

Review

A Comparison of Adhesion Behavior of Urea-Formaldehyde Resins with Melamine-Urea-Formaldehyde Resins in Bonding Wood

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Abstract: This paper reports a comparison of adhesion behavior of urea-formaldehyde (UF) with those of melamine-urea-formaldehyde (MU) resins in bonding wood by analyzing the results published in literatures. For this purpose, the adhesion behavior of UF resins prepared by blending low-viscosity resin (LVR) with high-viscosity resin (HVR) at five different blending and two formaldehyde/urea (F/U) molar ratios (1.0 and 1.2) was compared with those of two MUF resins synthesized by either simultaneous reaction (MUF-A resins) or multi-step reaction (MUF-B resins) with three melamine contents (5, 10, and 20 wt%). As the blending (LVR:HVR) ratio increased from 100:0 to 0:100, the viscosity and molar mass (M_w and M_n) of the blended UF resins increased while the gelation time decreased. The interphase features such as maximum storage modulus (E'_{max}), resin penetration depth, and bond-line thickness of the UF resins increased to a maximum and then decreased as the blending ratio increased. In addition, both MUF-A and MUF-B resins also showed an increase in the M_w and M_n as the melamine content increased from 5% to 20%. However, the E'_{max} , resin penetration depth, and bond-line thickness of the MUF resins decreased as the molar mass or melamine content increased. These results indicated that the adhesion of UF resins heavily depends on the interphase features while that of the MUF resins highly depends on the cohesion of the resins.

Keywords: amino resins; molecular weight; interphase adhesion; adhesion behavior



Citation: Park, S.; Jeong, B.; Park, B.-D. A Comparison of Adhesion Behavior of Urea-Formaldehyde Resins with Melamine-Urea-Formaldehyde Resins in Bonding Wood. *Forests* **2021**, *12*, 1037. <https://doi.org/10.3390/f12081037>

Academic Editor: Angela Lo Monaco

Received: 22 July 2021

Accepted: 3 August 2021

Published: 5 August 2021

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1. Introduction

Formaldehyde-based resins are still being used as adhesives for the manufacturing of wood-based composite panels such as particleboards (PB), oriented strand board (OSB), plywood, and medium-density fiberboard (MDF). Among these resins, amino resins such as urea-formaldehyde (UF) resins and melamine-urea-formaldehyde (MUF) resins are mainly used for the production of plywood, PB, or MDF panels. These resins are dominantly used as adhesives, owing to their low cost, high reactivity, fast curing time, colorlessness, and good adhesion [1]. In spite of these advantages, there are two drawbacks for UF and MUF resins: low water resistance and formaldehyde emission. In particular, the formaldehyde emission from wood-based composite panels bonded with these resins has been a serious issue of these amino resins [2]. Since the 1980's, the formaldehyde emission has been a main issue because it caused indoor air pollution, leading to a risk for health [3]. It is reported that the residual-free formaldehyde in UF resins is responsible for the formaldehyde emission in a short term while the hydrolysis of UF resins causes to emit formaldehyde in a long term [4].

Thus, various approaches of using scavengers [5] and ammonia chambers [6] have been attempted to reduce such emissions from wood-based panel products. One of the most effective and reliable method is to lower formaldehyde-to-urea (F/U) molar ratio in

their synthesis [4]. However, such low-molar-ratio UF resins cause some disadvantages such as lower reactivity, high curing energy, longer gelation time, and worse adhesion strength than those of higher F/U molar ratios [7]. In other words, the low-molar-ratio (≤ 1.0) UF resins give a low emission of formaldehyde at the expense of the adhesion. Thus, low-molar-ratio UF resins are quite different from those resins used 20 years ago. The low-molar-ratio UF resins have crystalline structures, which lead to worse adhesion than those of the high-molar-ratio counterparts that have amorphous structures [8–10]. Stulgross and Koutsky [11] showed the relationship between the crystallinity and performance of low-molar-ratio UF resins by determining the degree of crystallinity in these resins. Park and Causin [12] reported that the crystallinity of UF resins increased as the F/U molar ratio decreased from 1.6 to 1.0. In recent years, Wibowo and Park [13] reported that 1.0 F/U molar-ratio UF resins had low molecular weight in linear molecules, and these molecules formed a lamellar structure of the crystalline domain through hydrogen bonding using atomic force microscopy (AFM) and transmission electron microscopy (TEM).

A strong, durable, and excellent adhesion in wood bonding requires us to understand the adhesion process that is a complex physical and chemical phenomenon. In fact, there are many studies to understand the impact of adhesion aspects of various formaldehyde-based resin properties such as curing kinetics, adhesion, and resin penetration [14–23]. In particular, the adhesion strength of particleboards improved with higher molar mass of phenol-formaldehyde (PF) resins [14]. They also reported that the low adhesion strength of particleboards was attributed to over-penetration by low-molar-mass species. The adhesion is also influenced by thermal curing behaviors of UF resins with different F/U molar ratios [16]. In general, UF resins with high F/U molar ratio result in better adhesion

In addition, phenol-formaldehyde (PF) resins with different degrees of polymerization were used in the 1990s [24]. It is well known that a strong adhesion bond in wood requires a combination of low-molar-mass species with those of high molar mass in PF resins [25]. In general, low-molar-mass species are penetrated into wood tissues to form a strong interphase adhesion while high-molar-mass species are remaining to give a strong cohesive strength to the bond line. Dynamic mechanical analysis on PF resin-bonded wood composites also showed that low-molar-mass species penetrated into wood while high-molar-mass species exerted the interphase adhesion [26]. He and Riedl [27] suggested that the storage modulus (E') could be used for the evaluation of the rigidity of the resin network of amino resins. In addition, the E'_{max} of DMA analysis related to the F/U molar ratio of UF resins. In other words, low-molar-ratio UF resin resulted in lower E'_{max} while high-molar-ratio UF resins had high E'_{max} [28].

However, differences in the adhesion behavior of these amino resins are not well understood even though their synthesis reaction, chemical structure, or performance are well known. This paper reports a comparison of the adhesion behavior of UF and MUF resins in bonding wood by focusing on the interphase features such as resin penetration into wood, bond-line thickness and interphase strength, the adhesion strength, and the cohesion.

2. Methodology

As discussed in the Introduction, the adhesion of amino resins such as UF, MUF, or MF resins to wood is a complex process. One of the advantages of using MUF resins over UF resins as adhesives is to provide better resistance to moisture or water with bonded-wood products. However, most of the literature deals with the adhesion or bond quality of either only UF resins or only MUF resins [17–20,28]. In other words, a comparison of the adhesion behavior of UF resins with that of MUF resins has not been done yet. It is expected that the addition of multi-reactive melamine to UF resins to synthesize MUF resins could change the network structure of UF resins, which would be a much more branched structure when they are cured. Thus, it is expected that the cohesion of MUF resins could be different from that of UF resins in terms of the molecular structure. Therefore, this paper attempted to compare the adhesion behavior of UF resins with that of MUF resins. In fact, two papers on

UF and MUF resins with different molecular weights and melamine contents were recently published [29,30].

3. Materials and Methods

3.1. Synthesis of UF and MUF Resins

Details of the resin preparation are described in the publications [28,29]. Briefly, two different formaldehyde/urea (F/U) molar ratios (1.0 and 1.2) were employed to synthesize low-viscosity resin (LVR) and high-viscosity resin (HVR) for UF resins in a two-step reaction. In brief, the LVR resins were prepared by the condensation reaction with the target viscosity of a bubble viscosity (VG-9100, Gardner-Holdt viscometer, Gardco, Pompano Beach, FL, USA) scale of the “D” and “E”. By contrast, The HVR resins were prepared at the target viscosity scale of the “S” and “T” scale using the same bubble viscometer. For each of the two molar ratios, five different UF resins were prepared by blending LVR with HVR at five different ratios to obtain different molecular weights of UF resins [29].

By contrast, two different synthesis methods were employed to obtain MUF-A resins prepared by the simultaneous reaction of melamine, urea, and formaldehyde, and MUF-B resins were prepared by a multi-step reaction of melamine and formaldehyde and then urea [30].

3.2. Method

Details of gel permeation chromatography (GPC), differential scanning calorimeter (DSC), dynamic mechanical analysis (DMA), light microscopy (LM), confocal laser scanning microscopy (CLSM), and plywood properties (tensile shear strength (TSS)) of the UF and MUF resins are described in the publications [28,29]. These characterization methods are briefly described in this paper.

3.2.1. Characterizations

Molecular Weight Measurements of UF and MUF Resins

A gel permeation chromatography (GPC) system (YL9100, Younglin, Gyeonggi-do, Korea) equipped with a refractive index (RI) detector was used to measure the apparent molecular weight (MW) of the resins as reported [31]. The columns used were KD 801, 802, and 806 M (SHODEX, Showa Denko K.K., Tokyo, Japan), respectively. The GPC measurements were carried out at column and detector temperatures of 50 °C and a flow rate of 0.5 mL/min [23]. The UF resin samples were dissolved in a mixture of 10% DMSO and 90% DMF and kept in an oven at 50 °C for 3 h in order to achieve complete dissolution. Then, the sample solution was introduced into the GPC through a 0.45- μ m filter via the injection loop.

Curing Behavior of UF and MUF Resins

The curing behavior of UF and MUF resins was characterized with a differential scanning calorimeter (DSC, 25, TA Instruments, New Castle, DE, USA). About 5 g of each resin sample was mixed with 3% NH₄Cl (added in the form of a 20 wt% solution) based on the resin solid content prior to scanning. High-pressure pans were used in order to suppress the evaporation of water during the DSC run. All samples (5 mg) were scanned at four different heating rates (2.5, 5, 10, and 20 °C/min) in the temperature range of 30 to 200 °C under a flow of nitrogen gas at 50 mL/min. All thermo grams were used to obtain the peak temperature under the exothermic curve using a commercial software (TRIOS Software, v4.3.0, TA Instruments, New Castle, DE, USA).

Interphase Adhesion in UF or MUF Resins–Wood Composites

Either UF or MUF resins were used to bond two thin, Red Pine (*Pinus densiflora*) strips, with a glue spread of 125 g/m², to prepare a specimen measuring 100 × 8 × 0.2 mm (length × width × thickness) for evaluation by a dynamic mechanical analysis (DMA) (Q800, TA Instruments, New Castle, DE, USA) in the dual cantilever mode. All specimens

were pre-cured in an oven at 50 °C for 5 min prior to the DMA analysis. The storage modulus (E') of each specimen was determined at a frequency of 1 Hz, strain level of 0.005%, and heating rate of 5 °C/min in the scanning range of 30–300 °C.

Measurement of Resin Penetration and Bond-Line Thickness

Sample preparation: The bond-line samples were prepared by making two-ply parallel plywood of radiata pine (*Pinus radiata* D. Don) veneers (2 mm thick). A 3 wt% of NH_4Cl (20 wt% solution) based on the non-volatile resin solids' content was added to UF or MUF resins. Additionally, 10% wheat flour (based on liquid resin) was also mixed with the resins. Then, this glue mix was applied onto one of the two veneers at a spread of 170 g/m² using a rubber roller. The two-ply veneers were cold-pressed under 0.78 MPa pressure for 20 min, and then hot-pressed at 120 °C under the same pressure for 4 min.

Examination with confocal laser scanning microscope (CLSM): In this study, the “inter-phase region” is defined as the zone of resin penetration and the “interface” as the two-dimensional contact zone between resin molecules and the wood surface on a microscopic level, as reported [18]. The bond line is the adhesive region between the two pieces of joint parallel veneers. Cross sections (thickness: 70 µm) were prepared for microscope examination using a sliding microtome (Yamato KOHKI, Asaka, Japan). The samples were then stained with 0.05% aqueous toluidine blue O and mounted in air-free water on a glass slide prior to examination. A confocal laser scanning microscope (CLSM; LSM700, Carl Zeiss, Jena, Germany) was used to capture images in the fluorescence mode at two excitation wavelengths of 488 nm and 555 nm [22].

Examination under light microscope (LM): An LM (U-MDOB, Olympus Optical Co, Ltd., Tokyo, Japan) was used to capture images of the cross sections used for the CLSM, as reported by Nuryawan et al. [22]. Two images for each sample were acquired with a camera (PL-A662, Pixelink, Ottawa, ON, Canada), leading to 20 images. The average resin penetration depth was measured as the distance between the geometrical center line of the bond line and the tracheids penetrated by the resin.

Additionally, the distance between the interfaces of two veneers (geometrical contact zone between the resin layer and wood surface) was used as the average bond-line thickness without including individual filled tracheids further away from the bond line. Both the CLSM and LM images were used to measure the depth of resin penetration and bond-line thickness. The obtained images were processed using a software (IMT solution ver.22.5, Vancouver, BC, Canada) to obtain an average value and the standard deviation for the measurements.

Measurement of Tensile Shear Strength of Plywood

As a measure of adhesion strength, tensile shear strength (TSS) of three-ply plywood was determined using the same adhesive, glue spread, and pressing conditions as those used for the two-ply parallel plywood. The TSS of the plywood was determined according to a standard procedure (KS F 3101, 2016, Korea Standard Association, Seoul, Korea), using nine specimens (25 × 80 × 6 mm) at a crosshead speed of 2 mm/min in a universal testing machine (H50KS, Hounsfield, Redhill, England).

4. Resin Properties and Molar Mas

As expected, the viscosity and non-volatile solids' content of the blended UF resins increased, while the gelation time of the resins decreased when the blending ratio of LVR:HVR increased. Both the M_w and M_n of these resins also increased as the blending ratio increased. Tables 1 and 2 show the number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity (PD) of five UF resins at five blendings (LVR:HVR) and two F/U molar ratios, and two types of MUF resins, respectively. As expected, M_n , M_w , and PD of UF resins increased as the HVR proportion increased (Table 1). In addition, the M_n , M_w , and PD of the 1.2 F/U resin were higher than those of the 1.0 F/U resin, indicating there was higher molar mass due to a greater increase in

the molar mass. Additionally, the M_n , M_w , and PD of two types of MUF resins increased as the melamine content increased (Table 2). However, the M_n and M_w of MUF-A resins were lower than those of the MUF-B resins, indicating that more polymeric materials were formed in MUF-B resins and their molar mass increased at a higher melamine content. This could be due to the additional reaction of formaldehyde to melamine occurring more easily and more completely than that of urea [32].

Table 1. M_n , M_w , and PD of UF resins with different blendings and F/U molar ratios.

Blending Ratio (HVR: LVR)	1.0 F/U Molar Ratio			1.2 F/U Molar Ratio		
	M_n (g/mole)	M_w (g/mole)	PD	M_n (g/mole)	M_w (g/mole)	PD
100:0	354	1339	3.8	371	2234.1	6.0
75:25	365	1554	4.3	368	2806.3	7.6
50:50	335	2061	6.3	371	3595.9	9.7
25:75	350	2409	6.9	370	4564.8	12.3
0:100	358	2511	7.0	368	5076.7	13.8

Table 2. M_n , M_w , and PD of two types of MUF resins with three melamine contents.

Melamine Content (wt%)	MUF-A Resin			MUF-B Resin		
	M_n (g/mole)	M_w (g/mole)	PD	M_n (g/mole)	M_w (g/mole)	PD
5	407.1	803.1	1.9	435.4	913.5	2.1
10	407.4	1042.5	2.5	470.2	1207.3	2.5
20	500.9	1297.4	2.6	517.7	1332.1	2.6

5. Maximum Storage Modulus of the Interphase between the Resins and Wood

The resin penetration depth and bond-line thickness in the bond line was measured at the cross section of two-ply parallel plywood bonded with either UF or MUF resins. Furthermore, the depth of resin penetration was determined by measuring the distance between the geometrical center line of the bond line and the tracheids penetrated by the resin. Similarly, the bond-line thickness was determined as the distance between the interfaces of two veneers (geometrical contact zone between the resin layer and wood surface), not including individual filled tracheids further away from the bond line. A typical image of CLSM for the measurement of the resin penetration into wood and bond-line thickness is displayed in Figure 1. MUF resins present in the lumen or bond line were a yellow or green color, while wood cell walls were a red color, owing to their own fluorescence. As displayed, the resin penetrated into the tracheid lumens away from the interface between the resin and wood in the bond line. The depth of resin penetration was determined by counting all tracheids that were partially or fully filled.

For the comparison of the adhesion in the interphase between the resins and wood, the resin–wood composites were prepared and used to measure the maximum storage modulus (E'_{max}), using DMA. Tables 3 and 4 present the E'_{max} values of the resin–wood composites for UF and MUF resins, respectively. As the LVR:HVR blending ratio increased, the E'_{max} of UF resin–wood composites increased to a maximum and then decreased thereafter (Table 3). Both 1.0 and 1.2 F/U UF resins showed the highest E'_{max} at M_w of 2000–2400 g/mol and 3500–4500 g/mol, respectively, suggesting that a combination of a low-molar-mass species with a high-molar-mass species gave the best adhesion in the interphase region. This is quite reasonable to assume that a mixture of low- and high-MW species provides a strong adhesion bond in wood, as reported for PF resins by [25].

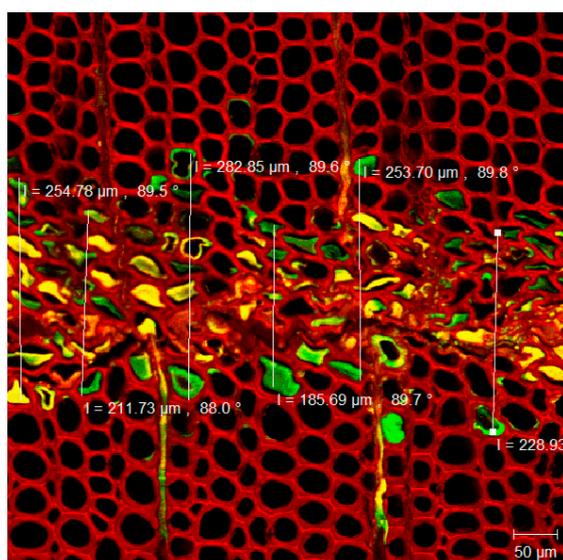


Figure 1. A typical CLSM image of MUF-A resins with 20% melamine in the bond line for its thickness measurement, showing MUF resins in yellow or green, and wood in red.

Table 3. E'_{max} of UF resin–wood composites prepared with different blending and F/U molar ratios.

Blending Ratio (HVR: LVR)	E'_{max} (GPa)	
	1.0 F/U Molar Ratio	1.2 F/U Molar Ratio
100:0	22.50 ± 0.87	22.74 ± 1.25
75:25	34.59 ± 0.52	24.49 ± 0.98
50:50	41.04 ± 1.36	41.46 ± 1.57
25:75	40.82 ± 0.89	40.60 ± 1.71
0:100	34.59 ± 0.92	29.43 ± 1.50

All values are presented with an average with standard deviation.

Table 4. E'_{max} of two types of MUF resin–wood composites as a function of melamine content.

Melamine Content (wt%)	E'_{max} (GPa)	
	MUF-A Resins	MUF-B Resins
5	36.23	38.72
10	21.01	30.26
20	16.44	18.10

Those E'_{max} values of MUF resin–wood composites are presented in Table 4. MUF-B resins had higher E'_{max} value than those of MUF-A resins in the resin–wood composite. As the melamine content increased, the E'_{max} value decreased, regardless of the synthesis method. The 5% melamine content for two types of MUF resins showed the highest E'_{max} value, which also resulted in the highest depth of resin penetration, as presented in Table 6, possibly owing to a strong interphase between wood and the resins. MUF-A and -B resins with 20% melamine content had the failure in the interphase regions and resulted in low E'_{max} values. A greater E'_{max} of MUF-B resins could be due to their higher cohesive strength because they had a higher molar mass (in particular, M_w) than that of MUF resins. These results indicate that the cohesion of the resin was improved with more cross links in their network with an increase in the melamine content.

It is interesting to compare the E'_{max} values of UF and MUF resins. As discussed, the E'_{max} values of UF resins increased to a maximum and then decreased, while the E'_{max} values of MUF resins decreased with an increase in the melamine content. These results indicate that the E'_{max} values of UF resins were mainly affected by the adhesion

in the interphase while those of MUF resins were mainly affected by the cohesion in the interphase. In other words, the lower-molar-mass species could penetrate more into wood and make a strong interphase to provide strong adhesion, while the high-molar-mass species remained in the bond line, giving strong cohesive strength.

6. Depth of the Resin Penetration into Wood in Bond Line

For the comparison, the penetration depth of UF resins with different blending and F/U molar ratios and two types of MUF resins with three melamine contents is presented in Tables 5 and 6, respectively. As shown in Table 5, the maximum resin penetration of 1.0 and 1.2 F/U ratio resin appeared at M_w of 2400 and 3500 g/mol, respectively, and this was similar to the range of the E'_{max} . Additionally, both LM and CLSM analyses showed a similar trend of two molar ratios of UF resins. By contrast, the resin penetration depth of MUF resins appeared quite different from those of UF resins, as presented in Table 6. As the melamine content increased, the resin penetration depth decreased for LM and CLSM measurements. Lower melamine content caused greater penetration, suggesting that low-molar-mass species in MUF resins preferably penetrated into wood tissues. Additionally, the resin penetration of MUF-A resins was slightly higher than those of MUF-B resins. This could be due to a smaller fraction of low-molar-mass species in MUF-A resins [29].

Table 5. Penetration depths of UF resins with different blendings and F/U molar ratios.

Blending Ratio (HVR: LVR)	1.0 F/U Molar Ratio		1.2 F/U Molar Ratio	
	LM (μm)	CLSM (μm)	LM (μm)	CLSM (μm)
100:0	187.0 \pm 35.63	239.2 \pm 21	263 \pm 28.5	175 \pm 27
75:25	212.4 \pm 24.0	249.6 \pm 20	296 \pm 21.5	221 \pm 45
50:50	209.1 \pm 32.03	260 \pm 30	399 \pm 14.5	385 \pm 31
25:75	240.5 \pm 37.85	380.9 \pm 58	295 \pm 10.3	213 \pm 35
0:100	206.1 \pm 38.27	295.1 \pm 32	291 \pm 15.3	202 \pm 31

All values are presented with an average with standard deviation.

Table 6. Penetration depths of two types of MUF resins with three melamine contents using LM and CLSM.

Melamine Content (wt%)	MUF-A Resins		MUF-B Resins	
	LM (μm)	CLSM (μm)	LM (μm)	CLSM (μm)
5	443.44 \pm 106.51	477.06 \pm 96.09	340.14 \pm 55.58	329.83 \pm 90.02
10	338.84 \pm 88.62	367.45 \pm 49.01	261.02 \pm 76.46	284.21 \pm 91.08
20	289.27 \pm 72.40	321.72 \pm 95.31	201.04 \pm 69.79	225.29 \pm 97.35

All values are presented with an average with standard deviation.

It seems that the resin penetration of UF and MUF resins was also related to the E'_{max} in interphase. In other words, the trend of E'_{max} values of both UF and MUF resins in Tables 3 and 4 is quite parallel with the trend of resin penetration into wood tissues in Tables 5 and 6.

The higher the E'_{max} values were, the greater the resin penetration was, regardless of the resin kinds. As is well known, the low-molar-mass species are preferably penetrated into wood tissues, while the higher-molar-mass species remained in the bond line to form the adhesion in the interphase in the bond line between resins and wood [16–19]. In addition, the critical M_w for the penetration into the softwood tissues was reported as 3000 g/mol of PEG [33]. Other factors such as cross linking during the resin curing also had a decisive role in the adhesion performance, as reported by Park et al. [7].

7. Bond-Line Thickness

Tables 7 and 8 show the bond-line thickness measurements for UF and MUF resins, respectively. As presented in Table 7, the 1.0 F/U resins had a considerably thinner bond line than those of the 1.2 F/U resins. The thinnest bond line appeared for the M_w of

2400 and 3500 g/mol, respectively, of the 1.0 and the 1.2 F/U resins. It is likely that the bond-line thickness was affected by the M_w of the resins and their depths of penetration. The bond-line thickness appeared closely related to the resin penetration. In fact, Hse [33] reported that the penetration depth was inversely proportional to the bond-line thickness in plywood. Furthermore, low-molar-mass species in the resins were preferentially absorbed into the porous wood, while high-molar-mass species remained on the bond line.

Table 7. Bond-line thicknesses of UF resins with different blendings and F/U molar ratios.

Blending Ratio (HVR: LVR)	Bond-Line Thickness (μm)	
	1.0 F/U Molar Ratio	1.2 F/U Molar Ratio
100:0	33.4 \pm 7.84	45.2 \pm 6.52
75:25	34.5 \pm 8.59	42.5 \pm 5.26
50:50	35.5 \pm 6.56	25.21 \pm 10.52
25:75	27.5 \pm 12.56	41.54 \pm 12.55
0:100	29.5 \pm 6.57	51.3 \pm 2.53

All values are presented with an average with standard deviation.

Table 8. Bond-line thicknesses of two types of MUF resins with three melamine contents.

Melamine Content (wt%)	Bond-Line Thickness (μm)	
	MUF-A Resins	MUF-B Resins
5	90.44 \pm 7.50	110.30 \pm 11.20
10	120.01 \pm 9.88	135.54 \pm 12.31
20	155.31 \pm 13.07	190.69 \pm 22.11

All values are presented with an average with standard deviation.

8. Adhesion Performance of UF and MUF Resins

Tables 9 and 10 present the tensile shear strength (TSS) of plywood bonded with UF and MUF resins, respectively. The highest TSS values of 1.0 and 1.2 F/U molar ratio resins were found at M_w of 2400 and 3500 g/mol, respectively (Table 9). Table 10 shows TSS and FE values of plywood bonded with two types of MUF resins with three melamine contents. When the TSS of two types of MUF resins were compared, the MUF-B resins showed higher TSS of plywood than those of MUF-A resins. TSS values improved as the melamine content increased.

It is interesting to compare TSS with the E'_{max} value, resin penetration, and bond-line thickness of UF and MUF resins. For UF resins at different blendings and F/U molar ratios, the maximum TSS was closely related to the maximum of E'_{max} value and resin penetration, but the minimum bond-line thickness. These results indicate that the adhesion in the bond line of UF resins was predominantly governed by the interphase adhesion in plywood. However, the E'_{max} value, resin penetration, and bond-line thickness of MUF resins were quite consistently parallel with the melamine content. In other words, the adhesion of MUF resins was mainly affected by the cohesion in the bond line. As discussed, an increase in the melamine content resulted in a more branched network structure than that of the UF resins, which consequently influenced the cohesion in bonding wood.

Table 9. Tensile shear strength and wood failure of plywood bonded with UF resins with different F/U molar ratios.

Blending Ratio (HVR: LVR)	1.0 F/U Molar Ratio	1.2 F/U Molar Ratio
	TSS (MPa)	TSS (MPa)
100:0	1.015 ± 0.048	0.904 ± 0.217
75:25	1.024 ± 0.079	1.123 ± 0.159
50:50	1.048 ± 0.059	1.345 ± 0.186
25:75	1.066 ± 0.120	1.19 ± 0.167
0:100	0.927 ± 0.028	1.223 ± 0.180

All values are presented with an average with standard deviation.

Table 10. Result of TSS and FE of plywood bonded with two types of MUF resins at three melamine contents.

Melamine Content (wt%)	MUF-A Resins	MUF-B Resins
	TSS (MPa)	TSS (MPa)
5	0.51 ± 0.08	0.84 ± 0.19
10	0.90 ± 0.14	0.96 ± 0.07
20	1.05 ± 0.05	1.05 ± 0.07

All values are presented with an average with standard deviation.

9. Conclusions

This review paper attempted to compare adhesion behaviors of UF and MUF resins in bonding wood. For this purpose, UF resins prepared by blending low-viscosity resin (LVR) with high-viscosity resin (HVR) at five blending ratios and two F/U molar ratios were compared for the molar mass, E'_{max} value, resin penetration, bond-line thickness, and tensile shear strength (TSS). As expected, the effects of molar mass of UF resins on the viscosity, curing kinetic, interphase, resin penetration, and bond-line thickness were closely related to their behavior as adhesive. The UF resin–wood composite showed the highest E'_{max} , at 2000–2400 g/mol for the 1.0 F/U resins and 3500–4500 g/mol for the 1.2 F/U molar ratio resins, respectively. The bond-line thickness was likely affected by the resin molar mass and their penetration depths. The highest UF resin penetration was related to the lowest bond-line thickness. As expected, the tensile shear strengths of the 1.2 F/U molar ratio resins were higher than those of the 1.0 F/U molar ratio resins. The combination of certain low-molar-mass and high-molar-mass proportions resulted in the highest E'_{max} , maximum resin penetration, thinnest bond line, and highest TSS. Compared with the synthesis methods, MUF-B resins had greater MWs at 20% melamine, smaller resin penetration, thicker bond line, greater E'_{max} , and higher TSS than those of MUF-A resins. These results indicate that the adhesion in the bond line of UF resins predominantly is governed by the interphase adhesion, while that of MUF resins is mainly affected by the cohesion in the bond line in bonding wood. In addition, the melamine content and synthesis method mainly affect the cohesive features of these resins, which eventually determined their adhesion performance in plywood.

Author Contributions: Conceptualization, B.-D.P.; methodology, B.-D.P. and B.J.; formal analysis, B.-D.P.; investigation, S.P., B.-D.P. and B.J.; writing—original draft preparation and revisions, S.P., B.-D.P., and B.J.; writing—review and editing, B.-D.P.; visualization, B.-D.P., B.J. and S.P.; supervision, B.-D.P.; project administration, B.-D.P.; funding acquisition, B.-D.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by National Research Foundation (NRF) of Korea funded by the Korean Government (MSIT), grant number 2020R1A2C1005042.

Acknowledgments: The authors are grateful for the National Research Foundation (NRF) of Korea funded by the Korean Government (MSIT) for the financial support.

Conflicts of Interest: The authors declare no conflict of interest.

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