The Chemistry and Development of Branched PRF Wood Adhesives of Low Resorcinol Content

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SYNOPSIS

Phenol–Resorcinol–Formaldehyde (PRF) resins of good adhesive performance, and of resorcinol content much lower than in traditional PRF cold-setting adhesives, were prepared by introducing small amounts of urea as a branching unit during preparation of the resin. Resorcinol contents as low as 10.6% were obtained by this method while still maintaining an acceptable pot-life of the resin. Resorcinol contents as low as 8%, still with a good adhesive performance, were obtained, although the pot-life obtained was too short. GPC, FT–IR and C^{13} NMR indicated that the small amount of urea branching unit used leads to the reduction of resorcinol content mostly by rapid doubling of the average linear length of the PF intermediates and of the final PF oligomers. Tridimensional branching in the liquid resin, contrary to what was previously thought, does not appear to be an important contributory factor and better adhesives are often prepared when branching is totally, or almost totally, absent. Reduction of resorcinol content is achieved simultaneously by two mechanisms: (i) the decrease of resorcinol percentage on resin solids due to the rapid lengthening (doubling) of average oligomers length and (ii) the need for these resins to operate at lower solids content, due to the increased viscosity obtained during their preparation.

INTRODUCTION

Phenol–resorcinol–formaldehyde (PRF) adhesives, have been used for many years as cold-setting adhesives for wood. They produce water and weather-resistant bonds.[1-3] PRF resins are mainly prepared by grafting resorcinol onto the active methylol groups of the low condensation resols obtained by the reaction of phenol with formaldehyde. Resorcinol is the chemical species that gives to the PRF adhesives their characteristic cold-setting behavior. Resorcinol gives to the phenolic resin accelerated and improved crosslinking at ambient temperature. Resorcinol is an expensive chemical, produced only in a few locations around the world, and is the determining factor in the cost of PRF adhesives. Significant reductions in the cost of such adhesives must by necessity be coupled with a decrease in their resorcinol content.

In the past, significant reductions in resorcinol content, at parity of adhesive performance, have been achieved when resorcinol–formaldehyde resins were substituted with PRF resins. Modern day commercial PRF resins have percentages by mass of resorcinol on the order of 16–18%, by mass, on total liquid resin. Although such resins have been commercial for more than 20 years, no system to further significantly decrease the resins' resorcinol content, without loss of performance, has been implemented. Recently, however, a step forward has been taken in the formulation of PRF adhesives of lower resorcinol content. Increasing branching of the liquid PRF resin during preparation of synthetic PRF adhesives results in a noticeable decrease in their resorcinol content without loss of performance.[4]

APPROACH

Traditional PRF adhesives are generally prepared by reaction of phenol with formaldehyde to form phenol–formaldehyde resols, which are mostly linear. Resorcinol is added to this resin often in excess of the $-CH_2OH$ methylol groups of the PF resin. Resorcinol is then linked by methylene bridges

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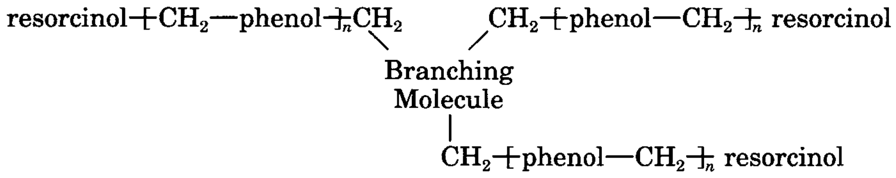
($-CH_2-$) to the PF resin skeleton. Thus, in the PRF resin the linear PF resin oligomers are in general terminated by resorcinol moieties. The PRF resin produced can be schematically represented as

$$\text{resorcinol}-CH_2-[\text{phenol}-CH_2]_n\ \text{resorcinol}$$

If a chemical molecule, capable of branching (three or more effective sites with an aldehyde), is used during or after the preparation of the PF resin, a branched PF, and consequently a branched PRF resin, is produced. This can be schematically represented as



$$\begin{array}{ccc} \text{resorcinol}[CH_2\text{—phenol}]_n CH_2 & & CH_2[\text{phenol—}CH_2]_n\ \text{resorcinol} \\ & \searrow\ \swarrow & \\ & \text{Branching Molecule} & \\ & | & \\ & CH_2[\text{phenol—}CH_2]_n\ \text{resorcinol} & \end{array}$$

where $n \geq 1$ in integer numbers.

Thus, in a linear PRF resin for every n moles of phenol, 2 moles of resorcinol are used; while only 1 mole of resorcinol for n moles of phenol is used in a "branched" PRF adhesive. The amount of resorcinol has thus been approximately halved in the case of a branched PRF resin. A second effect caused by branching is the noticeable increase in the degree of polymerization of the resin, with a consequent increase in the viscosity of the liquid adhesive solution. As PRF adhesives must be used within fairly narrow viscosity limits to give best performance, to return the viscosity of the liquid PRF resin within these limits its resin solids content must be lowered markedly, with a consequent further decrease of the amount of resorcinol on total liquid resin. Many substances can be used to branch a PF or a PRF resin during its manufacture. In theory, any molecule possessing three or more sites capable of reacting with formaldehyde might be able to branch the resin. Simple "branching" molecules that have been used are resorcinol, melamine, urea, and aniline,[4] although others can also be found to have the same effect.

In this article, urea was primarily used since it is relatively inexpensive. Urea is, in reality, only a three-point branching unit, since tetramethylolurea has never been isolated. The PRF resins prepared with urea as a brancher initially have an amber/greenish tint that changes to a deep ink-blue color within a week after preparation. Hence, the nickname of "Blue Glues" is used for these resins. When hardener is added to the resin, the glue mix has a dark grey-green color and after curing the resin is dark brown and cannot be distinguished from traditional PRF resins.

This article aims at clarifying what happens during the preparation of "branched" PRF resins and at showing that PRF resins of much lower resorcinol content and of good performance can be produced.

EXPERIMENTAL

Traditional Linear PRF Resin

A traditional PRF resin was produced according to the following formulation: Phenol (28.02 g: 2.98×10^{-1} mol) and concentrated sulphuric acid (7.50×10^{-2} g: 5.96×10^{-4} mol) were added and refluxed in an oil bath under continuous stirring. (Reflux temperature = 110°). 40% Formaldehyde solution (11.90 g: 1.46×10^{-1} mol) was added to the refluxing mixture dropwise over 20 min. The reaction mixture was refluxed for 30 min (reflux temperature = ~ 92°C). The reaction mixture was then cooled to 75°C, and on cooling a solution of 50% NaOH (2.80 g: 3.50×10^{-2} mol) and water (2.40 g: 1.33×10^{-1} mol) was added to the reaction mixture. This was then refluxed and a 40% formaldehyde solution (13.86 g: 1.71×10^{-1} mol) was added to it dropwise over 20 min. The reaction mixture is then allowed to reflux for 90 min. Resorcinol (18.70 g: 1.70×10^{-1} mol) was then added (reaction was exothermic), and the reaction mixture was further refluxed for 120 min. Resin was cooled down to 70°C and methanol (15.20 g: 4.75×10^{-1} mol) was added to it to decrease its viscosity.

Branched PRF Resin

This formulation is very similar to that of the traditional PRF resin above, except that after the PF intermediate was refluxed for 30 min plus 90 min, the urea brancher was added in each case and refluxed for a certain period of time before resorcinol was added.

The following is a general formulation for the "branched" PRF resin. Specific amounts of brancher, resorcinol, and reflux times are listed in the Tables of Results.

Phenol (28.02 g: 2.98×10^{-1} mol), water (2.50 g: 1.39×10^{-1} mol), and concentrated sulphuric acid (7.50×10^{-2} g: 5.96×10^{-4} mol) were added and refluxed in an oil bath under continuous stirring (reflux temperature = 100°C). A 30% methanol: 70% water solution (7.4 g) was added to the refluxing mixture. 96% paraformaldehyde powder (4.34 g: 1.36×10^{-1} mol) was then added slowly over 20 min to the reaction mixture. This was then refluxed for 30 min (reflux temperature = 92°C). The reaction flask was cooled to 75°C and on cooling a solution of 50% NaOH (2.80 g: 3.50×10^{-2} mol) and water (2.40 g: 1.33×10^{-1} mol) was added to the reaction mixture. The reaction mixture was once again allowed to reflux and a 30% methanol: 70% water solution (8.6 g) was added. 96% Paraformaldehyde powder (5.20 g: 1.71×10^{-1} mol) was then added slowly over 20 min. The reaction mixture was then allowed to reflux for 90 min. A certain amount of urea brancher was then added and refluxed for a certain period of time. A certain amount of resorcinol was then added and also refluxed for a certain period of time (amounts listed in Tables). Finally, the resin was cooled to 70°C and the viscosity was decreased with the addition of 70% methanol: 30% water solution.

Preparation of Glue Mixes

This was the glue mix formulation used for all the glue mixtures produced throughout this article: Gluemix = 5 parts liquid resin + 1 part hardener where hardener = (0,6 × 1 part) 96% paraformaldehyde + (0,4 × 1 part) 200 mesh wood flour. Beech strips of 100 × 25 × 3 mm were bonded with a 25 × 25 mm overlap joint, according to standard specifications BS 1204, 1965[8] and SABS 1349-1981,[9] with the above glue mixes. The bonded joints were clamped for 24 h at ambient temperature and then cured for a further 6 days also at ambient temperature. The pot-lives, strengths, and percentages of wood failure obtained are listed in the Tables of Results. Fifteen replicate specimens of each case were tested dry, after 24 h cold water soak and after 6 h boiling, according to the relevant specifications.[8,9] The results obtained are shown in Tables I–V.

Analysis

Resins were analyzed by Infrared studies on a JASCO FT/IR-5000 spectrometer, by Gel permeation chromatography (GPC) on a WATERS HPLC spectrometer using an 100 Å styragel column and methanol as a solvent. For controls of molecular mass in relation to GPC elution time pure phenol (M.W. = 94), pure catechin $C_{15}O_6H_{14}$ (M.W. = 290), isolated methylene bis catechin $C_{31}O_{12}H_{28}$ (M.W. = 592), and isolated dimethylene triscatechin $C_{47}O_{18}H_{42}$ (M.W. = 894), all phenolic materials for system consistency of comparison, were used. The results indicated that for each Δt of dilution = 1 min was equivalent to an increase of molecular mass of 160–170. The elution time to M_n relationship was found to be linear in the ranges indicated. Resins were also analyzed by C^{13} Nuclear magnetic resonance on a Bruker AC-200 Spectrometer (200.13 MHz) using deuterated methanol as a solvent.

C^{13}NMR, Resin 8 (intensity in bracket): 163.15 ppm (1.018; C = 0); 158.73 (20.386); 157.25 (3.274); 155.64 (1.049); 155.25 (1.757); 155.09 (1.609); 153.69 (1.124); 153.07 (0.665); 134.28 (1.755); 133.40 (0.833); 133.05 (0.732); 131.02 (9.782); 130.54 (13.129); 129.96 (2.894); 129.69 (2.504); 129.17 (1.383); 128.27 (1.092); 127.59 (1.212); 127.43 (0.900); 120.69 (5.234); 116.08 (16.524); 115.99 (7.896); 108.02 (17.236); 103.64 (10.372); 61.23 (1.105; $—CH_2OH$); 50.29 (0.988); 49.84 (35.526); 49.43 (6.323); 48.99 (6.946); 48.57 (6.118); 48.14 (3.235); 47.71 (1.024); 40.60 (1.108; $p,p—CH_2—$); 35.33 (1.353; $o,o—CH_2—$).

DISCUSSION

The results in Table I show that branched PRF adhesive resins of low resorcinol content, still presenting good performance, can be prepared. The lowest percentage of resorcinol, on liquid resin, which appeared still to give a resin satisfying the requirements of international specifications[7,8] for close-contact, cold-setting adhesives for wood, with still acceptable pot-life of the adhesive, was 10.6% (Table I, Resin 3). This is significantly lower than the 16%–18% of today's commercial PRF resins.

Linear PRF resins operate at 50%–55% resin solids content and show a marked decrease in performance when their percentage resin solids are decreased.[5] The branched PRF resins in Table I instead appear to be able to maintain good performance down to 45% resin solids content while

Table I Comparison of Results, Conditions of Preparation, and Physical Properties of a Few Urea-Branched PRF Resins

Resin No.	"Traditional" PRF Resin"	1	2	3	4	5	6	7
Amount of urea (g : mol)		3.0 g (5.0 × 10^{-2} mol)	1.5 g (2.5 × 10^{-2} mol)	1.5 g (2.5 × 10^{-2} mol)	1.5 g (2.5 × 10^{-2} mol)	1.5 g (2.5 × 10^{-2} mol)	1.5 g (2.5 × 10^{-2} mol)	1.5 g (2.6 × 10^{-2} mol)
"Branching" reflux time (min)		60	90	90	90	90	60	60
Amount of resorcinol (g : mol)	18.7 g (1.7 × 10^{-1} mol)	11 g (1.00 × 10^{-1} mol)	11 g (1.00 × 10^{-1} mol)	11 g (1.00 × 10^{-1} mol)	11 g (1.00 × 10^{-1} mol)	11 g (1.00 × 10^{-1} mol)	11 g (1.00 × 10^{-1} mol)	9 g (8.00 × 10^{-2} mol)
Resorcinol reflux time (min)	120	30	60	60	90	120	30	60
Viscosity	350	400	628	1200	1550	625	50 cps	1150
pH	9.10	10.20	9.80	9.74	10.41	11.13	—	10.18
Pot-life (min)	213	42	61	83	6	29	—	44
% Solids content	58.50	49.80	47.80	47.20	51.30	44.00	37.52	44.90
% Resorcinol in liquid resin	19.0	11.4	12.4	10.6	10.1	9.7	8.9	11.0
Strength (kN) (% wood fail)								
Dry	2.9 kN (96%)	3.0 kN (40%)	2.9 kN (76%)	2.7 kN (8%)	3.2 kN (6%)	2.8 kN (2%)	2.3 kN (1%)	3.4 N (71%)
Soak	2.6 kN (100%)	2.7 kN (84%)	2.9 kN (100%)	2.7 kN (80%)	2.9 kN (79%)	3.1 kN (48%)	1.6 kN (0%)	2.8 kN (79%)
Boil	2.4 kN (100%)	2.9 kN (89%)	2.6 kN (100%)	2.6 kN (100%)	2.8 kN (90%)	3.5 kN (100%)	2.55 kN (9%)	2.3 kN (100%)

Table II Comparison of Strength Results and Pot-Life of a Urea-Branched PRF Resin with pH as for Preparation and after pH Adjustment with Acetylsalicylic Acid

	Resin 3	Resin 3′
Viscosity	1200	1200
pH	9.74	9.03
Pot-life	83	173
Strength (kN) (% wood failure)		
Dry	2.7 kN (8%)	2.55 kN (9%)
Soak	2.7 kN (80%)	2.96 kN (77%)
Boil	2.6 kN (100%)	2.96 kN (97%)

usable pot-life is still acceptable (Table I, Resin 7). However, the results in Table I also indicate that at comparable performance the pot-life of branched PRF resins appear to be much shorter than for linear PRF resins. This is problematic because, while the pot-life of linear PRF resins can be easily lengthened by decreasing the resin's pH with an acid, this did not appear to be possible for the branched resins. The branched resins, upon addition of small amounts of diluted acid solutions, yielded instantaneous localized precipitation. This might be due to the greater degree of advancement of the resins during preparation, making them excessively sensitive to small water and water/methanol addition. Although the pH of the branched resins can be adjusted upward with ease, it was impossible to lower their pH by using acids of 10% or higher concentration. Formic, acetic, sulphuric, phosphoric, hydrochloric, and other acids diluted in water solution failed to solve this problem. Attempts with solid acids such as *p*-toluene sulphonic acid and trichloroacetic acid also failed. The pot-life of the branched PRF resins, however, was easily lengthened by adjusting downward the pH with very small amounts of acetylsalicylic acid. The results in Table II show an increase in pot-life from 83 to 173 min for a branched PRF resin in which the pH has been adjusted downward by the use of solid acetylsalicylic acid. The strength performance of the resin appears to be unaffected.

C^{13} NMR studies indicated that the small amount of urea brancher appeared to have coreacted, as expected, with the phenolic resin skeleton. The most indicative result in this respect was the value of the urea's C=O group's shift in the branched resin spectra. While the C^{13} NMR shift of the C=O group of unsubstituted urea is 161.2 ppm, that of a tetramethyl substituted urea is of 165.4 ppm.[9] In Table III are shown the shifts of the urea C=O group in a few of the branched PRF resins. Their values appear to indicate that the urea is mainly disubstituted. This shows that the greater part of the branched PRF resins were on average mostly constituted by more advanced linear PRF oligomers in which the urea connects just linear phenolic chains. It was initially believed then that the same effect, the decrease of resorcinol content of the final resin, could be achieved by just increasing the reaction period of the PF resin intermediate without addition of urea or other branching agents. This did not appear to be the case. Traditional linear PRF resins in which the PF intermediate was reacted for a much longer time, to achieve higher mol wt linear polymers, with a resorcinol content as low as that achieved with PRF resins containing urea, gave instead much poorer performance, as shown by the much lower values of percentage wood failure, which were much lower than standard requirements,[7,8] in Table IV. Thus, it can be deduced that the branching agent really functions as a facilitator in producing far more rapidly linear PF resin intermediates of much higher mol wt. The effect of resorcinol reduction, both on resin solids and by viscosity effect, is still maintained as instead of

$$m\ \text{Resorcinol}-(\text{CH}_2-\text{Phenol})_n\text{CH}_2-\text{Resorcinol}$$

Table III Assignment of C^{13} Chemical Shifts of Urea C=O Group, Indicating Urea Distribution

Resin No.	Chemical Shift (ppm)	Assignment
8	163.08	$\overset{\text{O}}{\overset{\Vert}{\text{C}}}$ of substituted urea
2	163.15	$\overset{\text{O}}{\overset{\Vert}{\text{C}}}$ of substituted urea
3	163.08	$\overset{\text{O}}{\overset{\Vert}{\text{C}}}$ of substituted urea
9	162.98	$\overset{\text{O}}{\overset{\Vert}{\text{C}}}$ of substituted urea

Table IV Composition and Comparison of Results of a Traditional Linear PRF Resin, a Traditional PRF Resin of Lengthened Reaction Time, and of a Linearly Lengthened Urea-Branched PRF Resin

Conditions	Traditional PRF	Traditional PRF with Increased Reflux Time	Branched PRF (Resin 3)
Amount of urea (g : mol)			1.5 g (2.5×10^{-2} mol)
"Branching" reflux time (min)	0	90	90
Amount of resorcinol (g : mol)	18.7 g (1.7×10^{-1} mol)	11 g (1.00×10^{-1} mol)	11 g (1.00×10^{-1} mol)
Resorcinol reflux time (min)	120	60	60
Viscosity (cps)	350	90	1200
pH	9.10	10.57	9.74
Pot-life (min)	213	243	83
% Solids Content	58.50	44.30	47.20
% Resorcinol in liquid resin	19.0	10.1	10.6
Strength (kN) (% wood fail)			
Dry	2.9 kN (96%)	2.7 kN (23%)	2.7 kN (8%)
Soak	2.7 kN (80%)	3.0 kN (26%)	2.7 kN (80%)
Boil	2.64 kN (100%)	2.7 kN (57%)	2.64 kN (100%)

small amounts of urea brancher addition will produce

$$\frac{m}{2}\ \text{Resorcinol}-(\text{CH}_2-\text{Phenol})_n\text{CH}_2$$

$$-\text{Brancher}-\text{CH}_2(\text{Phenol})_n\ \text{Resorcinol}$$

The net effect is still the approximate halving of resorcinol content while still maintaining good performance of the adhesive.

The reason for this behavior resides in the relative reactivities of phenol and urea moieties in alkaline environment. Urea does not form urea–formaldehyde polymers at a pH higher than 8, but only reacts

Table V Determination of Branching in PRF Resins by GPC/Viscosity Determinations[10]

Resin No.	10	11	12	13
Amount of urea (g : mol)	0	1 g (1.70×10^{-2} mol)	1.5 g (2.5×10^{-2} mol)	2.0 g (3.0×10^{-2} mol)
"Branching" reflux time (min)	60	60	60	60
Amount of resorcinol (g : mol)	18.7 g (1.8×10^{-1} mol)	11 g (1.00×10^{-1} mol)	11 g (1.0×10^{-1} mol)	11 g (1.0×10^{-1} mol)
Resorcinol reflux time (min)	60	60	60	60
Viscosity (cps)	165	1938	100	180
Average mol wt	286.65	298.09	260.10	341.00
Log. ave. mol. wt /(log viscosity)	1.110	0.753	1.207	1.120
% Solids content	45.0%	47.3%	45.3%	51.5%
% Resorcinol in liquid resin	17.11%	11.52%	11.25%	12.40%
Strength (kN) (% wood failure)				
Dry	3.3 kN (4%)	2.7 kN (0%)	2.9 kN (80%)	2.5 kN (0%)
Soak	3.2 kN (87%)	2.9 kN (21%)	2.7 kN (94%)	2.7 kN (16%)
Boil	3.0 kN (86%)	2.1 kN (32%)	2.9 kN (97%)	3.2 kN (78%)

very rapidly, more rapidly than phenol, with formaldehyde to form methylolated monomeric species. In a situation in which the only formaldehyde available to urea is in the form of the $-CH_2OH$ methylol groups on the PF resin intermediate, the urea will react rapidly with two of these $-CH_2OH$ groups, doubling the mol wt of the PF resin intermediate. Small amounts of urea can be very effective in this respect. The same effect cannot be achieved by adding phenol, which is much slower reacting under the same conditions, and hence cannot be obtained just by lengthening the reaction time of the PF resin without addition of urea or of a similar branching agent.

When small amounts of resorcinol, rather than urea, are instead used as a branching agent a much higher proportion of truly tridimensional branching is likely to occur. The liquid resin would then have a much higher proportion of truly tridimensionally branched chains, but of unusually high mol wt, which would also have difficulty in penetrating and wetting the wood surface. As a consequence a poor percentage wood failure results. This indeed has been reported.[4]

The most notable difference in the FT–IR spectra was between spectra of resins that gave "good" bonding performance and those that gave "poor" bonding performance. The difference lay in the relative intensities of the % transmission bands at ~ 1017 cm^{-1} and at 965 cm^{-1}. In "strong" resins, the band at ~ 1017 cm^{-1} was much more intense than that at ~ 965 cm^{-1} and in "weak" resins the intensities of these IR bands are reversed.

The band at ~ 1017 cm^{-1} is due to 1,2 and 1,4 substituted aromatic rings, which may be partly due to ortho- and para-methylolphenolic nuclei and this band is also due to the $C-O$ stretch of the methylol groups. The band at ~ 965 cm^{-1} appears to be primarily due to the $C-O$ stretch of resorcinol (as this peak appears very clearly in the resorcinol spectrum). It is understandable that in a "strong" adhesive, there are sufficient methylol groups to link up the resorcinol, hence the resorcinol band at ~ 965 cm^{-1} is less intense than the band at ~ 1017 cm^{-1}. The excess of free resorcinol would make the resin weaker as it would react preferentially with the formaldehyde in the hardener creating a defect of formaldehyde, slowing down the hardening process and hence weakening the resin. A FT–IR spectrum of a "weak" liquid resin, recorded after 2 months from preparation, appeared to be similar to that of a freshly prepared strong resin. This is expected since any resin left at ambient temperature will continue to react with time; consequently, the ratio of unreacted to reacted resorcinol will become lower. Thus, the intensity of the band at 965 cm^{-1} decreases relative to that at ~ 1017 cm^{-1}. Attempts to quantify exactly the amount of unreacted resorcinol in the liquid resin by this method were not successful. The IR bands inversion described is shown in Figure 1.

Molecular weight distribution plays an important role in the degree of penetration and of specific adhesion[3] of the resin to wood. This, in turn, influences the percentage wood failure results. GPC can be used to determine the degree of branching of a PF resin[10] and it was used here for the PRF resins. Gollob[10] proposed that an estimate of molecular branching is based on the influence of branching in measurements of viscosity. Viscosity is a function of mol wt, branching, and concentration of a polymer in solution, and may be used as a measure of mol wt. If mol wt is expressed per unit of viscosity, then differences between polymers of similar monomeric constitution in the same solvent and at the same concentration must be due to a structural feature such as branching. Branching is directly proportional to the value of the ratio of the log of the mol wt to the log of the viscosity. Larger ratios reflect a greater degree of branching, and vice versa.[10] Be-

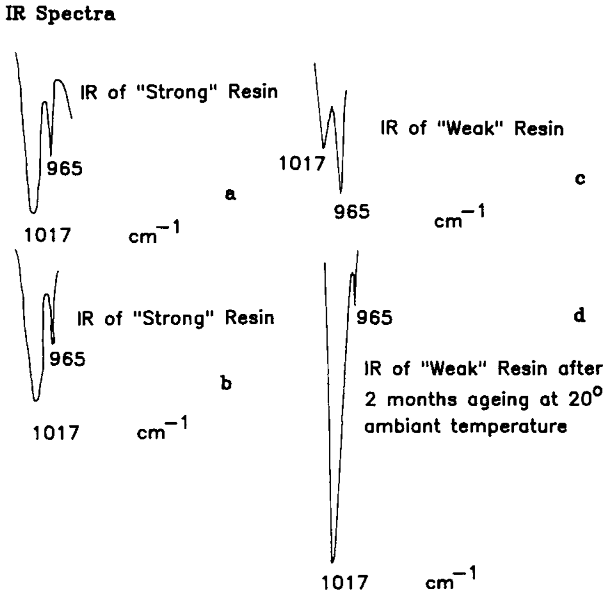


Figure 1 FT–IR spectra of strong and weak urea-branched PRF resins. Inversion of bands at 1017 and 965 cm^{-1} indicate the presence of low amounts of unreacted resorcinol in strong resins, and of higher amounts of unreacted resorcinol in weak resins. Note the decrease of the 965 cm^{-1} band of the weak resin after 2 months aging, indicating that the amount of unreacted resorcinol decreases with time (traces *c* and *d*).

cause the hydrodynamic volume of a highly branched molecule is smaller than for a less branched molecule, its ability to form entanglements with other molecules is also less. Thus, a relatively large mol wt per unit viscosity is indicative of a greater degree of branching. Table V reports GPC and viscosity results obtained by varying the proportion of urea brancher in the preparation of the PRF resin. The ratios of the log, average mol wt, and log of viscosity are an indication[10] of the degree of branching of the PRF resins. From the results in Table V, a number of conclusions can be drawn. First, it appears that the amount of resorcinol used can be decreased in two ways: (i) by true three-dimensional branching, as discussed before. Furthermore, (ii) by urea brancher addition a more advanced linear chain is obtained in which the resorcinol requirements are also approximately halved. The final strength of the resin appears to depend on both tridimensional branching as well as linear lengthening, rapid doubling in size, of the chain, with linear lengthening being the most important factor contributing to good performance of the adhesive.

An examination of the resins in Table V and Figure 2 in more detail reveals that resin 10 has no urea brancher present and behaves as a standard linear PRF resin with high resorcinol content. In resin 13, Table V, where 6% urea by mass of total resin solids was used, linear lengthening is also primarily experienced. Thus, the presence of too high a percentage of urea brancher appears to allow the formation of longer, linearly lengthened macromole-

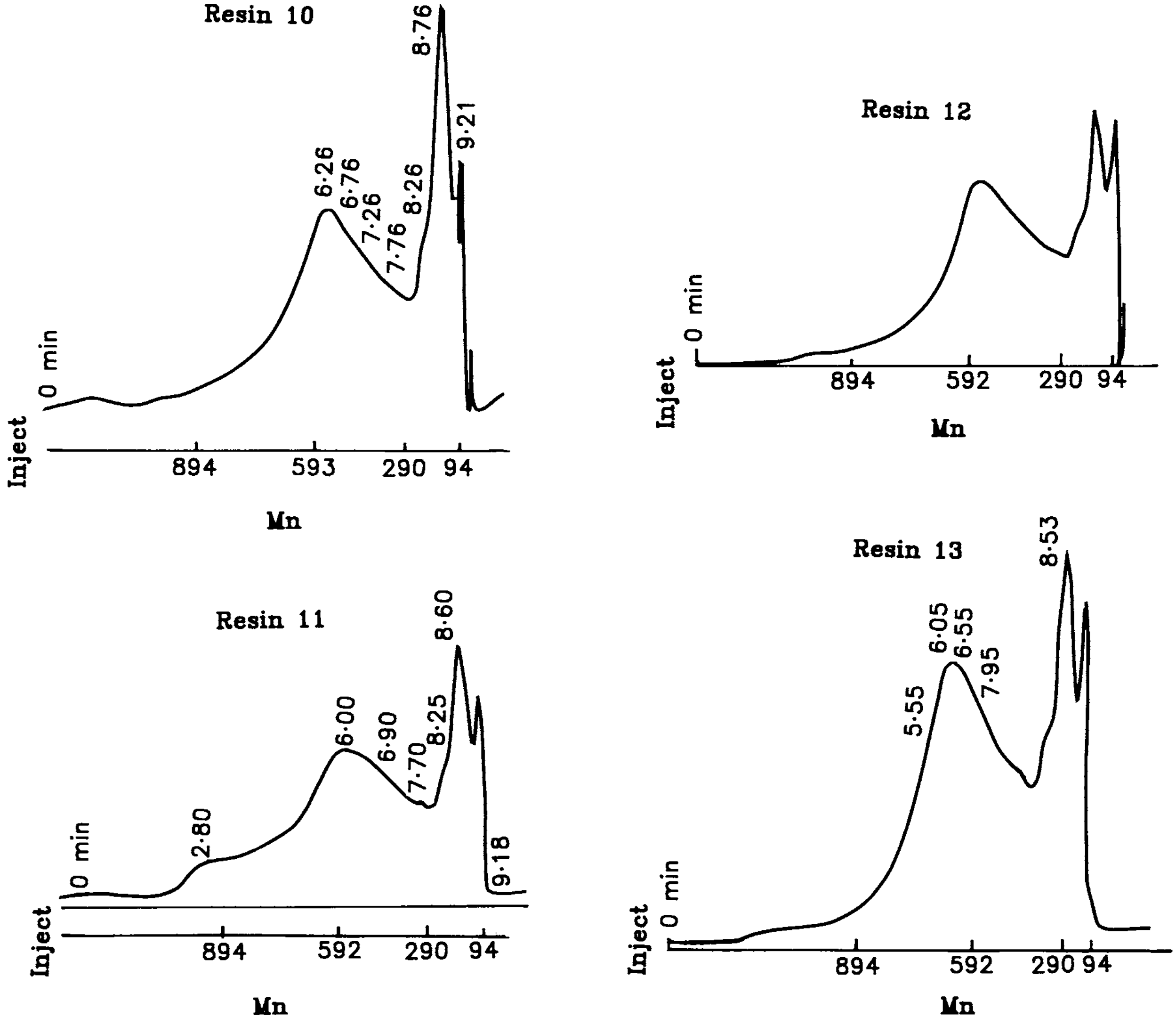


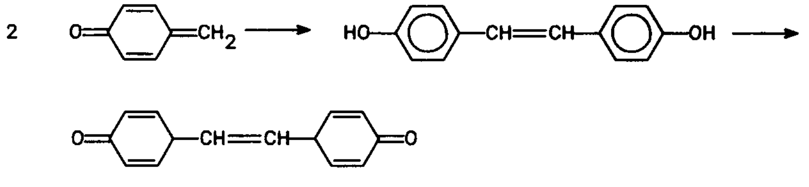
Figure 2 GPC traces (methanol eluent) of Resins 10, 11, 12, and 13 from Table V. Note the higher proportion of much higher mol wt species in Resin 11 and the similarity between Resins 10 (not branched) and 13.

cules. Thus, although the percentage resorcinol used is lower, these long chains cause poorer penetration and poorer adhesion of the resin to the substrate and hence low percentage wood failure. However, when too low a percentage of urea brancher is used, as in Resin 11 (Table V) where only 2% urea by mass of total resin solids was used, Gollob's method[10] estimates that Resin 11 is less branched than when there is no brancher at all (as in Resin 10). This indicates that the advancement of the polymer through linear lengthening is the favourite mechanism to decrease the percentage resorcinol in the resin. This is expected since sterically it is easier for urea to be disubstituted rather than trisubstituted being the relative substitution reactivities of the 1st, 2nd, and 3rd $-CH_2OH$ groups reacting with urea, respectively 9 : 3 : 1.[6] In Resin 11 (the one containing 2% urea by mass of the total resin solids), there does not appear to be sufficient urea to form excessively long linear macromolecules as in Resin 13 (6% urea), or even tridimensionally branched macromolecules as in Resin 12 (4% urea). When an optimal amount of urea brancher is used, as in Resin 12 (4% urea), it appears that a certain amount of tridimensional branching is forced to occur (9% much higher mol wt species are formed in Resin 12 than in Resin 10 where no brancher is used; *cf.* Fig. 2). Resin 12 is a good resin in that it displays good wood strengths and high percentages wood failure.

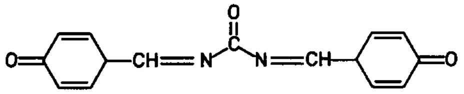
That the contribution to the decrease in resorcinol is mainly due to linear PRF oligomers obtained by doubling of the mol wt through urea distribution, rather than by tridimensionally branched polymers, can be seen, not only by C^{13} NMR (as already discussed), but also by the GPC elution traces of the resins in Table V. Figure 2 reports these GPC traces and indicates that the percentage of really tridimensionally branched oligomers appears indeed to be very low. The above estimate of 9% in Resin 12 being an approximate, uncommon maximum.

The results observed for Resin 13 indicate that if a certain branching level needs to be maintained, although this must be low, an increase in the percentage of urea brancher must be coupled to a corresponding increase in formaldehyde addition. This, however, would also imply an increase in the amount of available $-CH_2OH$ groups on the PF intermediate, leading finally to the necessity of increasing the proportion of resorcinol on resin solids. Thus, increasing both the amount of urea and formaldehyde in the formulation would have three effects on the amount of resorcinol required, namely: (i) a possible decrease in resorcinol due to an increased proportion of tridimensional branching, (ii) a necessary resorcinol increase due to the higher proportion of methylol groups present, and (iii) a decrease of resorcinol by viscosity effect (on liquid resin, not on resin solids). This again emphasizes that in "branched" PRF resins, a fine balance exists between the amount of urea branching unit used and the amount of resorcinol required. It is not a straightforward linear relationship, where the more branching unit that is used, the more tridimensionally branching that occurs and hence the less resorcinol that can be used. In fact, the best performance of the resin appears to be obtained when the level of tridimensional branching is very low or nonexistent, linear doubling of mol wt of the resin by urea branching unit accounting for the greatest proportion or even all of the resorcinol reduction with concurrent maintenance of adhesive good performance. Lower resorcinol percentages can also be obtained while maintaining the adhesive performance, as indicated by the results in Table IV. However, of the lower % resin solids content indicated in Table IV, the resin also present unacceptably short pot-lifes. The resin's balance is then affected: for good strength, short pot-lifes are obtained and for acceptable pot-lives, poor strength is obtained. Although, for particular applications, resin of such lower solids content might be useful, the difficulty of balancing the properties of strength and pot-lives indicate that the adhesive is over its limit, and that its behavior may be erratic. Such low % resin solids contents cannot be recommended for safe and consistent use of the resin in industrial applications.

A curiosity is the unusual intense blue color that these resins present a few days after preparation. In the mechanism of PF resols preparation, quinone methides have been suggested as reactive intermediates, which can then react with methylolphenols or other quinone methides to give dimers and further polymerize. The dimer of paraquinone methide (I) can be regarded as a stilbene derivative (II), which can be further oxidized to form a quinone dimer (III). This has been isolated by Adler[6,11]:



Due to its extensive conjugated system, Megson[6] suggested that this may possibly be the reason for the deep brown color of PF resin. The characteristic deep-blue color of the urea-branched PRF resins might be formed by a similar reaction. A conjecture could be that the presence of a dimer of structure



gives the unusual blue color. The conjugate system in this dimer is more extended and would give rise to a different chromophore, which might be the reason for the characteristic color of these resins.

CONCLUSIONS

Both applied adhesive results, GPC, FT-IR, and C^{13} NMR studies appear to indicate that PRF resins of much lower resorcinol content, hence of much lower cost, and of undiminished cold-setting adhesive performance can be prepared. However, tridimensional branching does not appear to be a great contributory factor, if at all. The main contribution to resorcinol decrease appears to be linear lengthening of the oligomers by mol wt doubling through the action of the urea brancher.

PRF resins of good adhesive performance, and of resorcinol content much lower than in traditional PRF cold-setting adhesives (which generally contain approximately 17–18% on liquid resin), were prepared by introducing small amounts of urea as a brancher during preparation of the resin. Resorcinol contents as low as 10.6% were obtained by this method while still maintaining acceptable pot-life of the resin. Resorcinol as low as 8% still with a good adhesive performance were obtained, although the pot-life obtained was too short. GPC, FT-IR, and C^{13} NMR studies indicated that the small amount of urea branching unit used leads to the reduction of resorcinol content, primarily by rapid lengthening of the average linear length of the PF intermediates and of the final PF oligomers. Tridimensional branching in the liquid resin does not appear to be an important contributory factor and better adhesives are often prepared when it is totally, or almost totally, absent: Reduction of resorcinol content is achieved simultaneously by two mechanisms: (i) The decrease of resorcinol percentage on resin solids due to the rapid lengthening of average oligomers length and (ii) the need for these resins to operate at lower solids content, due to the increased viscosity obtained during their preparation.

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