Dynamic Mechanical Analysis of Urea–Formaldehyde Resin Adhesives with Different Formaldehyde-to-Urea Molar Ratios

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ABSTRACT: As a part of abating formaldehyde emissions of urea–formaldehyde (UF) resin adhesives, using dynamic mechanical analysis (DMA), we attempted to investigate the influence of the formaldehyde to urea (F/U) molar ratio on the thermomechanical curing of UF resin adhesives with different F/U molar ratios. The thermomechanical curing of these UF resin adhesives was characterized with DMA parameters such as the gel temperature, maximum storage modulus, peak temperatures of the storage and loss moduli, and maximum tan δ. As the F/U molar ratio decreased, the gel temperature of UF resin adhesives increased, whereas the maximum storage modulus, an indicator of the rigidity of UF resin adhesives, decreased. The maximum tan δ increased with the F/U molar ratio decreasing, and this indicated that the UF resin adhesive with a low F/U molar ratio had greater damping than the one with a high F/U molar ratio. A decrease in the rigidity of the UF resin with a lower F/U molar ratio was explained by the calculated crosslinking density, which decreased with the F/U molar ratio decreasing. These results partially explained why UF resin adhesives with lower F/U molar ratios showed relatively poor adhesion performance when they were applied to the manufacture of wood panels. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 2045–2051, 2008

Key words: crosslinking; curing of polymers; resins; synthesis; thermal properties

INTRODUCTION

Urea–formaldehyde (UF) resin adhesives are most widely used for the manufacture of wood-based composite panels and particularly for plywood, particleboard, and medium-density fiberboard. Therefore, UF resin adhesives are considered as one of the most important wood adhesives and are mainly used for the production of wood-based composite panels. In the Republic of Korea, the production of formaldehyde-based resins was about 207,000 tons in 2005, which is 39% of the total production of adhesives. The production of UF resin adhesives was about 75% (i.e., about 155,000 tons) of the total production of formaldehyde-based resin adhesives.

UF resin adhesives are polymeric condensation products of formaldehyde with urea. The synthesis of a UF resin is commonly performed by a two-step procedure, that is, addition and condensation reactions. The addition reaction, or the so-called methylolation reaction, leads to the formations of monomethylol urea, dimethylol urea, and trimethylol urea under alkaline conditions. The condensation reaction under acidic conditions produces methylene or dimethylene ether linkages.[1]

UF resin adhesives possess some advantages such as fast curing, good performance in panels, water solubility, and a lower price. Disadvantages of using UF resin adhesives 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 resins and the hydrolytic degradation of UF resins under moisture conditions are known to be responsible for FE from wood-based panels.[2] In other words, unreacted formaldehyde in a UF resin after its synthesis could be emitted from wood panels even after hot-pressing at a high temperature. In addition, the reversibility of the aminomethylene link and its susceptibility to hydrolysis also explain the lower resistance against the influence of water and moisture and subsequently FE.[3] Therefore, the FE issue has been one of the most important issues for UF resins in the last few decades.[4–9]

Much attention has been paid to reducing or controlling FE from UF-resin-bonded panels through resin technologies. Therefore, lowering the formaldehyde to urea (F/U) molar ratio for the synthesis of UF resins has been adopted as one of the approaches to reducing FE of UF-resin-bonded panels.[8] An

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excellent literature review on the influence of the F/U molar ratio on FE as well as panel properties has been made.[10] According to the review, the gel time, used as an indicator of the resin reactivity, increased with a decreasing F/U molar ratio. In general, UF resin adhesives of lower F/U molar ratios reduce the emission of formaldehyde from the panel at the expense of deteriorated panel properties, particularly the internal bond strength and thickness swelling after water immersion for 24 h.[8,10–12]

In recent years, lower F/U molar ratios from 1.1 to 1.2 have started to be used for resin synthesis.[10] It was reported that an F/U molar ratio close to 1.0 produced quite similar structures and performance in a UF resin, and this led to the conclusion that the most important factor in the synthesis of UF resins was the F/U molar ratio.[13] However, the reason that UF resin adhesives with lower F/U molar ratios resulted in the deterioration of panel properties at the expense of lower FE was not fully explained.

Different methods of characterizing the curing behavior of UF resins have been employed. For example, thermal analysis includes thermogravimetric analysis,[14] differential thermal analysis,[15,16] differential scanning calorimetry (DSC),[17,18] and dynamic mechanical analysis (DMA).[19–22]

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

A UF resin adhesive becomes a thermosetting polymer via curing processes such as gelation, vitrification, and devitrification. The gel of a UF resin is a point of infinitely increasing molecular weight of the resin that drastically reduces resin flow and greatly increases its viscosity. After the gel, the UF resin continues to cure to reach a glass-transition temperature (T_g) at which the rubbery–elastic state of the UF resin changes to a glassy state. Thus, DMA could be used to monitor these curing processes of UF resins. For example, DMA as a tool for characterizing thermosetting adhesives has been widely used for phenol–formaldehyde (PF) resin adhesives.[19–22] Earlier work on PF resin showed that the results of DMA could be related to the degree of cure of PF resin adhesives and to the performance of wood composites.[22] The use of DMA also provided a characterization tool for PF resins, including the cure time, vitrification time, and other useful parameters.[21] In particular, the maximum of tan δ was interpreted as the vitrification point of a PF resin.[21] It was found that the area under the tan δ curve during isothermal scanning was related to an inverse of the measure of precure of a PF resin.[19,20]

By contrast, limited work has been done on the thermomechanical curing behavior of UF resin adhesives.[23–26] For example, DMA has been used for amine-modified UF resins,[23] low-level melamine fortification of UF resins,[24] and thermomechanical curing of different wood adhesive systems.[25]

Even though many authors have investigated the thermomechanical curing of UF resin adhesives, there are limited thermomechanical data available for UF resins prepared with different F/U molar ratios. Therefore, this study was conducted to investigate the influence of the F/U molar ratio on the thermomechanical curing behavior of UF resins with DMA as a part of abating the FE of UF resin adhesives.

EXPERIMENTAL

Preparation of UF resin adhesives

All UF resins used for this study were prepared in the laboratory by the traditional alkaline–acid two-step reaction. Formaldehyde (37%) was placed in the reactor and heated to 60°C, and then the reaction pH was adjusted 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 h. 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 to obtain F/U molar ratios of 1.6, 1.4, 1.2, and 1.0. For all resins prepared, the final pH was adjusted to 8.0 after the cooling.

Methods

Properties of the prepared UF resins

Nonvolatile solid content, pH, and viscosity measurement. About 1 g of a UF resin was poured into a disposable aluminum dish and then dried in a convective oven at 105°C for 3 h. The nonvolatile solid content was determined by the measurement of the weight of the UF resin before and after drying. An average of three replications was presented. The pH of the UF resin after synthesis was measured with an electronic pH meter at 25°C. The viscosity of the UF resin adhesives at 25°C was measured with a cone–plate viscometer (DV-II+, Brookfield, Middleboro, MA) with a no. 2 spindle at 60 rpm.

The UF resin (50 mL) in a mass cylinder was weighed to obtain its density at 25°C. The specific

gravity of the UF resin was determined by the division of the UF resin density by the density of water at 25°C. An average of three replications was presented.

Gel time measurement. The gel time was measured by the addition of 3 wt % ammonium chloride (NH_4Cl; 20 wt % solution) as a hardener at 100°C with a gel time meter. The measurements were performed with a gel time meter (Sunshine, Philadelphia, PA) with three replications for each UF resin with a different F/U molar ratio.

Determination of free formaldehyde. Free formaldehyde in the prepared UF resins was determined by a slightly modified sodium sulfite method.[27] A solution of 25 mL of 1*M* sodium sulfite mixed with 10 mL of HCl was added to 2–3 g of a UF resin sample dissolved in 100 mL of distilled water. The mixed solution, containing about 10 drops of 0.1% thymolphthalein, was neutralized with 1*N* sodium hydroxide. The percentage of free formaldehyde was determined by the equivalent of the amount of the consumed sodium hydroxide in titration.

Sample preparation for DMA

Because a UF resin adhesive is in an aqueous solution state, the use of DMA requires the solidification of the resin adhesive 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 temperatures (up to 300°C), not be hygroscopic, and have a porous structure.[20] A borosilicate glass microfiber filter (GF/C, Whatman, Fairlawn, NJ) was selected for the UF resin adhesive impregnation in this study.

For the sample preparation, 3% NH_4Cl (20% solution) was added to samples of UF resin adhesives with different F/U molar ratios based on the nonvolatile resin solid content and then thoroughly mixed. The glass microfiber filter (90 mm wide and 0.3 mm thick) was impregnated with the prepared resin and then dried at room temperature for 2 h. Preliminary experiments showed that the optimum resin loading ratio was 1.0 mg/mm^3. The air-dried glass filter was cut to a length of 60 mm and a width of 13 mm and then further dried for 48 h in a desiccator with phosphorous pentoxide (P_2O_5). A drying time shorter or longer than 48 h caused problems of sticking to the instrument or easy breaking of specimens. Prepared specimens were put on the grips of a DMA instrument (Diamond DMA7, PerkinElmer, Waltham, MA).

DMA measurements. All DMA measurements were made in a bending mode with the specimen clamped in a horizontal plane between the ends of two parallel arms. A fixed displacement mode with a 0.3-mm amplitude and a 1-Hz oscillation frequency was used. For a dynamic scan of DMA, the temperature was increased from room temperature to 300°C at a heating rate of 10°C/min. Nitrogen gas was used to prevent any oxidation of the sample and to purge the DMA chamber at a rate of 200 mL/min. Duplicate scans were made for each UF resin adhesive, and this resulted in similar curves without any significant difference. Thermomechanical parameters such as E', E', and tan δ (i.e., E''/E') were obtained from DMA curves.

RESULTS AND DISCUSSION

The properties of UF resins prepared at different F/U molar ratios are summarized in Table I. The nonvolatile solid content of UF resins prepared at different F/U molar ratios ranged from about 53 to 57 wt %. The specific gravity and pH values of the UF resins were not much different for the F/U molar ratios. However, the viscosity and gel time of the UF resin adhesives showed contrasting results. As the F/U molar ratio decreased, the viscosity and amount of free formaldehyde decreased, whereas the gel time increased. This result is quite reasonable because the reaction between urea and formaldehyde was much faster at a high F/U molar ratio, which resulted in a high-molecular-weight species of faster gelling in a given time. Another reason could be the amount of free formaldehyde in the UF resin after its synthesis. A greater amount of free formaldehyde in the UF resin produced more acids in curing when a hardener (usually NH_4Cl) was added, and this made the UF resin gel faster.[28]

Figure 1 shows DMA curves of UF resin adhesives with the F/U molar ratio of 1.0. Definitions of the thermomechanical parameters are also given in Figure 1. E' decreased to a minimum (E'_{min}) and then

TABLE I
Properties of UF Resins with Different F/U Molar Ratios

F/U molar ratio	Nonvolatile solid content (%)	pH	Specific gravity	Viscosity (mPa s)	Gel time at 100°C (s)	Free HCHO (%)
1.6	53.5	7.6	1.17	153.3	56	0.69
1.4	54.1	7.6	1.17	104.0	79	0.38
1.2	54.6	7.7	1.18	83.3	118	0.30
1.0	57.6	7.8	1.18	74.7	134	0.27

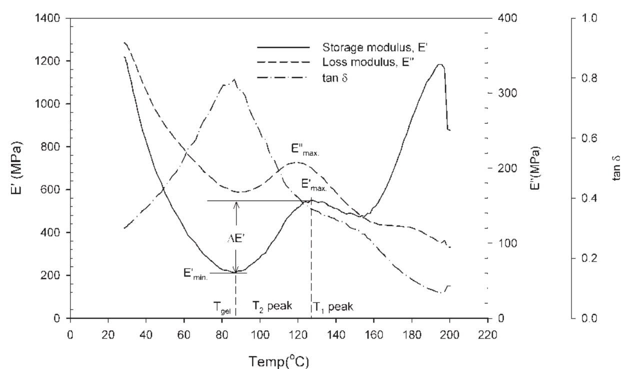

Figure 1 DMA curves of UF resins with an F/U molar ratio of 1.0.

increased to a maximum (E'_{max}) as the temperature increased. The difference between E'_{min} and E'_{max} was defined as $\Delta E'$. The temperature at which E' reached its minimum was defined as the gel temperature of the UF resin adhesive. The peak temperatures at which E'_{max} and the maximum loss modulus (E''_{max}) were reached were defined as the T_1 and T_2 peak temperatures, respectively.

As shown in Figure 1, the rigidity, represented as 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 increased. After E'_{min}, E' started to increase toward a maximum. This was possibly due to the gelation of the UF resin adhesive, during which an infinite molecular network began to be formed. Thus, this temperature was presented as the gel temperature. A similar definition of the gel time has been reported for an isothermal scanning of melamine-modified UF resins.[24]

An increase of E' after the minimum could possibly be ascribed to the change of the network structure of the UF resin adhesive from a gel state to a glassy state in which the amount of crosslinking increased as it went through the curing process. A decrease of E' after the maximum could be due to combined effects of many factors. One of the factors might be devitrification of the UF resin after its T_g. Another factor could be hydrolytic or thermal degradation of the UF resin as the temperature increased. Thus, as the resin adhesive went through gelation, E' continuously increased to a maximum at which the resin became vitrified. A further increase in the temperature resulted in a decrease of E', which could have resulted from devitrification of the UF resin.

Figure 1 also shows the presence of two peaks of E'. This observation could be explained by the curing process of the UF resin. In other words, the first peak occurred because of vitrification after its gelation, whereas the second peak might be due to another vitrification followed by devitrification. Further work is necessary to understand the presence of these two peaks.

E'' of the UF resin adhesive with the F/U molar ratio of 1.0 followed changes similar to those of E'. An initial decrease of E'' could be due to the softening of the UF resin as the rigidity decreased. E'' started to increase after reaching the minimum. This result also reflected the gelation of the UF resin, during which the polymerization reaction started to form a network, which resulted in efficient energy dissipation.

The E' curves of UF resin adhesives with different F/U molar ratios are shown in Figure 2. All the E' curves had similar patterns as the temperature increased. In other words, E' initially decreased to a minimum and then reached a maximum followed by a decrease. Figure 2 also shows the change of E'_{max} of UF resin adhesives, depending on the F/U molar ratio. As the F/U molar ratio decreased, E'_{max} increased to a maximum at the F/U molar ratio of 1.4 and then continuously decreased. This result indicated a reduction of the rigidity of the UF resin as the F/U molar ratio decreased. In particular, a lower E'_{max} value of the UF resin with a lower F/U molar ratio of 1.0 could have provided the resin adhesive with lower cohesive adhesion strength. This result partially explains a deterioration of the internal bond strength of particleboard bonded with UF resins of lower F/U molar ratios.[10,18]

However, E'_{min} slightly decreased with a decreasing F/U molar ratio and showed not much difference. $\Delta E'$, the difference between E'_{min} and E'_{max}, also increased up to the F/U molar ratio of 1.4 and then decreased. This result indicated that $\Delta E'$ was mainly dependent on E'_{max} rather than E'_{min}. In other words, the influence of the F/U molar ratio on the rigidity was more predominant on E'_{max} than E'_{min}. Therefore, $\Delta E'$ could be used as an indicator of the rigidity

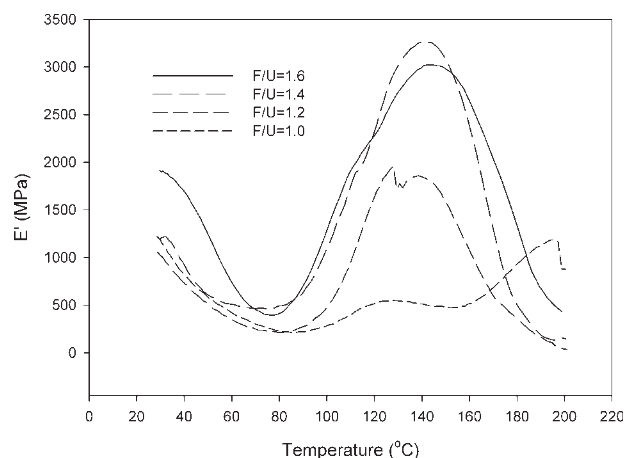

Figure 2 Typical E' curves of UF resins with different F/U molar ratios.

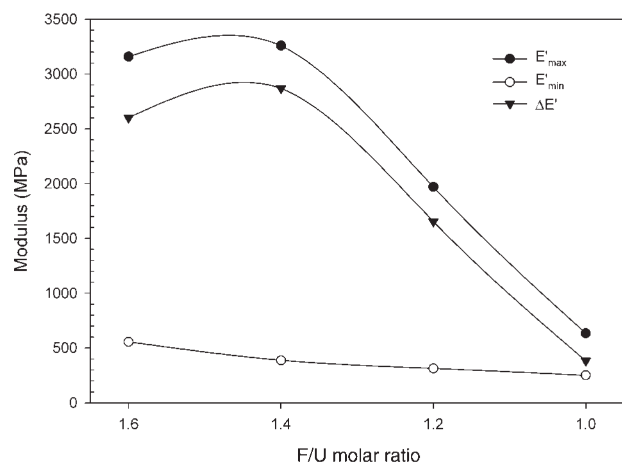

Figure 3 E'_{max}, E'_{min}, and $\Delta E'$ of UF resins with different F/U molar ratios.

of UF resins. In fact, $\Delta E'$ was used as a stiffening coefficient for the comparison of thermomechanical behaviors of different adhesive systems.[25]

Figure 3 shows E''_{max} of UF resin adhesives depending on the F/U molar ratios. E''_{max} showed a pattern similar to that of E'_{max} with a decreasing F/U molar ratio. E'' contributes the energy dissipation due to molecular friction because of the viscose flow of a material. Thus, the result indicated that the molecular friction of the cured UF resin adhesive was reduced as the F/U molar ratio decreased. A similar result was reported for a PF resole resin.[21] This could be attributed to the more branched network structure of a UF resin with a higher F/U molar ratio in comparison with those of lower F/U molar ratios. In other words, it seems that a UF resin of a lower F/U molar ratio was more flexible than those of higher F/U molar ratios, which required less energy dissipation under the oscillation. In fact, it was reported that UF resins with an F/U molar ratio of 1.0 were predominantly composed of linear methylene linkages.[29]

Figure 4 shows the gelation temperature and peak temperature of tan δ of UF resin adhesives versus the F/U molar ratio. In general, the gel temperatures of the UF resin adhesives increased with a decreasing F/U molar ratio, but they were quite different at F/U molar ratios below 1.4. This result indicated that a higher F/U molar ratio resin reached faster gelling than a lower F/U molar ratio resin, showing greater reactivity for the UF resin of a higher F/U molar ratio. This result is quite compatible with the results of PF resin adhesives[21] and is supported by the results of DSC.[18] The peak temperature of tan δ of the UF resin also showed a pattern similar to that of the gel temperature. This could be due to the gelation of the UF resin adhesive as the UF resin adhesive started to increase the amount of crosslinking.

Figure 5 shows peak temperatures of both E' and E'' of DMA curves. The T_1 and T_2 peak temperatures are the peak temperatures of E'_{max} and E''_{max}, respectively. As the F/U molar ratio decreased, the T_1 peak temperature slightly increased up to the F/U molar ratio of 1.4 and then gradually decreased afterward. This result suggests that the UF resin with an F/U molar ratio of 1.6 reached maximum rigidity faster than the other UF resins, and this resulted in a decreased T_1 peak temperature of E'. In other words, a decreased T_1 peak temperature with a decreasing F/U molar ratio could be due to a smaller value of E'_{max} of the UF resin with a lower F/U molar ratio. By contrast, the T_2 peak temperature gradually increased as the F/U molar ratio decreased. This result indicated that as the F/U molar ratio decreased, it took more time for

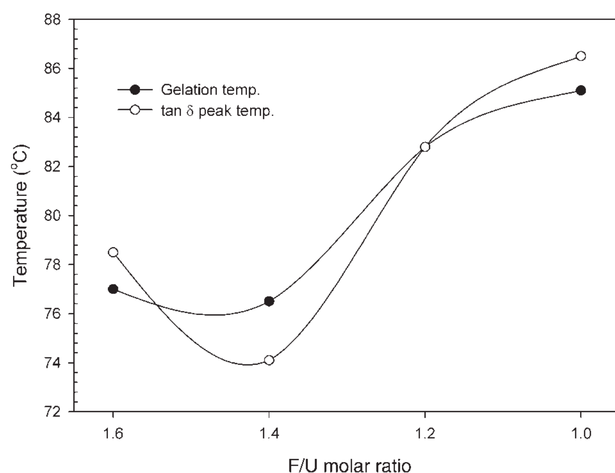

Figure 4 Gel temperature and peak temperature of tan δ of UF resins with different F/U molar ratios.

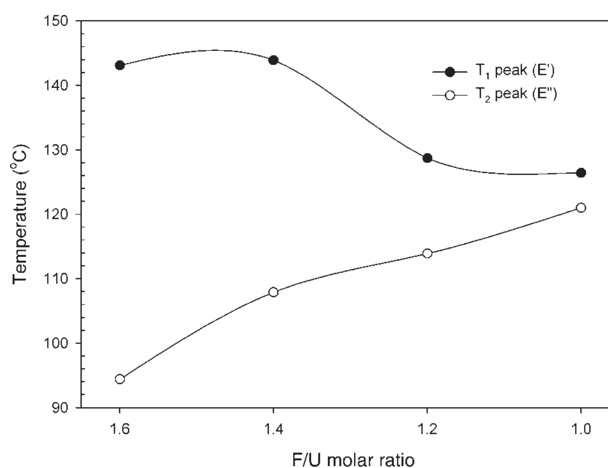

Figure 5 Peak temperatures of both E' and E'' of UF resins with different F/U molar ratios.

UF resins to reach the point of maximum energy dissipation.

The maximum tan δ of UF resin adhesives, depending on the F/U molar ratios, is shown in Figure 6. As the F/U molar ratio decreased, the maximum tan δ proportionately increased with the F/U molar ratio. As shown in Figure 1, the gelling of the UF resin resulted in a minimum E' value and a maximum tan δ value around the same temperature. In general, the maximum tan δ results from the gelling or vitrification of a thermosetting resin. Thus, this result could be due to increasing gel temperatures as the F/U molar ratio decreased. Furthermore, an increase of the maximum tan δ with a decreasing F/U molar ratio suggested that an elastic component of the UF resin decreased whereas a viscose component increased under oscillation. In other words, the damping behavior of the UF resin increased with the decreasing F/U molar ratio. A greater amount of the energy used to deform was dissipated into heat in the UF resin of a lower F/U molar ratio than in the one of a high F/U molar ratio.

The kinetic rubber theory of elasticity makes it possible to calculate the experimental value of the crosslinking density (ρ_c) on the basis of E' of DMA with the following equation:[30,31]

$$E' = 3\rho_c RT$$

where E' is the storage modulus at $T_g + 40°C$ in the rubbery plateau, R is the gas constant, and T is the absolute temperature (K). In this study, the gel temperature of UF resins was assumed to be T_g for the calculation of ρ_c of UF resins. The calculated results are shown in Figure 7. As expected, ρ_c of the UF resin decreased with a decreasing F/U molar ratio. This result provided a theoretical background explaining the lower rigidity of the UF resin with the lower F/U molar ratio. Furthermore, it was believed that this would have also contributed to the poor adhesion performance of the UF resin with the lower F/U molar ratio when it was applied to particleboard manufacture.

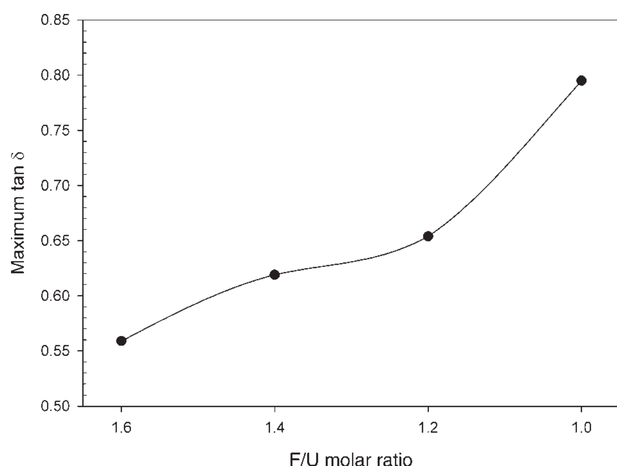

Figure 6 Maximum tan δ values of UF resins with different F/U molar ratios.

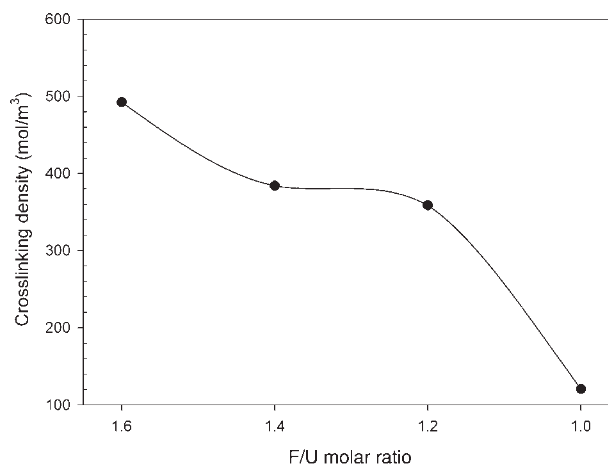

Figure 7 Calculated crosslinking density of UF resins with different F/U molar ratios.

CONCLUSIONS

As a part of abating FE of UF resin adhesive bonded wood-based panels, using DMA, we attempted to investigate the effects of the F/U molar ratio on the thermomechanical curing of UF resin adhesives with different F/U molar ratios such as 1.6, 1.4, 1.2, and 1.0. As the F/U molar ratio decreased, the thermomechanical parameters of DMA changed as follows: The gel temperature of the UF resin adhesives increased. E'_{max} as an indicator of the rigidity of UF resin adhesives increased to a maximum and then decreased. The T_1 peak temperature of E' decreased, suggesting faster vitrification of a UF resin of a lower F/U molar ratio. The maximum tan δ increased with a decreasing F/U molar ratio, indicating that a UF resin adhesive of a low F/U molar ratio had greater damping than one of a high F/U molar ratio. The calculated ρ_c values of the UF resin decreased with a decreasing F/U molar ratio. These results partially explained why a UF resin adhesive with a lower F/U molar ratio resulted in poor adhesion performance when it was applied to the manufacture of wood panels.

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