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Influence of the melamine content in melamine-urea-formaldehyde resins on formaldehyde emission and cured resin structure

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Abstract The effect of melamine content in melamine-urea-formaldehyde (MUF) resins on the formaldehyde emission and resin structure was investigated using six MUF resins synthesized with different F/(M + U) and M/U molar ratios. The formaldehyde emission from the plywood decreased as the F/(M + U) molar ratio decreased and the M/U molar ratio increased. In addition, the bond performance was enhanced as the M/U molar ratio increased in the MUF resins with a fixed F/(M + U) molar ratio. Quantitative solution ^{13}C -NMR spectra of MUF resins revealed that the MUF resins with a high melamine content consisted of more highly branched crosslinkage structure and free melamine compared to the resins with low melamine contents. Furthermore, solid-state ^{13}C CP-MAS NMR spectra of cured MUF resins proved that more methylol groups, dimethylene ether, and branched methylene structures were present in the MUF resins with a higher F/(M + U) molar ratio, leading to increased bond strength and formaldehyde emission. There is no significant difference in the linkage structure of the cured resins with the same F/(M + U) and different M/U molar ratios except the ratios of carbonyl carbon of urea and triazine carbon of melamine. Therefore, the lower formaldehyde emission from cured MUF resins with a higher M/U molar ratio might be ascribed to the stronger linkages between triazine carbons of

melamine than those of urea carbons. Consequently, the melamine contributed to strong crosslinking linkages in the cured resin structures, leading to lower formaldehyde emission and better bond performance.

Key words Formaldehyde emission · Melamine-urea-formaldehyde resin · Cured resin structure · Solid state ^{13}C -NMR analysis

Introduction

Melamine-urea-formaldehyde (MUF) resins have been used successfully for plywood, particleboard, medium-density fiberboard, and other wood products for three decades. Although the wood products bonded by MUF resins have seen widespread use because of their higher bond qualities than those of urea-formaldehyde (UF) resins, formaldehyde emission from the products has become an indoor air pollution problem, causing harm to human health, similar to the UF resins. A review of numerous reports^{1,2} suggests that formaldehyde is mainly emitted from the following three sources: (1) residual formaldehyde in the resin; (2) formaldehyde generated by a condensation reaction between hydroxymethyl groups and other aromatic carbons or two hydroxymethyl groups; and (3) formaldehyde released by hydrolytic degradation of cured resins, especially under high humidity and high temperature circumstances. Recent efforts are directed to the prevention or reduction of formaldehyde emissions from wood-based panels bonded with MUF resins. The most beneficial approach to reducing formaldehyde emission consists of lowering the formaldehyde/amino group molar ratio during synthesis of resin adhesives while maintaining the required reactivity and crosslinking. It has been proposed that the more substituted triazine and urea nuclei in the MUF resin provide lower amounts of formaldehyde as measured by ^{13}C nuclear magnetic resonance (NMR) spectroscopy.^{3,4} However, the effect of the melamine content in MUF resins on the cured resin structure and formaldehyde emission is still unclear.

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In this study, solution ^{13}C -NMR and solid-state ^{13}C -cross-polarization magic angle spinning (CP/MAS) NMR techniques were used to characterize the MUF resin structure before and after curing, respectively. The effect of the melamine content on the cured resin structure and formaldehyde emission is also discussed.

Experiment

MUF resin preparation

Urea, melamine, and 37% formaldehyde with an initial F/U/M molar ratio of 4.5/1.0/1.0 were added to a flask. The mixture pH was adjusted to 7.0–7.5 with an aqueous 1N NaOH solution while stirring the mixture. The mixture was then heated to 85°C in a waterbath for 30 min, keeping the same temperature for another 45–60 min. The degree of condensation was measured by a turbidity point method every 5 min; one drop of resin was dispersed in 100 ml of water. When the solution was turbid and not dissolved, the reaction was stopped. The pH was then corrected by adding 1N NaOH solution to a pH of 8.5–9.0. The resin was allowed to cool to 60°C. The required additional urea, melamine, or both were then added to the reaction mixture, and the resin was allowed to mature at 60°C for 60 min. Several characteristics of the synthesized resin then were determined in accordance with the Japanese Industrial Standard (JIS) K6801.

A series of MUF resin samples were weighed and then placed for 30 min in an oven kept at 110°C. The cured MUF samples then were ground thoroughly and prepared for solid-state ^{13}C -CP/MAS NMR analysis.

Preparation of plywood and testing

Red lauau (*Shorea spp.*) veneers with dimensions of 30 cm \times 30 cm \times 1.5 mm thickness were chosen for this study. Four three-ply plywood samples were bonded with each synthesized resin under the following conditions: veneer moisture content 6%–8%; glue spread 360 g/m² (double glue line); cold press 0.98 MPa for 30 min; hot press 0.98 MPa at 120°C with a pressing time of 135 s. All adhesive formulations were 100 g MUF resin, 15 g wheat flour, 10 g water, and 0.5 g ammonium chloride.

Bond performance test

A bond performance test was conducted using the delamination test of Japanese Agricultural Standard (JAS) for common plywood: 4 h of boiling, drying at 60°C for 20 h (one cycle), then 4 h of boiling and drying at 60°C for 3 h (two cycle). The rate of delamination was measured after each cycle. Four specimens cut into 75 \times 75 mm samples from one piece of plywood were subjected to the delamination test.

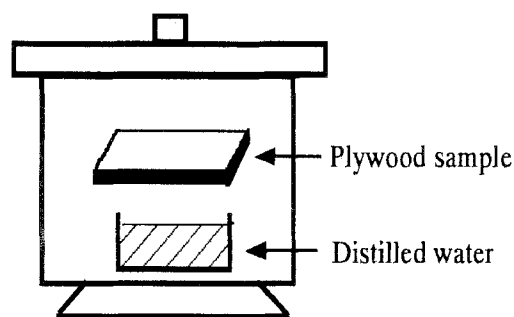


Fig. 1. Japanese Agricultural Standard (JAS) desiccator method for determining formaldehyde emissions from wood panels

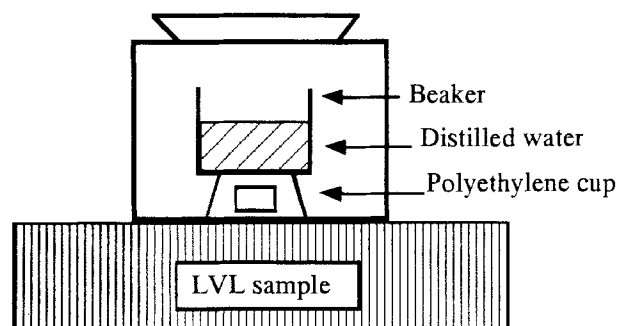


Fig. 2. Upside-down desiccator method for determining formaldehyde emissions from laminated veneer lumber (LVL)

Formaldehyde emission test

The formaldehyde emissions from the plywood samples were measured using two methods: the desiccator method prescribed in JAS for plywood (Fig. 1) and an upside-down desiccator method developed in our laboratory for laminated veneer lumber (LVL)⁵ (Fig. 2). Ten specimens cut into 150 \times 50 mm samples from 3 plywood pieces were subjected to the formaldehyde emission test using the desiccator method. One plywood (300 \times 300 mm) was subjected to the formaldehyde emission test using the upside-down desiccator method. The measurements were made just one time for each period: after 1 day, 1 week, 2 weeks, and 1 month of the sample preparation.

Solution ^{13}C -NMR spectra

Solution ^{13}C -NMR spectra were obtained with a JNA-LA400 FT-NMR spectrometer (400 MHz, Japan Electron Optics). The observed frequency was fixed at 100 MHz, operating frequency at 27 MHz, and irradiation frequency at 400 MHz for dimethylsulfoxide (DMSO- d_6). All spectra were run with a pulse width of 5 μs and a pulse delay of 30 s for 1000–5000 scans. Chemical shifts in DMSO- d_6 solution were calculated by defining a ^{13}C chemical shift of DMSO- d_6 at 39.5 ppm. Peak assignment and quantitative analysis were based on the signal intensities of total formaldehyde described in a previous paper.⁶

Solid-state ^{13}C -CP/MAS NMR spectra

Solid-state ^{13}C -CP/MAS NMR spectra were obtained on a Chemagnetics CMX300 spectrometer: contact time 3 ms, pulse delay 10 s; decoupling delay 35 μs ; H 90 pulse 4.5 μs , C 180 pulse 10 μs ; MAS speed 3.0 kHz. Two large and two small spinning sidebands were placed at a 40-ppm interval outside the center band of the carbonyl at 159 ppm. Chemical shifts were determined using a standard reference of methyl carbon (17.17 ppm) in hexamethylbenzene.

Results and discussion

Resin properties

The final $F/(M + U)$ and M/U molar ratios, melamine contents, and resin properties are summarized in Table 1. The gel time decreased and the viscosity increased as the melamine content increased. In general, the gel time and viscosity of thermosetting resins were related exponentially to the molecular weight. Therefore, it can be said that a high melamine content in MUF resin leads to more condensation and thus higher-molecular-weight resins compared to resin with a lower melamine content. Apart from that, no other significant difference was observed in the free formaldehyde content. In the bond performance test, all the plywood samples passed the one-cycle boiling test; however, the plywood samples bonded by the resins with an $F/(M + U)$ molar ratio of 1.125 had some problems during the two-cycle boiling. The bond quality deteriorated as the melamine content decreased. Only the MUF6 resin ($M/U = 1$), which had the highest melamine content of the resins with an $F/(M + U)$ molar ratio of 1.125, satisfied the bond performance in the boiling test as did the resins with an $F/(M + U)$ molar ratio of 1.5.

Formaldehyde emission

According to previous studies,^{3,4} formaldehyde emission is directly related to the $F/(M + U)$ molar ratio, irrespective

of the melamine content. However, the effect of the melamine content in the MUF resins with the same $F/(M + U)$ molar ratio on formaldehyde emission is unclear. Figure 3 shows the relation between melamine content expressed as the M/U molar ratio and formaldehyde emission from plywood samples measured by the JAS desiccator method. Formaldehyde emission of the plywood bonded by the resin with an $F/(M + U)$ of 1.5 was much greater than that of a resin with an $F/(M + U)$ of 1.125. In the resin with the $F/(M + U)$ of 1.5, formaldehyde emission decreased significantly as the M/U molar ratio increased. However, even with a M/U molar ratio of 1, the amount of formaldehyde emission could not be reduced below the JAS-Fc0 criteria (0.5 mg/l).

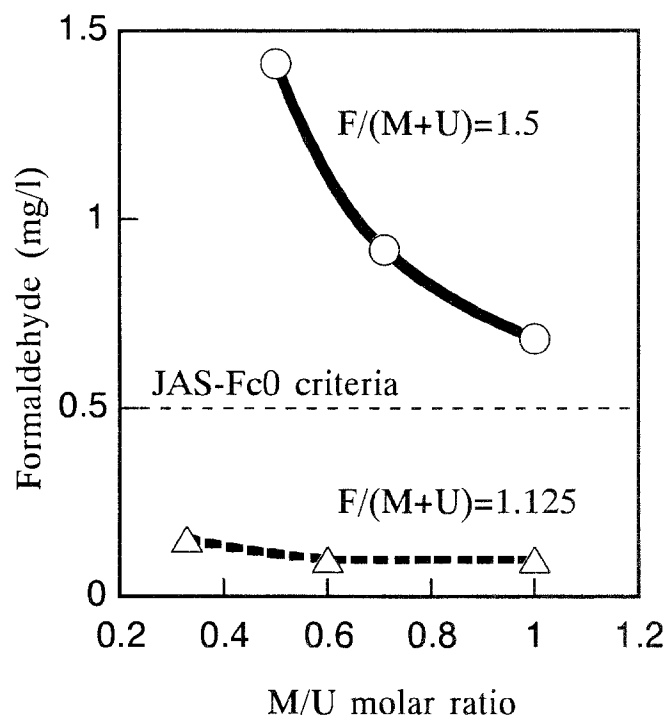


Fig. 3. Effect of melamine content expressed as the melamine/area (M/U) molar ratio in melamine-urea-formaldehyde (MUF) resins on formaldehyde emission measured by the JAS desiccator method

Table 1. Composition and properties of MUF resins

Parameter	MUF1	MUF2	MUF3	MUF4	MUF5	MUF6
Resins						
Final $F/(M + U)$ molar ratio	1.5	1.5	1.5	1.125	1.125	1.125
Final M/U molar ratio	0.5	0.7	1.0	0.3	0.6	1.0
Melamine content (wt% to MUF resin)	34	40	46	29	40	50
Property						
Viscosity (cp) at 25°C	40	100	150	55	75	110
pH at 28°C	8.0	9.9	8.9	8.1	8.3	8.4
Solid content (%)	56.9	59.5	59.7	59.0	59.2	59.3
Gel time at 50°C (min)	41	31	29	47	44	33
Free formaldehyde (%)	0.42	0.43	0.43	0.41	0.40	0.44
Bond performance test^a						
One-cycle delamination rate (%)	0	0	0	0	0	0
Two-cycle delamination rate (%)	0	0	0	100	25	0

MUF, melamine-urea-formaldehyde

^a Soaking delamination test: first cycle: 4 h boiling and 20 h drying at 60°C; second cycle: 4 h boiling and 3 h drying at 60°C

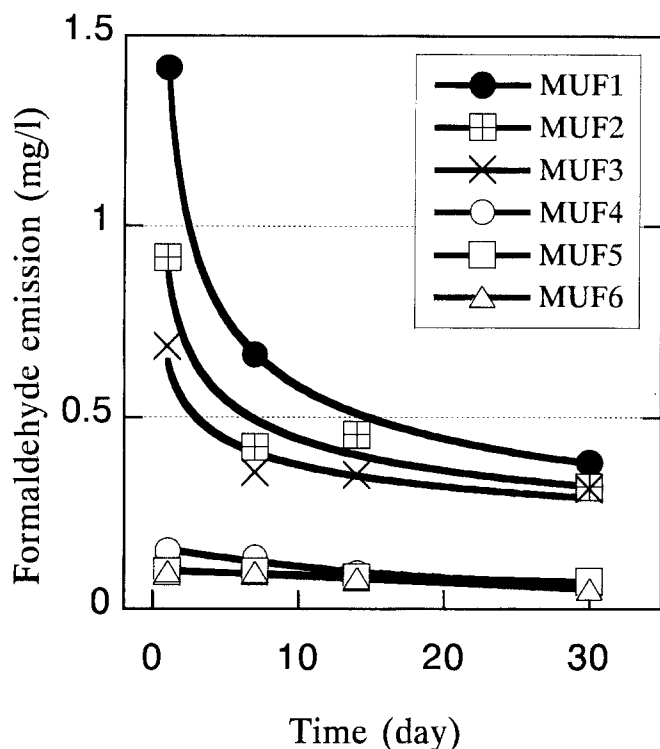


Fig. 4. Time dependence of formaldehyde emission measured by the JAS desiccator method. Samples were placed in a room at 20°C and 45% relative humidity (RH)

This result suggests that a reduction in formaldehyde emission by increasing the melamine content has limitations. On the other hand, all resins with an $F/(M + U)$ of 1.125 exhibited extremely low levels of formaldehyde emission, so there was no significant effect of the melamine content. The two low-melamine resins in the $F/(M + U)$ 1.125 series, however, had problems with their bond performances, as described above.

Figure 4 shows the time dependence of formaldehyde emission. The formaldehyde emission of all $F/(M + U)$ 1.125 resins decreased to <0.1 mg/l after 2 weeks. Although in the $F/(M + U)$ 1.5 resins formaldehyde emission rapidly decreased within 2 weeks down to the JAS-Fc0 level and kept on decreasing gradually after that, formaldehyde of approximately 0.3 mg/l was still emitted after 30 days. These results mean that even when using the resins with an $F/(M + U)$ molar ratio of 1.5, if the products are left in open air for 2 weeks, their formaldehyde emission could become quite low.

Figure 5 shows the formaldehyde emission obtained from the upside-down desiccator method. All formaldehyde emission values were much smaller than those measured by the JAS desiccator method. The most reasonable explanation is that the upside-down method can detect formaldehyde emitted only from one face of the board, not from the edge of the board. In contrast to the results of the JAS desiccator method, no clear relation between formaldehyde emission and time was observed during the 30 days of the upside-down desiccator measurements, and the values were consistently low. Practically, results of an experi-

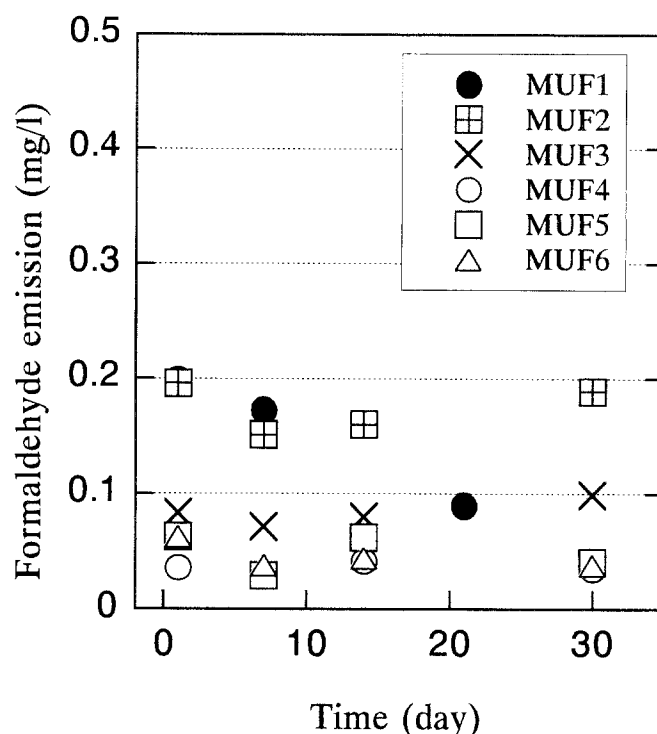


Fig. 5. Time dependence of formaldehyde emission obtained by the upside-down desiccator method. Samples were placed in a room at 20°C and 45% RH

ment using a full-scale model house^{7,8} showed that the upside-down desiccator method enabled estimation of formaldehyde concentration in indoor air.

MUF resin structure before curing

The chemical structure of all MUF resins before curing was investigated by quantitative ^{13}C -NMR spectroscopic analysis. Table 2 shows the integral ratios of various carbons to total formaldehyde. Comparing of the substituted triazine and urea or methylene bond in MUF1–MUF3 resins to those in MUF4–MUF6 resins shows that there were more condensation structures in the resins with a high $F/(M + U)$ molar ratio. The highly branched structure in resins causes an increase in viscosity and shortened gel times. For the same $F/(M + U)$ molar ratio, the MUF resins with a high melamine content consisted of more melamine free reaction sites (see triazine at 167.3–167.5 ppm) than those with a low melamine content. Additional melamine and urea would be consumed to produce methylene bonds compared to the control (CTRL) sample, which does not contain methylene bonds. Free formaldehyde in the high $F/(M + U)$ molar ratio resins was higher than in the lower $F/(M + U)$ resins. However, the differences were too small to affect the formaldehyde emission results. Therefore, formaldehyde emission can be ascribable to the formaldehyde produced during cure or to release after cure. The precise estimation of formaldehyde emission from resin component information appears difficult. Other factors such as the curing con-

Table 2. Solution ^{13}C -NMR spectroscopic integral ratios of various carbons to the total formaldehyde of MUF resin samples

Substance and structure	Peaks in Fig. 6	Chemical shift (ppm)	^{13}C -NMR spectroscopic integral ratio						
			MUF1	MUF2	MUF3	MUF4	MUF5	MUF6	CTRL
Methylene									
—NH—CH ₂ —NH—	a	45.9–47.3	0.11	0.10	0.09	0.11	0.12	0.11	0
—N(CH ₂ —)CH ₂ —NH—	b	53	0.03	0.02	0.01	0	0.01	0.01	0
—N(CH ₂ —)CH ₂ —N(CH ₂)—	c	60	0	0.00	0	0	0	0	0
Methylol									
—NH—CH ₂ OH	d	63.8–64.3	0.84	0.81	0.94	0.68	0.68	0.73	1.34
—N(CH ₂ —)CH ₂ OH		69.6	0.04	0.06	0.03	0.03	0.02	0.02	0.20
Methyl ether									
—NHCH ₂ OCH ₃		72.2	0.03	0.02	0.03	0.02	0.03	0.02	0.04
Dimethylene ether									
—NHCH ₂ OCH ₂ —NH—		67.8–68.5	0.09	0.23	0.17	0.12	0.10	0.09	0.52
—N(CH ₂ —)CH ₂ OCH ₂ NH—		72.3	0.08	0.05	0.05	0.04	0.04	0.05	0.08
Methanol									
CH ₃ OH		49.0–49.5	0.11	0.16	0.11	0.07	0.09	0.08	0.24
Methoxy									
—NHCH ₂ OCH ₃		54.6–56.1	0.18	0.16	0.14	0.09	0.11	0.10	0.21
Methylene glycol									
HOCH ₂ OH		82.3	0.02	0.01	0.01	0.01	0.01	0	0.03
HOCH ₂ OCH ₂ OH		86	0.01	0	0	0	0	0	0.01
HOCH ₂ OCH ₃		89.8	0.03	0.01	0.01	0.01	0	0	0.05
H(OCH ₂) _n OCH ₂ OCH ₃		93.2–97.2	0.04	0.03	0.02	0	0.01	0	0.02
Triazine									
=CNH ₂ —	f	167.3–167.5	0.11	0.34	0.38	0.09	0.33	0.55	0.15
=CNHCH ₂ OH—	f	166.0–166.5	0.24	0.36	0.35	0.18	0.22	0.29	0.38
=CN(CH ₂ OH) ₂ —	f	165.8–165	0.17	0.05	0.27	0.13	0.15	0.13	0.55
Urea									
NH ₂ CONH ₂	e	160.6	0.14	0.12	0.09	0.23	0.19	0.13	0.05
Mono-SubU									
—NHCONH ₂	e	159	0.37	0.26	0.20	0.32	0.27	0.21	0.24
Di,tri-subU									
=NCONH—, —NHCONH—	e	157.7	0.22	0.13	0.11	0.09	0.08	0.08	0.25
Total HCO			1.50	1.50	1.50	1.13	1.13	1.13	2.50
Total methylene			0.14	0.12	0.10	0.11	0.13	0.12	0.00
Total methylol			0.88	0.87	0.97	0.71	0.70	0.75	1.54
Total dimethylene ether			0.18	0.28	0.22	0.17	0.14	0.14	0.60
Total free formaldehyde			0.10	0.05	0.04	0.03	0.02	0.01	0.11

CTRL, Control: MUF resin before secondary additon [$\text{F}/(\text{M} + \text{U}) = 2.5$]; SubU, Substituted Urea

ditions, temperature and curing times, and time after curing should be taken into account.

Cured MUF resin structure

Solid-state ^{13}C -CP/MAS NMR spectra of cured MUF resins were measured to elucidate the effect of the cured resin structure on the formaldehyde emission and bond quality. It is difficult to allow the cure condition in an oven for neat resin to exactly represent the cured resin in a thin adhesion layer in plywood. Although the cure condition may not be in accordance with the hot-pressing situation at 120°C for 135 s, neat resins cured at 110°C for 15 min in an oven as a fully cured resin were selected for measuring solid-state ^{13}C -CP/MAS NMR spectra.

Figure 6 shows the solid-state ^{13}C -CP/MAS NMR spectra of MUF resins 1–3 (Fig. 6a) and MUF resins 4–6 (Fig. 6b), cured at 110°C for 15 min. Generally, peaks on solid-state ^{13}C -CP/MAS NMR spectra are much broader than those on the solution ^{13}C -NMR spectra. Therefore, the separation of peaks and quantification of each peak in the narrow region

of the chemical shift is difficult, although several peaks assigned to the identical functional groups in the spectra are comparable. The methylol groups (64 ppm: peak d), which comprise the major part of the solution resin, were observed to be limited in the cured resin. Instead of the methylol groups, methylene bonds (47, 53, and 60 ppm: peaks a, b, and c) were in a majority in the cured resins. There were more branched-type methylene bonds (53 ppm) than the linear-type methylene bonds (47 ppm: peak a) in the spectra of cured MUF resins with $\text{F}/(\text{M} + \text{U})$ 1.5, whereas more linear-type methylene bonds were observed in the spectra of cured resins with $\text{F}/(\text{M} + \text{U})$ 1.125. The observation suggests that the cured resin with a higher $\text{F}/(\text{M} + \text{U})$ molar ratio contained more crosslinked network structures. In addition, the melamine content influenced the cured resin structure by increasing the branched-type methylene bond. These are the same conclusions as for the resin structure before cure. The observations for the cured resin by solid-state ^{13}C -CP/MAS NMR spectrometry also supported the results of the bond performance test described above; the more crosslinked structure in the cured resin contributes to greater bond strength in the plywood. On the other hand,

Fig. 6. Effect of $F/(M + U)$ and M/U molar ratios of resins on the ^{13}C cross polarization magic angle spinning (CP/MAS) NMR spectra of MUF resins cured at 110°C for 15 min. Assignments of peaks *a*–*d* are listed in Table 2

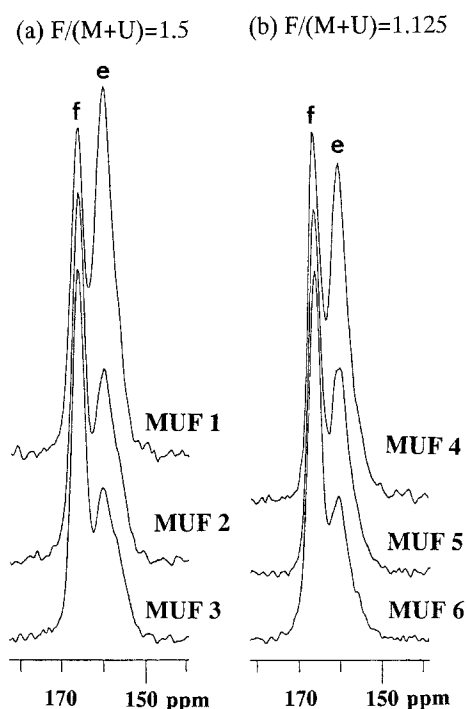
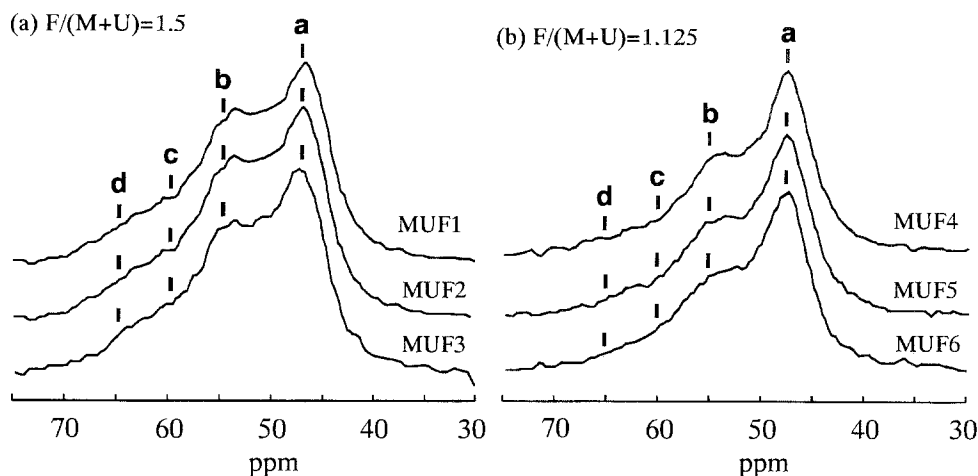


Fig. 7. Effect of $F/(M + U)$ and M/U molar ratios of the resins on the ^{13}C -CP/MAS NMR spectra of MUF resins cured at 110°C for 15 min. Assignments of peaks *e* and *f* are listed in Table 2

no significant differences in the spectra of the cured resins with the same $F/(M + U)$ molar ratio were found in the low-frequency region from 40 to 75 ppm in Fig. 6. The question of the effect of melamine content on the formaldehyde emission and cured resin structure thus remains.

Two independent peaks were observed in the region from 140 to 180 ppm on Fig. 7: melamine triazine carbon at around 169 ppm (peak *f*) and urea carbonyl carbon at around 160 ppm (peak *e*). The ratio of the two peaks was according to the M/U molar ratio. It was found that triazine carbon in melamine (165 ppm) increased and carbonyl carbon in urea (160 ppm) decreased as the melamine content increased. Although a peak of substituted and unsubstituted melamine or urea structure could not be distin-

guished because of peak broadness, the ratio of the melamine-melamine (M-M) and melamine-urea (M-U) linkages in the cured MUF resins should increase with increasing M/U molar ratio. In the same manner, the methylene and methylene ether linkage structure should comprise three patterns: U-U, U-M, and M-M. These linkages are assumed to be more in the high-melamine MUF resins, although it seems there is a similar shape of the ^{13}C -CP/MAS NMR spectra of the resins with the same $F/(M + U)$ and different M/U molar ratios in Fig. 6. In addition, Higuchi and coworkers reported⁹ that the degradation of methylene or methylene ether linkages (or both) in the cured resin with acid easily takes place in the following order: $\text{U-U} > \text{U-M} > \text{M-M}$. Therefore, the enhancing bond performance and the reducing formaldehyde emission in the high-melamine MUF resins might be ascribable to the stronger linkages between triazine carbons of melamine molecules in the cured MUF resins.

Conclusions

Formaldehyde emission decreased as the melamine content increased in MUF resins with the same $F/(M + U)$ molar ratio. The effect was higher in the resin with an $F/(M + U)$ molar ratio of 1.5 than in that with an $F/(M + U)$ molar ratio of 1.125. In the MUF resin with an $F/(M + U)$ molar ratio of 1.125, additional melamine was required to make the M/U molar ratio of 1.0 satisfy the criteria of the formaldehyde standard of JAS Fc0 (0.5 mg/l) and the bond performance. The melamine component contributed to the improved bond performance and formaldehyde emission, which might be ascribable to increasing branched methylene bonds and strong linkages between melamine molecules in the cured MUF resin structure.

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