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Adhesion Properties of Urea-Melamine-Formaldehyde (UMF) Resin with Different Molar Ratios in Bonding High and Low Moisture Content Veneers*1

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ABSTRACT

The objective of this research was executed to investigate the effect of molar ratio of formaldehyde to urea and melamine (F/(U+M)) of urea-melamine-formaldehyde (UMF) resin on bonding high and low moisture content veneers. For that purpose, UMF resin types with 5 different F/(U+M) molar ratios (1.45, 1.65, 1.85, 2.05, and 2.25) synthesized were used in present study. First, their curing behavior was evaluated by differential scanning calorimetry. Second, their adhesion performance in bonding high and low moisture content veneers was evaluated by probe tack and dry and wet shear strength tests. Curing temperature and reaction enthalpy decreased with the increase of F/(U+M) molar ratio. And the dry and wet shear strengthsof plywood manufactured from low moisture content veneers were higher than thoseof plywood manufactured from high moisture content veneers. Also, the maximum initial tack force on the low moisture content veneer was higher than that on the high moisture content veneer.

Keywords : urea-melamine-formaldehyde resin, adhesion performance, moisture content, veneer

1. INTRODUCTION

Veneer is essentially not different from lumber in the basic wood properties. The surface properties of veneer, however, can be drastically altered physically and chemically by cutting, drying, laminating into plywood, etc. in plywood manufacturing process. Thus, special knowledge and attention to these characteristics are required to ensure good wetting, flow, and penetration of adhesive.

Generally, conventional adhesives show satisfactory adhesion performance in the moisture content of veneer ranging from 6 to 14%. When an adhesive is specially formulated, however, the same result can be obtained even below and above this moisture content range. The optimum moisture content level for bonding a specific product with a specific adhesive is determined from practical experience and product performance.

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Aqueous adhesive tends to dry out when applied to wood below 6% moisture content (Simpson *et al.*, 1999). Bonding high moisture content veneers is a relatively new concept. Urea-formaldehyde (UF) plywood manufactured from veneers with moisture content of 18～20% in Japan and phenol-formaldehyde (PF) plywood produced from veneers with moisture content of 15～20% in America are the examples (Shi *et al.*, 1997). In bonding high moisture content wood, various methods can be used. For example, the methods of drying the wood surfaces with heated platens or air (Murphey *et al.*, 1971), grafting resorcinol onto a known glucose-urea-phenol-based resole (Clark, 1988), adding the resorcinol resin into PF resin (Shi *et al.*, 1997), and using one-component moisture curing isocyanate resin (Huang, 2005) etc. can be effective.

Hence, the present study was performed to investigate the effect of molar ratio of formaldehyde to urea and melamine (F/(U+M)) of urea-melamine-formaldehyde (UMF) resin on bonding high and low moisture content veneers.

2. MATERIALS AND METHODS

2.1. Synthesis of UMF Resin

To discuss the effect of molar ratio of formaldehyde (F) to urea (U) and melamine (M) of urea-melamine-formaldehyde (UMF) resin on bonding high and low moisture content veneers, the UMF resin types with 5 different F/(U+M) molar ratios (1.45, 1.65, 1.85, 2.05, and 2.25) were synthesized as follows. First, the base urea-formaldehyde (UF) resin with formaldehyde to urea (F1/U1) molar ratio of 1.42 was synthesized by reacting formaldehyde (F1) and urea (U1) at a pH of 8～9, and then a pH of 6.4 at a temperature of 90°C according to the conventional alkaline-acid method. Second, the intermediate UMF resin with formaldehyde to urea and melamine ((F1+F2)/(U1+M1)) molar ratio of 1.69 was synthesized by adding melamine (M1) and second formaldehyde (F2) to the base UF resin at a pH of 6.4 and a temperature of 90°C, and then adjusted to pH of 9.5 and cooled at room temperature. Finally, the resin type of $UMF_{1.45}$ with formaldehyde to urea and melamine ((F1+F2)/(U+M1+M2)) molar ratio of 1.45 was prepared by adding second melamine (M2) to the intermediate UMF resin. The other resin types of $UMF_{1.65}$, $UMF_{1.85}$, $UMF_{2.05}$, and $UMF_{2.25}$ were also made following the same procedure except for the adjustment of molar ratio of (F1+F2)/(U+M1+M2) to 1.65, 1.85, 2.05, and 2.25 in the final stage.

2.2. Wood Veneers

Rotary-cut softwood veneers with dimension of 300 × 300 × 2.1 mm and sliced hardwood veneers with dimension of 300 × 300 × 0.55 mm were used to produce 7-ply plywood consisting of 5 rotary-cut core veneers and 2 sliced face veneers in present study. The rotary-cut and sliced veneers were classified into two groups of 5～10% and 16～18% based on moisture content. The rotary-cut and sliced veneers with 5～10% moisture content were supplied from a company in South Korea and those with 16～18% moisture content were prepared by conditioning the veneers with 5～10% moisture content in a temperature & humidity chamber. The rotary-cut veneers with 5～10% and 16～18% moisture content and sliced veneers with 5～10% moisture content were used in plywood manufacture. The sliced veneers with 5～10% and 16～18% moisture content were used for probe tack test.

2.3. Differential Scanning Calorimetry (DSC)

Curing exotherm of UMF resin was determined through DSC analysis by the aid of a TA Instruments model Q-1000 equipped with a Thermal Analysis Data Station. This analysis was done using a sealed liquid type aluminum capsule pan under nitrogen atmosphere at 10°C/min. between 25°C and 200°C.

2.4. Probe Tack Test for Initial Tack

The UMF resin with different F/(U+M) molar ratios were coated onto sliced veneers with moisture content of 16～18% and 5～10% with a bar coater (PCT-200). Tack tests for initial tack were executed using a Texture Analyzer (TA-XT2i, Stable Micro Systems, Surrey, England) with a polished stainless steel cylindrical probe of 5 mm in diameter. Measurements were practiced at an open time of 5 min. and brought in contact with the probe at a probe contact time of 1 sec. and at a contact pressure of 100 g/cm^2. The probe was approached to the resin at a constant velocity (V_{app} = 10 mm/s) and was removed at a constant velocity (V_{deb}) of 0.5 mm/sec. This tack test was conducted in a constant temperature & humidity room at a temperature of 20°C and relative humidity of 50%.

2.5. Temperature of Adhesive Layer Inside and Outside of Plywood

Temperature was measured by inserting the sensor of digital thermometer into the innermost and outermost glue line of plywood.

2.6. Scanning Electron Microscope (SEM)

The adhesive depth of penetration into wood cells was determined using a mini-SEM (SNE-3000M). The acceleration potential used during this investigation was 20 kv. The samples were coated with gold to eliminate electron charging before measurement.

2.7. Plywood Shear Strength Test

For measuring shear strength, 7-ply plywoods, 300 × 300 × 2.1 mm, consisting of 5 rotary-cut core veneers and 2 sliced face veneers were manufactured from rotary-cut veneers with moisture content of 16～18% and 5～10% and sliced veneers with moisture content of 5～10%. Based on the solid weight of UMF resin, the adhesive was prepared by adding ammonium chloride powder and wheat flour in the proportion of 1% and 10%, respectively. Spread, i.e. the amount of prepared adhesive per unit area of wood surface, was 17 g/30 × 30 cm^2. Cold-pressing was taken for 30 min. at a pressure of 1 kg/cm^2, followed by hot-pressing at a pressure of 10 kg/cm^2, a temperature of 120°C, and a time of 20 sec./mm of thickness. The shear strength was measured in conformance with the procedure of Korean Standard (KS F 3101).

3. RESULTS and DISCUSSION

3.1. Differential Scanning Calorimetry (DSC)

The DSC curve of UMF resin by F/(U+M) molar ratio are shown in Fig. 1 And Fig. 2 shows the reaction enthalpy ($\triangle$H) which is proportional to the degree of conversion (α) during the curing process (Xing *et al.*, 2005) and the curing temperature which is the temperature at which the conversion rate reaches the maximum during the dynamic scan of the reaction. As shown in Fig. 2, the curing temperature and reaction enthalpy ($\triangle$H) decrease with the increase of molar ratio of F/(U+M) of UMF resin. In

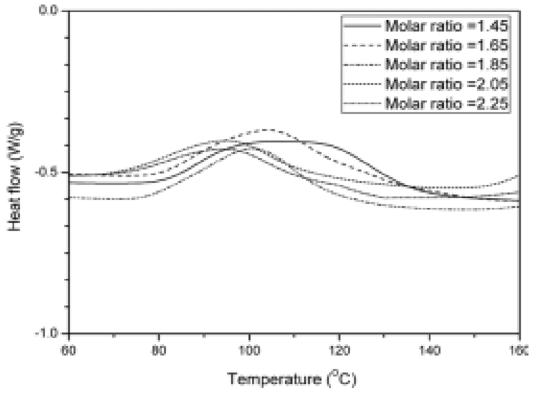

Fig. 1. DSC thermograms of UMF resin by F/(U+M) molar ratio.

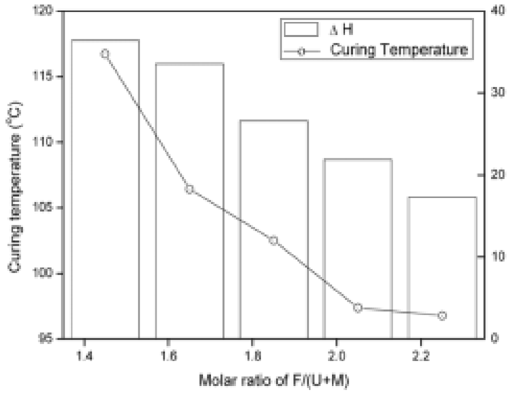

Fig. 2. Curing temperatures and reaction enthalpies (△H) of UMF resin by F/(U+M) molar ratio.

general, the curing of UMF resin was reported to involve the release of hydrochloric acid (HCl) through the reaction of NH_4Cl with formaldehyde, and this acid would bring the pH to very low level and speed up the curing rate (Higuchi *et al.*, 1979; Pizzi, 1983). Because free formaldehyde increased and consequently hydrochloric acid (HCl) released through the reaction of NH_4Cl with formaldehyde increased with the increase of molar ratio of F/(U+M) of UMF resin, the curing of UMF resin could be accelerated. This may mean that the UMF resin with higher F/(U+M) molar ratio requires lower curing temperatures. Also, the UMF resin of higher F/(U+M) molar ratio could produce more di hydroxymethylureas and trihydroxymethylureas and have the higher molecular weight with longer chains of methylene (-CH_2-) and methylene ether (-CH_2-O-CH_2-) bridges or much more branched chains, and thus the released energy might be reduced.

3.2. Probe Tack Force

Fig. 3 shows the maximum initial tack force of UMF resin by the F/(U+M) molar ratio at various open assembly times. With the increase of open assembly time, the water loss and the hardening reaction in the resin began to occur, and thus the viscosity and maximum initial tack force of resin would increase. With further loss of water from the resin, however, the maximum initial tack force decreased. As shown in Fig. 3, maximum initial tack force of UMF resin coated onto sliced veneer with 5～10% moisture content reaches maximum value faster than that with 16～18% moisture content, and the maximum value of the former is larger than that of the latter except for the UMF resin with the F/(U+M) molar ratio of 1.45. This is in partially agreement with Kim *et al.* (2005) and thought to be attributed to the more water absorption from the glue line by veneer with 5～10% moisture content of than that with 16～18% moisture content. Therefore, the veneer with higher moisture content was thought to be disadvantageous in allowing wet resin to tack the veneers together in cold-pressing

3.3. Temperature of Adhesive Layer Inside and Outside of Plywood

The temperatures of the innermost and outermost glue line of plywood by hot-pressing time are shown in Fig. 4. The innermost glue line was observed to be lower in the temperature

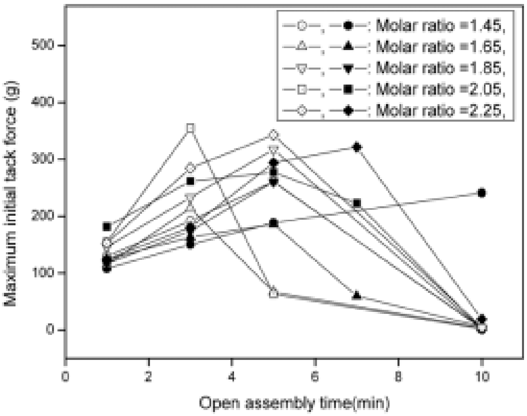

Fig. 3. Relationship of open assembly time and maximum initial tack force of UMF resin on sliced veneer by F/(U+M) molar ratio (○, △, ▽, □, ◇ : veneer with 5～10% moisture content ●, ▲, ▼, ■, ◆ : veneer with 16～18% moisture content).

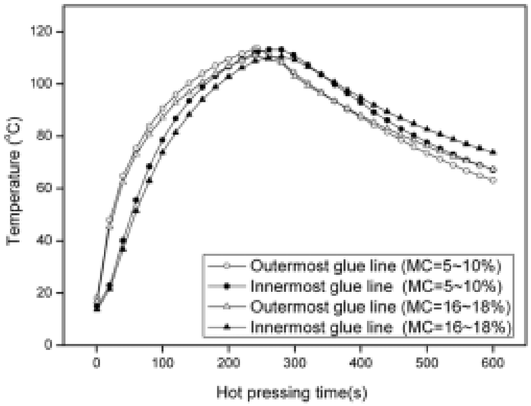

Fig. 4. Temperature of the innermost and outermost glue line of plywood by hot-pressing time.

than the outermost glue line, and this was thought to be attributed to the difference of heat transfer from hot platens to the innermost and outermost glue line of plywood during hot-pressing. Also, the plywood manufactured from high moisture content veneers was lower in the temperature than that produced from low moisture content veneers, which seemed to be caused by the difference of moisture content between the innermost and outermost glue line in plywood.

3.4. Scanning Electron Microscopy (SEM)

The SEM microscopic images of the innermost glue line of plywood are shown in Fig. 5. The penetration of resin into the veneer was deeper in plywood manufactured from veneers with 16～18% moisture content than in that produced from veneers with 5～10% moisture content veneers, like the report of Pommier (2005) who noted that it was possible to see a deeper penetration of adhesive in green wood (4 cells) compared with dry wood (2 cells) in the finger joints glued with the green and dry wood.

3.5. Plywood Shear Strength

Fig. 6 shows the dry and wet shear strengths of plywood glued with UMF resin by F/(U+M) molar ratio. In general, the dry shear strength of plywood increased but the wet shear strength decreased with increasing the F/(U+M) molar ratio. The increased dry shear strength seemed to be related to the increase of hydroxymethyl groups with the increase of F/(U+M) molar ratio because the hydroxymethyl group formed more covalent bonding with the hydroxyl group of wood. The decreased wet shear strength was thought to be caused by the hydrolysis of the hydroxymethyl group in the boiling water. In present study, the dry shear strengths of plywood manufactured from high and low moisture content veneers showed no significant increase with the increase of F/(U+M) molar ratio. Only the wet shear strength of plywood manufactured from high moisture content veneers showed a tendency to decrease slightly.

On the other hand, the plywood manufactured

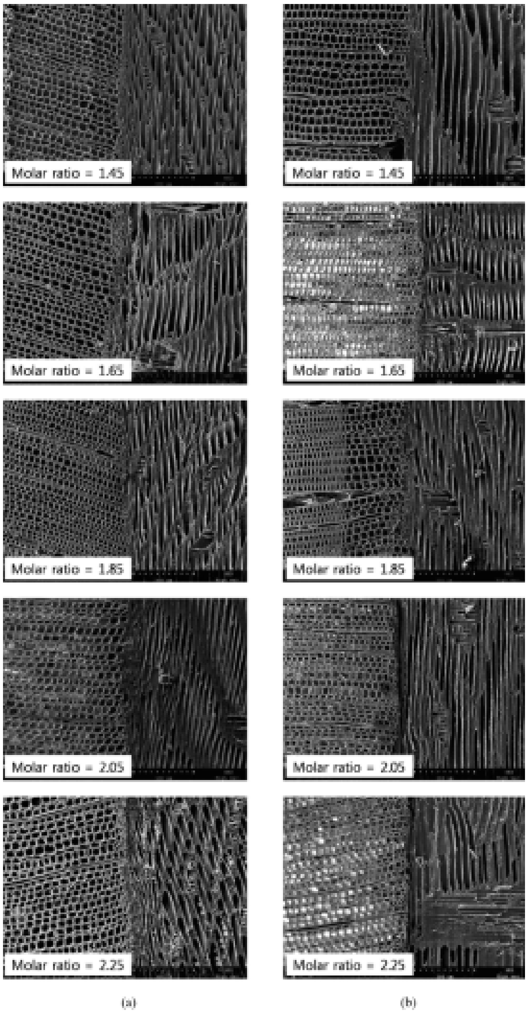

Fig. 5. SEM images showing the innermost glue line of plywood manufactured from veneers with 5～10% (a) and 16～18% (b) moisture content.

from veneers with 5～10% moisture content was higher in the dry and wet shear strengths than that produced from veneers with 16～18% moisture content. This result was thought to be attributed to the lower temperature, less hardening, and more starved joints in the glue lines due to more water in the plywood produced from high moisture content veneers during hot-pressing.

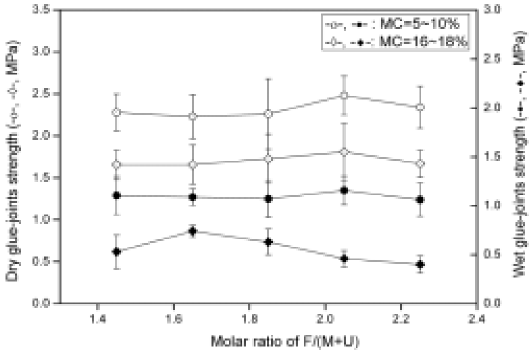

Fig. 6. Dry and wet shear strengths of plywood by F/(U+M) molar ratio of UMF resin.

4. CONCLUSIONS

This study was conducted to investigate the effect of F/(U+M) molar ratio of UMF resin on bonding high and low moisture content veneers under general hot-pressing condition. Curing temperature and reaction enthalpy decreased with the increase of F/(U+M) molar ratio. And the dry and wet shear strengths of plywood manufactured from low moisture content veneers were higher than those of plywood manufactured from high moisture content veneers. Also, the maximum initial tack force on the low moisture content veneer was higher than that on the high moisture content veneer.

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