

A ^{13}C -NMR Analysis Method for MF and MUF Resins Strength and Formaldehyde Emission from Wood Particleboard. I. MUF Resins

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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 melamine-urea-formaldehyde (MUF) resin strength and formaldehyde emission, is presented. The method relates results obtained by ^{13}C -NMR analysis of liquid MUF resins with their strength and formaldehyde emission in the resin hardened state. Sets of correlation equations are presented which can be used to predict some of the physical properties of a hardened MUF resin by studying the ^{13}C -NMR peak ratios of well-defined chemical groups in the liquid MUF resin. A true class of MUF resins, with characteristics all of their own, appear only to exist in the copolymers in which the mass ratio of M : U is in the approximate range 55 : 45 to 34 : 66, mass ratios outside this range resulting in resins which behave almost as pure melamine or as pure urea resins. Contrary to what was found for MUF glue mixes in which lower condensation pre-resins are used as scavengers and accelerators, in pure MUF resins, the ratios of NMR peaks of the downfield substituted and unsubstituted triazine and urea signals, while still important, do not exclusively dominate the correlation equations, other chemical groups such as methylene (Me), methylol (Mo), and methylene ether groups assuming considerable importance. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Melamine-formaldehyde (MF) and, particularly, melamine-urea-formaldehyde (MUF) resins are widely used for the manufacture of composite wood products, in particular but not only for particleboard, as well as for numerous other industrial applications. In their application to wood, the resins are tested by preparing laboratory particleboard and then strength testing the final bonded wood product to destruction. Thus, the evaluation of the cured strength of an MF or MUF adhesive 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. Testing is

further complicated 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 board.^{1,2}

Recently, ^{13}C -NMR methods were proposed that, from a single ^{13}C -NMR analysis of a liquid urea-formaldehyde (UF) resin, of a liquid phenol-formaldehyde (PF) resin, and from the relative proportions in the liquid glue mix of melamine resins, their accelerators and their formaldehyde scavengers are capable of predicting both the strength of particleboards bonded with such resins as well as their potential formaldehyde emission.³⁻⁵ These methods are based on the correlation found between the ratio of the NMR signal intensities of relevant chemical groups in liquid resin (or additives) spectra with the strength of the hardened resins, of the boards bonded with them, and of their formaldehyde emission values. Relevant groups likely to contribute significantly to the strength of hardened MF and MUF

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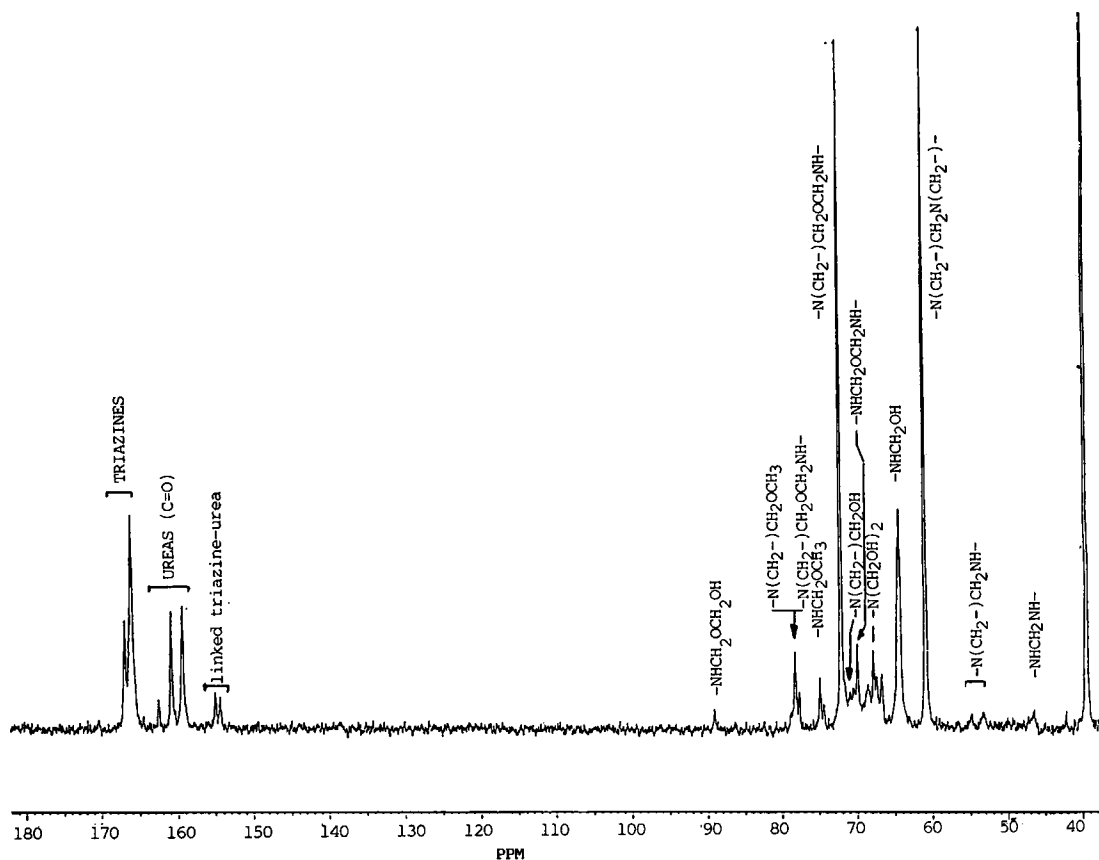


Figure 1 The ^{13}C -NMR spectrum and identification of relevant peaks for a resin of (M + U) : F molar ratio of 1 : 2.1 and M : U mass ratio of 34 : 66. Note that the intense peak at 62 ppm is not due to the resin but due to the $-\text{CH}_2-$ of the bis(hydroxyethyl)ether added after resin preparation as an external flexibilizer.

resins are also observable in the ^{13}C -NMR spectra of the liquid MF and MUF resins; their identification and shifts are well documented in the literature.⁶⁻¹¹

This article then presents a method to identify which of the main chemical groups in liquid MF and MUF resins contribute to its hardened strength and formaldehyde emission, as well as to correlate their ^{13}C -NMR signal ratios to both the IB (tensile internal bond) strength and potential formaldehyde emission of the particleboard bonded with it. The method is intended to be exclusively comparative and not absolute.

EXPERIMENTAL

Resin Preparation

A first series of MUF resins of (M + U) : F molar ratios of 1 : 2.1 and 1 : 1.7 and presenting M : U mass ratios of 80 : 20, 75 : 25, 66 : 34, 50 : 50, 40 : 60, 34 : 66, 25 : 75, and 15 : 85 were prepared.¹² A

second series of MUF resins of M : U mass ratios of 55 : 45, 50 : 50, 45 : 55, and 34 : 66 and of (M + U) : F molar ratios 1 : 2.4, 1 : 2.1, 1 : 1.7, 1 : 1.6, 1 : 1.5, 1 : 1.4, and 1 : 1.3 were prepared for final analysis.

All the resins were prepared according to the following procedure (described for a resin of M : U mass ratio of 45 : 55 and (M + U) : F molar ratio of 1 : 1.7): 61.5 parts by mass of formurea (57% formaldehyde and 23% urea) were mixed with 35 parts water and 8.5 parts of urea in a glass reactor equipped with a reflux condenser and mechanical stirrer and the pH was set to 10 with a 33% sodium hydroxide water solution. The temperature was then increased to 90°C under continuous mechanical stirring. In the resins in which additional formaldehyde was needed to satisfy the final molar ratio requirements, this was added as a 37% formalin solution during initial heating. The reaction was allowed to proceed until the turbidity point was reached and then 38.9 parts of melamine powder was added usually approximately 1 h after the be-

Table I Particleboard IB Strength and Formaldehyde Emission Results

M : U Mass Ratio	(M + U) : F Molar Ratio						
	1 : 2.4	1 : 2.1	1 : 1.7	1 : 1.6	1 : 1.5	1 : 1.4	1 : 1.3
Dry strength (MPa)							
55 : 45	0.841	0.764	0.592	0.193	—	—	—
50 : 50	—	0.596	0.580	—	0.548	—	0.524
45 : 55	—	0.684	0.648	—	0.516	—	0.332
34 : 66	0.426	0.377	0.313	0.227	0.178	0.147	—
Aged strength (MPa)							
55 : 45	0.403	0.388	0.121	0.008	—	—	—
50 : 50	—	0.136	0.126	—	0.100	—	0.076
45 : 55	—	0.220	0.126	—	0.044	—	0.010
34 : 66	0.220	0.184	0.132	0.124	0.083	0.068	—
Formaldehyde emission (mg/100 g board)							
55 : 45	21.3	9.5	5.9	4.0	—	—	—
50 : 50	—	17.1	19.5	—	14.4	—	11.3
45 : 55	—	17.3	20.9	—	7.2	—	4.9
34 : 66	39.2	34.1	14.6	7.2	18.7	12.9	—

gining of the reaction. For resins of an M : U mass ratio equal to or greater than 50 : 50, thus for resins of high melamine content, a total of 15 parts by mass of dimethylformamide and bis(hydroxyethyl)ether were also added, the latter of the two also added as an internal flexibilizer. The temperature was then raised to 95°C and the pH allowed to slowly fall with the proceeding of the reaction while monitoring the water tolerance of the resin until such a parameter had reached a value of 100–120%. The reaction was then immediately stopped by adjusting the pH to 10.2–10.5 and cooling the resin to ambient temperature by the use of an iced water bath. The resins were then characterized for gel time and viscosity and then stored.

Particleboard Preparation and Resins Strength

Duplicate one-layer core-only laboratory particleboard of *Pinus radiata* wood, of 350 × 350 × 12 mm dimension, were bonded with the MUF resins prepared to determine the strength of the cured resins. The sets of conditions used for the preparation of the particleboard were maintained the same throughout and were as follows: Pine wood particles of 1–40 mm in size, 8% MUF resin solids content on dry wood, and 3.3% NH₄Cl hardener used as a 20% water solution based on resin solids content; board pressing time was 7.5 min at a temperature

of 180°C and with a pressing cycle of 2 min from the pressplaten contact time to high pressure and high-pressure maintenance (23 kg/cm²) followed by 2.5 min at an intermediate pressure of 11 kg/cm², then followed, finally, by a holding period of 3 min at 4.5 kg/cm² before press opening.

Strength tests of the particleboard were carried out by subjecting small blocks of the board (50 × 50 × 12 mm thickness) to an internal bond (IB) tensile strength test on a Hounsfield tensometer. A series of specimens for each board were tested dry and a further series of specimens after an accelerated aging test consisting of 2 h immersion in boiling water followed by 16 h redrying at 105°C according to international standard specifications.^{1,2} The tensile force of rupture was applied perpendicular to the board surface, giving a reading in Newtons. The results in MPa compared with the requirements of standard specifications for MF- and MUF-bonded particleboard.^{1,2,13,14} The results obtained are shown in Table I.

Formaldehyde Release

Formaldehyde release from the particleboard prepared was determined by the WKI method as described by Roffael and Melhorn.^{15–17} The results obtained are reported in Table I.

Table II ^{13}C -NMR Spectra Peak Integrated Areas for MUF Resins of M : U Mass Ratios in the Range 55 : 45 to 34 : 66 and of (M + U) : F Molar Ratios in the Range 1 : 2.4 to 1 : 1.3

	M : U Mass Ratio							
	55 : 45				50 : 50			
	(M + U) : F Molar Ratio							
	2.4	2.1	1.7	1.6	2.1	1.7	1.5	1.3
Triazines								
167 ppm	9.273	5.033	5.066	41.160	7.072	10.844	15.445	14.539
166 ppm	21.030	7.153	4.469	34.290	14.351	17.009	15.968	9.880
Ureas								
163 ppm	0.905	3.390	0.468	4.148	2.606	3.082	6.869	8.248
161 ppm	3.825	4.656	1.472	7.073	9.657	11.747	18.536	14.472
160 ppm	5.169	4.259	1.056	2.953	9.051	10.468	11.134	6.655
<u>MCH₂U</u> carbons of linked triazines and ureas (not —CH ₂ —) (doublets or triplets)								
155 ppm	1.074	1.685	—	—	2.504	1.258	1.938	1.618
Others								
75 ppm	1.249	2.060	0.202	1.395	3.495	2.097	2.603	2.045
72 ppm	4.254	13.590	15.881	1.210	—	—	—	—
70–71 ppm	1.968	—	1.653	0.470	6.590	5.027	4.870	2.976
69 ppm	—	3.028	1.567	1.965	3.387	4.238	4.870	1.929
68 ppm	—	2.843	—	—	—	—	—	—
65 ppm	13.281	5.994	3.974	21.975	19.407	25.737	25.167	15.507
62 ppm	3.086	—	—	1.240	6.590	2.005	3.190	1.837
55 ppm	0.920	1.268	1.212	0.760	2.140	1.878	1.639	1.002
47 ppm	1.065	2.500	0.378	1.565	2.128	2.258	2.620	1.589

^{13}C -NMR Spectroscopy

^{13}C -NMR spectra of the liquid resins were obtained on a Bruker AC 200 FT-NMR spectrophotometer at a frequency of 50.3 MHz with the sample specimen at 35 Hz. Chemical shifts were calculated relative to $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_3\text{SO}_3\text{Na}$ as the external reference. $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_3\text{SO}_3\text{Na}$ was dissolved in dimethyl sulfoxide (DMSO), run separately, and the signal shifts of the trisilyl group were set. About 1 mL of liquid 55% solids resin, without hardener, was placed in an NMR tube and diluted with about 0.4 mL DMSO added directly to the sample. All spectra were run overnight. Acquisition time was 1.8 s with number of transients at 10,000. The spin-lattice relaxation time of ^{13}C -NMR is an important factor in setting the pulse intervals.^{18,19} Tomita and Hatono¹⁸ suggested that a pulse interval of 5 s was needed to obtain a reliable spectrum. All spectra were run with a relaxation delay of 5 s and chemical shifts were accurate to 1 ppm. The spectra were run with nOe enhancement, the spectral width was 15,000, and

the digital resolution was 0.825. The ^{13}C -NMR band areas reported in Table II are integrated areas. These were used for all the ratios investigated. The interpretation of the ^{13}C -NMR bands were taken from the literature.^{6–11} Identification of the NMR peaks is as reported in previous articles.^{3,5} Potentially significant peak integrated areas ratios are reported in Table III. The ^{13}C -NMR spectra of MUF resins can be split into four main areas of importance to the analysis at hand^{3,5}:

1. The substituted and unsubstituted melamine's triazine and urea carbonyl groups with their very sensitive signals in the 160–170 ppm region;
2. Methylene groups with signals from 45 to 62 ppm—thus, —CH₂— groups linking directly two amino or amido groups;
3. Methylol (N—CH₂OH) groups with signals from 65 to 72 ppm; and
4. Methylene-ether (N—CH₂OCH₂—N) groups with signals from 69 to 90 ppm,

Table II (Continued from the previous page)

	M : U Mass Ratio									
	45 : 55					34 : 66				
	(M + U) : F Molar Ratio									
	2.1	1.7	1.5	1.3	2.4	2.1	1.7	1.6	1.5	1.4
Triazines										
167 ppm	5.248	17.233	10.964	17.787	4.583	3.434	11.112	14.560	11.420	18.440
166 ppm	7.151	19.306	8.763	18.350	9.595	6.717	9.063	9.207	8.064	9.312
Ureas										
163 ppm	2.053	2.905	3.030	3.042	2.568	0.954	5.484	4.058	3.922	7.894
161 ppm	4.264	8.340	6.521	5.379	8.797	3.713	10.740	9.931	9.223	12.510
160 ppm	3.408	7.105	3.430	2.326	7.667	3.854	5.894	5.543	4.858	5.285
MCH ₂ U carbons of linked triazines and ureas (not —CH ₂ —) (doublets or triplets)										
155 ppm	1.757	1.969	1.274	0.600	2.610	1.185	2.739	2.437	1.231	0.959
Others										
75 ppm	1.738	1.668	1.178	1.463	3.886	1.619	4.819	3.341	1.749	2.248
72 ppm	14.490	30.170	—	—	17.962	21.260	46.913	22.590	17.070	0.948
70–71 ppm	1.393	2.351	2.016	1.491	1.362	1.515	5.793	1.741	1.252	—
69 ppm	1.816	3.325	1.437	1.385	7.625	2.661	2.580	3.260	2.720	2.910
68 ppm	2.043	2.770	—	—	—	2.444	4.414	—	—	—
65 ppm	4.071	20.220	5.925	6.928	16.622	6.838	9.069	10.426	10.987	10.727
62 ppm	—	—	1.508	1.399	3.739	—	—	2.354	1.724	1.375
55 ppm	0.471	1.394	0.550	0.590	1.022	0.630	1.130	0.932	0.850	0.843
47 ppm	1.064	2.065	1.196	0.952	1.345	0.690	2.219	1.856	1.317	1.429

where the zones of methylol and methylene ethers groups partly overlap.

There are also less important species at much lower concentrations but these were not considered. Correlation of the relevant NMR peak ratios with the IB strength and formaldehyde emission of the boards was carried out by an iterative Levenby-Marquardt polynomial approximation method.³⁻⁵

DISCUSSION

The absolute intensities or integrated areas of ¹³C-NMR bands can never be taken as a measure of the abundance of a particular chemical group. In a resin such as an MUF, as for MF resins, in which all the chemical groups are clearly interrelated, ratios of the integrated areas of peak characteristics of chemical groups known or suspected to contribute to the cured strength and formaldehyde emission appear to indicate excellent correlation with the experimental reality. All the MUF resins examined

were prepared according to the same procedure: After two series of resins of (M + U) : F molar ratios of 1 : 2.1 and 1 : 1.7 spanning the M : U mass ratios 80 : 20, 75 : 25, 66 : 34, 50 : 50, 45 : 55, 40 : 60, 34 : 66, 25 : 75, and 15 : 85,¹² it was found that resins of M : U mass ratios 80 : 20 to 66 : 34 behaved clearly as an MF resin, while resins of M : U mass ratios 40 : 60 to 15 : 85 behaved clearly as UF resins. For this reason, the study of the correlation of the ¹³C-NMR spectra with the IB strength and formaldehyde emission was limited to the M : U mass ratios of 55 : 45, 50 : 50, 45 : 55, and 34 : 66, thus in the range where quite clearly the properties of the resins differed from those of pure MF and UF resins. This was done throughout the (M + U) : F molar ratios of 1 : 2.4, 1 : 2.1, 1 : 1.7, 1 : 1.6, 1 : 1.5, 1 : 1.4, and 1 : 1.3. The average IB (tensile internal bond) strength and formaldehyde emission results of the boards manufactured under identical conditions are reported in Table I, while the experimental ¹³C-NMR bands integrated areas are reported in Table II. Table III shows the values of the peak integrated area ratios of species known or suspected to contribute

Table III ^{13}C -NMR Peak Ratios for MUF Resins

Mass Ratio M : U	$1/(2 + 3)$	Me/Mo	Me/(Me + Ethers + Mo)	(Me + Ethers)/Mo	Me/(Me + Mo)
<u>55 : 45</u>					
1 : 2.4	0.339	0.212	0.682	0.465	0.181
1 : 2.1	0.524	0.258	0.348	3.664	0.096
1 : 1.7	0.791	0.114	0.211	4.182	0.122
1 : 1.6	1.022	0.094	0.805	0.243	0.086
<u>50 : 50</u>					
1 : 2.1	0.292	0.144	0.620	0.611	0.126
1 : 1.7	0.356	0.139	0.633	0.577	0.122
1 : 1.5	0.488	0.137	0.649	0.539	0.121
1 : 1.3	0.734	0.133	0.690	0.447	0.117
<u>45 : 55</u>					
1 : 2.1	0.492	0.120	0.327	1.780	0.129
1 : 1.7	0.579	0.128	0.437	2.247	0.120
1 : 1.5	0.747	0.157	0.642	0.555	0.136
1 : 1.3	1.386	0.192	0.579	0.725	0.168
<u>34 : 66</u>					
1 : 2.4	0.274	0.088	0.453	1.194	0.080
1 : 2.1	0.307	0.106	0.329	1.750	0.257
1 : 1.7	0.574	0.128	0.309	4.902	0.109
1 : 1.6	0.755	0.143	0.347	1.885	0.147
1 : 1.5	0.933	0.149	0.384	1.605	0.150
1 : 1.4	0.972	0.158	0.700	0.427	0.156

or potentially contribute to the hardened strength of the resin. Table IV shows the ^{13}C -NMR species ratio correlation to IB strength for the different ratios for each series of resins: Most, but not all, group ratios appear to correlate well with the IB strength. It can also be deduced that ratios such as Me/Mo as in UF resins³ are likely to play an important role in the final IB strength of the board. The UF resin equation by Tomita and Hatono¹⁸ for possible crosslinking can also be considered for the MUF resins as summing up important contributions.

From the best correlations presented in Table IV, as for UF resins,³ the ratio primary/(secondary + tertiary) also appears to play a very important role in the final strength of the hardened resin and of the board bonded with it. The ether species appear to correlate considerably worse in some cases and, instead, rather well in others. From the correlation studies in Table IV, the situation for MUF resins appears to be rather different from what was observed for UF resins³ and rather similar to that observed for PF resins⁴: In the MUF series of resins, many of the possible ratios chosen show good cor-

relation (Table IV), which is not the case for UF resins. The difficulty then in the MUF resins case is in choosing not only what correlates well mathematically, but also what is likely to have real physical significance. Particular attention must be paid to make sure that the influence of some group is not counted twice or more times in the ratios used to introduce the correlation between IB strength and ^{13}C -NMR. Furthermore, having to consider both the correlation for the dry IB strength and the IB strength after 2 h boiling complicates further the choice available.

Due to the contribution of several terms, a composite equation can be derived to improve total correlation for all the resin series and explain the greater part of the phenomenon to a reasonable extent and in a conceptually correct manner as regards the expected contributions of chemical species to crosslinking. Thus, the $[1/(2 + 3)]$ ratio is the ratio of "primary" (unsubstituted) carbons belonging to the unsubstituted melamine's triazine and urea amino and amido groups; and of the sum of "secondary" carbons belonging to methylene-

Table IV Correlation Equations of Single ^{13}C -NMR Peak Ratios with Dry and Aged IB Strength Results and Related Correlation Coefficients

<u>M : U = 55 : 45</u>	
IB_{dry} (MPa) = $-0.9203 [1/(2 + 3)] + 1.213$	$r = 0.941$
IB_{aged} (MPa) = $-0.634 [1/(2 + 3)] + 0.6545$	$r = 0.920$
IB_{dry} (MPa) = $3.308 \text{ Me/Mo} - 0.0513$	$r = 0.945$
IB_{aged} (MPa) = $1.986 \text{ Me/Mo} - 0.123$	$r = 0.994$
IB_{dry} (MPa) = $3.234 \text{ Me}/(\text{Me} + \text{Mo}) - 0.0015$	$r = 0.884$
IB_{aged} (MPa) = $2.062 \text{ Me}/(\text{Me} + \text{Mo}) - 0.1172$	$r = 0.957$
<u>M : U = 50 : 50</u>	
IB_{dry} (MPa) = $-0.370 [1/(2 + 3)] + 1.572$	$r = 0.959$
IB_{aged} (MPa) = $-0.340 [1/(2 + 3)] + 0.432$	$r = 0.972$
IB_{dry} (MPa) = $15.165 \text{ Me/Mo} - 0.713$	$r = 0.972$
IB_{aged} (MPa) = $13.983 \text{ Me/Mo} - 1.667$	$r = 0.985$
IB_{dry} (MPa) = $-1.021 \text{ Me}/(\text{Me} + \text{ethers} + \text{Mo}) + 1.224$	$r = 0.928$
IB_{aged} (MPa) = $-0.886 \text{ Me}/(\text{Me} + \text{ethers} + \text{Mo}) + 0.672$	$r = 0.975$
IB_{dry} (MPa) = $0.966 (\text{Me} + \text{ethers})/\text{Mo} - 0.806$	$r = 0.938$
IB_{aged} (MPa) = $1.029 (\text{Me} + \text{ethers})/\text{Mo} - 0.263$	$r = 0.963$
<u>M : U = 45 : 55</u>	
IB_{dry} (MPa) = $-2.443 [1/(2 + 3)] + 2.985$	$r = 0.921$
IB_{aged} (MPa) = $-1.472 [1/(2 + 3)] + 1.225$	$r = 0.956$
IB_{dry} (MPa) = $-10.680 \text{ Me/Mo} + 2.987$	$r = 0.999$
IB_{aged} (MPa) = $-5.424 \text{ Me/Mo} + 1.028$	$r = 0.911$
<u>M : U = 34 : 66</u>	
IB_{dry} (MPa) = $-0.929 [1/(2 + 3)] + 1.321$	$r = 0.931$
IB_{aged} (MPa) = $-4.788 [1/(2 + 3)] + 1.277$	$r = 0.941$
IB_{dry} (MPa) = $-9.848 \text{ Me/Mo} + 1.990$	$r = 0.910$
IB_{aged} (MPa) = $-2.044 \text{ Me/Mo} + 0.403$	$r = 0.967$
IB_{dry} (MPa) = $-0.860 \text{ Me}/(\text{Me} + \text{Mo}) + 1.799$	$r = 0.931$
IB_{aged} (MPa) = $-0.176 \text{ Me}/(\text{Me} + \text{Mo}) + 0.356$	$r = 0.937$

and methylol-substituted melamine triazine rings and of "tertiary" carbons belonging to the mono- and multisubstituted amido groups of urea [e.g., from Table II: $(9.273 + 0.905)/(21.030 + 3.825 + 5.169) = 0.339$ of Table III, for the first case,

namely, the resin of M : U = 55 : 45, (M + U) : F = 2.4]

$$\text{IB}_{\text{dry}} \text{ (MPa)} = -0.576 [1/(2 + 3)] + 4.726 \text{ Me/Mo} + 0.229 [(\text{Me} + \text{ethers})/\text{Mo}]$$

with an estimated standard deviation = 0.12, and

$$\text{IB}_{\text{aged}} \text{ (MPa)} = 0.202 [1/(2 + 3)] + 2.318 [\text{Me}/(\text{Me} + \text{Mo})]$$

with an estimated standard deviation = 0.08. These two equations are valid for an M : U mass ratio range of 55 : 45–34 : 66 and the (M + U) : F molar ratio of 1 : 2.4–1 : 1.3, at an average board density of 0.685 g/cm³.

An important factor which can be deduced from the above is that the physical properties of a cured resin (such as IB strength) can be related to the ratio of species present in the liquid resin before curing. The Me/Mo and Me/(Me + Mo) ratios (with Me = methylene groups and Mo = methylol groups) are the ones which appear to contribute most to the IB strength. The higher the amount of Me in relation to Mo, the more prereacted is the resin and the greater the IB strength of the board. The ethers play a minor role for the dry IB strength and none at all for the aged boards' IB strength. The contribution of the $1/(2 + 3)$ term is approximately 30% of the total IB strength of the cured resin (the coefficient is only 12% of the Me/Mo term, but the values of the ratios are generally two or three times higher [Table III]). The importance of this term makes some sense because an increase in the unreacted (melamine + urea) content of an MUF resin should adversely affect the hardened resin strength and, hence, board strength. Thus, an increase of unreacted (primary peaks) melamine and urea at the expense of the reacted species (secondary and tertiary peaks) subtracts from the IB strength of the board and the coefficient of this term in the equation is negative. If the ratio considered would have instead been $(2 + 3)/1$, then the coefficient would be positive. The equations presented are not the only ones which could be found to describe the phenomena but are the ones which, with the data available, are both conceptually more correct as well as presenting the lowest standard deviation.

A similar approach can be taken for relating ^{13}C -NMR peak ratios of different chemical groups to the formaldehyde emission. This has been shown to correlate well with the F : (M + U) molar ratio at

which the resin has been prepared according to the equation

$$\begin{aligned} \text{Emission (mg HCHO/100 g board)} \\ = 8.915[F/(M + U)] \\ - 0.021[(Me + ethers)/Mo] \end{aligned}$$

with the standard deviation = 0.41.

As good as the correlation between the emission and ^{13}C -NMR is for such an equation, the equation is not usable when a resin of unknown molar ratio is analyzed by NMR. In this case, the most appropriate general equation for formaldehyde emission is as follows:

$$\begin{aligned} \text{Emission (mg HCHO/100 g board)} \\ = -4.138[1/(2 + 3)] \\ + 48.311[(Me + ethers)/Mo] \end{aligned}$$

with the standard deviation = 2.75, in which only terms derivable from the ^{13}C -NMR analysis are present. This indicates that in the absence of a free formaldehyde peak the methylene ether decomposition is the factor which influences most the amount of formaldehyde emission. It is well known²⁰ that the percentage of methylene ethers is relatively higher than in urea resins. Conversely, the negative sign of the coefficient of the $1/(2 + 3)$ term indicates that in such resins the proportion of still reactive amino groups is high and thus that part (5–10%) of the formaldehyde emitted is again captured by re-reaction with residual reactive sites of the resin itself (generally and principally the melamine moieties due to their much higher reactivity^{21–24}).

Of interest is the variation of the dry and aged IB strengths of the boards prepared with the initial MUF resins prepared at different M : U mass ratios. From these, it is clearly evident that in the M : U 80 : 20 to 55 : 45 mass ratio, with the melamine in mass excess (thus in the M : U molar ratio range 2 : 1 to 1 : 1.7), the resins behave more as melamine resins but quite differently: While the 80 : 20 ratio resin behaves as a pure melamine diluted with urea, copolymerization synergy favorable to the resins clearly occurs and increases proceeding through the 75 : 25 to 55 : 45 range. For the resins with a mass excess of urea in the M : U mass ratio range 45 : 55 to 15 : 85 (thus, in the molar ratio range 1 : 2.5 to 1 : 1.2), a similar effect occurs with the 15 : 85 and 25 : 75 mass ratios which behave more as urea resins diluted with melamine, while resins in the mass ratio range 45 : 55 to 34 : 66 benefit somewhat from the

copolymerization synergism between melamine and urea. The resins at a mass ratio of 50 : 50 (molar ratio 1 : 2.1 M : U) are somewhat more difficult to compare, their behavior in some cases resembling that of melamine, and in some others, that of urea resins.

Of some interest is also to report the equations of correlation of the IB strength of the board for variations of the M : U mass ratio with the ^{13}C -NMR peak ratios. Due to the profound character differences between resins prepared with the melamine mass excess which behaves mostly as melamine resins and between resins with melamine mass defects which behave mostly as urea resins, the field of resins of (M + U) : F molar ratios 1 : 2.1 and 1 : 1.7 had to be divided in two. Single reliable equations explaining the whole variation of IB strength vs. NMR peak ratios could not be obtained for the whole M : U mass ratio field 80 : 20 to 15 : 85. Some partial correlations could, however, be obtained. Thus, for the 1 : 2.1 molar ratio for the M : U mass ratios 55 : 45, 45 : 55, and 40 : 60,

$$\text{IB}_{\text{dry}} = 0.467[1/(2 + 3)] + 0.169 \quad r^2 = 0.999$$

$$\text{IB}_{\text{dry}} = \ln(0.721[1/(2 + 3)] + 1.139) \quad r^2 = 0.999$$

indicating that the range of values of the ratio $1/(2 + 3)$ is insufficient to distinguish between a linear and an ln fit. For the mass ratios M : U 40 : 60, 34 : 66, and 25 : 75,

$$\text{IB}_{\text{aged}} = \ln(0.911[1/(2 + 3)] + 1.189) \quad r^2 = 0.999$$

$$\text{IB}_{\text{aged}} = 0.682[[1/(2 + 3)] + 0.179] \quad r^2 = 0.998$$

For the (Me + ether)/Mo ratio for the M : U mass ratios 55 : 45, 34 : 66, 15 : 85,

$$\begin{aligned} \text{IB}_{\text{aged}} = \ln(1.289[(Me + ether)/Mo] \\ + 1.1495) \quad r^2 = 0.993 \end{aligned}$$

$$\begin{aligned} \text{IB}_{\text{aged}} = 0.733[(Me + ether)/Mo] \\ + 0.408 \quad r^2 = 0.984 \end{aligned}$$

Equally for the (M + U) : F molar ratio of 1 : 1.7 for the resins of M : U mass ratios 80 : 20, 75 : 25, and 66 : 34,

$$\text{IB}_{\text{aged}} = -1.834[1/(2 + 3)] + 1.250 \quad r^2 = 0.999$$

$$\text{IB}_{\text{aged}} = e(-1.88[1/(2 + 3)] - 0.234) \quad r^2 = 0.999$$

and for the mass ratios 40 : 60, 25 : 75, and 15 : 85,

$$IB_{\text{dry}} = e(0.950[1(2 + 3)] - 1.434) \quad r^2 = 0.986$$

$$IB_{\text{dry}} = 0.480[1/(2 + 3)] + 0.138 \quad r^2 = 0.974$$

These last few results at least show that there is definitely some evidence to show that the correlation between ^{13}C -NMR peak ratios and cured resin strength which exists for MUF resins as a function of changing formaldehyde content may also exist for the variation of the relative proportions of melamine and urea. It also shows that correlations between the M : U mass ratio and resin strength while appearing to exist indicates a series of complex interactions to which many parameters are likely to contribute, as would be expected by the kinetics of polycondensation gelling^{12,25} of mixtures of hexafunctional (melamine), trifunctional (urea), and difunctional (formaldehyde) reagents.

CONCLUSIONS

In conclusion, sets of equations can be used to predict some of the physical properties of a hardened MUF resin, thus also of a wood particleboard bonded with it, by studying the ^{13}C -NMR peak ratios of well-defined chemical groups in the liquid MUF resin. The equations presented are valid for the resins presented and under the conditions of preparation and application used. If the chemical groups involved remain the same and different resins are used, all of what needs to be recalculated is the set of coefficients of the equations. Of interest is also to remark that a class of true MUF resins, with peculiar characteristics all of their own, only appear to exist in the copolymers in which the mass ratio of M : U is in the approximate range 55 : 45 to 34 : 66, different mass ratios giving resins which behave almost as pure melamine resins or as pure urea resins. Differently from what was found for the correlation of ^{13}C -NMR spectra vs. IB strength and HCHO emission for MUF glue mixes obtained by addition of pre-resins such as accelerators and scavengers where the $1/(2 + 3)$ ratio dominates completely the correlation equations⁵ due to the preponderance of monomeric species, in MUF resins, as in UF and PF resins, the relative amounts of Me (methylenes) and Mo (methylols) and methylene ethers groups also have a considerable influence. This is due to the higher total degree of condensation of a pure MUF resin.

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