Effect of Melamine Allocation Proportion on Chemical Structures and Properties of Melamine-Urea-Formaldehyde Resins

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Melamine-urea-formaldehyde (MUF) resin was synthesized by adding melamine with a first and second portion of urea, named M1 and M2, respectively. Different allocation proportions of M1:M2 (4:0, 3:1, 2:2, 1:3, and 0:4) were used to develop five MUF (MUF-1, 2, 3, 4, and 5) resins with an F/(U+M) molar ratio of 1.05. The chemical structures, curing behaviors, and cross-section morphology of the resins were characterized. Three-ply plywood was fabricated to evaluate wet shear strength and formaldehyde emission. Results showed that when the melamine allocation proportion was increased from 0:4 to 4:0, the total methylene ether group content increased, the curing rate was elevated, and a heterogeneous cross-section of the cured resin formed, which led to a wet shear strength increase of 42.11%. When the melamine allocation proportion decreased, the free melamine content increased, the pot life was prolonged, and a highly homogeneous morphology was formed, which resulted in a decrease of 42.86% in formaldehyde emission of the resulting plywood. These results suggested that a high melamine allocation proportion, meaning that more of the MUF resin was added initially, improved the water resistance of the resulting resin, whereas a low melamine allocation proportion decreased the formaldehyde emission reduction of the resulting plywood.

Keywords: MUF resin; Melamine allocation proportion; Chemical structures and properties

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INTRODUCTION

Urea-formaldehyde (UF) resin is one of the most important adhesives in the wood composites industry. UF resin is especially useful for bonding interior wood-based composite boards such as plywood, particleboard, and medium density fiberboard. In recent years, bio-based adhesives prepared from renewable natural resources have been widely researched, such as starch, tannin, and protein (Qiao *et al.* 2014; Zhang *et al.* 2014; Zhang *et al.* 2015). Bio-based adhesives, however, cannot fully replace UF resins in the short period because of their high cost and low production efficiency. UF resin has a formaldehyde emission issue, and an effective method to reduce formaldehyde emission is by lowering the overall formaldehyde/urea (F/U) molar ratio (Myers and Koutsky 1990); however, a low mole ratio UF resin tends to result in poor bond strength, low water resistance, and poor assembly properties. Another effective method is introducing melamine to develop a melamine-urea-formaldehyde (MUF) resin. Melamine has a higher reactivity than urea and thus captures more formaldehyde and results in reducing the formaldehyde emission of bonded panels. Meanwhile, the ring structure of melamine increases the crosslinking extent of the cured resin and leads to an elevated bond strength; therefore, MUF resins have been widely investigated and applied (Sun *et al.* 2011; Zhou *et al.* 2013).

In the present study, MUF resins were prepared based in a UF resin synthesis procedure. A commonly used synthesis procedure of UF resin is a three-step resin procedure, undergoing alkaline hydroxymethylation (the first step), acidic condensation (the second step), and alkaline post urea addition (the third step) (No and Kim 2007). Melamine is added in the first and/or third step for modifying the UF resin to obtain different MUF resin formulations. The synthesis mechanism of MUF resin is similar with that of UF resin. If melamine is added in the alkaline hydroxymethylation step, it replaces part of the urea to react with formaldehyde to form various hydroxymethylmelamines. Then, the condensation reaction is carried out in a slightly acidic condition, which is complex and involves the condensation between hydroxymethylmelamines and/or hydroxymethylureas (Kim *et al.* 2006). If melamine is added in the alkaline post-urea addition step, it reacts with residual free formaldehyde, and the condensation reaction is performed in the curing process of resin. The reaction schematic of MUF resin synthesis is shown in Fig. 1.

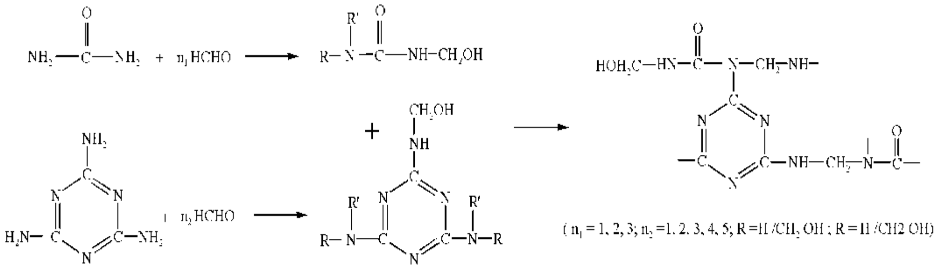

Fig. 1. The reaction schematic of MUF resin synthesis

Although possessing good performance attributes, MUF resin formulations with high melamine content have not been widely applied in the wood industry because of the higher cost of melamine than that of urea. In addition, high melamine content leads to a limited stability of the MUF resin due to the poor solubility of melamine. Therefore, a low melamine dosage (6% based on the weight of liquid MUF resin) was considered in the present study. The performance of MUF resins closely relies on the resin formulation and synthesis parameters. Lei *et al.* (2006) found that formulations resulted in different variations of molecular mass distribution during the progress of reaction and ageing of MUF resins. Xu *et al.* (2009) investigated the curing behavior and adhesion performance of a MUF resin synthesized by the staged addition of melamine. The study found that the MUF resin with the addition of melamine initially with the urea and formaldehyde showed the lowest thermal stability, rigidity, temperature of tan δ maximum, wet shear strength, and pH value of the cured resin. Paiva *et al.* (2012) studied the effect of the pH of the condensation reaction on the performance of the MUF resin synthesized using a strong acid process. It was reported that the condensation reaction at a pH below 3.0 was fast and difficult to control, but at a pH above 5.0 it became excessively slow. The particleboard bonded by MUF resin synthesized with a condensation reaction pH between 4.5 and 4.7 showed good internal bond strength and formaldehyde emission. Zhang *et al.* (2013) found that the MUF resin with melamine addition in the second stage had a low cross-linking degree, high activation energy, and low heat of reaction during the curing process. Recently, a series of works on melamine-modified UF resins were reported by Mao and coworkers (Mao *et al.* 2013a,b,c,d). They revealed the effect of methylene-ether groups in MUF resins on the bond strength and the formaldehyde emission of particleboard. Results showed that the formaldehyde contents of produced boards were mainly due to the methylene-ether-type groups in the UF and MUF resins.

Although these experiments were carried out to study the effect of the melamine addition stage on resin synthesis and adhesion performance, the reaction mechanism of the melamine in MUF resin synthesis process is still unclear. The investigation of the melamine addition stage on the resin structure and functional groups allowed for improving the MUF resin performance and reducing its cost. In the present study, five types of MUF resins were prepared by allocating melamine in the first (M_1) and third (M_2) steps of synthesis at different proportions (M_1:M_2= 4:0, 3:1, 2:2, 1:3, and 0:4). The effect of different formulations on the structure and performance of the resins were investigated. The chemical structures of the resins were characterized by ^{13}C nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) spectroscopy. Differential scanning calorimetry (DSC) was used to study the curing behavior of the resins. The cross sections of the cured resins were detected using a scanning electron microscope (SEM). Three-ply plywood was fabricated, and its wet shear strength and formaldehyde emission were measured.

EXPERIMENTAL

Materials

Formaldehyde solution (37%), sodium hydroxide, ammonium chloride, and formic acid were reagent grade and purchased from Tianjin Chemical Reagent Company, China. Urea and melamine were industrial reagents and provided by Lanyi Chemical Co., China. Poplar veneers with 8.0% moisture content and dimensions of 400 × 400 × 1.5 mm were obtained from Wen’an City, Hebei Province, China.

Methods

Preparation of MUF resins

Five types of MUF resins with 6% melamine content (based on the weight of liquid resin) and F/(U+M) molar ratio of 1.05 were prepared following typical alkali-acid-alkali synthesis procedure. First, 284.1 g of formaldehyde solution (37%) was placed in a reactor and adjusted to a pH of 7.5 to 8.0 with 20% sodium hydroxide solution. Then, the first amount of urea (U_1) and melamine (M_1) was added to give a F/(U_1+M_1) molar ratio of 2.0. The mixture was then heated to 90 °C for 1 h. The acidic reaction was brought by adding formic acid (30%) to obtain a pH of 5.5 to 6.0, and the condensation reaction was carried out until a target viscosity was reached (24-26 s, 30 °C, No 4 Cup). The pH of the mixture was adjusted to 7.5 to 8.0. The second amount of urea (U_2) and melamine (M_2) was added, and the F/ (U_1+U_2+M_1+M_2) molar ratio became 1.4. After 0.5 h at 80 °C, the third amount of urea (U_3) was added and the final F/ (U+M) molar ratio was 1.05. The mixture was further stirred at 80 °C for 0.5 h. The melamine was added in the alkaline hydroxymethylation step (M_1) and/or alkaline post amino addition step (M_2), and the relative allocation proportions were M_1:M_2= 4:0, 3:1, 2:2, 1:3, and 0:4, respectively. After cooling the resins, the pH was adjusted to 8.0. The formulation of the staged addition of the melamine in the MUF resin synthesis procedure is shown in Table 1.

Table 1. Melamine and Urea Addition of Different MUF Resin Formulations

Resins	Synthesis Parameters				
	U_1 (g)	M_1 (g)	U_2 (g)	M_2 (g)	U_3 (g)
MUF-1	90.8	30.0	45.1	0.0	50.0
MUF-2	94.4	22.5	41.5	7.5	50.0
MUF-3	98.0	15.0	38.0	15.0	50.0
MUF-4	101.5	7.5	34.4	22.5	50.0
MUF-5	105.1	0.0	30.8	30.0	50.0

Resin physical property measurement

The solid content of the adhesive was measured based on an oven-drying method. About 2 g of resin was placed into an oven for 3 h at a temperature of 120 ± 2 °C. The pot life of the resin was measured according to the China National Standard (GB/T 14074-2006). About 50 g of resin and 2 mL of ammonium chloride solution (25%) were placed in a water bath at 25 °C. The variation of viscosity of the catalyzed resin was checked every 10 min until completely cured. The viscosity of the adhesive was measured using a Brookfield DV-II viscometer using the 61# rotor with a spinning rate of 100 rpm. An average of three replications was used for each measurement.

^{13}C nuclear magnetic resonance (NMR) spectroscopy

The ^{13}C NMR spectra of the resins were obtained using a DELTA2 600 NMR spectrometer from JEOL RESONANCE Inc., Japan. The liquid resins were dissolved in deuterated dimethyl sulfur oxide (DMSO-D6). The resolution, pulse-width, relaxation-delay, and repetition time were 1.45 Hz, 12.75 μs (30°), 20 s, and 20.69 s, respectively, and used for quantitative results with 2560 scans accumulated for each sample. A decoupling method was used to minimize the nuclear Overhauser effect.

Fourier transform infrared (FTIR) spectroscopy

The resins were placed in an oven at 120 ± 2 °C until they reached a constant weight to cure completely, then ground into fine powder. The powder was mixed with KBr crystals at a mass ratio of 1/100, and pressed in a special mold to form a sample folium. The FTIR spectra were recorded using a Thermo Nicolet 6700 FT-IR (USA) over the range of 400 to 4000 cm^{-1} with a 4 cm^{-1} resolution and 32 scans.

DSC measurement

The resins were mixed with 1% solid ammonium chloride (based on the weight of liquid resins) and then freeze-dried for 12 h. About 5 mg of the freeze-dried resins were placed in an aluminum pan. The pan was sealed and then heated from -10 °C to 130 °C at a heating rate of 10 °C/min using a TA Instrument (DSC Q2000, Waters Company, USA). Each measurement was done under 50 mL/min flow of N_2 for protection.

Scanning electron microscope (SEM) test

The resins were placed in an oven at 120 ± 2 °C to cure completely. The cured MUF resins were fractured, and the fractured cross-sections were tested. During testing, the samples were first placed on an aluminum stub. A coating of 10 nm Au/Pd film was applied to the samples using a Q150T S Turbo-Pumped Sputter Coater/Carbon Coater (Quorum Technologies Ltd., UK). The coated samples were then examined and imaged using a JSM-6500F field emission scanning electron microscope (FESEM) (JEOL USA Inc., Peabody, MA).

Preparation of plywood samples

Three-ply poplar plywood was prepared at a 1.0 MPa pressure and a 120 °C hot pressing temperature. The ammonium chloride of 0.8% (based on the liquid MUF resin) was used as the curing agent. The adhesive spread rate was 160 g/m^2 (single glue line) and the hot pressing time was 6 min. After hot pressing, the plywood was stored under ambient conditions for at least 24 h before the wet shear strength was tested. Three plywood panels were made for each formulation of the resin.

Formaldehyde emission measurement

The formaldehyde emission of the plywood was determined using the desiccator method in accordance with the procedure described in China National Standard (GB/T 17657-2013). After being stored in a ventilation environment for 20 days, the plywood was prepared with dimensions of 50 mm ×150 mm. Then specimens of each panel were put into a 9 to 11 L sealed desiccator at 20 ± 2 °C for 24 h. The emitted formaldehyde was absorbed by 300 mL deionized water in a container. The water was measured by a visible spectrophotometer to obtain the formaldehyde emission value. The average value of formaldehyde emission was calculated from three panels and recorded.

Wet shear strength test

The wet shear strength of the plywood was determined in accordance with the China National Standard GB/T 9846.3-2004 for Type II plywood. The plywood pieces prepared were cut into shear specimens (gluing area of 25 mm × 25 mm) and then submersed in water at 63 °C for 3 h. The wet shear strength values of the wood specimens were tested using a common tensile machine operated at a speed of 10.0 mm/min. The force (N) at which the bonded wood specimen was damaged was recorded. The reported strength data of the adhesives were the average of ten replications from two plywood. Wet shear strength (MPa) was calculated using the following equation (Eq. 1):

$$\text{Wet Shear strength (MPa)} = \frac{\text{Force (N)}}{\text{Gluing area (m}^2\text{)}} \tag{1}$$

RESULTS AND DISCUSSION

^{13}C-NMR Spectroscopy Analysis

Figure 2 shows the ^{13}C-NMR spectra of the five MUF resins. Integrated areas of peak intensities and the associated percentage values (P) were calculated based on the total urea/melamine carbons or formaldehyde-derived carbons and are shown in Table 2. Chemical shift values were referenced to the peak of DMSO-D6 at 39.52 ppm. The definition and assignment of carbon groups were determined according to previous works (Kim 2000, 2001; Kim *et al.* 2003).

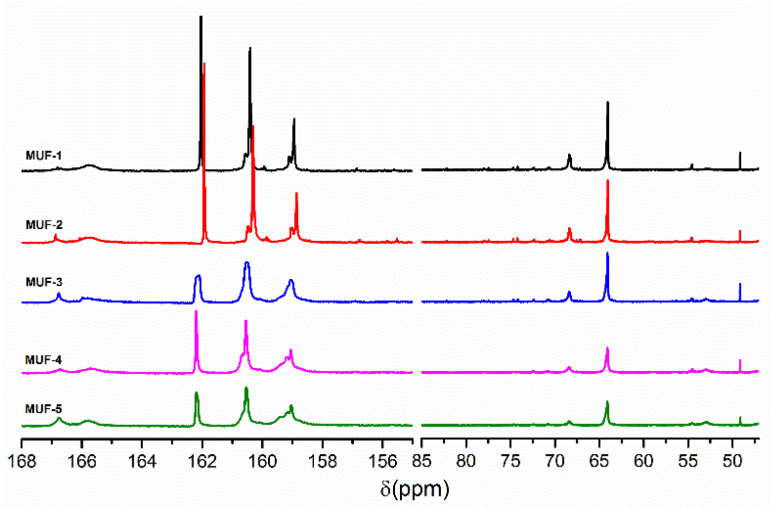

Fig. 2. The ^{13}C-NMR spectra of the MUF resins

Table 2. Assignments and Percentage Integration Values for Various Methylenic and Carbonyl Carbons of the MUF Resins

Carbon Groups	**Chemical shift**	**Resins**				
		MUF-1(%)	MUF-2(%)	MUF-3(%)	MUF-4(%)	MUF-5(%)
Total methylene		10.76	14.18	22.49	38.08	39.31
Type I	47.12 - 47.47	8.19	10.80	14.26	22.10	20.56
Type II	53.83 - 54.20	0.64	1.21	5.70	12.28	15.30
Type III	55.49 – 55.73	1.93	2.17	2.53	3.69	3.45
Total hydroxylmethyl		59.36	58.99	57.03	47.10	49.89
Type I	64.96 -65.29	57.89	57.98	55.32	46.05	48.77
Type II	75.14 – 75.40	1.47	1.02	1.70	1.05	1.12
Total methylene ether		28.87	25.71	19.31	13.83	10.02
Type I	69.39 – 69.62	28.07	23.87	18.25	13.51	9.56
Type II	75.22 – 75.40	0.56	1.44	0.88	0.26	0.45
Type III	78.40 – 78.55	0.24	0.39	0.17	0.06	
Free formaldehyde	83.14 – 83.42	0.07	0.08	0.02	0.05	0.05
Cyclic urea	155 - 157	0.67	1.10	0.38	0.29	0.40
Mono-substituted urea	161.24 – 161.74	49.67	48.42	46.12	41.37	40.42
Di, tri-substituted urea	159.97 – 160.79	23.90	25.66	30.90	40.55	39.69
Free urea	163.07 – 163.40	25.77	24.83	22.60	17.79	19.49
Total urea		100	100	100	100	100
Substituted melamine	166.80 – 167.04	83.49	78.26	64.44	59.42	52.17
Free melamine	167.80 – 167.96	16.51	21.74	35.56	40.58	47.83
Total melamine		100	100	100	100	100

As shown in Table 2, the total methylene ether group content of resin decreased with a decrease of the melamine allocation proportion, and the MUF-1 resin had the highest methylene ether group content of 28.87% in all MUF resins. According to other research (Mao *et al.* 2013c,d), a high methylene ether content of MUF resin resulted in a good performance; therefore, high allocation proportion was beneficial to increase the bond strength of bonded plywood. Meanwhile, the total methylene group content increased with the melamine allocation proportion decreased, and the MUF-5 resin possessed the highest methylene ether group content of 39.31% in all MUF resins. This may be attributed to the more melamine added in the third step of the synthesis process, which caused the methylene ether group to be rearranged into a methylene group (Despres *et al.* 2007).

The free melamine content increased from 16.51% in the MUF-1 resin to 47.83% in the MUF-5 resin as the melamine allocation proportion decreased from 4:0 to 0:4. Owing to the high reactivity, melamine can react with more formaldehyde molecules than urea to capture free formaldehyde during curing; therefore, a low melamine allocation proportion is beneficial for the formaldehyde emission reduction of the resulting panel.

When the melamine allocation proportion was at 4:0, 3:1, and 2:2, the synthesized MUF resins showed higher hydroxylmethyl group contents than at 1:3 and 0:4. The obvious increase in hydroxylmethyl groups provided more reactive sites for the crosslinking reaction and resulted in higher crosslinking density and compact crosslinking structure of the cured resins, which may resulted in the improved bond strength; therefore, the increase in melamine allocation proportion was in favor of enhancing the bond strength of the resulting plywood.

FTIR Spectroscopy Analysis

The FTIR spectra of the cured MUF resins are shown in Fig. 3. The broad band at 3340 cm^{-1} was assigned to the N-H stretching of primary amines. The C=O stretching of primary amides was the main absorption band of the UF resin infrared spectrum, which was recorded at 1639 cm^{-1}. The occurrence of the 1543 cm^{-1} band was assigned to the C-N stretching of secondary amines. The peak at 1378 cm^{-1} was assigned to the C-N stretching of CH_2-N. The peak at 1243 cm^{-1} was the C-N and N-H stretching of tertiary amines. The peak around 1130 cm^{-1} was the C-O stretching of aliphatic ether. The bands from 1030 to 1050 cm^{-1} were assigned to C-N or N-C-N stretching of the methylene linkage in the resins. The spectra of all the MUF resins exhibited a small band at 814 cm^{-1}, which is assigned to the typical stretching of the triazine ring of melamine (Reimschuessel and McDevitt 1960; Kandelbauer *et al.* 2007; Sun *et al.* 2011; Gao *et al.* 2012).

As shown in Fig. 3, the spectra of five MUF resins were quite similar to each other, and all of them specific absorption peaks did not change their position regardless of the melamine addition method. Moreover, no new absorption bands were observed in the FTIR spectra. These results may be attributed to the reaction similarity of the five MUF resins. Melamine and urea were incorporated into the cured network by the methylene and methylene ether linkage.

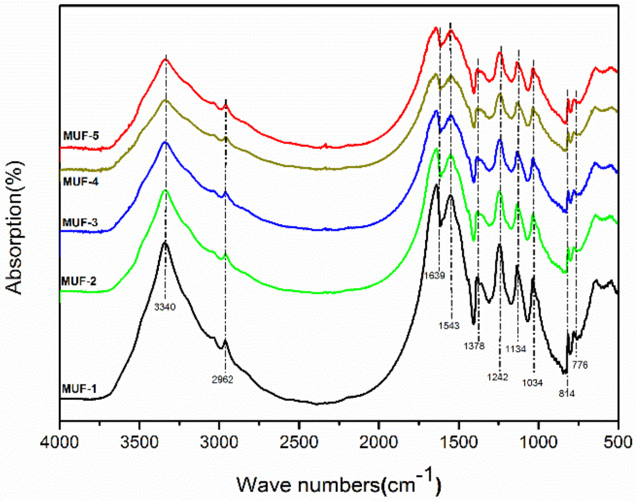

Fig. 3. The FTIR spectra of the cured MUF resins

DSC Analysis

Figure 4 shows the DSC curves of the MUF resins at a heating rate of 10 k/min. The curing process of MUF resin is usually considered as the continuation of condensation reaction and involves the evaporation of water and releasing of free formaldehyde. The condensation reaction was an exothermic reaction, which is attributed to the heat released from the polycondensation reaction of the primary amino groups of the free urea/melamine with hydroxymethyl groups. In addition, the branched-type methylene bridge cross-links were formed by the reaction between free melamine and hydroxymethyl groups in the curing process (Zhang *et al.* 2013). With a decrease in the melamine allocation propertion from 4:0 to 0:4, the peak temperature increased from MUF-1 to MUF-5, and the values were 95.43 °C, 95.71 °C, 97.02 °C, 98.24 °C, and 102.56 °C, respectively. In the peak temperature, the fastest curing reaction was produced. The results suggested that the curing rate of the MUF resins declined as the melamine allocation proportion was decreased. This may be attributed to an increased free melamine content from MUF-1 to MUF-5. Owing to its buffer function as an alkali compound, melamine impacted the decrease in pH after adding a catalyst to the curing process. According to the ^{13}C-NMR analysis, the free melamine content increased from MUF-1 to MUF-5, which indicated that the MUF-5 resin had the highest buffer capacity; therefore, when the same amount of catalyst was added, the pH of the MUF-5 resin hardly decreased and the curing rate was reduced. This resulted in an increase in peak temperature of the MUF-5 resin, which may cause incomplete curing and low bond strength under the same curing conditions.

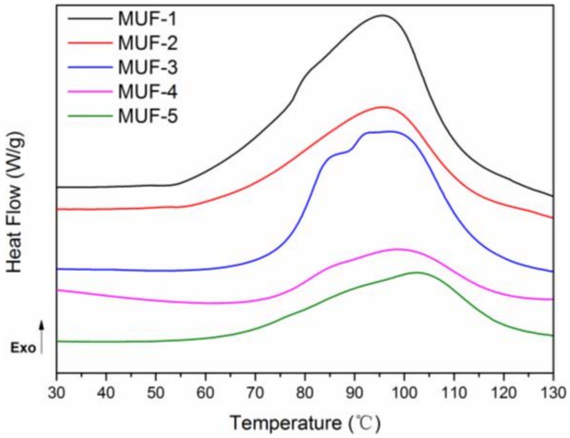

Fig. 4. The DSC curves of the MUF resins

Morphology of Cross-sections of Cured Resins

All of the formaldehyde-based resins have been considered to be in a colloidal state, which can have a remarkable influence on the performance and stability of the resin, especially the MUF resin (Zanetti *et al*. 2002). Figure 5 shows the cross-sections of the cured MUF resins. As shown in Fig. 5, the cured MUF-1 resin possessed a heterogeneous cross-section. With the melamine allocation proportion decreased, the resulting cross-section became more uniform, and a highly homogeneous morphology was formed in the MUF-5 resin. For MUF-1 resin, all melamine was introduced at the first step of synthesis process and took part in the acidic condensation reaction, which resulted in the formation of large colloidal particles with low solubility in water. These insoluble particles dispersion would show a heterogeneous morphology after agglomerating in curing process. Moreover, the insoluble colloidal particles in the MUF-1 resin would lead to a increased bond strength because of the high condensation (Ferra *et al.* 2010). Similarly, the MUF-5 resin showed a highly homogeneous cross-section, which might possibly explain the low bond strength resulting from this resin formulation procedure.

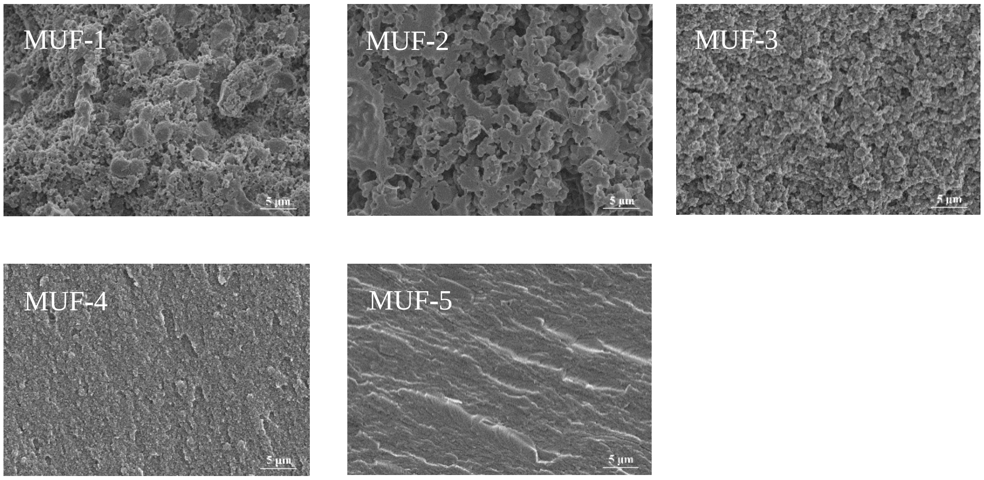

Fig. 5. Cross-sections of the cured MUF resins

Wet Shear Strength and Formaldehyde Emission Measurement

Physical properties of the prepared MUF resins and the performance of the resulting plywood are summarized in Table 3. These tested values for the different formulations are as expected and are also within the range of industrial values. The melamine addition method had a significant effect on viscosity and pot life of the resins. When the melamine allocation proportion was decreased, more free melamine remained, as shown by the results of NMR analysis. The curing rate of resin declined as the observation of DSC analysis. These influences led to an increased pot life from MUF-1 to MUF-5 resin. Meanwhile, MUF-5 resin showed the highest viscosity in all resins, which may be due to the continuous reaction of melamine in an alkaline condition. As expected, the MUF-1 resin has the highest wet shear strength of 1.08 MPa and showed an increase of 42.11% compared with the MUF-5 resin. In addition, the MUF-5 resin possessed the lowest formaldehyde emission of 1.12 mg/L and showed a decrease of 42.86% compared with the MUF-5 resin.

Table 3. Physical Properties of the MUF Resins

Resin	Solid content (%)	Viscosity (cP)	Pot life (min)	Wet shear strength (MPa)	Formaldehyde emission (mg/L)
MUF-1	54.45 ± 1.20	29.5 ± 2.3	561 ± 5	1.08 ± 0.32	1.96 ± 0.22
MUF-2	53.92 ± 1.68	32.0 ± 2.8	578 ± 5	1.04 ± 0.38	1.88 ± 0.36
MUF-3	53.88 ± 1.33	43.7 ± 3.2	582 ± 5	0.97 ± 0.22	1.84 ± 0.42
MUF-4	53.78 ± 1.14	83.1 ± 3.6	596 ± 5	0.83 ± 0.25	1.16 ± 0.32
MUF-5	53.59 ± 2.06	102.9 ± 5.6	720 ± 5	0.76 ± 0.13	1.12 ± 0.24

CONCLUSIONS

The melamine addition method was shown to have a remarkable influence on the performance of the MUF resin. With the different melamine allocation proportions, the bonded plywood exhibited different wet shear strength and formaldehyde emission.

A high allocation proportion of 4:0 (all melamine were added in the first alkaline hydroxymethylation) increased methylene ether group content of the synthesized MUF resin, and most melamine went through the acidic condensation reaction, thus resulting in an increase of the bond strength. On the contrary, a low allocation proportion of 0:4 (all melamine were added in the alkaline post urea addition) led to most free melamine remaining in the synthesized MUF resin, which was beneficial for decreasing the formaldehyde emission. In order to obtain a high bond strength of the resulting plywood while the formaldehyde emission is in an acceptable range, melamine should not be solely added in a synthesis step, and an appropriate allocation proportion is need depending on the target application.

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