E''_{max} decreased with decreasing F/U mole ratio. The loss modulus contributes the energy dissipation due to molecular friction of the viscose flow of a material. Thus, the result indicated that molecular friction of cured UF resin adhesive was reduced as F/U mole ratio decreased. This could be ascribed to more branched network structure of UF resin with higher F/U mole ratio than those of lower F/U mole ratios. In other words, it seemed that UF resin of lower F/U mole ratio

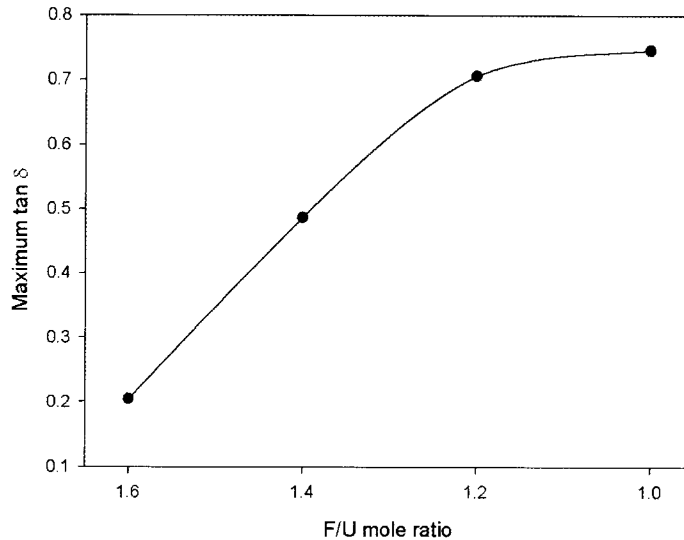

Fig. 7. Maximum tan δ of UF resins with different F/U mole ratios.

was more flexible than those of higher F/U mole ratios, which required less energy dissipation under oscillation. Similar result was reported for PF resole resin (Kim *et al.*, 1991).

The maximum tan δ of UF resin adhesives depending on F/U mole ratios was shown in Fig. 7. As the F/U mole ratio decreased, the maximum tan δ proportionately increased with F/U mole ratio. As shown in Fig. 1, the gelling of UF resin resulted in a minimum E' and a maximum tan δ at the almost same temperature. In general, the maximum tan δ results from the gelling or vitrification of thermosetting resin. Thus, this result could be due to increasing gel temperatures as F/U mole ratio decreased.

4. CONCLUSIONS

As a part of abating formaldehyde emission of UF resin adhesive bonded wood-based panels, this study was conducted to investigate the effects of formaldehyde to urea (F/U) mole ratio on thermomechanical curing of UF resin adhesives with different F/U mole ratios such as 1.6, 1.4, 1.2, and 1.0 using DMA. As the F/U mole ratio decreases, the minimum storage modulus regarded as the gel temperature of UF resin adhesives increased. The maximum storage modulus as an indicator of the rigidity of UF resin adhesives decreased with decreasing F/U mole ratio. The peak temperature of tan δ increased with decreasing F/U mole ratio, indicating that the vitrification occurred faster for high F/U mole ratio of UF resin adhesives than for the lower F/U mole ratio ones. As the F/U mole ratio decreased, the E''_{max} decreased while the maximum tan δ increased. These results partially explained the reason why UF resin adhesive with lower F/U mole ratio resulted in a poor adhesion performance when they were applied to the composite panel manufacturing.

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