

# COMPARISON OF MODIFIERS FOR DURABILITY IMPROVEMENT OF UREA-FORMALDEHYDE RESIN

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## ABSTRACT

Several common organic modifiers, having varying degrees of reactivity and functionality, were evaluated at different levels of addition for their improvements to the relative durability of urea-formaldehyde (UF) glue-wood bonds. The recently developed thermal-softening technique was used to determine the thermal sensitivity of cured samples of these modified resins. Urea-formaldehyde resin containing modifiers with aromatic character and high potential reactivity, such as melamine, furfuryl alcohol, and resorcinol, showed significant increases in thermal-softening points compared with unmodified resin. Accelerated-aging tests on Douglas-fir laminates bonded with UF resins modified with either melamine, 2-imidazolidinone, or furfuryl alcohol showed that durability ranking correlated closely to the softening points of these adhesives. One inorganic modifier, aluminum powder, gave an improvement in softening point, but exhibited poor durability with wood bonds in aging tests.

*Additional keywords:* Douglas-fir laminates, melamine, furfuryl alcohol, aluminum powder, resorcinol, softening point, accelerated aging, thermal sensitivity.

## INTRODUCTION

Wood-bonding adhesives are categorized as satisfying exterior- or interior-use requirements primarily on the basis of their response to moisture and temperature. Phenolic resins, at present the major adhesive family used in exterior-grade wood products, have recently experienced severe price fluctuation because of their dependence on petroleum as a raw material source. The strong reliance of plywood, particleboard, and laminated products on phenolic resins makes any large increases in adhesive prices an important factor in competition with other materials. To remain competitive, the wood-products industry will likely seek alternatives to phenolic resins that can make use of existing plant equipment and offer an economic advantage, while still maintaining the bond quality for exterior exposures.

Two directions are apparent: development of a new nonpetroleum durable adhesive, or modification of an existing interior-grade resin to improve its durability. This study is concerned with the latter approach to urea-formaldehyde (UF) resins, with special emphasis on the chemical character

of various modifiers and their ability to improve resin properties.

Urea-formaldehyde resins are restricted to interior use because of their tendency to hydrolyze at higher temperatures in the presence of water (Troughton 1968). Recent thermal-softening studies of cured resins further indicate that molecular motion resulting in free-volume changes within the polymer also contributes to the instability of UF resin above the 60–70°C range (Chow 1973). Melamine added, either in monomeric form or co-reacted with formaldehyde, is known to markedly improve UF glue-bond durability (Yanagawa and Matsumura 1962; Blomquist and Olson 1964). The last authors have indicated that the greatest benefit to durability of plywood made from Douglas-fir, birch, or poplar veneer is achieved at 20 parts melamine-formaldehyde (MF) fortification of UF resin. The durability, however, never reaches that of MF resin alone, while processing limitations such as reduced resin solubility and the need for higher cure temperatures are present (Yanagawa and Matsumura 1962). Resorcinol provides effective fortification for UF resins, al-

TABLE I. *Properties of modified UF resins*

Modification	Mole %	Weight (g)			Viscosity* (cps)	Gel time <sup>†</sup> (min.)
		UF stock solution	Modifier	2nd Urea		
Control	-	300	-	21.4	2850	6.5
Melamine	5	"	11.3	16.1	2400	15
"	10	"	22.6	10.7	2880	29
"	15	"	33.9	5.4	2525	60
Furfuryl alcohol	5	"	8.8	16.1	1800	3.0
"	10	"	17.6	10.7	1710	3.0
"	15	"	26.5	5.4	1920	3.0
2-Imidazolidinone	5	"	7.7	16.1	1480	6.0
"	10	"	15.5	10.7	1580	7.0
"	15	"	23.2	5.4	1830	8.0
Resorcinol	5	"	9.9	16.1	††	8.0 <sup>δ</sup>
"	10	"	19.8	10.7	††	7.5 <sup>δ</sup>
"	15	"	29.7	5.4	††	5.5 <sup>δ</sup>

\*Measured at 25 C

<sup>†</sup> Measured at 50 C<sup>††</sup> Continually increasing because of room temperature reactivity of mixture<sup>δ</sup> Determined 30 minutes after resorcinol addition

though the presence of excess formaldehyde may affect pot life of the adhesive mixture (Blomquist and Olson 1964). Other modifiers, such as furfuryl alcohol (Brown and Stigger 1961; Nakarai et al. 1963), polyvinyl acetate (Gillespie et al. 1964), phenol and blood (*ibid.*) have also been examined.

Although it appears that present standards for exterior glueline durability cannot be achieved by these UF-resin modifications, little information exists on a relative comparison of modifier effectiveness for increasing glue-bond durability. Since formaldehyde-to-urea molar ratio governs to some extent the ultimate durability of a wood-glue bond (Steiner 1973), comparisons may be more meaningful if resin preparations are designed to attain a common final molar ratio as co-reactants are added. Hopefully, such background data will help provide some insight for further improving the durability of interior-grade resin systems that may have special importance in situations where only intermediate quality (i.e. somewhere between interior and exterior grade) is required.

#### EXPERIMENTAL

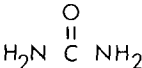
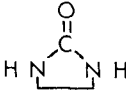
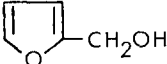
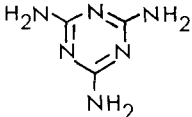
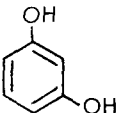
For modifications examined here, cure time and temperature are held constant, while both accelerated-aging tests on wood-glue bonds and softening temperatures of cured resins are used as a means of durability evaluation.

##### *Resin synthesis and characterization*

A stock UF resin of molar ratio F/U = 2.38 was prepared as follows:

Initially, 3000 g of 46.9% formaldehyde solution (46.9 moles) and 1184.4 g of urea (19.7 moles) were placed in a reaction vessel, and pH was adjusted to 8.4 with a 50% NaOH solution. The solution was heated to 70 C and the temperature maintained for 30 min, whereupon the solution was adjusted to pH = 5.4 with 10% HCl and then refluxed for 2 h. The mixture was cooled and then neutralized with NaOH solution. Water was removed under vacuum to bring the total solids content to 62.5%.

A control resin of F/U = 1.9 was prepared by adding additional urea (hereafter called second urea) to a portion of the stock

Modifier	Structure	Functionality*	$\frac{\text{Functionality}}{\text{molecular weight}}$
Urea		4 <sup>†</sup>	0.067
2-Imidazolidinone		2	0.023
Furfuryl alcohol		2	0.020
Melamine		6	0.048
Resorcinol		3 <sup>††</sup>	0.027

\*Number of *potentially* reactive positions for addition or condensation in the presence of formaldehyde.

<sup>†</sup> Studies of model compounds indicate that only three of these four positions are reactive.

<sup>††</sup> Assumes that only ortho and para positions are activated.

FIG. 1. The structure and functionality of various organic modifiers.

resin (see Appendix for detailed calculation).

Organic modifiers were added to the stock solution, together with the appropriate amount of second urea to give a final molar ratio of formaldehyde to urea and modifier of 1.9. Table 1 lists calculated formulations for these modifications. Inorganic modifiers were added directly as a weight percentage to the F/U = 1.9 control resin.

All modified solutions, with the exception of those containing resorcinol, were heated at 50 C with stirring for 30 min to obtain a homogeneous mixture. Resorcinol was mixed into solution at room temperature. Viscosities of the mixtures were measured at

25 C using a Brookfield LVF viscometer. Gel times were determined at 50 C with samples containing 25 g of resin and 0.5 g NH<sub>4</sub>Cl.

Thermal softening measurements were carried out using an apparatus and method described previously (Chow 1973; Chow and Pickles 1971). The resins examined included modifiers that were not evaluated by the accelerated aging tests on laminated samples. The resins were cured as a thin film on a glass plate with 2% (w/w) NH<sub>4</sub>Cl overnight at 60 C and then ground to pass 120 mesh while retained by 140 mesh. A heating rate of 9 C/min was used for all samples.

TABLE 2. *Shear strength and percentage wood failure for accelerated aging tests on various UF resin modifications*

Modification	Mole %	Cycle*									
		0		1		2		3		4	
		psi	% WF	psi	% WF	psi	% WF	psi	% WF	psi	% WF
Control resin <sup>δ</sup>	-	1134	92	543	61	469	74	delaminated			
Melamine	5	2043	95	1890	99	1527	83	1708	95	1400	87.5
"	10	1540	95	1325	98	1356	98	1065	98.5	1038	100
"	15	2200	97.5	2005	96.5	1963	92	1725	97	1513	92
2-Imidazolidinone	5	1773	93	1331	91	846	76	324	47	631	68
"	10	1924	92	1306	75	908	41	516	45	135	12
"	15	1302	98	475	91	487	99	510	83	448	67
Furfuryl alcohol	5	1718	78	1618	90	1610	83.5	1532	69	1439	77
"	10	1258	97.5	1087	100	1198	99	689	93	699	91
"	15	1457	90	1313	96.5	1243	98.5	1096	98	963	82
Aluminum powder	0.1 <sup>†</sup>	1287	97.5	815	96	682	79	659	90	767	97
"	0.25 <sup>†</sup>	1305	100	751	97	721	97.5	559	98	654	92
"	0.5 <sup>†</sup>	1291	100	874	82	592	89	425	72	409	57

\*Average of 6 shear specimens

<sup>δ</sup>F/U = 1.9, 20% 2nd urea<sup>†</sup>Weight percent of resin added*Bonding and testing*

The wood used was clear, straight-grain, tangentially matched Douglas-fir boards of dimension  $101.6 \times 19.1 \times 1.9$  cm ( $40 \times 7\frac{1}{2} \times \frac{3}{4}$  inch), of moisture-content range from 9 to 10% and average growth rate of 31 rings/inch. This material's differential degree of swelling, between the tangential and the radial directions, under water-saturated conditions created large glueline stresses in laminated samples exposed to the cyclic conditions used in this experiment. Before gluing, the boards were planed to 1.6 cm ( $\frac{5}{8}$  inch) thickness. In all cases, glue containing 2% (w/w)  $\text{NH}_4\text{Cl}$  based on resin, but no filler or extender, was spread in amounts of  $0.31 \text{ kg/m}^2$  (63 lbs/1000 sq ft) of single glueline. Total assembly time was kept below 15 min.

For each modification tested, two boards were hot pressed with grain parallel to each other at 60 C under  $120 \times 10^4 \text{ N/m}^2$  (175 psi) pressure for a period of 17 h. Strips of 10 cm (4 inches) were cut from both ends of each laminated board and discarded. The remaining board portion was cut and sequentially numbered from one

end into ten, 19.1 cm ( $7\frac{1}{2}$  inches) tangential  $\times$  7.6 cm (3 inches) longitudinal, sample strips. The two innermost sample strips, 5 and 6, were retained for control purposes, while 1 to 4 and 7 to 10 were treated in a vacuum-pressure tank filled with water (10 C) for a cycle of 2 h vacuum at  $84.4 \times 10^3 \text{ N/m}^2$  (25 inches) mercury, 2 h pressure at  $55.2 \times 10^4 \text{ N/m}^2$  (80 psi) and then dried in a forced-draft oven (air velocity 450 ft/min) for 17 h at  $70 \pm 1$  C. Two sample strips from each laminate were removed at the end of each cycle.

Three standard block-shear specimens were cut from each sample (giving 6 shear specimens for each cycle of a tested modification) according to ASTM D-905. The block-shear specimens were tested to failure at 9 to 10% MC using a Tinius-Olsen tester with a head speed of 0.061 cm/min (0.024 inch/min). Both shear strength and percentage wood failure were recorded.

## RESULTS AND DISCUSSION

The structure and functionality of organic modifiers evaluated in this study are summarized in Fig. 1. The monomers were

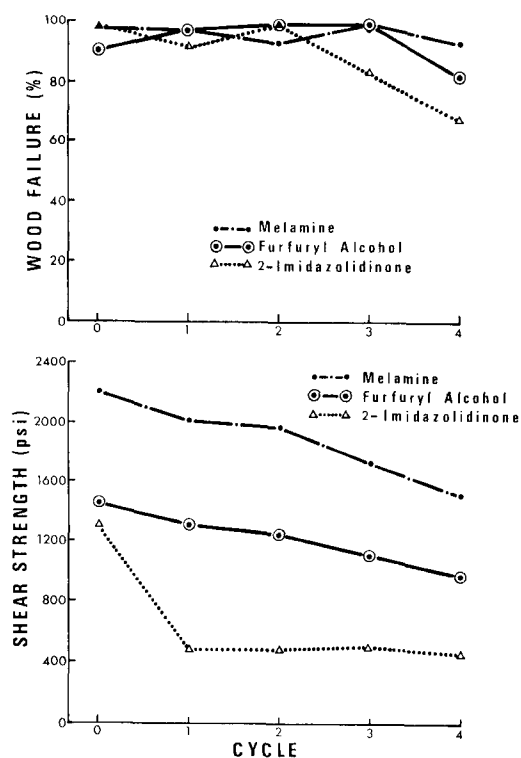


FIG. 2. Shear strength and wood failure percent for UF resin containing 15 mole percent modification (average of six samples for each point).

chosen to range from saturated linear and cyclic systems, through a five-membered ring structure of partial aromatic character to, finally, the fully aromatic character of resorcinol. One expects that the resonance stabilization provided by increased conjugation and aromatization will lead to increased bond strengths between molecules, resulting in more rigid and thermally stable compounds. Additionally the modifier's functionality provides an indication of potential reactivity in the presence of formaldehyde. Urea has the highest functionality per weight unit while furfuryl alcohol has the lowest.

Table 1 lists some properties of resin systems containing modifiers. Notably, the melamine modification greatly increases the gel time, suggesting that room-temperature cure is made more difficult with this monomer. On the other hand, furfuryl alco-

hol decreases the gel time, indicating increased reactivity with this additive. Resorcinol is intermediate; initially gel time increases, but then shows a decrease with higher percentages of resorcinol added to the UF resin. Both reactivity and compatibility of a monomer with UF resin need to be considered to establish the suitability of a modification to industrial application.

#### *Accelerated-aging tests*

Rather than perform numerous aging tests on a large series of compounds in the first part of the study, we tested only certain modifiers that represented various chemical categories. For example, melamine was chosen to be representative of an aromatic modifier that would include the resorcinol and phenol compounds. The thermal-softening portion of this study was expanded to include these other modifiers.

The results of four vacuum-pressure-drying cycles on UF resins with several selected modifiers are shown in Table 2. The unmodified control resin showed some delamination after one cycle, as expected with a drying temperature of 70 C. This temperature was purposely chosen to be slightly higher than the softening temperature of UF resin, thus creating accelerated bond degradation.

In contrast, the modified resins showed varying degrees of durability during these accelerated tests, with those having some aromatic character exhibiting significant improvements in bond stability.

A comparison of shear strengths and percentage wood failure, at a 15 mole percent modification level, as shown in Fig. 2, clearly indicates on the basis of strength that the melamine and furfuryl alcohol modifications are more durable than the imidazolidinone system. Wood failure showed less of a variation between the modifiers. At other modification levels, resins having imidazolidinone added, exhibited a rapid decrease in both shear strength and percentage wood failure. By considering the percentage decrease in wood failure and shear strength between cycles 0 and 1 (Fig. 3), a convenient relative comparison of both

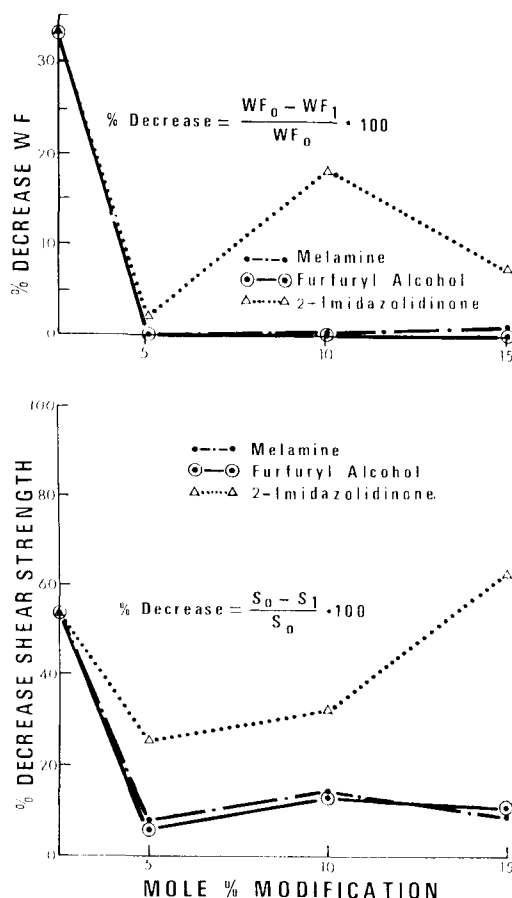


FIG. 3. Percentage decrease in wood failure (WF) and shear strength (S) between cycles 0 and 1 for various modifiers in UF resins. All negative percentage changes are set to 0.

original bond quality (adhesion character before exposure) and durability (adhesion character after exposure for a period of time) at various amounts of added modifier is obtained. This takes into account the initial variability between different wood laminates. The percentage decrease for the control UF resin was about 60% for shear strength. Again it is evident that melamine and furfuryl alcohol are superior fortifiers of UF resin compared to imidazolidinone, with the latter showing a decrease in bond stability with increasing amounts of mono-mer added.

Apart from the above modification, involving substances that can form covalent

bonds with UF resins, other interactions between resin and modifier, such as electron sharing through complex formation (chelation) or Van der Waal's interactions, may also take place. Studies of imidazolidinone (Berni et al. 1963) and urea (Penland et al. 1957) have shown that the carbonyl and amide portion of the molecule can readily form metal-ion complexes with zinc (II), iron (III), cobalt (II), and copper (II), which result in increased thermal stability. Russian workers have also reported that  $\text{AlCl}_3$  or  $\text{FeCl}_3$  increases the heat resistance of UF molding compounds (Tarakhtunov 1968).

Addition of aluminum powder (200–250 mesh, containing traces of aluminum oxide) to a standard UF resin ( $F/U = 1.9$ , 20% second urea) was undertaken to examine the effects on wood-glue durability of a substance that has the potential of complexing with the resin. The results shown in Table 2 indicate a marked reduction in shear strength with increasing cycles of testing at all levels of modification. Somewhat surprisingly, the percentage wood failure of the 0.1% and 0.25% modification still remains high throughout the entire test.

#### Thermal softening measurements

It is well known that the accelerated-aging method of evaluating bond durability, although not completely representative of natural weathering, does provide a relative indication of durability in a wood-glue bond treated under specific conditions. In testing a number of new adhesives, however, this can still be a very time-consuming task. Chow (1973) has shown that the thermal-softening method of evaluating cured adhesives does distinguish between adhesive families of different durabilities. The time-saving involved in determining thermal-softening points encouraged us to consider the correlation between this method and the above accelerated-aging durability tests.

A typical series of softening-point curves for modified UF resins are presented in Fig. 4. The softening point ( $T_i$ ) is the temperature at which the curve initially departs

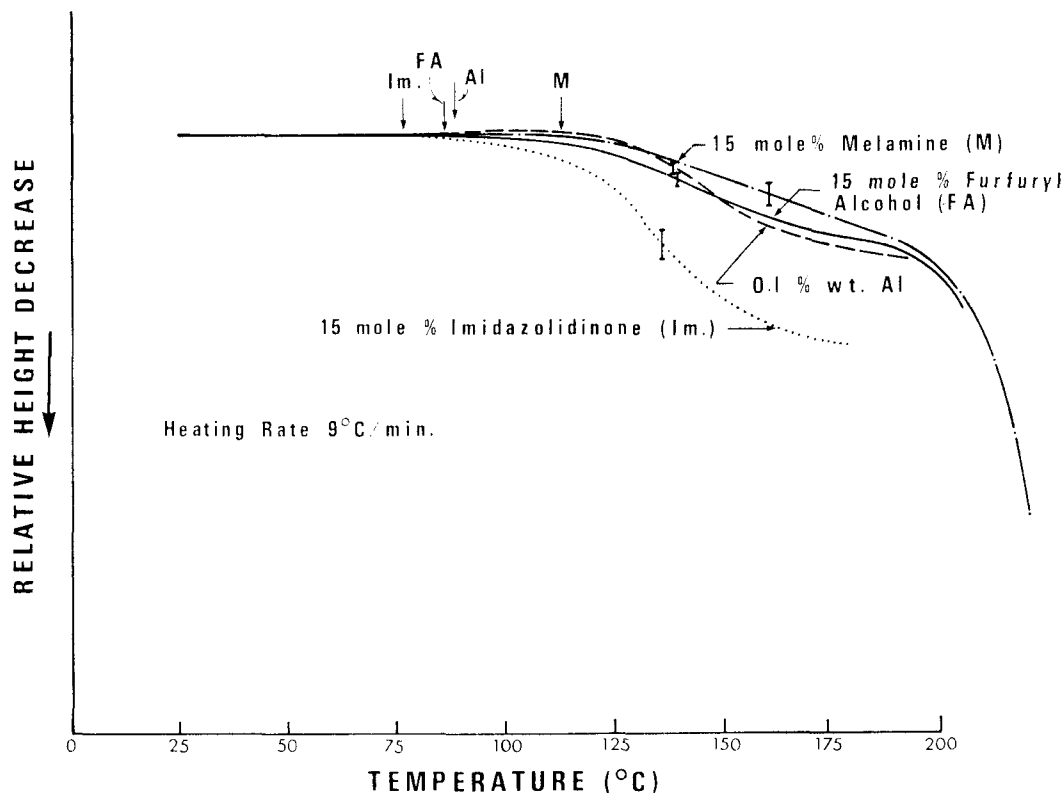


FIG. 4. Thermal-softening curves for cured UF resins containing various modifiers. The arrows and vertical lines indicate  $T_i$  and  $T_g$ , respectively.

from the baseline. In amorphous polymers, this corresponds to the onset of significant conformational motion in the polymer chains. As this motion increases, the polymer transforms from a rigid to a semi-rubbery state with a corresponding decrease in free volume, resulting in an increased slope in the softening curve. At this stage, the accessibility of the polymer lattice to external solvents is greatly increased. This maximum change in slope is often designated as the "glass-transition temperature" of the solid and will be referred to as  $T_g$  here.

The softening temperatures of a number of organic and inorganic modified UF resins are shown in Table 3. Only melamine and resorcinol at 15 mole percent fortify UF resin sufficiently to attain a softening temperature greater than 100°C. Furfuryl alcohol, although showing a large increase

in  $T_i$  at 5% addition, tends to provide little more improvement at higher concentrations.

While a reasonable correlation exists between wood-glue bond durability and softening temperature for these modifiers, the aluminum powder case appears to be an exception. Here one finds a large increase in  $T_i$  at 0.25 and 0.5 weight percent concentrations but, as was previously shown, a severe strength loss during accelerated aging. Although a clear understanding of this apparent anomaly requires further experimentation, a comparison of both  $T_i$  and  $T_g$  for melamine and aluminum powder modifications does provide some additional information (Fig. 5). In the case of melamine, as  $T_i$  increases  $T_g$  also increases, as would be expected from structural alterations in the polymer arising from co-polymerization. On the other hand, for

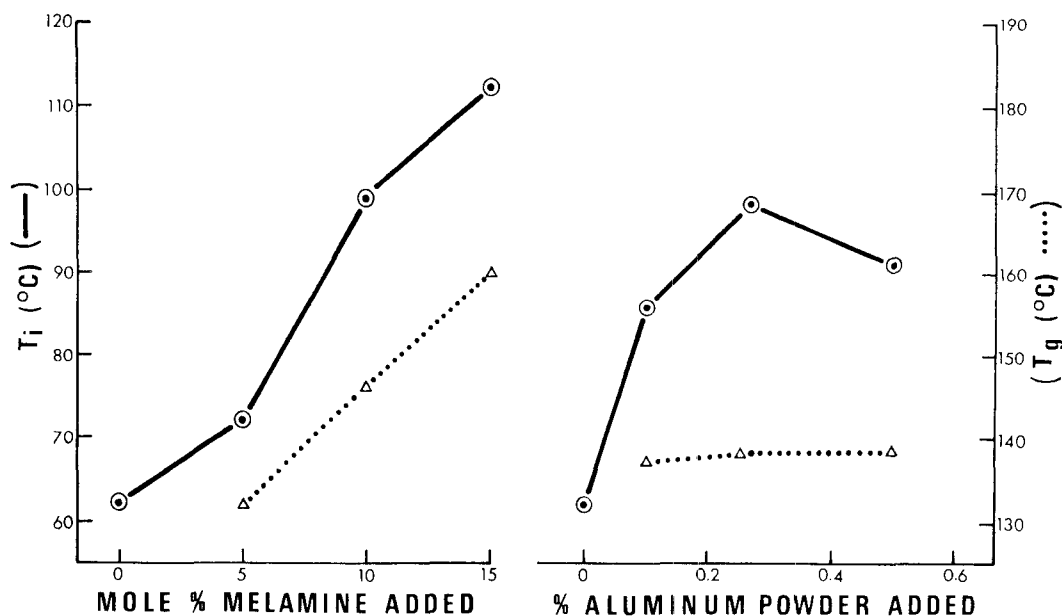


FIG. 5. Comparison of softening temperatures ( $T_i$  and  $T_g$ ) for melamine and aluminum powder modifications of UF resins.

TABLE 3. Softening temperatures ( $T_i$  and  $T_g$ ) of modified UF resin

A. Organic modifiers						
Modifier*	Softening temperatures (°C) of mole percent modifications					
	5%		10%		15%	
	$T_i$	$T_g$	$T_i$	$T_g$	$T_i$	$T_g$
Melamine	72	132	99	146	112	160
Furfuryl alcohol	84	133	82	140	86	138
Resorcinol	77	137	91	142	101	145
2-Imidazolidinone	69	133	76	129	76	136

B. Inorganic modifiers						
	Softening temperature (°C) of weight percent added					
	0.1%		0.25%		0.5%	
	$T_i$	$T_g$	$T_i$	$T_g$	$T_i$	$T_g$
Al powder	86	137	98	138	91	138
ZnCl <sub>2</sub>	-	-	-	-	69	118
FeCl <sub>3</sub>	-	-	-	-	80	136
CaSO <sub>4</sub>	-	-	-	-	85	140

\* Control: F/U = 1.9, 20% 2nd urea;  $T_i$  = 65°C;  $T_g$  = 127°C  
 Commercial UF plywood resin;  $T_i$  = 62°C,  
 $T_g$  = 99°C (Chow 1973).

$T_i$  = The temperature at which the adhesive shows the initiation of softening.

$T_g$  = The temperature at which the adhesive shows the maximum rate of softening

aluminum powder, as  $T_i$  increases  $T_g$  remains relatively stable, suggesting a temperature-sensitive complex exists between this modifier and the resin which influences the polymer characteristics only up to  $T_i$ , but not in the  $T_g$  range.

#### SUMMARY AND CONCLUSIONS

This limited study of fortifiers has shown that relatively small amounts of modifiers, post-added as monomers to UF resins, result both in increased wood-glue bond durability and in increased softening temperature of the cured resin. Additives having a higher degree of aromatic character and greater functionality for covalent bond formation proved most beneficial as modifiers. For instance, a comparison of the effects of furfuryl alcohol and imidazolidinone, both having the same functionality, indicates that furfuryl alcohol's aromatic character greatly improves resin durability. Addition of minor amounts of aluminum powder appears to have little effect on improving bond durability.

The increase in thermal-softening temperature of cured modified resins was found to



follow closely the durability ranking of these systems, with the exception of the aluminum powder addition, where apparent complex formation provided increased softening temperatures, but resulted in little change in bond durability. The thermal-softening method thus provides, in the case of organic modifiers, a convenient method of screening resins without initially carrying out time-consuming accelerated-aging tests.

Although melamine, one of the best modifiers tested, does not attain the bond quality of exterior-grade phenolic resins, it is likely that aromatic, highly functional molecules offer the greatest potential for modifying UF resins to approach exterior durability. The fact that relatively small amounts of the proper modifier create such significant changes in durability suggests that the UF system is very sensitive to minor changes that alter the configurational and conformational character of the cured resin.

Finally, it should be realized that all modifications considered here involve addition of monomers to prepared resins. Although the stock resin likely has a low degree of polymerization, quite different polymer networks would arise from direct co-polymerization of modifier, urea, and formaldehyde at the beginning of resin preparation.

#### APPENDIX

Method for calculating the amount of second urea required to adjust molar ratio from  $F/U = 2.38$  to  $1.9$  from a  $300$  g solution containing  $62.5\%$  solids:

total weight of solids =  $187.5$  g  
 letting  $x$  = weight of urea  
 and  $187.5 - x$  = weight of formaldehyde,  
 then

$$\frac{F}{U} = 2.38 = \frac{\frac{187.5-x}{30}}{\frac{x}{60}} \quad (1)$$

Solving (1) gives  $x = 85.6$ .

This portion of the stock solution then contains  $85.6$  g urea and  $101.9$  g of formaldehyde. To achieve a final molar ratio of  $1.9$ ,

the new amount of urea,  $y$ , now required is obtained from the expression

$$\frac{F}{U} = 1.9 = \frac{\frac{101.9}{30}}{\frac{y}{60}} \quad (2)$$

Solving (2) gives  $y = 107$ , indicating that  $21.4$  g of second urea are required to bring this stock solution to  $F/U = 1.9$ .

This method of calculation assumes that the stock solution is a prepolymer containing very few methylene condensation linkages and that no formaldehyde is lost during the cooking process.

#### REFERENCES

- BERNI, R. J., R. R. BENERITO, W. M. AYRES, AND H. B. JONASSEN. 1963. Metal ion complexes of 2-imidazolidinone (ethylene urea). *J. Inorg. Nucl. Chem.* 25:807-818.
- BLOMQUIST, R. F., AND W. Z. OLSON. 1964. Durability of fortified urea-resin glues exposed to exterior weathering. *For. Prod. J.* 14:461-466.
- BROWN, L. H., AND E. K. STIGGER. 1961. Furfuryl alcohol as a resin modifier. *Mod. Plast.* 39(4):135.
- CHOW, S. 1973. Softening temperature and durability of wood adhesives. *Holzforschung* 27: 64-68.
- CHOW, S., AND K. J. PICKLES. 1971. Thermal softening and degradation of wood and bark. *Wood Fiber* 3:166-178.
- GILLESPIE, R. H., W. Z. OLSON, AND R. F. BLOMQUIST. 1964. Durability of urea-resin glues modified with polyvinyl acetate and blood. *For. Prod. J.* 14:343-349.
- NAKARAI, Y., T. WATANABE, AND M. ONO. 1963. The effect of modification by furfuryl alcohol to urea-formaldehyde resin adhesive. *Wood Ind. (Japan)* 18(4):171-176.
- PENLAND, R. B., S. MIZUSHIMA, C. CURRAN, AND J. V. QUAGLIANO. 1957. Infrared absorption spectra of inorganic co-ordination complexes. X. Studies of some metal-urea complexes. *J. Am. Chem. Soc.* 79:1575-1578.
- STEINER, P. R. 1973. Durability of urea-formaldehyde resins: Effect of molar ratio, second urea and filler. *For. Prod. J.* 23:(12)32-38.
- TARAKHTUNOV, O. A. 1968. Influence of aprotic acid on properties of urea-formaldehyde resins. *Sov. Plast.* 37-38.
- TROUGHTON, G. E. 1968. Accelerated aging of glue-wood bonds. *Wood Sci.* 1:172-176.
- YANAGAWA, R., AND O. MATSUMURA. 1962. The study of wood adhesives I. The effect of melamine to fortify urea-formaldehyde resin adhesives. *J. Jap. Wood Res.* 8:62-67.