

Urea-Resorcinol-Formaldehyde Adhesives of Low Resorcinol Content

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SYNOPSIS

Low resorcinol content cold-setting urea-resorcinol-formaldehyde (URF) resins were prepared. Most of these adhesives had water-resistant properties, whereas some also presented weather- and boil-proof adhesive characteristics and performance. URF resins of acceptable adhesive performance were also prepared by inducing branching by introducing a certain amount of resorcinol or of polyflavonoid mimosa tannin extract as a branching unit. Resorcinol content as low as 12.7 and 12.15% on total liquid resin were obtained by this method while still maintaining adhesive performance and water-resistant properties.

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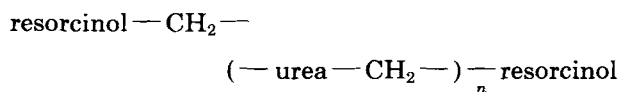
INTRODUCTION

The field of adhesives for wood has been dominated during the last half-century by two main classes of synthetic resins: aminoplastic and polyphenolic adhesives. The latter have been used mostly for the production of weather- and boil-proof wood adhesives. Among phenolics, phenol-resorcinol-formaldehyde (PRF) resins are the ones used as cold-setting adhesives for the preparation of weather-proof structural glulam and fingerjointing.¹ Since resorcinol is an expensive chemical, significant reductions in the cost of such adhesives must, by necessity, be coupled with a decrease in their resorcinol content. Recently, a step forward has been reported² in the formulation of PRF adhesives of lower resorcinol content. This was the mistakenly called the "branching principle"²; in practice, a very rapid doubling of the average molecular mass of the liquid resin obtained by the use of small amounts of very reactive tri- or polyfunctional monomer units.³ In this article, the same approach already reported for PRF resins has been used to prepare urea-resorcinol-formaldehyde (URF) resins of low resorcinol

content. This is a more difficult undertaking than for PRF resins, because of an additional effect militating against such resins: Although a decrease of resorcinol appears, in principle, possible (as for the PRF), too low an amount of resorcinol, while possibly still affording good dry strength of the bonded joint, may not be able to protect the urea-formaldehyde (UF) backbone of the resin from water degradation, possibly causing catastrophic strength loss in the wet strength of the joints.

APPROACH

Supposing that the average degree of polymerization of the UF resin before resorcinol addition is n , then the URF resin produced can be schematically represented as^{2,3}



where $n \geq 1$ in integer numbers.

If a chemical molecule capable of extensively branching, or of rapidly doubling linearly the molecular weight, of the UF and URF resins is used after the preparation of the UF resin, then a URF of lower resorcinol content will be produced. Thus,

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warm, a certain amount of wattle tannin extract was added to the resin. On cooling, the resulting resins were diluted to a usable viscosity with 30% methanol : 70% water solvent.

Method of Preparation of a Branched URF Resin

A UF resin of U : F ratio 1 : 0.5 was prepared as described above. The appropriate amount of brancher was added as a 50% brancher : 50% solvent (30% methanol : 70% water) by mass solution. The reaction mixture was allowed to react under continuous stirring at 55–60°C for a maximum period of 4 h or until the reaction mixture thickened excessively. After addition of the brancher, the pH of the reaction mixture was adjusted to ~ 9 and maintained at this pH throughout the branching reaction period with 22% sodium hydroxide solution. The appropriate amount of terminal 50% resorcinol : 50% solvent (30% methanol : 70% water) solution was added whose pH had been preadjusted to ~ 9 with 22% sodium hydroxide solution. A reaction period of 1 or 2 h was allowed at 55–60°C. The pH of the reaction mixture was maintained between 9 and 10. While the resin was still warm, 15% wattle tannin extract by mass of undiluted resin was added to thicken the resin. On cooling, the resin was diluted to a usable viscosity with 30% methanol : 70% water solution.

Analysis of Resins

Resins were analyzed using IR and ¹³C-NMR analytical techniques. IR spectra were recorded on Jasco FT/IR5000 and PYE UNICAM PU 9512 infrared spectrometers. ¹³C-NMR spectra were recorded on a Bruker AC-200 spectrometer (200.13 MHz) with the samples dissolved in D₂O.

Though UF resins are characteristically white in color, on addition of the resorcinol, they become brown. The mimosa polyflavonoid tannin extract gives them a darker brown tint. However, on addition of a hardener, both the resorcinol- and wattle tannin-extract branched URF resins become dark brown after curing and cannot be distinguished from traditional PRF resins.

RESULTS AND DISCUSSION

The preparation of URF resins has been reported several times,⁹ although these resins have not been used very much due to the fear that their durability might not be as good as that of their phenolic counterparts. Traditional URF resins of acceptable performance (cf. results of resins 1 and 2 in Table I) operate at 55–58% resin solids content. This is slightly higher than for linear PRF resins. The viscosity of these resins at this percentage solids content is low and they cannot be further diluted with-

Table I Preparation Parameters and Results of Linear URF Resins

	Resin URF No.			
	1	2	3	4
U : F ratio	1 : 0.5	1 : 0.5	1 : 0.5	1 : 0.5
% Resorcinol in undiluted liquid resin	25.0	22.5	20.0	17.0
Reaction time at 60°C (min)	360	360	360	240
% Solids content	57.1	55.9	47.6	55.1
% Resorcinol in total liquid resin	17.4	16.0	12.0	12.4
Viscosity (cps)	155	395	225	500
Pot life (min)	76	80	90	75
Shelf life (days)	> 40	> 40	> 40	5
% Wattle by mass in undiluted liquid resin	15	15	15	5
Strength (kN)				
Dry	2.57	2.50	2.50	2.65
Soak	2.20	2.20	1.70	1.00
Boil	2.20	2.20	1.60	0.90
Wood failure (%)				
Dry	70	43	27	94
Soak	75	75	42	3
Boil	87	83	43	2

out deterioration in their performance. Resorcinol-branched URF adhesives operate in a much wider percentage solids content range. For instance, resin URF 6 and resin URF 11 (cf. Table II) display good performance and operate at 48.8 and 59% resin solids content, respectively. In general, resorcinol-induced branching in URF resins does not appear to have a significant effect on the viscosity of the resins. The resins produced have a viscosity comparable to that of "linear" URF resins. Mimosa tannin-branched URF resins are, however, slightly more viscous than are the corresponding resorcinol-branched URF resins. This increase in viscosity could be attributed to the larger molecular weight of the wattle tannin macromolecules that have condensed onto the URF resin. These resins also operate in a much narrower range of percentage resin solids content (56–58%) (cf. results of URF 14W and URF 16W in Table II).

The lowest percentages resorcinol by mass on total liquid resin that gave acceptable performance in "traditional" URF and resorcinol-"branched" and tannin-"branched" URF resins are 16, 13.4, and 12.7%, respectively (cf. results of URF 1.6 and 16 W in Table II). The results in Table II also clearly

show that there is an optimum level of resorcinol for each type of URF resin.

URF resins to which resorcinol as an additional branching unit was added and URFs without an additional branching unit had pot lives longer than did urea-branched PRF resins³ (Fig. 1). URF resins in which mimosa polyflavonoid tannin was the additional branching unit gave, instead, a much shorter pot life (Fig. 1). Such URF resins presented the same sensitivity to a pH decrease as did their PRF counterparts.³ Again, only acetylsalicylic acid³ was capable of correcting the resin pH downward with consequent lengthening of pot-life. Any other acid, in solution or solid, caused localized precipitation of the resin.

Another problem encountered in URF resins was their stability (shelf life). Whereas traditional and branched PRF resins are stable and display long shelf lives, this was a problem in the production of URF resins. A decrease in the formaldehyde/urea molar ratio resulted in a more stable resin with a much longer shelf life. The most stable U : F ratio was found to be 1 : 0.5 (cf. results in Table III).

As urea has three reactive sites, and also as a result of its reactivity, most UF resins are shown to

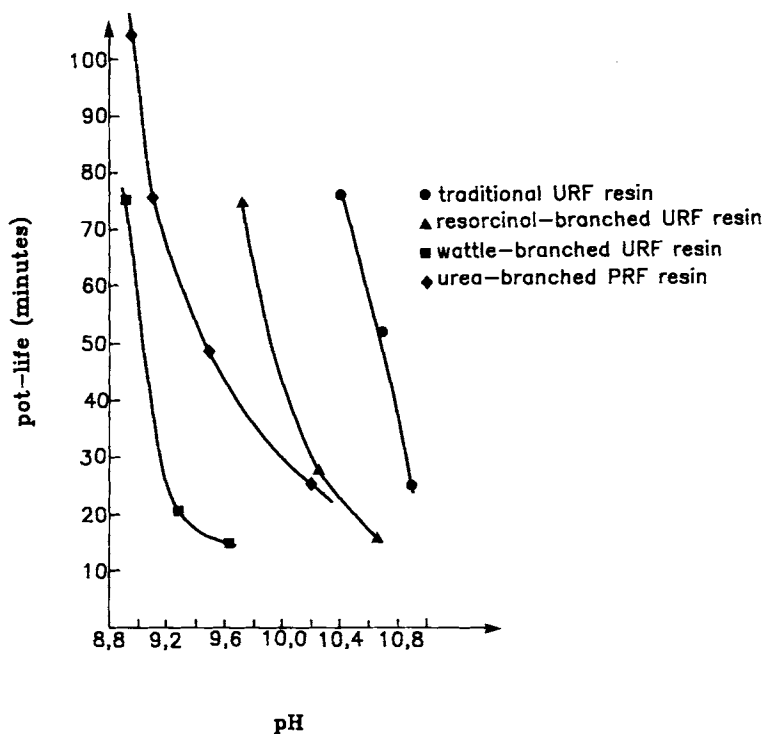
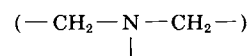


Figure 1 Resins pot lives as a function of resin glue-mix pH: (●) traditional URF resin; (▲) Resorcinol-branched URF resin; (■) wattle tannin extract-branched URF resin; (◆) urea-branched PRF resin.

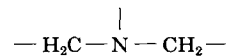
Table III Preparation Parameters and Results of URF Resins of Different Urea : Formaldehyde Molar Ratios

	Resin URF No.																	
	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34
U : F ratio	1 : 1.5	1 : 1.25	1 : 1.1	1 : 1	1 : 0.8	1 : 0.5	1 : 1.5	1 : 1.25	1 : 1.1	1 : 1	1 : 0.8	1 : 0.5	1 : 1.5	1 : 1.25	1 : 1.1	1 : 1	1 : 0.8	1 : 0.5
% Resorcinol in undiluted liquid resin	17.4	17.4	17.4	17.4	17.4	17.4	14.0	14.0	14.0	14.0	14.0	14.0	10.5	10.5	10.5	10.5	10.5	10.5
Reaction time at 55°C (min)	110	105	176	205	202	240	66	72	78	84	90	150	40	44	54	62	75	120
% Solids content	57.2	55.7	58.7	59.9	60.2	57.4	55.5	57.7	58.1	59.1	59.8	60.1	59.6	—	—	61.1	64.4	59.8
Viscosity (cps)	1000	≥ 1000	975	975	≥ 1000	230	2900	350	≥ 1000	1650	500	652	16,000	≥ 1000	—	2100	2000	515
Shelf life (days)	1	1	2	2	1	> 40	1	2	1	2	3	12	1	1	< 1	2	2	11
Strength (kN)	1.80	1.65	1.84	1.93	2.57	2.77	1.74	1.86	1.88	2.07	2.61	2.87	1.68	2.26	2.37	2.31	2.81	2.76
Dry Wood failure (%)	25	35	48	47	72	80	21	30	43	46	58	78	20	28	30	34	42	66

be naturally branched or potentially branched. This is quite different to traditional PF resins that appear to be mostly linear.¹⁰ It must be stressed that what are referred to as traditional URF resins in this article are not necessarily linear: They are merely URF resins in which additional induced branching has not been introduced by the addition of another branching unit during its preparation. Also, it was not possible to distinguish between mono-, di-, and trisubstitution on the resorcinolic nucleus by a change in the chemical shift of the resorcinolic C's in ¹³C-NMR spectroscopy. Thus, ¹³C-NMR spectroscopy was not used to identify tridimensional branching or linear lengthening on the resorcinolic nuclei, but rather just on the urea molecules. The peak that was used as an identification whether tridimensional branching occurred is at $\delta \approx 55$ ppm:



On this basis, URF resins to which resorcinol has not been added as a branching unit show an increase of branching on the UF backbone of the resin when total terminal resorcinol is increased. Conversely, URFs in which additional branching has been induced by introduction in the midreaction of a small amount of resorcinol branching units show a decrease of branching with a resorcinol decrease. This can be observed by the absence, or presence, and intensity, of the



band at $\delta = 55$ –56 ppm in ¹³C-NMR. Thus, in the noninduced-branching URF resins 1 and 2 (Table I) of, respectively, 25 and 22.5% terminal resorcinol content, this ¹³C-NMR band is, respectively, absent and present (but small). This result could be interpreted as that by decreasing the percentage of resorcinol more free formaldehyde and methylol groups are still available for reaction, increasing the probability of UF branching.

In induced-branching, the reverse applies. Thus, induced-branching URF resins 35 and 38 (Table IV) of, respectively, 25 and 22.5% total terminal resorcinol content have the ¹³C-NMR band at $\delta = 55$ –56 ppm present and absent, respectively. Applied results indicated that as the amount of resorcinol brancher increased in branched URF resins the percentage wood failure results decreased (Table II).

By examining the ¹³C-NMR spectra, it was possible to note differences that can be used to understand why the applied results are such. When only

Table IV Effect of Methanol in Branched URF Resins

	Resin URF No.					
	35	36	37	38	39	40
U : F ratio	1 : 0.5	1 : 0.5	1 : 0.5	1 : 0.5	1 : 0.5	1 : 0.5
% Resorcinol in undiluted liquid resin	25.0	25.0	25.0	22.5	22.5	22.5
% Resorcinol in total liquid resin	17.4	17.1	16.9	16.0	16.8	15.8
Reaction time at 60°C (min)	360	360	360	360	360	360
Methanol : water ratio in solvent	30 : 70	15 : 85	45 : 55	30 : 70	15 : 85	45 : 55
% Solids content	57.1	56.2	55.3	55.9	58.8	55.0
pH	10.42	8.81	9.31	9.65	8.43	9.31
Viscosity (cps)	155	160	105	395	160	100
Pot life (min)	76	83	79	80	70	62
Shelf life (days)	> 40	> 40	> 40	> 40	> 40	> 40
% Wattle by mass in undiluted liquid resin	15	15	15	15	15	15
Strength (kN)						
Dry	2.57	2.62	2.60	2.50	2.23	2.61
Soak	2.20	1.51	1.24	2.20	1.03	0.89
Boil	2.20	1.66	1.18	2.20	1.60	1.27
Wood failure (%)						
Dry	70	68	100	43	29	77
Soak	75	32	15	75	28	25
Boil	87	44	30	83	23	20

2.9×10^{-2} mol to 7.2×10^{-2} mol of resorcinol brancher is used (URF 10 and 11, Table II), tridimensional branching on the urea molecule appears to occur as the peak at $\delta = 55.90$ – 56.04 ppm is clearly evident (Figs. 2 and 3). Resin URF 11 (with 7.2×10^{-2} mol of resorcinol brancher) experiences the greatest tridimensional branching on the urea molecule according to the ^{13}C -NMR spectrum, yet it also exhibits the highest percentages wood failure. When the amount of resorcinol brancher is further increased, then it appears from the ^{13}C -NMR spectra that tridimensional branching on the urea molecule is eliminated as the $-\text{N}-(\text{CH}_2)_2$ peak at $\delta = 56$ ppm disappears. The amount of branching resorcinol may be sufficient enough to allow the macromolecule to lengthen linearly. This linear lengthening appears to decrease the percentages wood failure, probably as a consequence of the decreased ability of the polymer to wet the substrate. The optimum amount of brancher appears to be 7.2×10^{-2} mol to 8.2×10^{-2} mol of resorcinol brancher for approximately 15% of terminal resorcinol used by mass of liquid resin. Though, as expected, linear lengthening is the favorite mechanism for decreasing the resorcinol required, it appears that in branched URF resins the macromolecules produced are too large. This causes poor specific adhesion and is manifested in poor wood failure results.

By substituting the resorcinol brancher with mimosa tannin extract, it was hoped that the percentage resorcinol by mass on total liquid resin would decrease. It was, however, feared that the percentage wood failure results would be lower because condensation of the macromolecule on the URF resin would imply an increase in the molecular weight of the resin.

The applied results showed that if the amount of resorcinol brancher did not prove to be excessive in the branched URF resin, optimum results were also achieved when an equivalent amount of tannin extract was used as a brancher. (cf. results in Table II). The surprising result was that the introduction of the tannin extract as a brancher decreased the percentage of resorcinol by mass on total liquid resin without deteriorating the percentage wood failure results. A possible explanation of this is the difference in the molecular geometry created when branching occurs on a small resorcinol molecule compared with that created when it occurs on a large tannin macromolecule. When resorcinol is used as a branching molecule, it has a much more rigid structure than when tannin extract is used. The molecular geometry of branching in the latter is not as densely packed. The reactive sites on the wattle tannin macromolecule are also more widely spaced than those on resorcinol. The more widely spaced

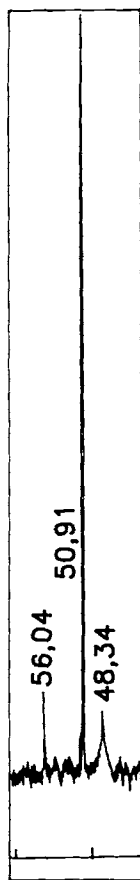
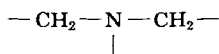


Figure 2 ^{13}C -NMR spectrum region 44–61 ppm of resin URF 10; note that the 56.04 ppm band indicates branching.

and more flexible molecular geometry introduced when polyflavonoid tannin is used as a brancher may be allowing better adhesion of the resin to the wood, resulting in higher percentages wood failure. Ordinarily higher molecular weights cause poorer wetting—hence, poorer wood failure, but in this case, it appears that the molecular geometry caused by branching molecules has a significant effect on the ability of the adhesive to wet the substrate. ^{13}C -NMR spectroscopy (16W, Table II and Fig. 4) also indicates that when tannin extract is used tridimensional branching on the urea molecule is even more encouraged than when resorcinol is used. The peak at $\delta = 55$ ppm



is even more intense in these spectra. This further supports the hypothesis that branching on the polyflavonoid tannin occurs more readily due to the better steric availability of the reactive sites.

Both applied and analytical results showed that

the optimum conditions to produce a branched URF with good performance are

- (i) the use of 4.5×10^{-2} mol of polyflavonoid tannin extract as a branching unit for 176.4 g of 1 : 0.5 UF liquid resin and a 4 h branching period at 60°C ; and
- (ii) 7.4×10^{-1} moles of terminal resorcinol for 176.4 g of 1 : 0.5 UF liquid resin and a reaction time of 2 h at 60°C .

The amount of methanol used in the solvent also affected the performance of both traditional and branched URF resins. In traditional URF resins, it was observed that if the amount of methanol in the solvent used was increased the percentage wood failure in the dry test improved, but the water-resistant properties of the resin deteriorated (Table IV).

Methanol is known to be a retarder in the UF resin synthesis. Methanol retards the process whereby paraformaldehyde release formaldehyde

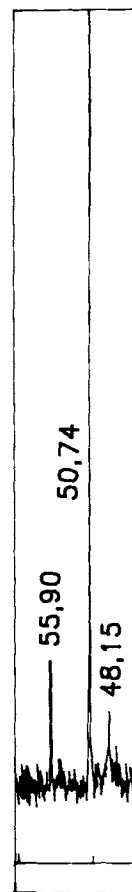


Figure 3 ^{13}C -NMR spectrum region 44–61 ppm of resin URF 11.

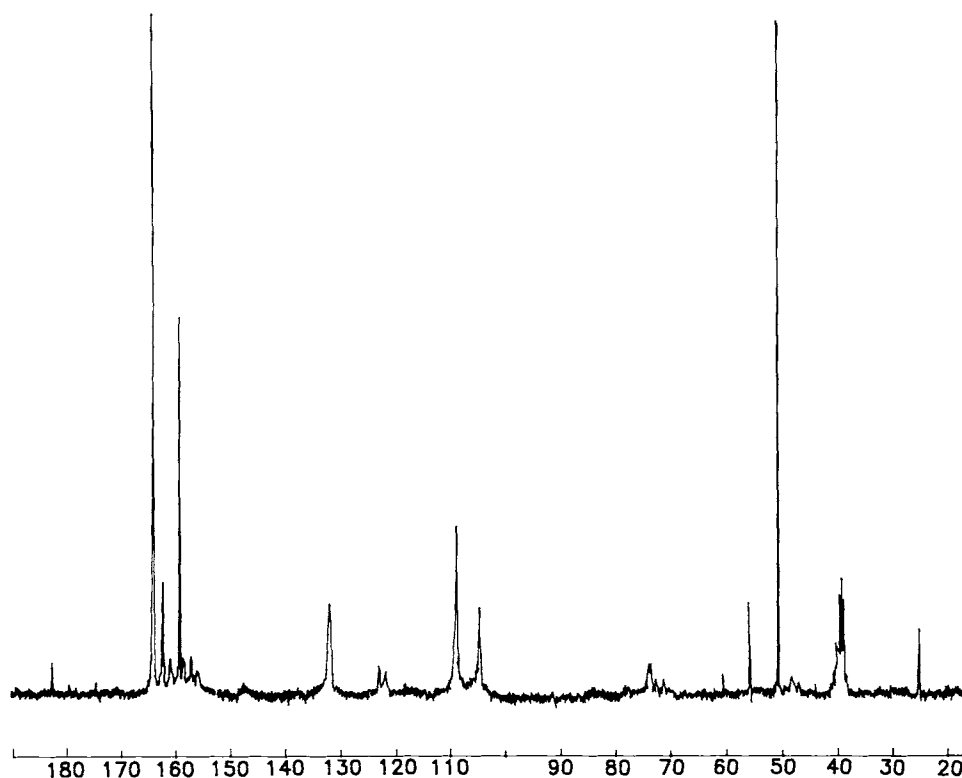


Figure 4 ^{13}C -NMR spectrum of resin URF 16W wattle (mimosa) tannin extract-branched.

that can then react with urea to form methylol groups. As fewer reactive methylol groups results, shorter UF polymer chains are formed. Specific adhesion to lignocellulosic substrates of lower molecular weight resins is greater¹¹. For this reason, it was believed that higher percentages wood failure in the dry test would result, as indeed they did (cf. results in Table IV). However, it has been reported¹² that methanol content makes a considerable difference in the water resistance of UF resins. This effect is due to the formation of methylated UF resins, which, on curing, remain unchanged and because of their easy solubility in water destroy the water resistance of the cured, bonded joint. The same effect is being observed in traditional URF resins in which 45% by mass of methanol was used in the solvent mixture (Table IV).

^{13}C -NMR spectroscopy indicated a possible explanation for the above phenomenon. Resins URF 1 and 35 (Tables I and IV) are traditional URF resins with 17.4% of resorcinol by mass on total liquid resin. Resin URF 37 is its corresponding resin but with 45% of the solvent being methanol, whereas in the former, only 30% was methanol. The applied results indicated an increase in percentages wood failure in the dry test but a weakening of the water

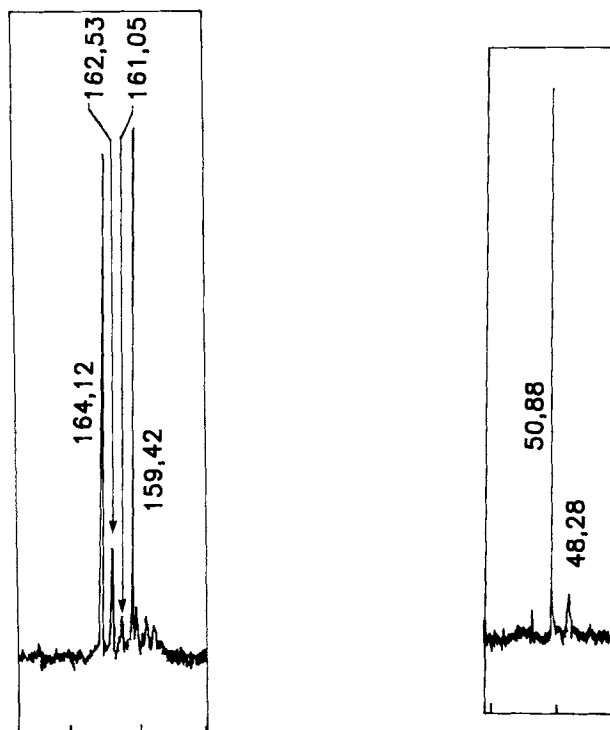


Figure 5 ^{13}C -NMR spectrum regions 41–61 ppm and 150–180 ppm of resins URF 1 and URF 35. Note absence of 55 ppm band.

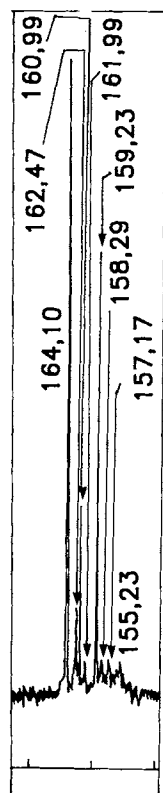


Figure 6 ^{13}C -NMR spectrum region 149–173 ppm of resin URF 37.

resistance. If one examines the ^{13}C -NMR spectra of these resins (Fig. 5), one notes that with an increase in percentage methanol used in the solvent there is an increase in the amount of monomeric urea and methylenebisurea present. This is deduced by an increase in intensity of the bands at $\delta = 164.10$ ppm (C=O of urea) and at $\delta = 161.99$ ppm (C=O peak of methylenebisurea) in the spectrum of URF 37 (Fig. 6) relative to the intensity of the same peaks in the spectrum of URF 1 and 35 (Fig. 5). The presence of this increased amount of monomeric urea and methylenebisurea may be causing weakening in the water-resistant properties of URF 37. Another possible explanation is that in the presence of a larger percentage methanol the decrease of reactivity of the formaldehyde causes a slower degree of polymerization of the resin. Though this may be causing stronger adhesion in the dry test due to better penetration of the resin into the wood, it also may be simultaneously weakening the cohesive forces of the resin. This may be to the extent that if the cured resin is exposed to severe water attack conditions the resin exhibits impaired water resistance. The percentage methanol in the solvent also affects the results of branched URF resins. For instance, resin URF 6 (Table II) is a branched URF resin with 14.9% of resorcinol by mass on total liquid

Table V Effect of Methanol in Branched URF Resins

	Resin URF No.					
	41	42	43	44	45	46
U : F ratio	1 : 0.5	1 : 0.5	1 : 0.5	1 : 0.5	1 : 0.5	1 : 0.5
Mass of liquid resin (g)	176.4	176.0	176.4	176.4	176.4	176.4
Methanol : water ratio in solvent	30 : 70	45 : 55	30 : 70	45 : 55	30 : 70	45 : 55
Branching resorcinol (mol)	0.041	0.041	0.082	0.082	0.160	0.160
Branching time at 60°C (min)	240	240	240	240	40	50
Terminal resorcinol (mol)	0.74	0.74	0.74	0.74	0.74	0.74
Terminal resorcinol time at 60°C (min)	120	120	120	120	120	120
% Resorcinol in liquid resin	16.6	16.3	14.9	17.4	18.3	17.7
% Solids content	56.7	55.3	48.8	57.2	56.1	54.2
pH	9.22	9.16	9.73	9.20	8.86	8.90
Viscosity (cps)	116	150	155	195	220	95
Pot life (min)	75	75	75	70	87	77
Shelf life (days)	> 40	> 40	> 40	> 40	> 40	> 40
% Wattle by mass in undiluted liquid resin	15	15	15	15	15	15
Strength (kN)						
Dry	2.60	2.80	2.60	2.50	3.15	2.43
Soak	2.10	2.07	1.75	1.86	2.10	0.88
Boil	2.02	1.75	1.74	2.10	2.40	1.39
Wood failure (%)						
Dry	36	100	70	100	35	5
Soak	76	60	75	84	65	26
Boil	88	86	95	92	50	24

resin. URF 44 is its corresponding resin except that once again 45% of the solvent is methanol instead of only 30%. Applied results showed an increase in percentages wood failure on dry test, but no deterioration on the soak and boil tests (Tables II and V, resin 6 vs. 44). The ^{13}C -NMR spectrum of resin URF 44 does show an increase in the amount of urea compared to that in resin URF 6 (Figs. 7 and 8). The relative intensity of the peak at $\delta = 164.10$ ppm ($\text{C}=\text{O}$ of urea) in relation to the rest of the spectrum is much more intense in the spectrum of URF 44 than in URF 6. However, there is no difference in relative intensity between the $\text{C}=\text{O}$ peak of methylenebisurea ($\delta = 161.9$ ppm) in the two spectra. This implies that there does not appear to be an increase in the amount of methylenebisurea as in URF 37 (Fig. 6) (the traditional URF resin with 45% methanol in the solvent). From the ^{13}C -NMR results, one can only conclude that too large a percentage of methylenebisurea in the resin appears to have a weakening effect on the water-resistance properties of the resin. This is perhaps the

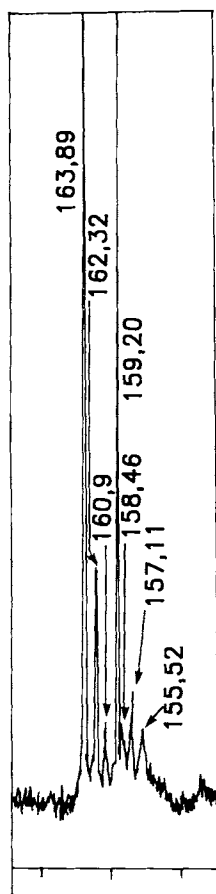


Figure 7 ^{13}C -NMR spectrum region 145–175 ppm of resin URF 6.

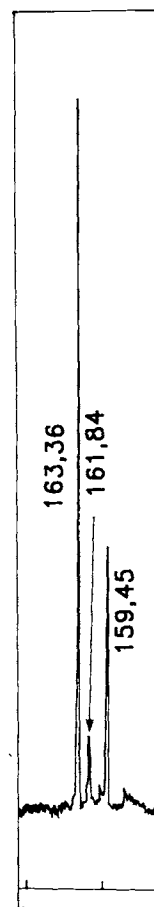


Figure 8 ^{13}C -NMR spectrum region 152–171 ppm of resin URF 44.

first clear analytical indication of the water lability of the $-\text{NH}-\text{CH}_2-\text{NH}-$ bond.

CONCLUSION

In conclusion, effects that appear to influence the results of branched URF resins include the

- (i) amount of brancher, with amounts of resorcinol brancher between 0.07 and 0.08 mol giving the best balanced performance;
- (ii) type of brancher, with polyflavonoid tannins (0.045 mol) allowing greater decrease of resorcinol content;
- (iii) temperature of reaction, with lower reaction temperatures (50–60°C) giving much better results;
- (iv) amount of final resorcinol, with resorcinol contents as low as 12–13% still giving resins of acceptable performance;

- (v) amount of methanol used in solvent, with increasing methanol increasing percentage wood failure but progressively impairing water resistance of the cured linear resins, but not of the cured branched resins; and
- (vi) physical properties such as pH and viscosity.

Though these effects also influenced the results of branched PRF resins,³ it appears that the range in which these effects overlap to produce acceptable results in branched URF resins is much narrower than in branched PRF resins.

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