Mokchae Konghak 38(5) : 414~420, 2010

Effect of pMDI or HDI Content in UMF Resin on Bonding High Moisture Content Veneers*1

Guang-Zhu Xu*2, Young-Geun Eom*2†, Byoung-Ho Lee*3, and Hyun-Joong Kim*3

ABSTRACT

The effect of polymeric diphenyl methane-4,4-diisocyanate (pMDI) or 1,6-hexamethylene diisocyanate (HDI) in the UMF resin was discussed for improvement of the dry and wet shear strengths of plywood manufactured from high moisture content veneers. The curing behavior of UMF resin by pMDI or HDI content was examined by DSC and TGA, and its adhesion performance was evaluated by dry and wet shear strength tests of plywood. With the increase of pMDI content in the UMF resin, the curing temperature, reaction enthalpy (ΔH), and thermal stability consistently increased. With the increase of HDI content in the UMF resin, however, the curing temperature and reaction enthalpy (ΔH) decreased consistently and the thermal stability slightly increased in the range of 200 to 400°C but decreased beyond 400°C. Also, the dry tensile shear strength increased up to the pMDI content of 5% and then decreased with its further addition but the wet tensile shear strength showed slight tendency to increase with the increase of pMDI content in the UMF resin. As the HDI content increased, however, the dry and wet tensile shear strengths of plywood consistently increased.

Keywords : UMF resin, pMDI, HDI, high moisture content veneer, tensile shear strength, plywood

1. INTRODUCTION

The associated methylene bridged polyphenyl polyisocyanates known as polymeric diphenyl methane-4,4-diisocyante (pMDI) is a versatile compound that comes from the polyurethane industry, and has become one of the important wood adhesives in forest products industry. Compared with conventional wood adhesives, pMDI has some unique characteristics of fast curing rate, formaldehyde emission-free, good weather resistance, and small spread (amount of prepared adhesive per unit area of wood surface) (He and Yan, 2005).

For upgrading the performance of conventional wood adhesives, hybrid resins such as urea-formaldehyde with pMDI (Pizzi *et al.*, 1993; Simon *et al.*, 2002), melamine-formaldehyde with pMDI (Pizzi *et al.*, 1993), phenol-formaldehyde with pMDI (Pizzi and Walton 1992; Pizzi *et al.*, 1993;

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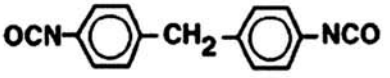
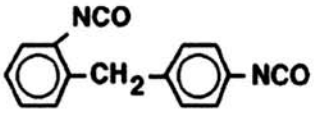
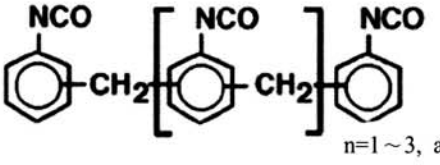
pMDI:



4,4′-MDI, typically with at least 95% of monomer fraction



2,4′-MDI



Isomeric mixture of methylene bridged polyisocyanates

HDI:

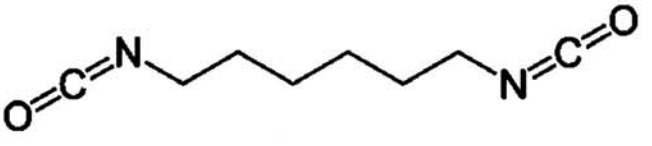


Fig. 1. Chemical structures of pMDI and HDI.

Zheng and Frazier 2000), phenol-urea-formaldehyde with pMDI (Osman *et al.*, 2005), and phenol-melamine-urea-formaldehyde with pMDI (Lei *et al.*, 2006) resins have already been developed and characterized.

In present study, the effect of pMDI content in the conventional UMF resin on improving the dry and wet tensile shear strengths was investigated in the plywood made from high moisture content veneers. Also, the result obtained from pMDI was compared with that from HDI.

2. MATERIALS and METHODS

2.1. UMF Resin with pMDI or HDI

The UMF resin type with F/(U+M) molar ratio of 2.0, solid content of 52.5%, and pH of 9.5 used in present study was synthesized as follows. First, the base urea-formaldehyde (UF) resin with formaldehyde to urea (F1/U1) molar ratio of 1.68 was prepared by reacting formaldehyde (F1) and urea (U1) at a pH of 8～9, and then adjusted to pH of 6.4 at a temperature of 90°C according to the conventional alkaline-acid method. Second,

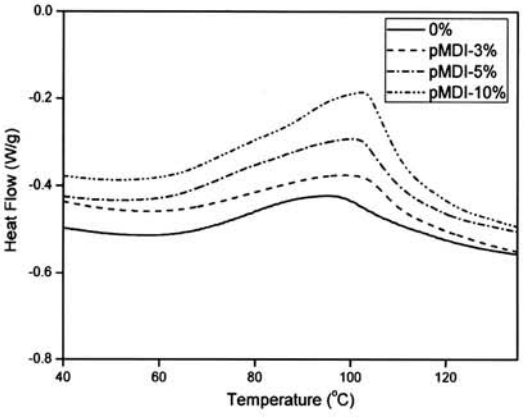


Fig. 2. DSC thermogram of UMF resin by pMDI content.

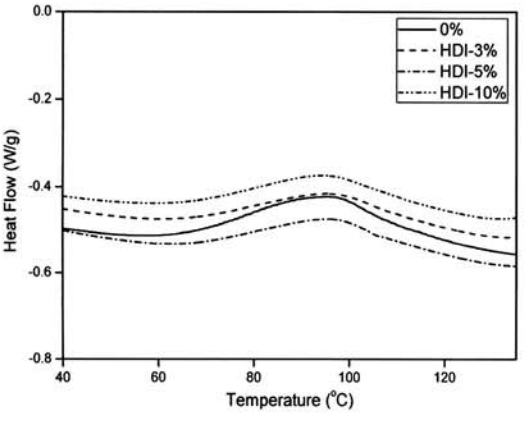


Fig. 3. DSC thermogram of UMF resin by HDI content.

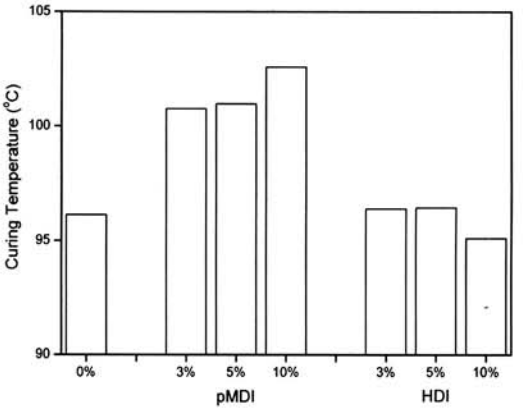


Fig. 4. Curing temperature of UMF resin by pMDI or HDI content.

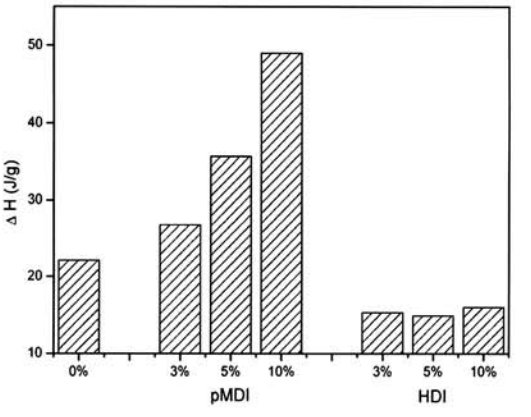


Fig. 5. Reaction enthalpy (△H) of UMF resin by pMDI or HDI content.

the UMF resin with formaldehyde to urea and melamine ((F1+F2)/(U1+M1)) molar ratio of 2.0 was prepared 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, adjusting to pH of 9.5, and cooling at a room temperature.

And pMDI and HDI was used as the compound with NCO functional group for strengthening of the conventional UMF resin and their chemical structures are depicted in Fig. 1.

2.2. Wood Veneers

In present study, rotary-cut softwood veneers with dimension of 300 × 300 × 2.1 mm and sliced hardwood veneers with dimension of 300 × 300 × 0.55 mm supplied from a company in South Korea were used to produce 7-ply plywood consisting of 5 rotary-cut core veneers and 2 sliced face veneers. The sliced face veneers with 5～10% moisture content and the rotary-cut core veneers with 16～18% moisture content by conditioning the veneers with 5～10% moisture content in a temperature & hu-

midity chamber were used.

2.3. Differential Scanning Calorimetry (DSC)

Curing exotherms of all UMF resin blends were 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. Thermogravimetric Analysis (TGA)

All the UMF resin blends were dried at 66°C for 4 hours for evaporating most of the liquid and then completely cured at 150°C for 1 hour. After completion of curing, they were analyzed in nitrogen at a heating rate of 20°C/min by a thermogravimetric analyzer. Ten milligrams of each cured sample were placed on a balance located in the furnace and heated from room temperature to 600°C.

2.5. Plywood Tensile Shear Strength

For measuring tensile shear strength, 7-ply plywoods, 30 cm × 30 cm × 0.21 cm, were made from 5 rotary-cut core veneers with moisture content of 16~18% and 2 sliced face veneers with moisture content of 5~10%. The pMDI or HDI was added in the proportion of 3, 5, and 10% to the UMF resin based on the weight of liquid resin. Ammonium chloride powder as a hardener was added in the proportion of 1% to the UMF resin based on the weight of ovendried resin and wheat flour as an extender in the proportion of 10% to the UMF resin based on the weight of liquid resin. Spread, i.e. the amount of prepared adhesive per unit area of wood surface, was 17 g/(30 cm × 30 cm). 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 tensile 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 curves of UMF resin by pMDI and HDI content are shown in Figs. 2 and 3, respectively. From Figs. 4 and 5 showing the curing temperature and reaction enthalpy ($\triangle$H), the increases of curing temperature and reaction enthalpy ($\triangle$H) were identified with the increase of pMDI content in the UMF resin. Differently from pMDI, the curing temperature slightly decreased but the reaction enthalpy decreased at first and then remained constant later with the increase of HDI content in the UMF resin. Also, the curing temperature of UMF resin with pMDI was higher than that of UMF resin with HDI. This result is in agreement with Rogulaska *et al.* (2007) who noted in studies on thermoplastic polyurethanes based on new diphenylethane-derivative diols that the HDI-based PURs exhibited definitely lower Tg (glass transition temperature) and better microphase separation in comparison with the MDI-based ones. Moreover, the higher $\triangle$H value in the DSC thermogram of the UMF resin with pMDI in comparison with that of UMF resin with HDI might be related to higher ability to crystallize in the former than in the latter.

3.2. Thermogravimetric Analysis (TGA)

The thermal decomposition and stability of cured UMF resin with pMDI or HDI were examined using TGA. Figs. 6 and 8 show the weight

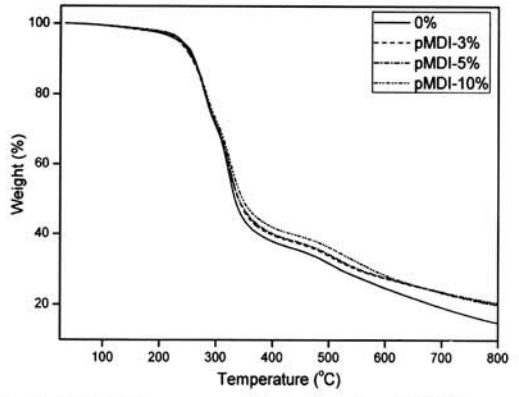


Fig. 6. Weight loss curve of cured resin of UMF resin by pMDI content.

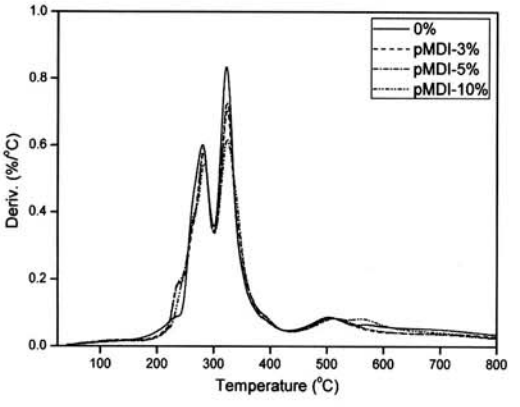


Fig. 7. DTG curve of cured resin of UMF resin by pMDI content.

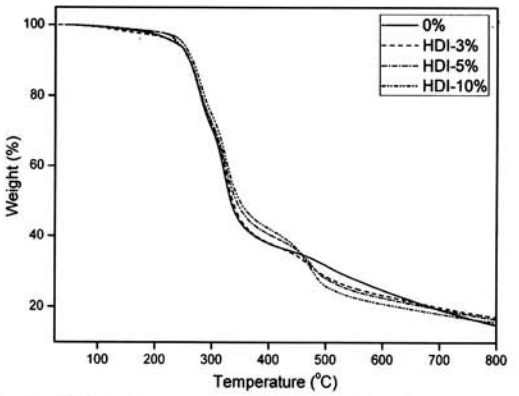


Fig. 8. Weight loss curve of cured resin of UMF resin by HDI content.

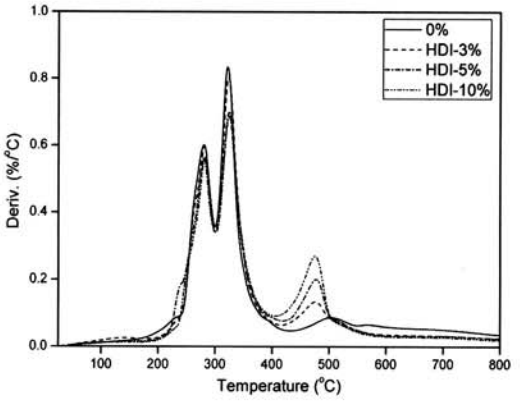


Fig. 9. DTG curve of cured resin of UMF resin by HDI content.

loss and Figs. 7 and 9 exhibit its 1st derivative over a temperature range from 25 to 800°C under nitrogen atmosphere, respectively. The UMF resin with pMDI or HDI exhibited thermal stability up to 200°C but the weight loss significantly increased over 200°C. Between 200 to 400°C, its primary weight loss was observed and its thermal decomposition decreased with the increase of pMDI or HDI content in the UMF resin. But there was no significant difference in the thermal decomposition between the UMF resin with pMDI and HDI. Above 400°C, however, its thermal decomposition decreased with the increase of pMDI content in the UMF resin but increased with the increase of HDI content in the UMF resin. This result seemed to be attributed to the increased rigidity of polymer molecules by aromatic pMDI with the bulky double phenyl ring, differently from the aliphatic HDI with flexible CH_2 chain. The similar results were also identified by Kweon *et al.* (2000), Du *et al.* (2007), and Kim *et al.* (2005).

3.3. Plywood Tensile Shear Strength

Dry and wet tensile shear strengths of plywood glued with the UMF resin by content of pMDI or HDI are shown in Fig. 10. As the

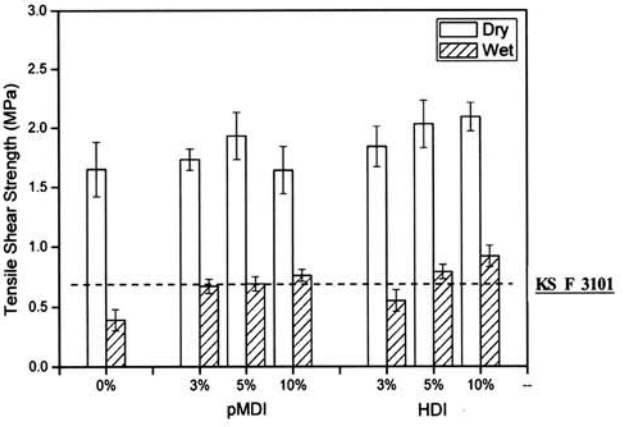


Fig. 10. Dry and wet tensile shear strengths of plywood by pMDI or HDI content. The dotted line indicates the requirements of tensile shear strength in KS F 3101.

pMDI content in the UMF resin increased, the dry tensile shear strength increased a little at first but decreased later and the wet tensile strength showed slight increasing tendency. With the increase of HDI content in the UMF resin, however, the dry and wet tensile shear strengths continuously increased. Because both the pMDI and HDI have the isocyanate group capable of reacting with any hydroxyl group, the tensile shear strength of plywood made from high moisture content veneers was thought to increase with the increase of pMDI or HDI content in the UMF resin.

In copolymerizing UMF resin with pMDI, generally, two mechanisms are involved. The first one is based on the reaction of isocyanate group of pMDI with the active methylol group of the UMF resin. The second one is the reaction of methylol group of UMF resin with the activated aromatic ring of pMDI (Pizzi *et al.*, 1992; Simon *et al.*, 2002). In addition, the reactivity of pMDI is higher than that of HDI and thus isocyanate group of pMDI can easily react with water in the UMF resin. The wet tensile shear strength of plywood was higher in the UMF resin with pMDI than in that with HDI at lower content of pMDI or HDI. Both the dry and wet tensile shear strengths, however, were lower in the UMF resin with pMDI than in that with HDI at higher content of pMDI or HDI. This might be caused by the higher rigidity of pMDI than that of HDI, the isocyanate group of pMDI capable of reacting with water relatively faster than that of HDI, and the methylol group of UMF resin capable of reacting with the activated aromatic ring of pMDI. In the case of tensile strength, also, the UMF resin with pMDI or HDI content of 5% or more satisfies the requirements of Korean Standard (KS F 3101).

4. CONCLUSIONS

This study was conducted to discuss the effect of pMDI or HDI in the UMF resin on improvement of the dry and wet tensile shear strengths of plywood. With the increase of pMDI content in the UMF resin, the curing temperature, reaction enthalpy ($\triangle H$), and thermal stability increased. The dry tensile shear strength increased up to the pMDI content of 5% and then decreased with its further addition but the wet tensile shear strength slightly increased as its content in the UMF resin increased. With the increase of HDI content in the UMF resin, the

curing temperature and reaction enthalpy ($\triangle H$) decreased and the thermal stability slightly increased in the range of 200 to 400°C but decreased beyond 400°C. As the HDI content increased, the dry and wet tensile shear strengths of plywood showed the increasing tendencies. In the improvement of adhesion strength of plywood, pMDI appeared to be more effective than HDI at lower content but HDI more effective than pMDI at higher content.

ACKNOWLEDGEMENTS

This work was supported in part by the research program 2010 of Kookmin University in Korea and the Korea Forest Service Program (500-20080132).

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