A ^{13}C-NMR Analysis Method for Phenol–Formaldehyde Resin Strength and Formaldehyde Emission

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SYNOPSIS

A method based on the use of ^{13}C-NMR relative peak intensity ratios for different characteristic chemical groups, known or supposed to contribute to phenol–formaldehyde (PF) resin strength and formaldehyde emission is presented. The method relates results obtained by ^{13}C-NMR analysis of liquid PF resins with the strength and formaldehyde emission in the resin-hardened state. Correlation of different peak ratios with experimental results allows the proposal of equations relating the sum of different ^{13}C-NMR peak ratios with the two mentioned physical properties of the same resins in their hardened state. The equations presented appear to have some applied value in predicting physical properties of hardened industrial-type PF resins from a single ^{13}C-NMR spectrum of the original liquid resin, as well as to render easier comparison between different PF resin formulations. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Phenol–formaldehyde (PF) resins are widely used as adhesives for the manufacture of exterior grade wood products, in particular for wood-based particleboard, as well as numerous other industrial applications. In their application to wood, these resins are tested by preparing a bonded wood joint on laboratory particleboard and then strength testing the final bonded wood product to destruction. Equally laborious is the testing of the formaldehyde released by the PF binder during the board service life, although this is low in the case of the PF series. Thus, the evaluation of the cured strength of a PF adhesive and the determination of its capacity of formaldehyde emission, once it has become the hardened binder of the board, is a long procedure requiring extensive repetitive testing. This is because such a procedure is subject to fairly large experimental errors induced by the need to pass through the board manufacturing stage. The testing is further compli-

cated by the need to test the strength of the resin glue line after 2 h boiling, an accelerated test used to determine the extent of resin cure and weather durability of the bonded joint.[1]

Recently a ^{13}C-NMR method was proposed that, from a single ^{13}C-NMR analysis of a liquid urea-formaldehyde (UF) resin, is capable of predicting both the strength of a UF-bonded particleboard, hence the strength of the board resin, as well as its potential formaldehyde emission.[1] This method is based on the correlation found between the ratio of the NMR signal intensities of relevant chemical groups in the liquid UF resin spectrum with the strength of the hardened UF resin, of the board bonded with it, and its formaldehyde emission. Relevant groups likely to contribute significantly to the strength of hardened PF resins are also observable in the ^{13}C-NMR spectra of the liquid PF resins; their identification and shifts are well documented in the literature.[2,3] This article then presents a method to identify which one of the main chemical groups in a liquid PF resin contribute to its hardened strength and formaldehyde emission, as well as to correlate their ^{13}C-NMR signals ratios to both the IB strength (tensile internal bond = IB) and potential formaldehyde emission of the particleboard bonded with it.

EXPERIMENTAL

Resin Preparation

A series of PF resins of P : F molar ratios 1 : 1.1; 1 : 1.3; 1 : 1.5; 1 : 1.8; 1 : 2.0; and 1 : 2.2 were prepared as follows (series A): 94 g phenol technical grade (SASOL) and the relative amount of paraformaldehyde (fine powder 96% technical grade, Degussa). To obtain the F : P molar ratios indicated above 40 g of a water/methanol 80/20 were added and while mixing mechanically, two amounts of 4 mL 33% NaOH solution were added at 15 min intervals at ambient temperature. The reaction mixture was brought to reflux over a period of 30 min, and during this period two other amounts of 4 mL 33% NaOH were added at 10 min intervals to reach a pH of 11. The mixture was refluxed under mechanical stirring for $\frac{1}{2}$ h, then cooled to ambient temperature in 10–15 min, and stored. Before application, the pH of the resins was adjusted to 12.5 by the addition of 33% NaOH.

Another series of resins (B-series) was prepared by stepwise addition of one of the reagents, according to the following procedure: 100 parts by mass of phenol (technical grade, SASOL), in 66.8 parts water and 15.6 parts of a 40% NaOH water solution was heated for 1 h under mechanical stirring and in a reaction vessel equipped with reflux condensers and stabilized to 70°C. The required amounts of 37% formalin solution (technical grade, Merck, 9% methanol stabilizer), to obtain the molar ratio indicated in the tables, was added in a number of equal

aliquots, over a period of $2\frac{1}{2}$ h at 10 min intervals, while monitoring the reaction under mechanical stirring at 70°C. During the last half hour period of formalin addition, the temperature of the reaction mixture was increased to 77–80°C. This reaction mixture was maintained at this temperature for a 6 h period under mechanical stirring. The reaction was then halted by rapidly cooling to ambient temperature in an ice bath, and stored for further use.

Particleboard and Resin Strength

Triplicate (*Pinus radiata*) one-layer core-only particleboards, 12 mm thick, were prepared from the modified resins to determine the strength of the cured resin. The following set of conditions were kept the same for each of the boards prepared. Pine chips varying in size from 2 to 25 mm, 8% PF solids content, and 12% glue particle moisture content was maintained. Pressing time for each board was 7.5 min: 2 min at 23.5 kg/cm², 2.5 min at 11.7 kg/cm², and 3 min at 3 kg/cm² at a pressing temperature of 190°C. The boards were left for 2 weeks before analysis.

Strength tests of the particleboard was done by subjecting small blocks of the boards (50 × 50 × 12 mm thickness) to a series of IB tensile-strength tests when dry, after 2 h boiling followed by 16 h drying at 105°C (tested dried),[4] and after 2 h boiling (tested wet)[5] (DIN 68763-V100). Densities were measured on 20 samples of each board by micrometer and weight according to DIN 68763. IB strengths were measured by bonding the two faces of each sample

Table I Averaged Results for Strength Tests and Formaldehyde Emission of Triplicate Particleboards Prepared with PF Resins of A and B Series

Resin Sample	Average Density (g cm⁻³)	Dry IB Strength (MPa)	Average Density (g cm⁻³)	2 h Boil IB Strength Tested (MPa)	
				Dry	Wet
1 : 2.2A	0.730	0.79	0.748	0.69	0.27
1 : 2.2B	0.750	0.94	0.739	0.64	0.26
1 : 2.12B	0.698	0.79	0.680	0.62	0.25
1 : 2.0A	0.692	0.54	0.695	0.29	0.17
1 : 2.0B	0.745	0.76	0.720	0.49	0.22
1 : 1.8A	0.684	0.29	0.689	0.08	0.11
1 : 1.8B	0.707	0.39	0.672	0.10	0.12
1 : 1.5A	0.690	0.08	—	—	—
1 : 1.5B	0.688	0.13	—	—	—
1 : 1.3A	0.702	0.11	—	—	—
1 : 1.1A	0.716	0.07	—	—	—
1 : 1.1B	0.665	0.12	—	—	—

Table II   ¹³C-NMR Assignments for Phenol–Formaldehyde Resins

Functional Group	Relative Position	Chemical Shift² (ppm)	Chemical Shift³ (ppm)
Methylene bridges			
Ph—CH₂—Ph	ortho–ortho	29.21	30.8–31.4
	ortho–para	34.93	35.5–35.9
	para–para	39.67	41.0
Methylol Species			
CH₃OH		50.70	
CH₃O—CH₂OH		56.29	
Methylol Species			
Ph—CH₂OH	ortho	61.4–61.5	
Ph—(CH₂OH)₂	di-ortho	61.6–62.3	
Ph—CH₂OH	para	65.52	
Ether Species			
Ph—CH₂OCH₂OH	ortho	65.67	
Ph—CH₂OCH₂OCH₂OH and	ortho		
Ph—(CH₂OCH₂OH)₂	di-ortho	67.10	
Ph—CH₂OCH₂OH	para	70.57	
Ph—CH₂OCH₂OCH₂OH	para	71.16	
Ph—CH₂OCH₂—Ph		70.77	
HOCH₂OH		83.73	
HOCH₂OCH₂OH		87.29	
Ph—CH₂OCH₂OCH₂OH	ortho	87.3	
	para		
Ph—CH₂OCH₂OH	para	89.27	
	ortho	89.59	
CH₃O-CH₂OH		91.3	
Ph—CH₂OCH₂OCH₂OH	para	92.2	
	ortho	92.87	
Blocked sites on the phenolic ring			127.6–133.9
ortho Free positions on the phenolic ring			115.4–116.0
para Free positions on the phenolic ring			119.9–120.9
meta Free positions on the phenolic ring			127.4–132.9

to high density plywood with an epoxy resin and applying a testing rate of 5 mm/s on an Instron universal testing machine.

Formaldehyde Release

The desiccator[1,6–8] method was used for the determination of the formaldehyde released by the particleboards made with PF resins. A 200 mL glass filled with 100 mL distilled water was placed inside a 2 L desiccator.

The particleboard specimens were cut (25 × 25 mm × thickness), weighed, and suspended over the water in a porcelain desiccator plate. The released formaldehyde was supposed to dissolve in distilled water. The desiccators were kept at room temperature for 24 h; eventually they were subjected to the temperature fluctuation during the total period of emission, that is, approximately +18 to +19 during the day time and 0 to −1 during the night. An average of six samples (two samples per time) per board were analyzed.

The fluorometric acetylacetone standard method[9–11] (with Hantzsch reagent) was used at 410 nm for the determination of the formaldehyde content present in the distilled water. The method was used exactly according to the standard reported in the literature.[9–11]

Table III ^{13}C-NMR Peak Integrated Areas for Different PF Series

F/P Molar Ratio	Total Groups		Total Sites	
	Me^a (29.21–41.0 ppm)	Mo^b (61.4–65.32 ppm)	$(o + p)^c$ (115.4–130.9 ppm)	$(m + b)^d$ (127.4–133.9 ppm)
A-Series				
1.1	4.53	21.08	84.35	130.06
1.3	3.87	21.79	62.37	121.60
1.5	9.87	48.71	91.11	257.60
1.8	7.55	45.50	18.17	102.58
2.0	3.84	28.69	9.74	87.28
2.2	6.39	42.62	2.33	101.40
B-Series				
1.1	4.01	15.04	77.54	92.96
1.3	5.81	27.65	95.46	146.77
1.5	3.20	17.91	50.47	115.78
1.8	3.49	29.74	34.72	123.48
2.0	4.49	51.46	33.17	149.55
2.12	1.96	7.23	2.74	19.77
2.2	2.80	18.80	7.11	93.78

^{a} Methylenes.
^{b} Methylols.
^{c} Free *ortho* + *para* sites.
^{d} Free *meta* + blocked (*ortho* + *para*).

Table IV ^{13}C-NMR Peak Ratios

	A-Series					
F/P	1.1	1.3	1.5	1.8	2.0	2.2
Y_1	4.65	5.63	4.93	6.02	7.47	6.66
Y_2	0.66	0.51	0.35	0.17	0.11	0.02
Y_3	0.25	0.35	0.53	2.50	2.94	18.24
Y_4	18.55	16.11	9.22	2.40	2.53	0.36
Y_5	0.30	0.41	0.64	2.91	3.34	20.97
Y_6	0.16	0.17	0.18	0.44	0.32	0.42
Y_7	0.03	0.03	0.03	0.07	0.04	0.06
Y_8	0.37	0.33	0.26	0.15	0.10	0.02
Y_9	0.019	0.02	0.02	0.06	0.04	0.06
Y_{10}	0.089	0.11	0.14	0.25	0.29	0.41

	B-Series					
F/P	1.1	1.3	1.5	1.8	2.0	2.12	2.2
Y_1	3.75	4.75	5.37	8.39	11.44	3.68	6.70
Y_2	0.38	0.65	0.43	0.29	0.22	0.13	0.07
Y_3	0.19	0.29	0.34	0.85	1.55	2.63	2.64
Y_4	19.34	16.41	15.76	9.87	7.37	1.39	2.53
Y_5	0.24	0.35	0.40	0.95	1.68	3.34	3.03
Y_6	0.16	0.18	0.14	0.24	0.34	0.36	0.20
Y_7	0.04	0.04	0.02	0.03	0.03	0.099	0.03
Y_8	0.45	0.39	0.30	0.25	0.18	0.12	0.071
Y_9	0.02	0.01	0.01	0.02	0.025	0.08	0.028
Y_{10}	0.08	0.11	0.10	0.20	0.28	0.32	0.18

Table V   Regression Equations and Respective Coefficient of Correlation Describing Variation of ¹³C-NMR Species Ratios as a Function of F : P Molar Ratio

Series Resin		
A	$Mo/Me = 2.645P + 1.670$	0.86
B	$Mo/Me = 8.347P - 6.110$	0.96
A	$(o + p)/(m + b) = -0.578P + 1.260$	0.99
B	$(o + p)/(m + b) = -0.646P + 1.489$	0.98
A	$Mo/(o + p) = 3.725P - 5.838$	0.96
B	$Mo/(o + p) = 2.717P - 4.919$	0.95
A	$(o + p)/Me = -17.633P + 37.295$	0.96
B	$(o + p)/Me = -16.151P + 38.120$	0.97
A	$\ln[(Mo + Me)/(o + p)] = 3.671P - 5.589$	0.96
B	$\ln[(Mo + Me)/(o + p)] = 2.746P - 4.791$	0.90
A	$\ln[(Mo/(m + b)] = 0.948P - 2.892$	0.89
B	$\ln[(Mo/(m + b)] = 0.723P - 2.646$	0.74
A	$Me/(m + b) = 0.027P - 0.003$	0.69
B	$Me/(m + b) = 0.015P + 0.017$	0.25
A	$(o + p)/\{(o + p) + (m + b)\} = -0.329P + 0.751$	0.99
B	$(o + p)/\{(o + p) + (m + b)\} = -0.328P + 0.817$	0.99
A	$\ln[Me/\{(o + p) + (m + b)\}] = 0.990P - 5.102$	0.97
B	$\ln[Me/\{(o + p) + (m + b)\}] = 1.510P - 5.683$	0.91
A	$\ln[Mo/\{(o + p) + (m + b)\}] = 1.399P - 3.975$	0.99
B	$\ln[Mo/\{(o + p) + (m + b)\}] = 1.471P - 4.209$	0.98

The standard solutions[9-11] for the calibration curve were prepared by dissolving a known amount of 37% formaldehyde solution (Merck, AR grade) in distilled water and diluting to the required concentrations.

Ten milliliters of the sample or the standard solution and 10 mL of the Hantzsch reagent were mixed and heated to 60°C for 15 min (pH = 5.5–6.5). After cooling, the fluorescence of the solution was measured using a Perkin–Elmer LS-5 Luminescence Spectrophotometer. Excitation took place at 410 mn and emission measured at 510 nm. The results of the standard solutions were plotted on a graph and used for determination of formaldehyde absorbed by the water from the particleboard in the desiccator.

¹³C-NMR Spectroscopy

¹³C-NMR spectra of the liquid resins were obtained on a Bruker AC200 FT-NMR spectrometer, at a frequency of 50.3 MHz with the sample spectra

Table VI   ¹³C-NMR Species Ratio Correlation to Dry and 2 h Boil Internal Bond (IB) Strength

	NMR Species Ratio	Correlation for Series			
		Dry IB Strength		2 h Boil, Dried IB Strength	
		A	B	A	B
Y_1	Mo/Me	0.93	0.98	0.71	0.47
Y_2	$(o + p)/(m + b)$	0.98	0.98	0.99	0.98
Y_3	$Mo/(o + p)$	0.90	0.98	0.87	0.97
Y_4	$(o + p)/Me$	0.84	0.97	0.89	0.92
Y_5	$(Me + Mo)/(o + p)$	0.90	0.96	0.87	0.93
Y_6	$Mo/(m + b)$	0.78	0.59	Very low	Very low
Y_7	$Me/(m + b)$	0.60	0.31	Very low	Very low
Y_8	$(o + p)/\{(o + p) + (m + b)\}$	0.99	0.97	0.99	0.99
Y_9	$Me/\{(o + p) + (m + b)\}$	0.98	0.93	0.95	0.95
Y_{10}	$Mo/\{(o + p) + (m + b)\}$	0.98	0.99	0.96	0.98

Table VII ^{13}C-NMR Species Ratio Correlation to Formaldehyde Emission

	NMR Species Ratio	Correlation for Resins	
		A Series	B Series
Y_{10}	Mo/[$(o + p) + (m + b)$]	0.98	0.98
Y_{11}	Free F/[$(o + p) + (m + b)$]	0.99	0.90
Y_{12}	Ethers/[$(o + p) + (m + b)$]	0.99	0.91

at 35 Hz. Chemical shifts were calculated relative to $(CH_3)_3Si(CH_2)_3SO_3Na$ for NMR control. $(CH_3)_3Si(CH_2)_3SO_3Na$ was dissolved in D_2O, run separately, and the shifts for the four signals were set. About 1 mL of liquid resin at 50% resin solids concentration was placed in an NMR tube and diluted with 0.4 mL D_2O added directly to the sample. All spectra were run overnight. Acquisition time was 1.8 s with number of transients at 10000. All spectra were run with relaxation delay of 5 s and were accurate to 1 ppm. The spectra were run with nOe enhancement, spectral width was 15000 Hz, and digital resolution was 0.825. Typical spin lattice relaxation times were not measured but standard values shown in the literature were used.[12] The ^{13}C-NMR band areas reported in the tables are integrated areas. These were used for all the ratios investigated. No direct quantitative correlation results with resin strength could be obtained from the raw data, but by considering the peak ratios of certain species, some information between the various synthesis parameters and the final resin's properties could be deduced and some quantitative correlations derived. The ^{13}C-NMR spectra of PF resins can be split into four main areas[2,3]:

1. free meta-sites (m) on phenolic aromatic nuclei and already reacted *ortho* and *para* sites (b) with signals from 127.4 to 133.9 ppm;
2. free *ortho*-(o) and *para*-(p) sites on phenolic aromatic nuclei with signals from 115.4 to 120.9 ppm;
3. methylol groups with signals from 61.4 to 65.3 ppm;
4. methylene groups connecting two aromatic nuclei, with signals from 29.2 to 41.0 ppm.

In the two series of PF resins prepared, no methylene ether signals, and no, or very small, free formaldehyde signal (84 ppm) were observed. Peak assignments and relative integrated areas are reported in

Table II. Peak relative integrated areas are reported in Table III. Regression equations and their coefficients of correlation between potentially significant ^{13}C NMR peak intensity ratios and the F : P molar ratio are reported in Table V.

DISCUSSION

The absolute integrated areas of ^{13}C-NMR peaks can never be taken as a measure of the abundance of a particular chemical group. In a resin such as a PF resol in which all chemical groups are closely interrelated, ratios of the integrated areas of peaks characteristic of chemical groups known or suspected to contribute to cured strength appear to indicate excellent correlation with experimental results. In PF resins, the smaller variety of chemical groups likely to contribute to strength appear to allow better correlation with hardened resin strength than is the case of the UF series.[1] The two series of PF resins (P : F molar ratios 1 : 2.2; 1 : 2.12; 1 : 2.0; 1 : 1.8; 1 : 1.5; 1 : 1.3; 1 : 1.1) were prepared by two different methods. The resins of one series were prepared by reacting, from the start of the reaction, phenol and formaldehyde in the wanted final molar ratios required (series A). The PF resins in the other series were instead brought to the final P : F molar ratio by the addition of formaldehyde in several steps (series B). Both methods are used for the preparation of industrial PF resins, the second one being the most commonly used for industrial high performance resins.

In Table I the experimental results for IB strength and formaldehyde emission are reported; the experimental ^{13}C NMR results and assignment of peaks are reported in Figure 1, Tables II and III. Tables IV and V show the values of the peak integrated areas of species known to contribute or potentially contribute to the hardened strength of the resin and its formaldehyde emission. For the IB strength the raw results shown in Table I were normalized by fitting the following nonlinear multivariable polynomials by Levenby–Marquardt modelling.
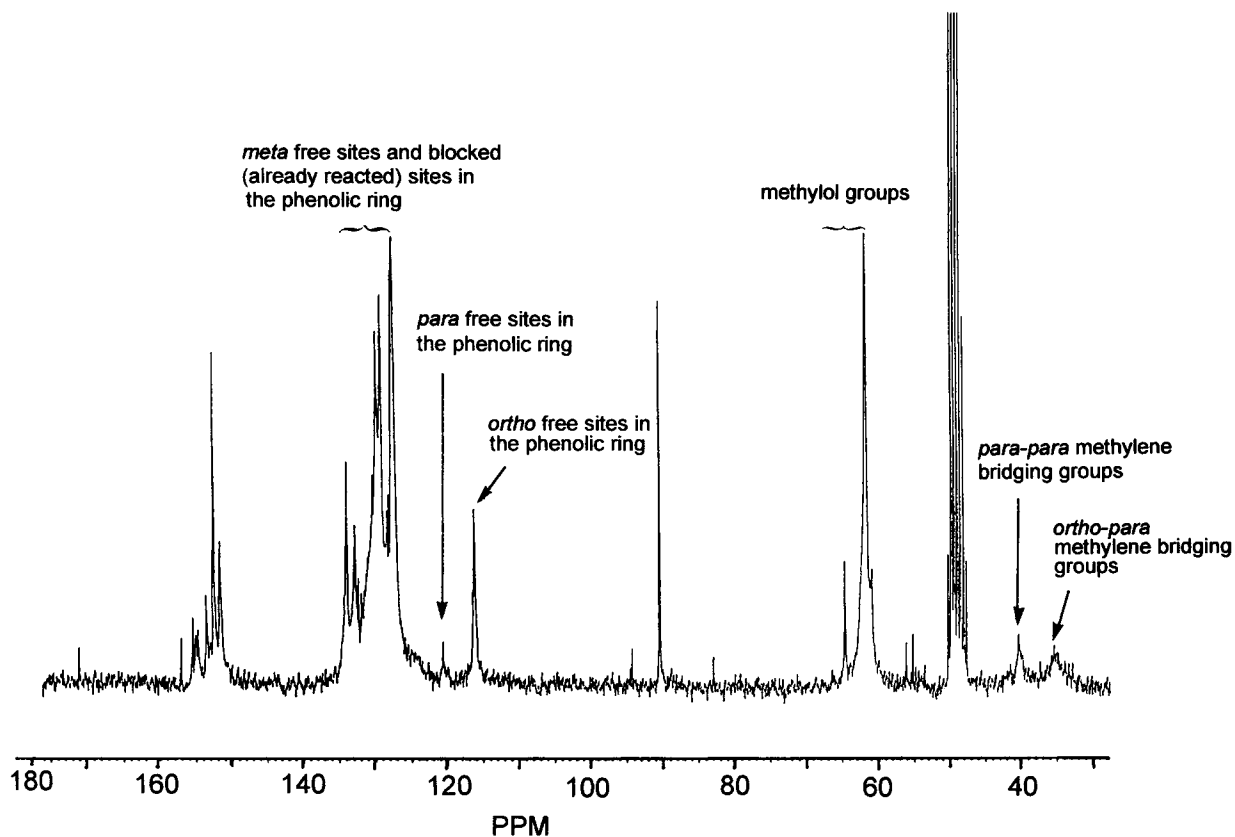
Series A

$$IB = 0.144 + 0.115P + 0.379P^2 - 0.219D^{4.441}$$

Series B

$$IB = -0.089 - 0.179P + 0.307P^2 - 0.014D^{2.846},$$

where IB is IB strength in MPa, P is the F : P molar ratio, and D is the board density in g cm^{-3}, where

Figure 1 ^{13}C-NMR of PF resin of molar ratio P : F = 1 : 2.2 (B-series) indicating the signals of groups taken in consideration for peak intensity ratios.

the exponents of each variable are numerical values obtained from the nonlinear multivariable regression analysis of the data.

The peak ratios tested were chosen among others not only because they are potentially significant to the physical reality of the situation but also because they correlated well with the variation in F : P molar ratios (Table V). While the equations in Table V are important, they are of no use for analysis of a resin for which the F : P molar ratio is unknown. Table VI shows the ^{13}C NMR species ratio correlation to IB strength for the two series of resins. As can be seen, several, but not all of the group's ratios appear to correlate well with the IB strength. It can also be further deduced that ratios such as those involving Me, Mo, and ($o + p$) are likely to play an important role in the final IB strength of a board. From the correlation studies in Table VI the situation appears rather different in PF resins from what was observed in the UF series.[1] In the PF series many of the possible ratios chosen show good correlation, which is not the case for the UF series. The difficulty in the PF series is then to choose not only

what correlates better mathematically, but also what is likely to have real physical significance. Having to consider both the correlation with dry IB strength and IB strength after 2 h boiling complicates the choice over the case of the UF resins. The ideal contributory ratios should then be those that give good correlation coefficients for both types of IB strength. From this point of view there is no doubt that ratios $Y_2((o + p)/(m + b))$ and $Y_8((o + p)/\{(o + p) + (m + b)\})$ are the ones best fulfilling this requirement. However, they also describe the same influence, the influence of the same still free reactive sites on the phenolic aromatic nuclei. For this reason only one of them should be used in any equation to avoid double counting. The one finally preferred was Y_8. Good correlation equations could also be attained using Y_2, an illustration that for PF resins, different from the case of the UF series, a wide variety of equally or almost equally good correlation equations can be presented. The equations presented are not then exhaustive of the possibilities, because as can be seen from Table VI, several others, equally effective, can be deduced. Thus for dry IB strength

equations in function of $(Y_1 + Y_2)$, $(Y_1 + Y_8)$, or $(Y_8 + Y_9 + Y_{10})$ can describe the phenomenon equally well. The $(Y_1 + Y_8)$ equation for the A-series resins is

$$IB = 0.120Y_1 - 1.885Y_8$$

with a standard deviation of 0.164, for an IB strength range of 0.07–0.796 MPa. For the B-series of resins is

$$IB = 0.055Y_1 - 0.368Y_8$$

with an estimated standard deviation of 0.021, for an IB strength ratio of 0.124–0.944 MPa.

The same hypothesis should not be advanced for the IB strength after 2 h boiling (wet IB), simply because Y_1 in Table VI shows a bad correlation. As a consequence of this, the A-series equation of $(Y_1 + Y_8)$ gives an unacceptably high standard deviation; in the case of the B-series resins the $(Y_1 + Y_8)$ equation:

$$\text{wet IB} = 0.028Y_1 - 0.309Y_8$$

gives still an acceptable standard deviation of 0.045 (for a range 0.105–0.648 MPa). Although this illustrates the problem, this approach to the wet IB problem is conceptually incorrect. Again the correct approach, fitting the correlations both mathematically and physically without redundancies and double counting, is to express both dry and wet IB values as a function of $f(Y_8 + Y_9 + Y_{10})$, because these ratios express well defined, nonredundant physical realities and have excellent correlations both for the dry and wet IB strengths. Thus, the general equation describing both the strength of a hardened PF resin, and of particleboard bonded with it should be:

$$IB \text{ strength} = a\{(o + p)/[(o + p) + (m + b)]\}$$
$$+ b\{Me/[(o + p) + (m + b)]\}$$
$$+ c\{Mo/[(o + p) + (m + b)]\}$$

where the coefficients a, b, and c are characteristic for each type of resin series preparation used and for an IB dry or wet.

For the two series of resins considered then the IB equations are: A-series

$$IB \text{ dry} = -0.470Y_8 + 3.734Y_9 + 1.431Y_{10}$$
$$(SD = 0.04)$$

$$IB \text{ boil/dry} = -1.812Y_8 + 11.674Y_9 + 0.002Y_{10}$$
$$(SD = 0.10)$$

IB boil/wet (V100)

$$= -0.743Y_8 + 1.915Y_9 + 0.488Y_{10}$$
$$(SD = 0.07)$$

B-series

$$IB \text{ dry} = -0.389Y_8 + 2.754Y_9 + 1.874Y_{10}$$
$$(SD = 0.02)$$

$$IB \text{ boil/dry} = -0.187Y_8 + 0.887Y_9 + 1.883Y_{10}$$
$$(SD = 0.006)$$

IB boil/wet (V100)

$$= -0.134Y_8 + 0.059Y_9 + 0.967Y_{10}$$
$$(SD = 0.07)$$

with IB strength and standard deviations (SDs) expressed in MPa. The number of samples involved were of 180 IB dry test samples for each series, and 90 samples each for each series for the two wet tests.

An important factor that can be deduced is that for the PF series and the UFs, the physical properties of a hardened resin (such as IB strength) can be related to the ratio of species present in the resin before cure. It is interesting to note that for all the equations the sign of the coefficient of the term $(o + p)/[(o + p) + (m + b)]$ is always negative. This is physically correct because the negative sign indicates that the higher is the amount of still free *ortho* and *para* sites on the phenolic nuclei, the lower the degree of condensation of the resin, and potentially lower the density of cross-linking at parity of still available methylol groups.

A similar approach can be taken to relate ^{13}C NMR peak ratios of different chemical groups to the formaldehyde emission. Although formaldehyde emission is not of major importance in PF, emission from particleboard bonded with this resin being generally low, it is nonetheless of interest to see if correlation between ^{13}C-NMR peak ratios and emission exist.

Table VII shows the ^{13}C-NMR ratio correlation to formaldehyde emission for the two series of resins. From these an equation can be obtained unique for a specific homologous series of PF resins. This is also unique to the particular formaldehyde emission determination method.[2,6–8,13] In the form given below the results are given in the WK1 method, mg/100 g board.

$$F = a\left(\frac{\text{Mo}}{(o + p) + (m + b)}\right) + b\left(\frac{\text{free F}}{(o + p) + (m + b)}\right)$$
$$+ c\left(\frac{\text{methylene ethers}}{(o + p) + (m + b)}\right)$$

Therefore these ratios can be related to the formaldehyde emission for the specific series of resins by taking the respective experimental data and obtaining the following equation for the A-series resins:

$$F = -39.378\,Y_{10} + 38.231\,Y_{11} + 105.032\,Y_{12}$$

with an estimated SD of 0.410 mg/100 g board. Similarly for the B-series resins:

$$F = 17.893\,Y_{10} + 2.440\,Y_{11} - 43.866\,Y_{12}$$

with an estimated SD of 0.887.

It is of interest to note the sign of the coefficients a, b, and c in the formaldehyde emission equations. The a coefficient is negative for the A series and positive for the B series; this indicates that in the A-series resins, a considerable amount of methylols lead to methylene ether bridges during hardening, subtracting from the value of formaldehyde emission. In the B series instead the amount of methylols leading to methylene ethers on hardening is low. This finding is consistent with the processes of preparation of the two series of resins. In the B series the proportion of methylols is much lower than in the A series, as expected. This behavior is confirmed by the sign of the c coefficient. In the A series part of the high proportion of methylene ether formed reorganizes readily to methylene linkages contributing significantly to hardened resin formaldehyde emission. This is not the case for the lower proportion of methylene ethers in the B-series resins. The sign of the b coefficient is always positive, indicating that free formaldehyde always contributes to formaldehyde emission.

The above set of equations can be used in predicting some of the physical properties of the hardened PF resin by studying the ¹³C-NMR peak ratios of certain species in the liquid PF resin.

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