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Original Article

Performance of Melamine-Urea-Formaldehyde Resin Adhesives at Various Melamine Contents for Bonding Glued Laminated Timber Under High Frequency Heating[1]

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ABSTRACT

This work attempted to manufacture glued-laminated timber (Glulam) bonded with melamine-urea-formaldehyde (MUF) resin adhesives at various melamine contents from 20% to 50% under high frequency (HF) heating for a very short time. Two preparation methods were employed to prepare MUF resin adhesives with different melamine contents: one-batch method of synthesizing MUF resins in a single batch, and two-batch method of mixing urea-formaldehyde (UF) resin with melamine-formaldehyde (MF) resin that had been synthesized separately. As the melamine content increased, the gelation time and peak temperature of MUF resins decreased. The adhesion performance of plywood showed that the one-batch MUF resin adhesive with 50% melamine content only satisfied the standard requirement of water resistance. Thus, the one-batch MUF resin adhesive with 50% melamine content was applied for bonding wood lamina from four softwood species such as Japanese larch, Korean red pine, Korean pine and Japanese cedar to manufacture Glulam under HF heating. All Glulam samples bonded with the one-batch MUF resin adhesives with 50% melamine content except those from Korean Red Pine satisfied the requirement in water soaking or boiling water delamination test as an exterior grade Glulam. The presence of rosin in Korean Red Pine was believed to be responsible for its poor adhesion. These results showed that the one-batch MUF resin adhesives with 50% melamine content provided acceptable water resistance with exterior grade Glulam manufactured under HF heating.

Keywords : MUF resins, melamine content, Glulam, softwood species, exterior grade

1. INTRODUCTION

The use of wood adhesive is one of the important ways of efficiently utilizing timer resources. For example, wood adhesives enable to bond lumbers from small diameter logs into large and structural members for timber structures. Thus, a varieties of wood adhesives

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are being used for manufacturing glued-laminated timber (Glulam), structural composite lumbers, or wood-based composite panels such as plywood, particleboard and fiberboard. In general, cold-setting resin such as resorcinol-formaldehyde (RF) resin or phenol-resorcinol-formaldehyde (PRF) resins are being applied for manufacturing Glulam under conventional cold pressing for more than twenty-four hours under room temperature. PRF resins are preferably used for manufacturing structural Glulam because of its high bonding strength under wet condition even though it is relatively expensive (Messmer, 2015; Shim *et al.*, 2005). In the cold pressing system, adhesives are spread on the surface of wood laminae, and then pressed by clamps under certain pressure to cure the resin. A long curing time of cold pressing to manufacture Glulam results in a low productivity, which consequently increases the unit cost of structural Glulam production. Therefore, it is highly necessary to develop a Glulam manufacturing system which can reduce the curing time. A way of reducing the cold pressing time is to use high frequency (HF) heating that has been used for gluing wood for long time (Bierwirth and Hoyler, 1943). In principle, the HF heating is a process in which a high-frequency alternating electric field, or radio wave heats a dielectric material (Pereira *et al.*, 2004). The HF heating generates heat by friction of dipole molecules in rotation under the dielectric. The heat generation is known to be related to the relative loss factor of materials. The relative dielectric constant and the loss factor was changed by the oscillated frequency, and the selection of frequency range was important to heat materials. The HF heating system has already commercially been used in the manufacturing of glued laminated board or laminated veneer lumber (LVL) (Sven and Hans, 2003).

In addition, PRF resins are expensive owing to the cost of resorcinol. So, a few results have been reported on the application of melamine-urea-formaldehyde (MUF) resin adhesives for manufacturing Glulam (Properzi *et al.*, 2001; Sauget *et al.*, 2014). For example, Properizi *et al.*, (2001) showed that honeymoon MUF resin adhesives with various melamine contents were very successful in manufacturing exterior grade Glulam. They combined a high performance MUF resin adhesive (a non-volatile solids content of 72～73%) with a hardener to bond Glulams at room temperature. In addition, these MUF resins showed excellent performance of water resistance for severe conditions in an accelerated aging test (Sauget *et al.*, 2014).

However, in general, cold-setting adhesives requires a longer time for clamping to manufacture Glulam. It took 16 hours of clamping and 7 days of aging for Glulam manufacturing (Properizi *et al.*, 2001). In recent years, it took 3 hours only for manufacturing exterior grade Glulam using honeymoon MUF resins (Sauget *et al.*, 2014). An advantage of using HF heating for manufacturing Glulam is to reduce the production time of Glulam. In order to taking the advantage of HF heating, this work attempted to manufacture Glulam under HF heating, using

MUF resin adhesives with various melamine contents, which were less expensive than RF or PRF resins, and expected to provide water resistance with Glulam prepared. Therefore, the objective of this work is to investigate the adhesion performance of MUF resin adhesives for manufacturing Glulam from four different softwood species under HF heating system.

2. MATERIALS and METHODS

2.1. Materials

Commercially available urea (99%), melamine (99%), formalin (37%), formic acid, and sodium hydroxide were used for MUF resin synthesis. Commercial rosin (#603, Leto Musical Instrument Co., Ltd., Austria) for violin was also used for the gel time measurement of MUF resins.

2.2. MUF Resin Synthesis

Technical grade of urea (99%), melamine (99%), and formalin (37%) were used for the synthesis of UF resin, MF resin and MUF resin. One-batch method of preparing MUF resins were synthesized in a batch, using four-neck reactor under continuous stirring at 80℃. In two-batch method, MF resin and UF resin were synthesized separately, and then mix them together to obtain melamine contents from 20% to 50% in MUF resins on the basis of resin solids. To evaluate bonding performance of glulam manufactured under HF heating system, four softwood species such as Japanese Larch (*Larix kaempferi* Carriere), Korean Pine (*Pinus koraiensis* Siebold & Zucc.), Korean Red Pine (*Pinus densiflora* Siebold & Zucc.) and Japanese Cedar (*Cryptomeria japonica* D.Don) were selected for this research. Laminae were 30 mm thick, 190 mm wide, and 1,800 mm long with an average moisture content of 10%. 10% wheat flour based on the total resin mass and 3% ammonium chloride based on the resin solids content was added to MUF resins were mixed as extender and hardener, respectively. And MUF resin adhesives were spread at 170 g/m^2 on the surface of each lamina.

2.3. Characterization of MUF Resins

2.3.1. Non-volatile Solids Content and pH

About 1 g of MUF resin was poured into a disposable aluminum dish, and then dried in a convective oven at 105℃ for 3 hours. Non-volatile solids content was determined by measuring the weight of MUF resin before and after drying. An average of three replications was presented.

2.3.2. Viscosity

The viscosity of UF resin adhesives at 25℃ were measured using a cone-plate viscometer (DV-II+, BROOKFIELD, USA) with no. 2 spindle at 60 rpm.

2.3.3. Gel Time Measurement

The gel time of MUF resins with different melamine contents was measured by adding 3 wt% NH_4Cl (20 wt% solution) as hardener at 100℃, using a gel time meter (Sunshine gel time meter, Davis Inotek Instrument, Charlotte, NC, USA) with three replications. The gel time of MUF resins with different additions of rosin was also done by the same procedure.

2.3.4. DSC Measurement

A differential scanning calorimetry (DSC) (TA Q10, TA Instrument, New Castle, DE, USA) with high-pressure cells was used to evaluate curing behaviors of MUF resins synthesized at four heating rates such as 2.5, 5, 10, and 20℃/min. About 3～5 mg of the MUF resins was weighed in high-pressure cell prior to scanning with at least two replications per sample. For each sample, the peak temperature (*Tp*) was used to calculate activation energy (*Ea*). A multi-heating rate scan method was used to calculate the *Ea* of MUF resins.

2.3.5. ^{13}C-NMR Spectroscopy

The prepared liquid MUF resins were dissolved in deuterated dimethyl sulfuroxide (DMSO-*d6*) as a solvent for ^{13}C-NMR spectroscopy. The ^{13}C-NMR spectra were obtained with 9.5 seconds pulse width (30) and a pulse delay of 4 seconds, using 300 MHz model (Bruker AMX-R300). By using the gated decoupling method to minimize the nuclear Overhauser effect, about 20,000 scans were accumulated to obtain reliable spectra.

2.4. Adhesion strength of plywood

2.4.1. Plywood preparation

Prior to fabricating Glulam, we prepared 3-ply plywood using Radiata pine veneers to screen MUF resin adhesives with different melamine contents. Glue-mix of the MUF resins with different melamine contents was spread on the surface of veneers, and then were cross-laminated. The assembled veneers were cold pressed for 2 hour at room temperature, and then hot-pressed at 120℃ for 4 minutes under a pressure of 784.5 kPa.

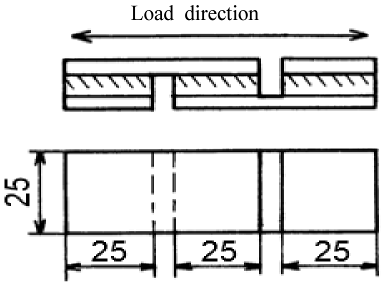

Fig. 1. The specimen geometry for tensile shear strength test for 3-ply plywood (unit: mm).

2.4.2. Tensile shear strength of plywood

As a way of screening MUF resins with different melamine contents, tensile shear strength of the plywood specimen as shown Fig. 1 was determined according to a standard procedure (KS F 3729). In other words, the plywood specimens were treated in boiling water for four hours, and then dried for 20 hours at 60℃ to determine water resistance of the sample.

2.5. Adhesion performance of Glulam

2.5.1. Fabrication of Glulam

As shown in Fig. 2, the HF heating system for manufacturing Glulam is composed of dielectric heating system to heat MUF resin adhesives for cure and hydraulic press system to

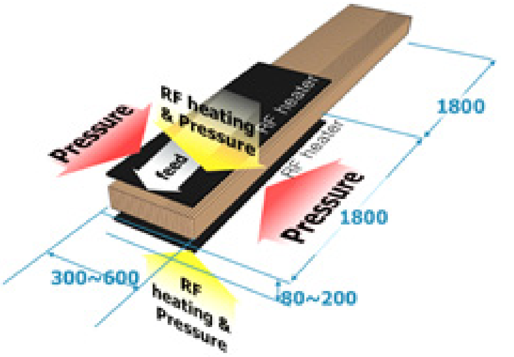

Fig. 2. Schematic diagram of the HF heating system for the glulam manufacturing.

press laminae. The targeted frequency for HF heating oscillator was set as 5 MHz and the output power was set as 60 kW. Using the HF system, glulam was manufactured with five laminae of 30 × 190 × 1,800 mm to manufacture 150 × 190 × 1,800 mm Glulam. To equalize dielectric heating under constant electric field, the glued laminae were arranged in the center of the press and polyethylene (PE) plates were filled in the remaining area of press. The glued laminae with a glue spread of 200 g/m^2 were pressed under 980.7 kPa pressure. Then the bonding lines were heated by HF oscillator. The applied oscillating conditions was set as 2 A of anodic current capacity, 10 min. of applied time and 10 min. of cooling.

Temperature change at bond-line and lamina was measured with a thermocouple when the Glulam was being fabricated. Fig. 3 shows the location of temperature measurement at the bond-line using a fiber optic thermocouple (FOBS-2, OMEGA, Quebec, Canada).

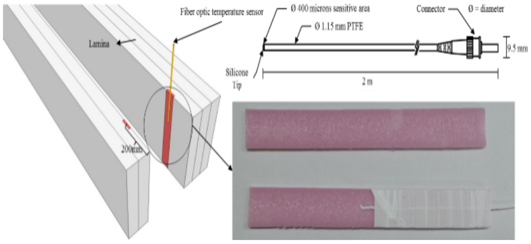

Fig. 3. Schematic diagram of measuring temperature at the bond-line, using a fiber optic thermocouple.

2.5.2. Bonding performance of Glulam

We measured shear block strength, water soaking delamination, and boiling water delamination of the Glulam bonded with MUF resin adhesives to determine their performance of Glulam prepared. The shear block strength was tested according to a standard procedure (KS F 3021, 2013), while two types of delamination tests were done by the procedure of a standard (KS F 2160, 2008).

3. RESULTS and DISCUSSION

3.1. Properties of MUF resins

The properties of MUF resins prepared at different melamine contents are summarized in Table 1. MUF resins prepared by two methods showed quite contrasting trend for the resin solids, viscosity, and gel time. As the melamine content increases, the non-volatile solids content of MUF resins increased for the reins prepared by the one-batch method while it did not change much for those prepared by the two-batch method. In addition, the viscosities of MUF resins prepared by one-batch method decreases while those of two-batch method MUF

Table 1. Properties of MUF resins at different melamine contents

Resin type	Melamine content (%)	Non-volatile solid content (%)	Viscosity (mPa.s)	Gel (s)	*Ea* (kJ/mole)
One-batch MUF resin	20	58.48	118.0	151.3 (5.2)[a]	67.42
	30	62.07	122.0	127.7 (7.4)	87.87
	40	66.15	124.7	103.0 (3.3)	72.88
	50	72.62	204.0	61.0 (3.3)	76.45
Two-batch MUF resin	20	57.56	183.3	109.0 (4.5)	61.22
	30	58.52	168.7	91.0 (5.3)	93.11
	40	59.28	163.3	78.0 (5.3)	89.91
	50	59.85	149.3	42.0 (5.1)	69.71

[a] Values in parentheses are standard deviations

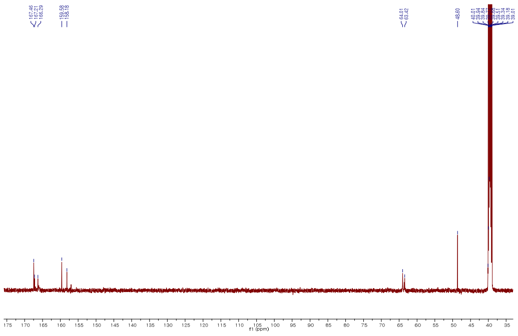

Fig. 4. ^{13}C-NMR spectrum of MUF resins with 50% melamine prepared by the one-batch method.

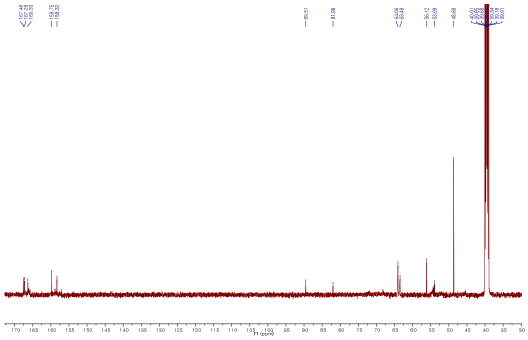

Fig. 5. ^{13}C-NMR spectrum of MUF resins with 50% melamine prepared by the two-batch method.

resins increases. However, the gel time of MUF resins decreased with an increase in the melamine content, regardless of the preparation method. These results indicate that the reactivity of MUF resin increases with an increase in the melamine content.

As shown in Table 1, the activation energy of MUF resins decreased as the melamine content increased with an exception of 20% melamine content. The activation energy is a minimum energy level of MUF resin to start its curing reaction. Thus the result suggest that a heterogeneity of MUF resin is reduced with an increase in the melamine content, which is compatible with the gel time result as shown in Table 1.

Figs. 4～5 show ^{13}C-NMR spectra of two types of MUF resins with 50% melamine contents. The MUF resins prepared by the one-batch method displays methylene bridges and hydroxymethyl groups (Fig. 4). Two ^{13}C-NMR spectra of MUF resins clearly shows that two types of MUF reins are composed of urea (158～160 ppm) and melamine (166～168 ppm), which are resulted from substituted carbonyl groups of urea (Kim, 1999) and sub-

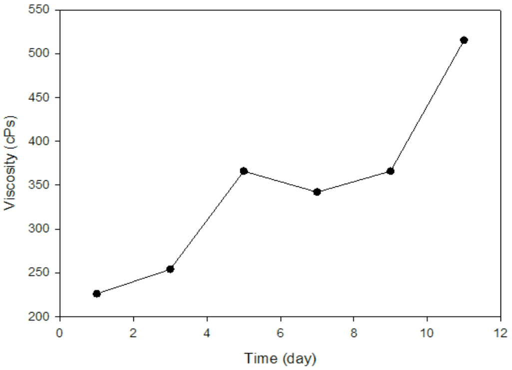

Fig. 6. Change of the viscosity of one-batch MUF resin with 50% melamine content as a function of storage time at room temperature (25℃).

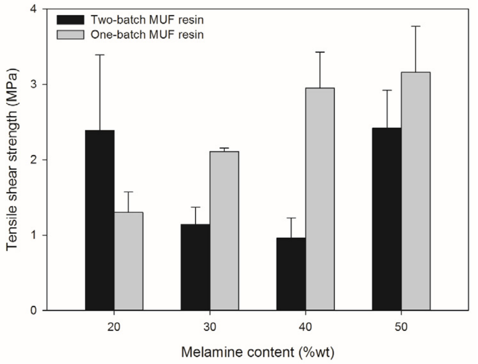

Fig. 7. Tensile shear strength of plywood bonded with MUF resins that have been prepared by two different synthesis methods.

stituted triazine ring of melamine (Tomita and Ono, 1979). Fig. 5 shows ^{13}C-NMR spectrum of two batch MUF resins with 50% melamine content. An interesting chemical shift of the two-batch MUF resin is that it contains free formaldehyde peak at around 90 ppm (Park *et al*., 2008). This could be due to the free formaldehyde in either UF or MF resin after its synthesis.

Fig. 6 shows changes of the viscosity of one-batch MUF resin as a function of storage time. As expected, the viscosity gradually increased with the elapsed time. After seven days of storage, the viscosity rapidly increased. This result indicates that the one-batch MUF resin should be used within a week for the Glulam production.

3.2. Adhesion strength of plywood

As shown in Fig. 7, the result of tensile shear strength of plywood is quite interesting. As the melamine content increases, the two-batch MUF resins decreases, and then increases. By contrast, tensile shear strength of plywood bonded with one-batch MUF resin consistently increases with an increase in the melamine content. One interesting point is the fact that the tensile shear strength of the one-batch MUF resin is much greater than that of the two-batch MUF resin at the same 50% melamine content. This result suggests that MUF resin prepared by the one-batch method show better water resistance than that of the counterpart at 50% melamine content. So, we selected the one-batch MUF resin with 50% melamine for the fabrication of Glulam.

3.3. Temperature profile of Glulam under HF heating

In order to understand HF heating, we measured temperature profiles at bond-line of Glulam made of Japanese larch. As shown in Fig. 8, the temperature at the bond-line rapidly increased at the initial stage of HF heating, re-

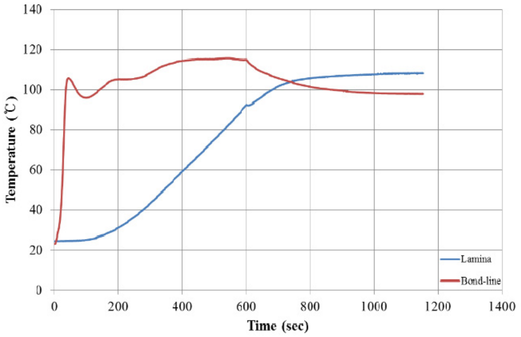

Fig. 8. Temperature profile at lamina and bond-line of Glulam during RH heating.

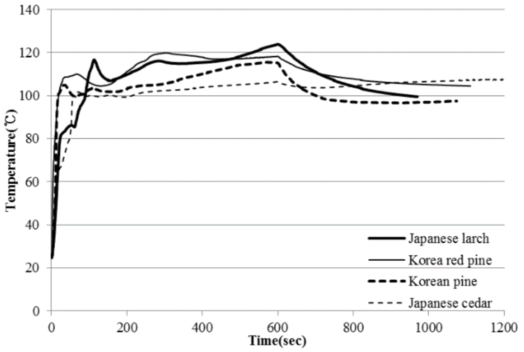

Fig. 9. Temperature profile at the bond-line of Glulam made of different softwood species during HF heating.

sulting from a rapid heating of water in the MUF resin at the bond-line. However, temperature at the lamina gradually and slowly increased as the HF heating time increased. This is quite natural because the lamina contains much less water that in the bond-line.

Fig. 9 also shows temperature profiles of Glulam made of four different softwood species. The maximum temperatures at the initial HF heating were relatively lower for Glulam made of Korean pine, Japanese cedar, and Korea red pine than that of the one made of Japanese larch. It is not clear which factors make this happen, which deserves further study. However, higher temperature at the bond-line is expected to accelerate the curing of MUF resin under HF heating. Thus, block shear strength of the Glulam seems closely related to the maximum temperature at the bond-line as shown Fig. 10∼11.

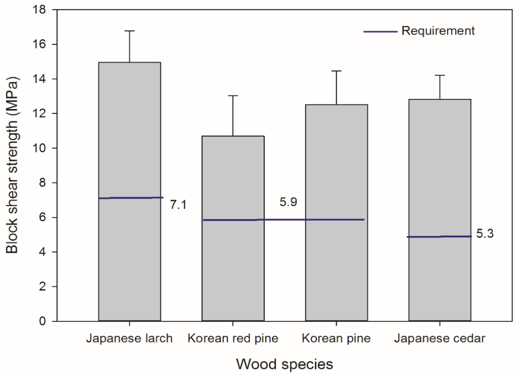

Fig. 10. Block shear strength of Glulam bonded with one-batch MUF resin adhesives.

3.4. Performance of Glulam

In order to evaluate adhesion performance of Glulam, block shear strength and two types of delamination tests were done for all Glulam prepared with different softwood species in this work, and the results were displayed in Figs. 10 and 11. All block shear strengths of Glulam bonded with the one-batch MUF resin with 50% melamine content were above the requirement level (Fig. 10). The block shear strength was the highest for the Glulam made of Japanese larch. This is believed to be related to the maximum temperature at the bond-line under HF heating as shown Fig. 9. And block shear strength decreased in the order of Korean

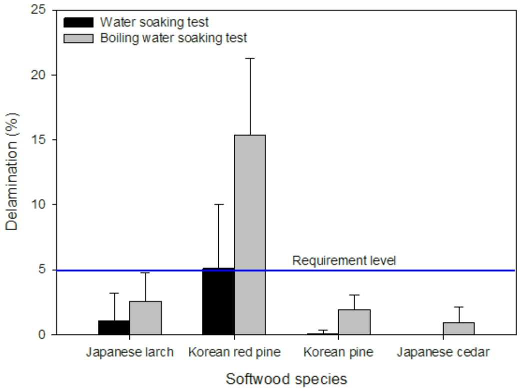

Fig. 11. Delamination percentage of glulam bonded with one-batch MUF resin after water soaking and boiling water soaking test.

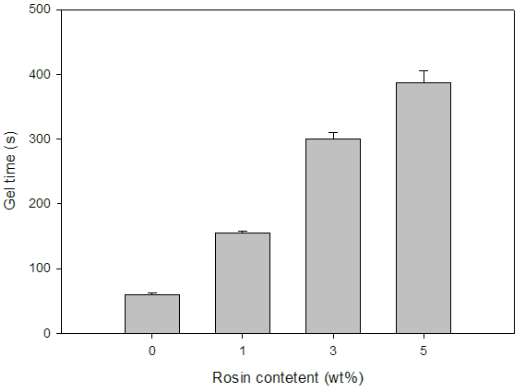

Fig. 12. The gel time of MUF resins with 50% melamine content as a function of a commercial rosin content.

red pine, Korean pine, and Japanese cedar. As expected all block shear strengths satisfied the standard requirement level for each wood species. And they are greater than those of Glum bonded with the one-batch MUF resin with 50% melamine content.

In addition, we also conducted delamination tests in water soaking and boiling water soaking to determine water resistance of the Glulam. Delamination test results of Glulam bonded with MUF resins are presented in Fig. 11, showing that all delamination percentages of the Glulam are above the requirement level (below 5%) of the Korean standard except the Glulam made of Korean Red Pine. In addition, the Glulam made of Korean Pine and Japanese Cedar resulted in lower delamination percentage than the one of Japanese Larch.

The delamination percentage of Glulam made of Korean Red Pine did not satisfy the standard requirement. Even many factors such as wood factors, processing factors, or wood-adhesive interaction factors did influence to the bonding of Glulam made of Korean Red Pine. We believed that the rosin present in Korean Red Pine might have influenced the bonding performance of Glulam. In order to understand the impact of rosin present in Korean Red Pine, we mixed commercial rosin with the MUF resin with 50% melamine content to measure the gel time as a function of rosin content. The results are presented in Fig. 12. As expected, the gel time of MUF resin increased as the rosin content increased. This result help explaining why the Glulam made of Korean Red Pine does not satisfy the delamination percentage of the standard requirement.

4. CONCLUSIONS

This study attempted to manufacture Glulam under HF heating, using four different softwood species and MUF resin adhesives prepared by two different synthesis methods at various melamine contents. The results showed that properties of MUF resins such as solid content, viscosity, and gel time heavily depended on the melamine content. The adhesion performance of plywood made it possible to select MUF resin with 50% melamine with acceptable water resistance for the fabrication of Glulam. When one-batch MUF resin with 50% melamine content was applied for manufacturing Glulam using HF heating system, all block shear strengths satisfied the standard requirement level. All delamination percentages of Glulam after water soaking and boiling water soaking test was also above the requirement level except the one made of Korean red pine. These results indicate that one-batch MUF resin with 50% melamine content satisfy the adhesion performance level of exterior grade Glulam, except the one made of Korean red pine. A poor adhesion of the Glulam made of Korea red pine was ascribed to the presence of resin canal, which increased the gel time of MUF resin.

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