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Original Article

Effect of Urea-Formaldehyde Resin Adhesive Viscosity on Plywood Adhesion[1]

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ABSTRACT

This work was conducted to investigate on the effect of urea-formaldehyde (UF) resin viscosity on plywood adhesion. The viscosity of UF resin was controlled either by adjusting the condensation reaction during its synthesis to obtain different target viscosities (100, 200 and 300 mPa.s) at two levels of formaldehyde/urea (F/U) mole ratios (1.0 and 1.2) or by adding different amounts (10, 20 and 30%) of wheat flour into the resins for the manufacture of plywood. When the viscosity of UF resin increased by the condensation reaction, the adhesion strength of plywood bonded with UF resin of 1.2 F/U mole ratio consistently increased, while those bonded with the 1.0 F/U mole ratio resin slightly decreased, suggesting a difference in the adhesion in plywood. However, the adhesion strength of plywood decreased as the viscosity increased by adding wheat flour, regardless of F/U mole ratio. The manipulation of UF resin viscosity by adjusting the condensation reaction was much more efficient than by adding wheat flour in improving the adhesion performance of plywood. These results indicated that a way of controlling the viscosity of UF resin adhesives has a great influence to their adhesion in plywood.

Keywords : urea-formaldehyde resin, viscosity, condensation, wheat flour, adhesion

1. INTRODUCTION

Urea-formaldehyde (UF) resin adhesives have been extensively used for the manufacture of wood-based composite panel, such as plywood, medium density fiberboard (MDF) and particleboard (PB). Therefore, UF resin adhesives are regarded as one of the most important types of adhesive in wood-based panel industry. UF resin is a polymeric condensation product of the chemical reaction of formaldehyde with urea, the synthesis of a UF resin is commonly performed by a two-step procedure, that is, addition and condensation reaction. The addition reaction, or methylolation reaction, leads to the formation of monomethylol urea, dimethylol urea, and trimethylol urea under alkaline conditions. Then, the condensation reaction under acidic condition produces methylene or dimethyl ether linkages. Compared to other wood

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

In general, the parameter, influencing the bond strength can be classified into three categories. First, wood-related parameters include wood species, grain direction, diameter of lumen, density, strength of the wood tissue, wettability of wood surface, and surface free energy. Second, resin-related parameters are types and properties of the resin, chemical structure and composition of resin, degree of condensation, molar mass distribution, F/U mole ratio, viscosity, level of adhesive spread, extender such as wheat flour, and rate of resin curing. Third, manufacture process-related parameters are assembly time, temperature in the bond line during a hot press cycle, applied pressure, and press time.

In particular, the viscosity of resin could be one of the most important factors, affecting the bond strength. Commonly, the viscosity of resin is dependent on the size and shape of the adhesive molecules, the solids content of resin adhesive and amount of additives like fillers or extenders. It is also deeply related to the flow of the adhesive and penetration into wood. Therefore, high viscosity of the resin adhesive leads to a poor penetration into the wood, resulting in a decrease in the bond strength (Osemeahon *et al*., 2007; Gavrilović-Grmuša *et al*., 2010a, b, 2012) A similar result was also published by Nuryawan *et al.* (2014) who reported that a greater F/U mole ratio and higher viscosity of UF resin adhesives led to an increase in the bond-line thickness. Also, Derkyi *et al.* (2008) investigated the influence of extender content on the bond strength of plywood. They used wheat flour and cassava flour as extender, and used five extender levels such as 15.6, 31.2, 46.8, 62.4, and 78.1%. They reported the effect of extender type on plywood bonding strength was insignificant, while the level of extender addition had highly significant effect on the bond strength of plywood.

There are some reviews that have been conducted to investigate characteristics of UF resin adhesive. For example, Myers (1984) reviewed that an influence of F/U mole ratio on the properties of UF resins and wood-based composite panels bonded with them. They found that the gel time as an indicator of resin reactivity increased when the F/U mole ratio decreased, and concluded that lower F/U mole ratio of UF resin caused a loss of panel properties such as bond strength, modulus of rupture (MOR), and thickness swelling. Park *et al.* (2006, 2008) also studied to investigate the influence of F/U molar ratio on thermal curing behavior of UF resin and properties of PB. They found that the gel time, onset and peak temperatures, and heat of reaction ($\triangle$H) increased as the F/U mole ratio decreased from 1.6 to 1.0. But, the properties of PB were also deteriorated with a decrease in the F/U mole ratio of UF resins used.

Although a few research work on the influence of the viscosity and characteristics of UF resin adhesives have been done in the past, studies regarding the effect of UF resin adhesive's viscosity on the adhesion strength of plywood has not been investigated yet. Therefore, the objective of this study was to investigate the effect of UF resins adhesive's viscosity that was controlled either by adjusting the condensation reaction or by adding different amounts of wheat flour into UF resin on the bond strength of plywood.

2. MATERIALS and METHODS

2.1. Synthesis of UF resins

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 40℃ and then adjusted the reaction pH to 7.8-8.0 with sodium hydroxide (20 wt %). Subsequently, 1^{st} urea was placed in the reactor, and the mixture was heated to 90℃ for 1 h. Then, the reaction pH was adjusted to 4.6 with formic acid (20 wt %) for condensation. The condensation reactions were carried out until reached a target viscosity, which was measured using a bubble viscometer (VG-9100, Gardner-Holdt Bubble Viscometer, USA). Once the viscosity was reached, a different amount of 2^{nd} urea was placed in the reactor. After all of the urea had dissolved, the mixture was cooled to 23-25℃, and then the pH was adjusted to 8.1. Different amounts of the second urea were added for the synthesis to obtain the F/U mole ratio of 1.0 and 1.2.

2.2. Viscosity control of UF resins

Two methods of controlling the viscosity of UF resin adhesives were used in this work. Firstly, the viscosity of UF resins was adjusted by controlling the duration of condensation reaction under acidic condition. The condensation reaction was carried out to obtain three target viscosities such as 100, 200 and 300 mPa.s. Secondly, different amounts of wheat flour such as 10, 20 and 30 wt % based on the total mass of the resin were added into the neat UF resin with a viscosity of 200 mPa.s.

2.3. Properties of UF resins

Properties of UF resin such as non-volatile solids content, viscosity and gel time was measured. The non-volatile solid content of UF resin was obtained by drying about 1 gram of UF resin in a oven for 3 hours at 105℃ and by measuring the weight of the UF resin before and after the drying. An average of three replications was presented. The viscosity of UF resins was measured using a viscometer (DV-II+, Brookfield, USA) with spindle no. 2 before the addition of wheat flour and with spindle no. 4 after the addition of wheat flour at 60 rpm at 25℃. The gel time of UF resins was measured at 100℃, as a hardener, using a gel time meter (Davis inotek instruments, Charlotte, NC) after the addition of 3 wt % NH_4Cl (20 wt % solution).

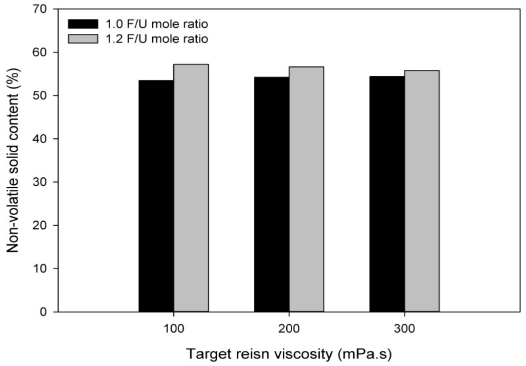

Fig. 1. Non-volatile solids content of UF resins at different viscosities and F/U mole ratios.

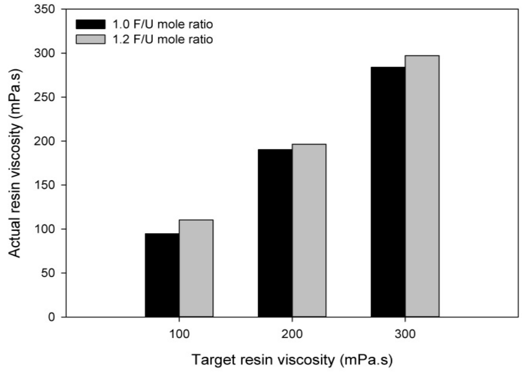

Fig. 2. Relationship between the target and actual viscosity of UF resins at different F/U mole ratios.

2.4. Manufacture of plywood

A calculated amount of the glue mix spread (170 g/m^2) per face were spread onto three veneers (2 mm thick) from *pinus radiata* to make 3-ply plywood. As a control, 10% of the wheat flour were added to all UF resins with different viscosities that were controlled by the condensation reaction during the resin synthesis. By contrast, viscosities of UF resins that had been adjusted by adding different amounts of wheat flour were also used to prepare plywood. And 3% of NH_4Cl based on the non-volatile solids content of UF resins was added to all the resins. And then, all plywoods were cold-pressed under 8 kgf/cm^2 for 20 min, and then hot-pressed for 4 min at 120℃ and 8 kgf/cm^2.

2.5. Tensile shear strength test

Tensile shear strength of plywood was measured by a standard procedure (Korean Standard, KS F 3101, 2006). Nine specimens (25 mm × 80 mm × 6 mm) were prepared for tensile shear strength. Tensile shear strength was calculated using the peak load that had been determined by a universal testing machine (H50KS, Hounsfield, Redhill, England) with a cross head speed of 2 mm/min.

3. RESULTS and DISCUSSION

Properties of UF resins were showed in Figs. 1 ∼ 3. As shown in Fig. 1, the non-volatile solids content increased as the viscosity of the UF resin increased, ranging from about 54 to 56 wt %. Those of UF resins of 1.2 F/U mole ratio were higher than those of 1.0 F/U mole ratio resins. Fig. 2 displays a relationship between the target and actual viscosity of UF resins that has been controlled by the condensation reaction. As expected, the target viscosity measured by the bubble viscometer scale was quite consistent with the actual viscosity of UF resins after their synthesis. But, the viscosity of UF resins of 1.2 F/U mole ratio was higher than those of 1.0 F/U mole ratio. This could be due

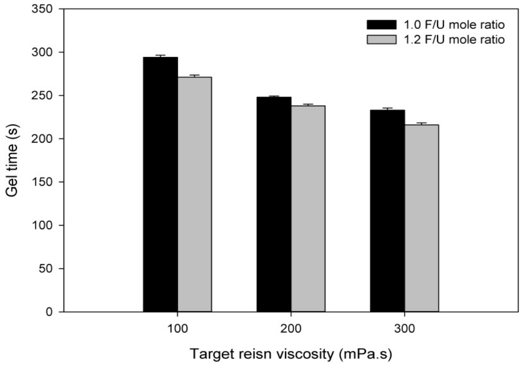

Fig. 3. Gel time of UF resins with different viscosities controlled by the condensation reaction at two F/U mole ratios.

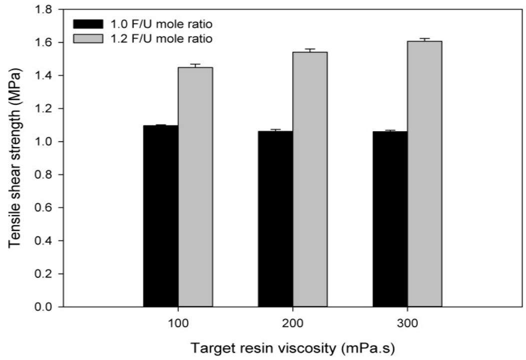

Fig. 4. Tensile shear strength of plywood bonded with UF resins at different viscosities controlled by the condensation reaction.

to a greater reactivity of the UF resin at high F/U mole ratio as presented in Fig. 3.

Fig. 3 shows the results of gel time measurements of UF resins of different viscosities adjusted by the condensation reaction. The gel time of all resins became shorter with an increase in the viscosity of UF resins. As expected, the gel time of UF resins of 1.2 F/U mole ratio was shorter than those of the 1.0 F/U mole ratio. These results indicated that the reactivity of UF resins was improved as the viscosity increased. This was probably due to the fact that high viscosity UF resins contained much greater molecular weight than those of low viscosity resins, resulting in a short time for the formation of network structure. And UF resins of higher F/U mole ratios also showed shorter gel time than those of low F/U mole ratio resins, which was compatible with the reported results (Park *et al.*, 2006; Gavrilović-Grmuša *et al.*, 2010a and b, 2012). Another reason could be the greater free formaldehyde content in high F/U mole ratio UF resins, which had released more hydrochloric acid when ammonium chloride was used as a hardener (Pizzi, 2003; Park *et al.*, 2008, 2011). This made UF resins of 1.2 F/U mole ratio were gelled faster than that of 1.0 F/U mole ratio did.

Fig. 4 presents tensile shear strengths of plywood bonded with UF resins with different viscosities that were adjusted by the condensation reaction. It is very interesting result that as the viscosity of the resin adhesive increases, the bond strength of plywood bonded with UF resins of 1.0 F/U mole ratio slightly decreases, while those of UF resins of 1.2 F/U mole ratio proportionately increases. A slight decrease of the adhesion strength upon an increase in the viscosity could be responsible for the formation of crystals in 1.0 F/U mole ratio UF resins. It was known that the crystalline structures have been formed in 1.0 F/U mole UF resins (Sigh *et al.*, 2014; Nuryawa *et al.*, 2017). In other words, the crystalline structures were found in the cured and solids (Sigh *et al*., 2014) and liquid UF resins of 1.0 F/U mole ratio (Nuryawa *et al*., 2017). Thus, it was believed that these crystalline structures prevented the penetration of UF resin molecules into wood cell walls, and were remained in the bon-line of plywood, leading to a reduction of the adhesion strength. In addition, the adhesion strength of plywood bonded with UF resins of 1.2 F/U mole ratio was greater than those of the resin adhesive of 1.0 F/U mole ratio. It could be attributed to higher reactivity of the UF resin adhesives that could form tighter network structure in their cure state (Park and Kim, 2008).

In addition, these results also showed that the viscosity of UF resin certainly had a significant effect on the bonding strength of plywood as reported by Osemeahon *et al.* (2007). They found that an increase in the viscosity of UF resin adhesives led to increase in the bond strength, which affected the flow ability of UF resin adhesives, and eventually inhibited the resin penetration into wood tissues. In general, the flow ability of UF resin is likely related to its viscosity that is also dependent on its F/U mole ratio. Low flow ability of UF resin adhesive with high-viscosity causes a poor penetration of the resin adhesive into wood. Therefore, the penetration of UF resin adhesives into wood became poorer for UF resins with higher viscosity (Nuryawan *et al*., 2014). They reported that higher viscosity of UF resin adhesives resulted in a decrease in the average resin penetration and an increase in the bond-line thickness as the F/U mole ratio of UF resin

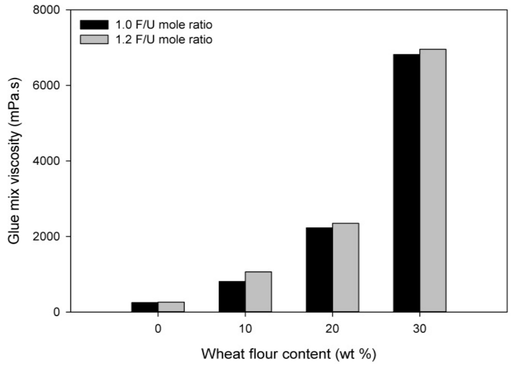

Fig. 5. Change of the glue mix viscosity of UF resins as a function of wheat flour addition and F/U mole ratio.

increased.

In order to compare the way of controlling the viscosity of UF resins by the condensation reaction, we also adjusted the resin viscosity by adding different amounts of wheat flour as extender for plywood manufacturing. Fig. 5 displays the glue mix viscosity change of UF resins as a function of the wheat flour addition and F/U mole ratio. As expected, the glue mix viscosity of UF resins exponentially increased as the addition of extender increased from 0 to 30 wt %. Glue mix viscosities of UF resins of 1.2 F/U mole ratio were slightly greater than those of 1.0 F/U mole ratio UF resins, which was believed due to their higher reactivity as shown in Fig. 3.

Fig. 6 presents tensile shear strength of plywood bonded with UF resins at different viscosities controlled by adding different amounts of wheat flour and two F/U mole ratios. As expected, tensile shear strength consistently decreased as the glue mix viscosity increased by adding wheat flour into UF reins adhesives.

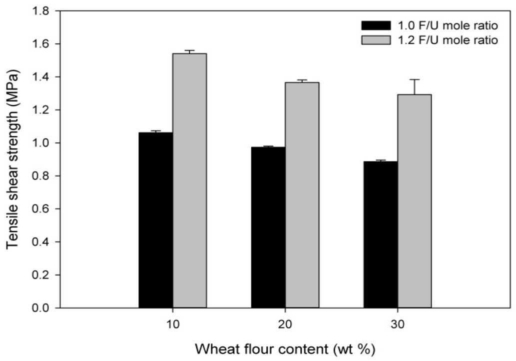

Fig. 6. Tensile shear strength of plywood bonded with UF resins at different viscosities controlled by adding different amounts of wheat flour and two F/U mole ratios.

These results could be explained by that a greater glue mix viscosity of UF resin adhesive by adding different amounts of wheat flour had resulted in a low flow ability of the resin adhesive and then consequently a poor penetration into wood tissues as reported (Nuryawan *et al.*, 2014). Another reason could be due to the fact that greater viscosity of UF resin adhesives by adding wheat flour resulted in a decrease of UF resin component in the glue spread for plywood manufacturing. In other words, an increase in the wheat flour in the glue mix reduced the amount of UF resin adhesive in the bond-line, which consequently decreased the adhesion strength for plywood. This result is quite compatible with the report published by Derkyi *et al.* (2008).

4. CONCLUSION

This study was conducted to investigate the effect of the viscosity of UF resin adhesives bonding strength of plywood. The viscosity of UF resin adhesives was controlled either by adjusting the condensation reaction during the resin synthesis, or by adding different amounts of wheat flour into the resin at two levels of F/U mole ratios (1.0 and 1.2) for the manufacturing of plywood. The results showed that the viscosity of UF resin adhesives has a significant influence on the adhesion strength of plywood. The following conclusions were obtained from this study:

1. An increase in the viscosity of UF resin adhesive controlled by the condensation reaction resulted in an increase in the non-volatile solids content and a decrease in the gel time.
2. As the resin viscosity increased, the adhesion strength of plywood bonded with UF resin of 1.2 F/U mole ratio consistently increased, while those bonded with the 1.0 F/U mole ratio resin slightly decreased, suggesting a difference in the adhesion in plywood.
3. An increase in the viscosity of UF resin adhesive controlled by adding wheat flour resulted in a consistent decrease in the adhesion strength of plywood regardless of F/U mole ratio.
4. Therefore, these results showed that the way of adjusting the viscosity of UF resin adhesive had a considerable influence on their adhesion strength in plywood.

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