Melamine-Bridged Alkyl Resorcinol Modified Urea–Formaldehyde Resin for Bonding Hardwood Plywood

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ABSTRACT: A powdery product was obtained by the reaction of methylolated melamine with alkyl resorcinols to form melamine-bridged alkyl resorcinols (MARs). The effects of the addition of this powder on the bonding strength and formaldehyde emission of urea–formaldehyde (UF) resins were investigated. Three types of UF resins with a formaldehyde/urea molar ratio of 1.3 synthesized by condensation at pH 1.0 (UF-1.0), pH 4.5 (UF-4.5), and pH 5.0 (UF-5.0) were fabricated. The addition of MAR to UF-4.5 and UF-5.0 for bonding hardwood plywood enhanced the bonding strength and reduced formaldehyde emission. For UF-1.0, the addition of MAR adversely affected the bonding strength. However, the UF-1.0 resin yielded the lowest formaldehyde emission of all of the UF resins in the study. The effects of the MAR addition were related to the molecular structures of the UF resins. UF-1.0 contained a large amount of free urea, a considerable number of urons, and a highly methylene-linked, ring-structured higher molecular weight fraction and had a smaller number of methylol groups. Therefore, the addition of MAR was considered to cause a shortage of the methylol groups, which in turn, led to incomplete resin curing. In contrast to UF-1.0, UF-5.0 contained a smaller amount of free urea and a linearly structured higher molecular weight fraction and had a larger number of methylol groups. In this case, MAR was considered to effectively react with the methylol groups to develop a three-dimensional crosslinked polymer network to enhance the bonding strength and suppress the generation of free formaldehyde to reduce formaldehyde emission. © 2010 Wiley Periodicals, Inc.† J Appl Polym Sci 116: 2840–2845, 2010

Key words: adhesives; ageing; catalysts; mixing; NMR

INTRODUCTION

Oil shale produced in Estonia contains a high percentage of an organic oily substance that mainly consists of water-soluble alkyl resorcinols (ARs), such as 5-methyl resorcinol, 2.5-dimethyl resorcinol, and 5-ethyl resorcinol.[1] These resorcinols (AR compounds) are extracted from the distillate obtained by the dry distillation of oil shale.[2] With their comparatively low price and high reactivity with formaldehyde, AR compounds have been extensively investigated as replacements for costlier resorcinols in the development of cold-setting structural wood adhesives.[3,4] Although the high reactivity is considered a desired property in resin applications, it has also created problems with controlling the reaction of formaldehyde addition in resin synthesis and also with pot life and the storage of the resins.[5,6]

To control the excessive reactivity of AR in resin preparation, acetone or other carbonyl compounds have often been added to form hydrogen-bonded complexes with phenolic hydroxyls to reduce the reaction rate of hydroxymethylation.[7,8] Nevertheless, even with complexing agents to reduce reactivity by a factor of 10, the hydroxlymethylation of AR is still eight times faster than the rate of resorcinol.[9] One study[10] showed that the acetone addition of up to 20 wt % of AR compounds was needed in the resin formulation to achieve the optimum reaction and performance of an AR resin.

In this study, we attempted to synthesize a melamine-bridged alkyl resorcinol (MAR) so that the AR derivative was insoluble in amino resins at room temperature but soluble at higher temperatures. This powdered MAR was considered to be capable of reacting with the methylol groups attached to the urea–formaldehyde (UF) resin molecules when heated. On the basis of this consideration, an MAR was synthesized by the reaction of methylolated melamine with AR. The effects of this powdered MAR as an additive for UF resins were investigated. The objective of this study was to evaluate the potential of an AR derivative to be used as a powdered fortifying agent for amino resin adhesives.

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TABLE I
Reaction Conditions for the UF Resins Prepared in the Laboratory

	First-stage reaction conditions				Second-stage reaction conditions			
UF resin	Molar ratio[a]	pH	Temperature (°C)	Time (min)	Urea addition (mol)	pH	Temperature (°C)	Time (min)
UF-1.0	3/1	1.0	65	75	1.31	8.0	80	55
UF-1.6	3/1	1.0	65	75	0.88	8.0	80	55
UF-4.5	2.5/1	4.5	85	120	0.92	7.0	85	55
UF-5.0	2/1	8.6–5.0[b]	85	90	0.54	7.0	85	30

[a] F/U ratio.
[b] The reaction occurred at pH 8.6 for 30 min and then at pH 5.0 for 60 min.

EXPERIMENTAL

Preparation of the MAR powder

A mixture of melamine (252 g, 2 mol), an aqueous 37% formaldehyde solution (324 g, 4 mol as HCHO), and sodium carbonate (0.2 g) was heated to 80°C over 20 min and kept at this temperature for 10 min. Then, an aqueous 70% AR solution (780 g, 4 mol equiv) was added to the methylolated melamine solution under stirring. The mixed solution was held at 70°C for 2 h to be solidified. The solid product was easily broken into pieces and air-dried. Finally, the product was ground in a mortar to pass a 400-mesh screen. The obtained powder was insoluble in water and liquid UF resin but was soluble in acetone.

Preparation of the UF resins

To facilitate UF resins with a wide range of chemical characteristics, four UF resins with a solid content of 58% were prepared in the laboratory [i.e., three UF resins synthesized at pH 1.0 (UF-1.0), pH 4.5 (UF-4.5), and pH 5.0 (UF-5.0) with a formaldehyde/urea (F/U) ratio of 1.3 and one UF resin synthesized at pH 1.0 with a F/U ratio of 1.6]. Also, a commercial resin with an F/U molar ratio of 1.3 containing a small amount of melamine (MUF) and a commercial UF resin with an F/U molar ratio of 1.3 without melamine (UF-0) were included in the study for the purpose of comparison. The four UF resins were prepared with two-stage reactions. The first stage was a reaction at a higher F/U ratio, and the second stage was a reaction with second urea addition to adjust the final F/U ratio to 1.3. The reaction conditions are summarized in Table I.

Analysis of the UF resins

Chemical analyses

The amounts of free formaldehyde were determined by the ammonium chloride method, and the amounts of total formaldehyde were determined by an acid hydrolysis/steam distillation/iodometry method.

^{13}C-NMR analysis

The resins were freeze-dried and dissolved in deuterated dimethyl sulfoxide. ^{13}C-NMR spectra were obtained with a JNM-GSX400 spectrometer (JEOL, Tokyo, Japan).

Preparation of the plywood specimens

Three-ply plywood specimens were prepared with 1 mm thick white meranti veneers (moisture content = 10%). The adhesives were roller spreaders. The adhesive formulations and pressing conditions were as follows:

1. Adhesive formulations:
    a. Control: 100 parts UF, 20 parts wheat flour, and 18 parts water.
    b. MAR 20%: 100 parts UF, 10 parts MAR, 20 parts wheat flour, and 28 parts water.
    c. MAR 40%: 100 parts UF, 20 parts MAR, 20 parts wheat flour, and 38 parts water.
2. Pressing conditions:
    a. Glue spread rate: 140 g/M^2 (single glue line, liquid base).
    b. Open assembly time: 0 min.
    c. Closed assembly time: 60 min.
    d. Cold pressing: 30 min under a pressure of 1 MPa.
    e. Hot-press temperature: 110°C.
    f. Hot-press time: 3 min.

Measurement of the bonding strength

The bonding strengths of the plywood specimens were measured by tensile shearing by use of Japanese Agricultural Standards (JAS) A type test pieces.[11]

TABLE II
Effects of the Addition of MAR Powder to the UF Resins for the Production of Plywood

		Bonding strength (MPa/WF %)					
			Water soak (60°C, 3 h)		Boiling for 1 h		
UF resin	Amount of MAR added	Dry (MPa)	Strength (MPa)/ wood failure (%)	Strength retention (%)[c]	Strength (MPa)/ wood failure (%)	Strength retention (%)[c]	Formaldehyde emission (mg/L)
UF-1.0	Control	1.09/15	0.48/0	44.0	0/0	0	0.93
	+20%	1.05/0	0.07/0	6.7	0/0	0	0.35
	+40%	1.06/0	0/0	0	0/0	0	0.35
UF-4.5	Control	1.87/87	1.14/08	61.0	0/0	0	4.84
	+20%	2.25/84	1.95/20	87.0	0/0	0	3.00
	+40%	1.76/100	1.54/85	87.0	0.44/0	25	2.47
UF-5.0	Control	2.14/96	1.20/05	56.1	0/0	0	6.64
	+20%	2.02/95	1.56/20	77.3	0/0	0	3.23
	+40%	2.20/80	1.91/23	86.8	0.46/05	20	2.27
UF-1.6	Control	2.11/92	1.03/0	48.8	0/0	0	10.80
	+40%	2.43/95	1.70/75	70.0	0.43/0	18	5.10
MUF[a]	Control	1.79/95	1.43/25	79.9	0/0	0	4.90
	+20%	1.60/95	1.56/50	97.5	0 49/04	31	2.90
	+40%	1.57/96	1.59/76	100	0.59/10	38	2.30
UF-0[b]	Control	1.80/90	1.47/50	81.7	0/0	0	5.00
	+20%	1.84/94	1.60/62	87.0	0/0	0	3.90
	+40%	1.87/100	1.69/86	91.4	0.42/05	23	2.80

[a] Commercial resin with an F/U molar ratio of 1.3 containing a small amount of melamine.
[b] Commercial resin with an F/U molar ratio of 1.3 containing no melamine.
[c] Bond strength retention after the aging treatment (calculated as the ratio of the strength after aging to the dry strength).
WR, wood failure.

Measurement of formaldehyde emission

Formaldehyde emissions were measured by a desiccator method according to JAS (for plywood specimens).[11]

RESULTS AND DISCUSSION

Table II summarizes average bonding strength, wood failure, and formaldehyde emission for each combination of adhesive formulations. Significant effects of MAR addition on the bonding strength and formaldehyde emission of the UF resins are presented, respectively, in Figures 1 and 2. The dry bonding strengths and percentage wood failures of the UF resins synthesized in the laboratory were highly comparable with those of the commercial UF resins used as controls with the exception of UF-1.0.

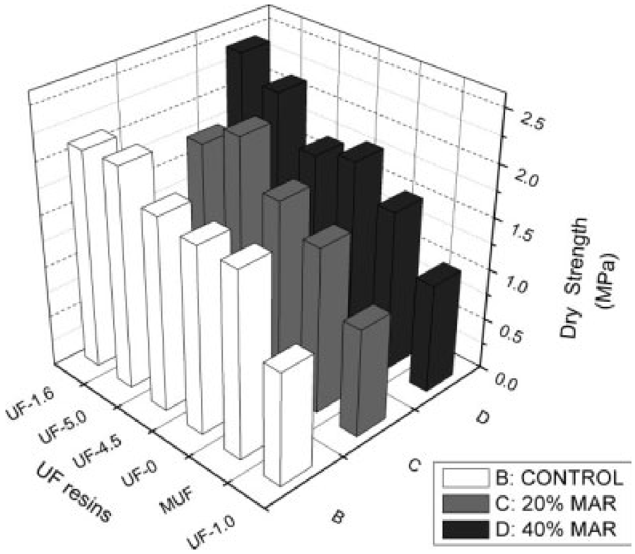

Figure 1 Effects of the addition of MAR powder on the bonding strength of hardwood plywood fabricated with UF resins.

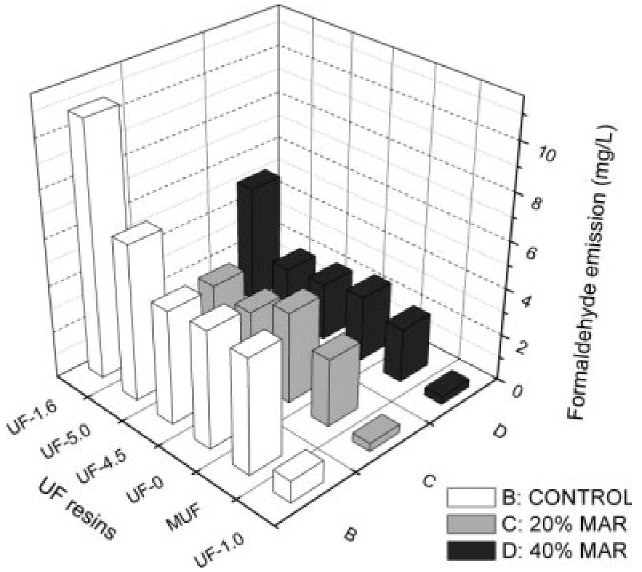

Figure 2 Effects of the addition of MAR powder on the formaldehyde emissions of hardwood plywood fabricated with UF resins.

TABLE III
Compositions of the Resins Fractionated with Ethanol (as Determined by Chemical Analysis)

	UF-1.0		UF-5.0	
Resin fraction	EtOH-soluble	EtOH-insoluble	EtOH-soluble	EtOH-insoluble
Amount of urea residues[a]	0.66	0.34	0.56	0.44
Amount of combined formaldehyde[b]	0.63	0.63	0.61	0.69
$F_{combined}$/U molar ratio[c]	0.95	1.84	1.09	1.56

[a] Determined by nitrogen analysis (by a Kjeldahl method).
[b] Determined by a combination of the acid hydrolysis/steam distillation/iodometry method with the ammonium chloride method.
[c] Combined formaldehyde to urea ratio.

UF-1.0 resulted in substantially lower bonding strength and percentage wood failure but yielded significantly lower formaldehyde emission. Overall, the addition of MAR significantly decreased the formaldehyde emission of the UF resins.

In general, the fortification effects on UF resins are most commonly evaluated by aging tests, such as water soaking or boiling treatments. After soaking in 60°C water for 3 h, the retention of the bonding strength increased as the addition of the MAR increased, again with the exception of UF-1.0. Furthermore, the percentage wood failure of all of the UF resins with MAR addition was significantly higher than that of UF resins without powder addition (i.e., control). These results demonstrate the potential for the application of AR derivatives as fortifying agents for amino resin adhesives.

The treatment with boiling water for 1 h resulted in an overall degradation of bonding strength and indicated that the boiling treatment was a much more severe accelerated aging method than water soaking. The average retention of bonding strength with the addition of 40% MAR powder ranged from completed glue-bond delamination for UF-1.0 to a strength retention of more than 37% for the MUF resin. Furthermore, with 20% addition of MAR, the MUF resin was the only one with a measurable retention of bonding strength (i.e., 31%). The results indicate that the MUF resins worked well with MAR to bond hardwoods to improve the bond durability. The effectiveness of melamine-modified UF resin for bonding various hardwoods with a wide range of wood densities was also shown in a previous study.[12]

One of the most interesting results of the study was the marked contrast between UF-1.0 and other resins (i.e., UF-4.5 and UF-5.0) in the effects of MAR addition. Therefore, the molecular structure of UF-1.0 was investigated to compare with it that of UF-5.0, which was selected as a representative reference.

We fractionated the resins into two fractions, ethanol-soluble and ethanol-insoluble (a white solid precipitate), by pouring 20 g of the resins into 500 mL of 99% ethanol under stirring. We then obtained the liquid resins in the ethanol-soluble fractions by evaporating off the ethanol under reduced pressure. These ethanol-soluble and ethanol-insoluble fractions were subjected to chemical analyses and ^{13}C-NMR analyses. The results of the chemical analyses are shown in Table III.

The amount of the ethanol-soluble fraction of UF-1.0 (66% in terms of urea residues) was greater than that of UF-5.0 (56%), whereas the combined formaldehyde/urea (F/U) molar ratio of the ethanol-soluble fraction of UF-1.0 (0.95) was less than that of UF-5.0 (1.09). On the other hand, the combined F/U molar ratio of the ethanol-insoluble fraction of UF-1.0 (1.84) was much greater than that of UF-5.0 (1.56).

Table IV shows the results of the ^{13}C-NMR analysis. The ethanol soluble fraction of UF-1.0 contained a larger amount of free urea (45% of the urea residues), a smaller number of methylene bonds (0.21 mol/mol of the urea residues), and a smaller number of methylol groups (0.66 mol/mol of the urea residues) compared to those of UF-5.0. On the other hand, the ethanol-insoluble fraction of UF-1.0 contained a considerable number of urons (0.18 mol/mol of the urea residues), a larger number of methylene bonds (1.08 mol/mol of the urea residues), and a smaller number of methylol groups (0.4 mol/mol of the urea residues). Moreover, it contained a considerable number of methylene bonds formed between tertiary amino groups.

From these data, the ethanol-insoluble fraction of UF-1.0 was considered to be a mixture of ring-structure oligomers, like the model shown in Figure 3(a). In contrast, the ethanol-insoluble fraction of UF-5.0 was considered to be composed of rather linearly structured oligomers, like the model shown in Figure 3(b).

It is generally recognized the curing of the UF resin proceeds through the condensation reactions of methylol groups with amino groups of urea and with methylol groups themselves. Therefore, the amounts of these functional groups are expected to relate to the effectiveness of the condensation reaction and, thus, to the performance of the cured resins. Consequently, the numbers of methylol groups and the primary and secondary amino groups were

TABLE IV
Chemical Structures of the Resins Fractionated with Ethanol (as Determined by ^{13}C-NMR Spectroscopy)

Resin fraction	UF-1.0		UF-5.0	
	EtOH-soluble	EtOH-insoluble	EtOH-soluble	EtOH-insoluble
Urea residues[a]	1.00	1.00	1.00	1.00
Urons[a]	004	018	0	0
Free urea[a]	0.45	0	0.28	0
$-NHCH_2NH-$[a]	0.05	0.13	0.10	0.36
$N(CH_2-)CH_2NH-$[a]	0.16	0.70	0.20	0.45
$N(CH_2-)CH_2N(CH_2-)$[a]	0	0.25	0	0
Total methylene structures[a]	0.21	1.08	0.30	0.81
$-NHCH_2OH$[a]	0.61	0.36	0.61	0.54
$-N(CH_2)CH_2OH$[a]	0.05	0.04	0.12	0.13
Total methylol groups[a]	0.66	0.40	0.73	0.67
Dimethylene ether and/or hemiformal[b]	0.01	0.01	0.06	0.05
Dimethylene ether of urons[b]	0.07	0.37	0	0
Methoxymethylool[b]	0	0	0	0.03

[a] The amounts are expressed as the molar ratio to urea residues.
[b] The amounts are expressed as the molar ratio of the methylene carbon to the carbonyl carbon of urea residues.

calculated from the data shown in Table IV, and the results are summarized in Table V.

In the reactions with methylol groups, the primary amino group is more reactive than the secondary amino group. As shown in Table V, the numbers of primary amino groups in UF-1.0 (0.61 mol/mol of the urea residues) exceeded that of the methylol groups (0.57 mol/mol of the urea residues). Therefore, the addition of the MAR was considered to cause the shortage of the methylol groups to complete the reaction, which in turn, led to an insufficient curing of the resin system.

In the case of UF-5.0, the number of methylol groups (0.70 mol/mol of the urea residues) was about twice that of the primary group (0.37 mol/mol of the urea residues); hence, MAR addition to the resin was considered to react effectively with the methylol groups to form bridges among the urea residues; this led to an increase in the water resistance of the glue bond and to a decrease in the formaldehyde emission.

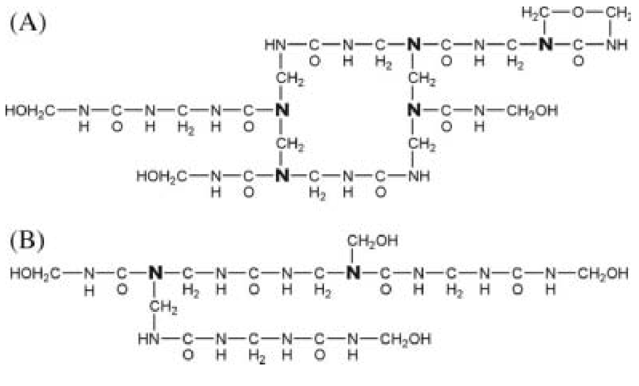

Figure 3 Models for ethanol-insoluble fractions of (A) UF-1.0 and (B) UF-5.0. **N** (in bold) indicates tertiary nitrogen; N (not in bold) indicates secondary nitrogen.

Among the resins tested, MUF and UF-0 were synthesized by procedures similar to that for UF-5.0, and their molecular compositions were considered to be very similar to that of UF-5.0. UF-4.5 did not have urons and methylene bonds linking tertiary amino groups and was also not much different in molecular structure from UF-5.0. Therefore, the addition of MAR to both resins (i.e., UF-5.0 and UF-4.5) resulted in increasing water resistance and decreasing formaldehyde emission, as expected.

The molecular structure of UF-1.6 was expected to be very similar to that of UF-1.0, but UF-1.6 contained a smaller amount of free urea because a smaller amount of urea was added after the condensation process. Thus, contrary to UF-1.0, UF-1.6 had a smaller number of primary amino groups to compete with MAR for methylol groups; this made more methylol groups in the resin system available to react with MAR and, in turn, increased the bonding strength and durability.

The formation of a high percentage of uron derivatives under strongly acidic conditions (UF-1.0) was rather interesting. The formation of these cyclic derivatives was not detected in resins made with either weakly acid or alkaline conditions (UF-4.5 and UF-5.0). The results indicate that resins formulated under strongly acidic conditions differed considerably from conventional UF resins formulated in the past. Experiences with UF resins used in the textile and paper industries have indicated that cyclic compounds are desirable compounds as crosslinking agents.[13] This study showed that the resin catalyzed under strongly acidic conditions resulted in the lowest formaldehyde emission, with emission values almost one order less than that of the other resins in the study. The result is particularly significant because formaldehyde release from glued wood

TABLE V
Amounts of the Functional Groups in the Resins

Resin fraction	UF-1.0 EtOH-soluble	UF-1.0 EtOH -insoluble	UF-1.0 Total	UF-5.0 EtOH-soluble	UF-5.0 EtOH-insoluble	UF-5.0 Total
Urea residues	0.66	0.34	1.00	0.56	0.44	1.00
$-NH_2$	0.61	>0	>0.61	0.37	0	0.37
$-NH-$	0.57	0.44	1.01	0.57	0.76	1.33
$-CH_2OH$	0.43	0.14	0.57	0.41	0.29	0.70

The values are molar ratios with respect to the total urea residues.

products is the most pressing environmental problem in the wood industry. Nevertheless, the UF resin prepared under strongly acidic conditions (UF-1.0) also yielded a substantially lower bonding strength and lower water resistance because of insufficient methylol content in the resin system. When the F/U ratio was increased to 1.6, the bonding strength and water resistance of the resin prepared under strongly acidic conditions (i.e., UF-1.6) increased, but the formaldehyde emissions also increased. It appeared that these two sets of divergent effects of a strongly acidic catalyst suggest that in general, a low-formaldehyde-emission UF/MAR resin system must be a compromise between strength and emission requirements.

CONCLUSIONS

The addition of MAR to UF resins synthesized by condensation at pH 5.0 and 4.5 resulted in significant improvements in bonding strength and decreased formaldehyde emission in plywood production. The MUF resin worked well with the addition of MAR to improve the bonding strength, particularly, the bonding strength after aging.

For UF-1.0, the addition of MAR adversely affected the bonding strength and caused the delamination of the plywood glue bond in the aging test. Nevertheless, the UF-1.0 resin yielded the lowest formaldehyde emission of all of the UF resins in the study. When the F/U ratio was increased to 1.6, the bonding strength and water resistance of the resin prepared under strongly acidic conditions (i.e., UF-1.6) increased, but the formaldehyde emissions also increased. It appeared that these two sets of divergent effects of a strongly acidic catalyst suggest that in general, a low-formaldehyde-emission UF/MAR resin system must be a compromise between strength and emission requirements.

The difference in the effects of MAR addition among the UF resins was ascribable to the difference in the molecular structures of the UF resins. The resin synthesized by condensation at pH 1.0 contained a large amount of free urea, a considerable number of urons, and a highly methylene-linked, ring-structure, high-molecular-weight fraction and had a smaller number of methylol groups. Therefore, the addition of the powder was considered to cause the shortage of the methylol groups, which led to incomplete curing of the resin. However, the resin synthesized by condensation at pH 5.0 contained a smaller amount of free urea and a linearly structured, high-molecular-weight fraction and had a larger number of methylol groups. In this case, the powder was considered to react effectively with the methylol groups to develop a three-dimensional crosslinked polymer network and suppress the generation of free formaldehyde during resin curing.

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