A ^{13}C-NMR Analysis Method for MUF and MF 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 chemical groups known to contribute to melamine–urea–formaldehyde (MUF) and melamine–formaldehyde (MF) resin strength and formaldehyde emission is presented. The method relates results obtained by ^{13}C-NMR analysis of liquid MUF and MF resins with their strength and formaldehyde emission in the hardened state. Correlation of different peak ratios with experimental results showed that, contrary to other formaldehyde-based resins, the NMR analysis for the MUF and MF resins needs only to take into account the triazine/substituted triazines and the urea/substituted ureas peak ratios to allow the proposal of equations correlating a single spectrum of the liquid resin with the physical properties of the boards bound with the same resin in its hardened state. Correlation equations are developed for both the case in which variation of the amine : formaldehyde molar ratio is directly induced at the resin preparation stage as well as the case in which it is induced at the glue-mixing stage, the latter by addition of different types of resin accelerators and resin scavengers. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Melamine–formaldehyde (MF) resins, and, in particular, their more economical important variant, melamine–urea–formaldehyde (MUF) resins, are widely used as adhesives for the manufacture of exterior and moisture-resistant wood products, in particular, for particleboard.[1] The evaluation of the cured strength of MUF and MF adhesives and the determination of their capacity for formaldehyde emission, once the resin has become the hardened binder of a board, is a long procedure needing repetitive testing as it is subject to fairly large experimental errors. These are induced by the need to pass through the board manufacturing stage. The testing is further complicated by the need to test the strength of the hardened resin in the board both dry and after 2 h boiling (or less, according to different standard specifications).[2,3] Determination of formaldehyde emission is vital, in general, in prod-ucts bonded with aminoplastic resins, but, in particular, for any adhesive in which urea is used even in part.

Recently, methods for the correlation of a single ^{13}C-NMR spectrum of a liquid resin to the strength and formaldehyde emission of wood products bonded with it, thus for the resin in its hardened state, were proposed for urea–formaldehyde (UF)[1,4,5] and phenol–formaldehyde (PF)[1,6] adhesive resins. These methods are based on the correlation found between the ratio of NMR peak intensities of relevant chemical groups in the liquid resin spectrum with the strength of the hardened resin, of the board bonded with it, and with its formaldehyde emission. The application of such methods appears considerably more complicated for MUF resins, in which NMR bands characteristic of MFs, UFs, and their copolymers are evident in the spectrum.

This article then presents a method to identify which of the main chemical groups in a liquid MUF resin contribute to its hardened strength and formaldehyde emission, as well as to correlate their ^{13}C-NMR signal ratios from a single spectrum of the liquid resin with both the I.B. strength (tensile

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Table I   (a) The Statistical Scheme Used for the Preparation of Adhesive Systems; (b) Results of Particleboard Prepared with Different MUF Adhesive Systems

(a)

Percentage Chart[a]			% Solids Chart[b]		
Resin Solids	Accelerator	Scavenger	Resin Solids	Accelerator	Scavenger
100%	0%	0%	8%	0%	0%
	0%	10%	7.2%	0%	0.8%
	0%	15%	6.8%	0%	1.2%
	0%	20%	6.4%	0%	1.6%
	10%	0%	7.2%	0.8%	0%
	10%	10%	6.4%	0.8%	0.8%
	10%	15%	6%	0.8%	1.2%
	10%	20%	5.6%	0.8%	1.6%
	15%	0%	6.8%	1.2%	0%
	15%	10%	6%	1.2%	0.8%
	15%	15%	5.6%	1.2%	1.2%
	15%	20%	5.2%	1.2%	1.6%
	20%	0%	6.4%	1.6%	0%
	20%	10%	5.6%	1.6%	0.8%
	20%	15%	5.2%	1.6%	1.2%
	20%	20%	4.8%	1.6%	1.6%

Table I *(Continued from the previous page)*

(b)

UF Accelerator on Adhesive Solids (%)[a]	UF Scavenger on Adhesive Solids (%)[a]	UF Accelerator, UF HCHO Scavenger						MF Accelerator, MF HCHO Scavenger					
		Board Density (g cm^{-3})	I.B.[d] Dry (MPa)	Board Density (g cm^{-3})	I.B. V100 (MPa)	HCHO Emission mg/100 g Board	Gel Time/ Minutes	Board Density (g cm^{-3})	I.B. Dry (MPa)	Board Density (g cm^{-3})	I.B. V100 (MPa)	HCHO Emission mg/100 g Board	Gel Time/ Minutes
None	None	0.709	0.803	0.699	0.401	75.96	1.88	0.709	0.803	0.699	0.401	75.96	1.88
None	0.8	0.685	0.680	0.697	0.220	54.84	2.07	0.721	0.696	0.716	0.346	52.73	2.46
None	1.2	0.690	0.728	0.697	0.260	42.91	2.33	0.728	0.675	0.713	0.261	47.43	2.90
None	1.6	0.702	0.663	0.680	0.185	37.80	2.77	0.712	0.568	0.719	0.200	43.78	3.48
0.8	None	0.691	0.690	0.688	0.211	65.63	1.81	0.692	0.712	0.694	0.311	67.87	2.53
0.8	0.8	0.709	0.752	0.711	0.200	54.74	2.17	0.733	0.680	0.716	0.178	52.15	3.02
0.8	1.2	0.706	0.640	0.705	0.084	45.26	2.27	0.727	0.626	0.717	0.190	48.01	3.98
0.8	1.6	0.700	0.586	0.699	0.078	34.43	2.47	0.715	0.603	0.699	0.131	47.27	5.58
1.2	None	0.713	0.604	0.712	0.145	84.84	1.68	0.706	0.703	0.711	0.217	87.06	2.68
1.2	0.8	0.721	0.734	0.713	0.067	50.77	1.90	0.701	0.576	0.699	0.155	58.64	3.60
1.2	1.2	0.703	0.653	0.700	0.053	41.31	2.00	0.703	0.613	0.697	0.164	56.19	4.33
1.2	1.6	0.718	0.744	0.736	0.052	37.73	2.57	0.712	0.559	0.726	0.098	50.47	5.65
1.6	None	0.705	0.652	0.703	0.135	72.53	1.65	0.701	0.711	0.696	0.275	77.15	2.88
1.6	0.8	0.696	0.697	0.696	0.089	55.39	2.07	0.703	0.587	0.687	0.098	56.43	3.67
1.6	1.2	0.736	0.736	0.698	0.085	42.88	2.55	0.696	0.437	0.717	0.079	55.70	5.40
1.6	1.6	0.701	0.456	0.718	0.015	38.39	2.85	0.702	0.523	0.694	0.074	52.66	7.80

MF Accelerator on Adhesive Solids (%)[a]	UF Scavenger on Adhesive Solids (%)[a]	MF Accelerator, UF HCHO Scavenger						UF Accelerator, MF HCHO Scavenger					
		Board Density (g cm^{-3})	I.B. Dry (MPa)	Board Density (g cm^{-3})	I.B. V100 (MPa)	HCHO Emission mg/100 g Board	Gel Time/ Minutes	Board Density (g cm^{-3})	I.B. Dry (MPa)	Board Density (g cm^{-3})	I.B. V100 (MPa)	HCHO Emission mg/100 g Board	Gel Time/ Minutes
None	None	0.709	0.803	0.699	0.401	75.96	1.88	0.709	0.803	0.699	0.401	75.96	1.88
None	None	0.685	0.680	0.697	0.220	54.84	2.07	0.721	0.696	0.716	0.346	52.73	2.46
None	1.2	0.690	0.728	0.697	0.260	42.91	2.33	0.728	0.675	0.713	0.261	47.43	2.90
None	1.6	0.702	0.663	0.680	0.185	37.80	2.77	0.712	0.568	0.719	0.200	43.78	3.48
0.8	None	0.692	0.712	0.694	0.311	67.87	2.53	0.691	0.690	0.688	0.211	65.63	1.81
0.8	0.8	0.684	0.582	0.656	0.138	66.82	2.62	0.684	0.541	0.713	0.139	59.20	2.97

Table I *(Continued from the previous page)*

MF Accelerator on Adhesive Solids (%)ᵃ	UF Scavenger on Adhesive Solids (%)ᵃ	MF Accelerator, UF HCHO Scavenger						UF Accelerator, MF HCHO Scavenger					
		Board Density (g cm⁻³)	I.B. Dry (MPa)	Board Density (g cm⁻³)	I.B. V100 (MPa)	HCHO Emission mg/100 g Board	Gel Time/Minutes	Board Density (g cm⁻³)	I.B. Dry (MPa)	Board Density (g cm⁻³)	I.B. V100 (MPa)	HCHO Emission mg/100 g Board	Gel Time/Minutes
0.8	1.2	0.707	0.620	0.687	0.138	53.62	3.05	0.711	0.467	0.718	0.099	51.65	3.03
0.8	1.6	0.694	0.628	0.695	0.119	43.91	3.15	0.695	0.509	0.714	0.124	47.17	3.47
1.2	None	0.706	0.703	0.711	0.217	87.06	2.68	0.713	0.604	0.712	0.145	84.84	1.68
1.2	0.8	0.697	0.676	0.701	0.182	60.51	3.05	0.732	0.603	0.719	0.170	64.96	2.83
1.2	1.2	0.686	0.583	0.706	0.098	50.11	3.22	0.695	0.466	0.717	0.079	52.34	3.22
1.2	1.6	0.694	0.571	0.704	0.092	34.65	3.75	0.692	0.463	0.714	0.113	43.65	3.47
1.6	None	0.701	0.711	0.696	0.275	77.15	2.88	0.705	0.652	0.703	0.135	72.53	1.65
1.6	0.8	0.730	0.559	0.695	0.094	49.04	3.18	0.744	0.732	0.693	0.191	42.62	2.58
1.6	1.2	0.714	0.554	0.684	0.047	47.29	3.57	0.725	0.545	0.703	0.095	39.86	2.70
1.6	1.6	0.725	0.558	0.696	0.060	44.88	4.52	0.708	0.569	0.725	0.082	28.62	3.97

MUF Accelerator on Adhesive Solids (%)ᵃ	MUF Scavenger on Adhesive Solids (%)ᵃ	MUF Accelerator, MUF HCHO Scavenger					
		Board Density (g cm⁻³)	I.B. Dry (MPa)	I.B. V100 (MPa)	Board Density (g cm⁻³)	HCHO Emission mg/100 g Board	Gel Time/Minutes
None	None	0.709	0.803	0.401	0.699	75.96	1.88
None	0.8	0.698	0.688	0.237	0.715	49.84	2.17
None	1.2	0.708	0.588	0.158	0.719	45.09	2.43
None	1.6	0.739	0.586	0.146	0.677	37.57	2.70
0.8	None	0.715	0.742	0.307	0.716	82.71	1.68
0.8	0.8	0.695	0.627	0.167	0.722	49.85	2.23
0.8	1.2	0.731	0.663	0.198	0.708	45.55	2.52
0.8	1.6	0.727	0.545	0.119	0.707	41.92	2.83
1.2	None	0.721	0.758	0.201	0.700	60.78	1.72
1.2	0.8	0.698	0.666	0.190	0.712	59.06	2.47
1.2	1.2	0.699	0.525	0.086	0.744	58.49	2.58
1.2	1.6	0.717	0.578	0.094	0.709	40.43	2.68
1.6	None	0.673	0.538	0.112	0.761	77.96	1.83
1.6	0.8	0.777	0.702	0.077	0.672	70.89	2.13
1.6	1.2	0.670	0.465	0.101	0.743	54.27	2.43
1.6	1.6	0.684	0.477	0.062	0.701	32.42	3.72

Total resin solids content on dry wood = 8%.
ᵃ Percentage based on MUF resin solids basis.
ᵇ Percentage on dry wood basis.
ᶜ Percentage on MUF resin solids content.
ᵈ I.B. values based on 10 specimens each.

Table II ^{13}C Peak Assignments for MF, MUF, and UF Resins

Name	Structure	Chemical Shift (ppm)		
		MF[a,b] Resin	MUF[b] Resin	UF[b] Resin
Triazine nucleus	$=\underline{C}NH_2$	167.2 (167.3)	167.2	—
	$=\underline{C}NHCH_2-$	166.5 (166.4)	166.3	—
	$=\underline{C}N(CH-)_2-$	166.2		—
Urea residue	$H_2N\underline{C}ONH_2$	—	163.2	163.6
	$H_2N\underline{C}ONH(CH_2-)$	—	161.4	161.9
	$(CH_2-)NH\underline{C}ONH(CH_2-)$	—	159.9	160.2
Methylenes	$-NH\underline{C}H_2NH-$	47.3 (47.9)	47.4	47.7
	$-N(CH_2-)\underline{C}H_2NH-$	52.2 (53.8)	53.6	53.8
	$-N(CH_2-)\underline{C}H_2N-$ $(CH_2-)-$	—	—	60.0
Methylol group	$-NH\underline{C}H_2OH$	64.8 (65.5)	65.0	65.1
	$-N(CH_2-)\underline{C}H_2OH$	69.8 (71.6)	71.3	71.7
Methyl ether of methylol group	$-NH\underline{C}H_2OCH_3$	73.0 (73.7)	73.2	73.2
	$-N(CH_2-)\underline{C}H_2OCH_3$	77.4 (78.2)	78.2	79.7
Dimethylene ether group and hemi formal form of methylol group	$-NH\underline{C}H_2OCH_2NH-$	69.8 (69.7)	69.3	69.4
	$-NH\underline{C}H_2OCH_2OH$	69.8 (69.7)	69.3	69.4
	$-N(CH_2-)\underline{C}H_2OCH_2NH-$	73.0 (75.0)	74.8	76.0
	$-N(CH_2-)\underline{C}H_2OCH_2OH$	73.0 (75.0)	74.8	76.0
Methanol methoxymethylene	$\underline{C}H_3OH$	50.7 (50.0)	50.0	50.0
	$-CH_2O\underline{C}H_3$	55.3 (55.6)	55.4	55.6
Methylene glycol species	$HO\underline{C}H_2OH$	82.1 (83.0)	83.0	83.1
	$HO\underline{C}H_2OCH_2OH$	85.2 (86.6)	86.6	86.6
	$HO\underline{C}H_2OCH_3$	89.5 (90.6)	90.6	90.7
	$H(OCH_2)_nO\underline{C}H_2OCH_3$	93.9 (95.0)	95.0	95.0
Hemiformal form of methylol group	$-NHCH_2O\underline{C}H_2OH$	86.2 (87.1)	87.1	87.1
	$-N(CH_2-)CH_2O\underline{C}H_2OH$	86.2 (87.1)	87.1	87.1

In MUF resin, parentheses values were calculated by method in footnote b.

[a] Chemical shift was calculated by defining ^{13}C of DMSO-d_6 as 39.5 ppm.

[b] Chemical shift in water was calculated by defining ^{13}C of external dioxane as 47.3 ppm.

strength perpendicular to the board surface = internal bond = I.B.) and formaldehyde emission of the particleboard bonded with it.

EXPERIMENTAL

Resins Preparation

Formurea, 132 parts by mass (a formaldehyde concentrate composed of 57% formaldehyde and 22% urea in water solution) and 4.5 parts of urea were mixed with 60 parts water in a laboratory glass reactor furnished with a reflux/distillation condenser and a mechanical stirrer. The mixture was heated under continuous mechanical stirring to 92–94°C and the pH adjusted to 10.0–10.4 with 33% NaOH solution. Heating at 94°C was continued for 1.5 h under continuous mechanical stirring. The pH was then adjusted to 9.5–10, and 41 parts by mass of melamine were added. The pH was maintained at 9.5–10 while checking the turbidity point every 10 min. Approximately 1 h later, when the hydrophobicity point is of approximately 300%, 6.5 parts by

Table III   Selected Integrated Peak Areas from NMR Spectra of MUF Resin Systems

(A) System: MUF Resin + UF Accelerator + UF Scavenger

	Resin Name	Triazine Nucleus		Urea Residue	
		Primary Peak	Secondary Peaks	Primary Peak	Secondary Peaks
1.	MUF A1	9.434	22.241	3.284	26.324
2.	MUF A2	7.901	15.287	6.620	45.692
3.	MUF A3	4.882	9.111	5.930	34.602
4.	MUF A4	8.754	13.352	11.580	55.057
5.	MUF A5	21.265	68.688	11.681	154.23
6.	MUF A6	5.893	11.226	6.344	37.697
7.	MUF A7	6.226	11.146	9.309	47.946
8.	MUF A8	4.041	5.903	7.834	30.704
9.	MUF A9	4.343	11.305	2.099	28.252
10.	MUF A10	6.610	12.477	4.679	39.027
11.	MUF A11	18.637	32.887	25.111	149.535
12.	MUF A12	20.147	28.418	33.402	151.188
13.	MUF A13	15.474	51.215	9.440	137.459
14.	MUF A14	9.701	21.301	12.106	92.418
15.	MUF A15	15.613	26.304	21.418	127.500
16.	MUF A16	20.913	29.326	36.260	197.317
17.	UF activator	—	—	—	22.062
18.	UF scavenger	—	—	37.515	15.704

(B) System: MUF Resin + MF Accelerator + MF Scavenger

	Resin Name	Triazine Nucleus		Urea Residue	
		Primary Peak	Secondary Peaks	Primary Peak	Secondary Peaks
1.	MUF B1	6.746	21.103	2.052	32.418
2.	MUF B2	8.247	22.827	2.352	26.467
3.	MUF B3	15.324	26.109	3.699	32.166
4.	MUF B4	18.482	30.894	4.599	36.546
5.	MUF B5	7.331	20.531	2.479	34.061
6.	MUF B6	45.088	77.886	9.336	117.454
7.	MUF B7	55.344	76.610	9.401	96.899
8.	MUF B8	6.875	9.044	1.236	8.036
9.	MUF B9	2.070	5.268	1.193	10.257
10.	MUF B10	8.616	16.134	1.732	18.285
11.	MUF B11	16.981	27.489	3.139	31.741
12.	MUF B12	14.230	18.232	2.501	19.536
13.	MUF B13	6.015	15.141	1.242	20.274
14.	MUF B14	30.467	51.950	5.177	46.174
15.	MUF B15	28.075	38.996	4.671	35.361
16.	MUF B16	16.274	22.400	11.173	13.268
17.	MF activator	12.910	19.456	—	—
18.	MF scavenger	10.233	7.520	—	—

Table III   *(Continued from the previous page)*

(C) System: MUF Resin + MF Accelerator + MF Scavenger

	Resin Name	Triazine Nucleus		Urea Residue	
		Primary Peak	Secondary Peaks	Primary Peak	Secondary Peaks
1.	MUF C1	14.680	46.828	5.988	76.591
2.	MUF C2	9.361	17.426	7.055	48.718
3.	MUF C3	28.004	41.365	13.070	103.864
4.	MUF C4	16.169	31.596	19.384	93.405
5.	MUF C5	20.875	54.908	7.498	93.648
6.	MUF C6	31.050	52.741	12.237	112.383
7.	MUF C7	25.040	34.643	9.665	90.283
8.	MUF C8	20.996	35.821	13.188	78.162
9.	MUF C9	8.692	23.033	2.190	23.376
10.	MUF C10	16.589	27.314	11.899	61.140
11.	MUF C11	13.457	17.579	7.626	46.760
12.	MUF C12	58.096	94.115	56.152	258.527
13.	MUF C13	12.699	32.723	4.020	62.284
14.	MUF C14	19.809	29.727	14.449	80.336
15.	MUF C15	18.909	23.454	16.398	74.402
16.	MUF C16	15.429	15.638	19.267	67.724
17.	MF activator	18.137	28.077	—	—
18.	UF scavenger	—	—	55.475	25.485

(D) System: MUF Resin + UF Accelerator + MF Scavenger

	Resin Name	Triazine Nucleus		Urea Residue	
		Primary Peak	Secondary Peaks	Primary Peak	Secondary Peaks
1.	MUF D1	6.223	20.837	1.465	28.538
2.	MUF D2	15.964	26.496	2.736	41.544
3.	MUF D3	12.480	19.934	2.318	19.243
4.	MUF D4	87.807	107.496	11.938	110.538
5.	MUF D5	22.343	49.876	15.082	130.657
6.	MUF D6	8.618	22.014	3.153	41.352
7.	MUF D7	48.364	56.508	12.355	78.122
8.	MUF D8	44.102	41.040	10.623	52.860
9.	MUF D9	36.537	70.465	27.236	220.004
10.	MUF D10	24.537	22.969	10.371	59.138
11.	MUF D11	27.026	21.026	10.158	51.321
12.	MUF D12	5.694	3.688	2.036	7.284
13.	MUF D13	3.886	14.013	1.551	38.050
14.	MUF D14	11.599	25.504	3.535	56.036
15.	MUF D15	22.296	35.803	5.585	53.730
16.	MUF D16	22.677	30.248	5.378	42.327
17.	UF activator	—	—	—	22.062
18.	MF scavenger	10.233	7.520	—	—

Table III *(Continued from the previous page)*

		Triazine Nucleus		Urea Residue	
	Resin Name	Primary Peak	Secondary Peaks	Primary Peak	Secondary Peaks
1.	MUF E1	10.698	31.498	2.035	68.679
2.	MUF E2	21.803	43.265	11.158	84.057
3.	MUF E3	32.594	48.408	10.135	73.098
4.	MUF E4	38.310	44.938	13.134	77.778
5.	MUF E5	10.104	27.621	3.206	49.827
6.	MUF E6	12.604	21.801	4.382	41.626
7.	MUF E7	41.142	55.289	10.674	99.185
8.	MUF E8	25.077	29.587	9.332	63.301
9.	MUF E9	12.467	38.646	2.817	53.921
10.	MUF E10	1.818	3.307	0.461	4.984
11.	MUF E11	30.714	40.491	8.261	78.593
12.	MUF E12	12.815	15.510	4.105	32.965
13.	MUF E13	8.657	25.171	2.346	43.784
14.	MUF E14	19.637	32.215	5.254	60.395
15.	MUF E15	41.942	51.734	13.306	114.144
16.	MUF E16	54.239	62.396	14.522	117.451
17.	MUF activator	5.843	13.415	2.370	35.722
18.	MUF scavenger	2.646	—	26.237	30.138

The title row above the subheaders reads: (E) System: MUF Resin + MUF Accelerator + MUF Scavenger

mass of the second urea were added to the reaction mixture. The reaction was allowed to proceed at 94°C until a water tolerance point of 160% is reached (in about 20 min). The resin was then cooled down in an ice bath and then the pH adjusted to 9.8–10 and the resin stored. As the molar ratio of the resin was of M : U : F = 1 : 2.3 : 6.6—hence, of (M + U) : F = 1 : 2, the control MF and UF resins and the MF resin reported in Table VII were prepared according to procedures and formulations already reported.[4,5,7]

Scavenger Preparation

A set of UF, MF, and MUF formaldehyde scavengers were synthesized, maintaining an amine : HCHO molar ratio of 1 : 0.4 as follows: Water, 163 parts by mass, 265 parts of methanol stabilized 35% formalin solution, and 60 parts by mass of NaCl were mixed and stirred until complete dissolution at 25°C, at pH 4.5. Diethanolamine, 0.6 parts by mass, 2.5 parts hexamine, and 0.5 parts dimethylformamide were added to the mixture and stirred until all solids were dissolved and were then followed by the addition of 33% NaOH solution as needed to correct the pH to 7.5. The required amounts of urea or melamine or both (in a 55 : 45

urea : melamine mix by mass) to reach a molar ratio of (M + U) : F = 1 : 0.4 were then added under mechanical stirring. Ammonia solution, 15 parts, 0.5 parts of ammonium chloride, and 1.0 parts of dimethyl formamide were also added at the same time. The pH was adjusted to 10 with 33% NaOH solution, heated at 30–35°C for 16 h, and then the solution stored at ambient temperature before use. When melamine was involved in the preparation, the pH was never allowed to fall under 9.

Accelerators Preparation

The corresponding set of accelerators were prepared maintaining the amine : HCHO molar ratio = 1 : 2.25, although later results indicated that for a (M + U) : F = 1 : 2 molar ratio resin accelerators of a higher molar ratio would be better for acceleration power (i.e., 1 : 3). To 160 parts of water were added 124 parts NaCl and 311 parts of methanol-stabilized 37% formalin solution and the mixture stirred to dissolution. The pH was adjusted to 9 with 33% NaOH solution. The required amount of urea/melamine were added to reach the required molar ratio while maintaining the pH at approximately 9. The mixture was maintained at 30–35°C for 16 h, the

Table IV ¹³C-NMR Peaks Integrated Areas Ratios for Different MUF Adhesive Systems

Resin Name	Triazine Nucleus Primary : Secondary	Urea Residue Primary : Secondary + Tertiary
1. MUF A1	1 : 2.358	1 : 8.016
2. MUF A2	1 : 1.935	1 : 6.902
3. MUF A3	1 : 1.866	1 : 5.835
4. MUF A4	1 : 1.525	1 : 4.754
5. MUF A5	1 : 3.230	1 : 13.203
6. MUF A6	1 : 1.905	1 : 5.942
7. MUF A7	1 : 1.790	1 : 5.150
8. MUF A8	1 : 1.461	1 : 3.919
9. MUF A9	1 : 2.603	1 : 13.460
10. MUF A10	1 : 1.888	1 : 8.341
11. MUF A11	1 : 1.764	1 : 5.955
12. MUF A12	1 : 1.411	1 : 4.526
13. MUF A13	1 : 3.310	1 : 14.561
14. MUF A14	1 : 2.196	1 : 7.634
15. MUF A15	1 : 1.685	1 : 5.953
16. MUF A16	1 : 1.402	1 : 5.442
17. UF activator	—	—
18. UF scavenger	1 : 0.735	1 : 0.419

Resin Name	Triazine Nucleus Primary : Secondary	Urea Residue Primary : Secondary + Tertiary
MUF B1	1 : 3.128	1 : 15.798
MUF B2	1 : 2.768	1 : 11.253
MUF B3	1 : 1.704	1 : 8.696
MUF B4	1 : 1.672	1 : 7.947
MUF B5	1 : 2.801	1 : 13.740
MUF B6	1 : 1.727	1 : 12.581
MUF B7	1 : 1.384	1 : 10.307
MUF B8	1 : 1.315	1 : 6.502
MUF B9	1 : 2.245	1 : 8.598
MUF B10	1 : 1.873	1 : 10.557
MUF B11	1 : 1.619	1 : 10.112
MUF B12	1 : 1.281	1 : 7.819
MUF B13	1 : 2.517	1 : 16.324
MUF B14	1 : 1.705	1 : 8.919
MUF B15	1 : 1.389	1 : 7.570
MUF B16	1 : 1.376	1 : 1.188
MF activator	1 : 1.507	—
MF scavenger	1 : 0.735	—

Resin Name	Triazine Nucleus Primary : Secondary	Urea Residue Primary : Secondary + Tertiary
MUF C1	1 : 3.190	1 : 12.769
MUF C2	1 : 1.862	1 : 6.905
MUF C3	1 : 1.477	1 : 7.947
MUF C4	1 : 1.954	1 : 4.819
MUF C5	1 : 2.630	1 : 12.490
MUF C6	1 : 1.699	1 : 9.184
MUF C7	1 : 1.384	1 : 9.341
MUF C8	1 : 1.706	1 : 5.938
MUF C9	1 : 2.650	1 : 10.674
MUF C10	1 : 1.647	1 : 5.138
MUF C11	1 : 1.306	1 : 6.132
MUF C12	1 : 1.620	1 : 4.604
MUF C13	1 : 2.577	1 : 15.494
MUF C14	1 : 1.501	1 : 5.560
MUF C15	1 : 1.240	1 : 4.537
MUF C16	1 : 1.014	1 : 3.515
MF activator	1 : 1.548	—
UF scavenger	—	1 : 0.459

Resin Name	Triazine Nucleus Primary : Secondary	Urea Residue Primary : Secondary + Tertiary
MUF D1	1 : 3.348	1 : 19.480
MUF D2	1 : 1.660	1 : 15.184
MUF D3	1 : 1.597	1 : 8.302
MUF D4	1 : 1.224	1 : 9.259
MUF D5	1 : 2.232	1 : 8.6630
MUF D6	1 : 2.554	1 : 13.115
MUF D7	1 : 1.168	1 : 6.323
MUF D8	1 : 0.931	1 : 4.976
MUF D9	1 : 1.929	1 : 8.078
MUF D10	1 : 0.936	1 : 5.702
MUF D11	1 : 0.778	1 : 5.053
MUF D12	1 : 0.648	1 : 3.578
MUF D13	1 : 3.606	1 : 24.533
MUF D14	1 : 2.199	1 : 15.852
MUF D15	1 : 1.606	1 : 9.620
MUF D16	1 : 1.334	1 : 7.870
UF activator	—	—
MF scavenger	1 : 0.735	1 : 2.575

Resin Name	Triazine Nucleus Primary : Secondary	Urea Residue Primary : Secondary + Tertiary
MUF E1	1 : 2.944	1 : 33.749
MUF E2	1 : 1.984	1 : 7.533
MUF E3	1 : 1.485	1 : 7.212
MUF E4	1 : 1.173	1 : 5.922
MUF E5	1 : 2.734	1 : 15.542
MUF E6	1 : 1.730	1 : 9.499
MUF E7	1 : 1.344	1 : 9.292
MUF E8	1 : 1.180	1 : 6.783
MUF E9	1 : 3.010	1 : 19.141
MUF E10	1 : 1.819	1 : 10.811
MUF E11	1 : 1.318	1 : 9.514
MUF E12	1 : 1.210	1 : 8.030
MUF E13	1 : 2.908	1 : 18.633
MUF E14	1 : 1.641	1 : 11.495
MUF E15	1 : 1.233	1 : 8.578
MUF E16	1 : 1.150	1 : 8.088
MUF activator	1 : 2.296	1 : 15.073
MUF scavenger	—	1 : 1.149

Table V Coefficients of Correlation of ^{13}C-NMR Peak Ratios with I.B. Strength and Formaldehyde Emission

	Triazine/Substituted Triazine (Y_1)		Urea/Substituted Urea (Y_2)	
	Dry	Boil/Dry	Dry	Boil/Dry
I.B. dry				
Resin series A	0.725	0.911	0.637	0.882
Resin series B	0.887	0.956	0.754	0.804
Resin series C	0.814	0.938	0.745	0.867
Resin series D	0.791	0.682	0.691	0.643
Resin series E	0.798	0.862	0.830	0.853
HCHO emission				
Resin series A	0.971		0.968	
Resin series B	0.926		0.780	
Resin series C	0.973		0.909	
Resin series D	0.969		0.895	
Resin series E	0.932		0.961	
% Scavenger content				
Resin series A	0.990		0.991	
Resin series B	0.975		0.990	
Resin series C	0.988		0.960	
Resin series D	0.966		0.942	
Resin series E	0.996		0.986	

pH readjusted to 9, and then cooled in an ice bath and stored at ambient temperature.

Adhesive Resins Systems

Adhesive resin systems were prepared taking the resin solids content of each resin into consideration according to the statistical scheme in Table I. NH_4Cl hardener, 2%, was added as a 25% water solution on a total resin solids basis for the glue mix.

Particleboard Preparation and Testing

Duplicate (*Pinus radiata*) one-layer core-only particleboards of 350 × 350 × 12 mm dimensions were prepared from the modified resins to determine the strength of the resin. The following set of conditions were kept the same for each of the boards prepared: Total resin solids, 8% (including accelerator and scavenger solids content) was used for all panels, with a glued particle moisture content of 10–11%. The pH of the resins before use were in the range 9.8–10.0. A light water spray was applied to the sur-

faces of the panels' furnish before pressing. The total pressing time used was 7.5 min to bring the panels to their ultimate strength, with a cycle of 2 min from press contact to maximum pressure and maximum pressure holding, with a pressure of 23 kg/cm², followed by 2.5 min at 12 kg/cm² and 3 min at 3 kg/cm² at a press temperature of 180°C. After pressing, the panels were cooled and left standing in a well-vented room for 2 weeks before analysis. Internal bond (I.B.) strength dry, I.B. strength after 2 h boiling followed by 16 h drying at 105°C, and HCHO emission measurement by the WKI method[8] and sodium sulfite titration method[9] were carried out.

^{13}C-NMR Spectroscopy

^{13}C-NMR spectra of the liquid resins were obtained on a Bruker AC 200 FT–NMR spectrometer, at a frequency of 50.3 MHz with the sample spectra 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 signals for the four signals were set. About 1 mL of liquid 55% solids resin glue mix, without a hardener, was placed in an NMR tube and diluted with about 0.4 mL deuterium oxide added directly to the sample. All spectra were run overnight. Acquisition time was 1.8 s with the number of transients at 10,000. The spin-lattice relaxation time of ^{13}C-NMR is an important factor in setting the pulse intervals.[10,11] Tomita and Hatono[12] 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 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 the tables are integrated areas. These were used for all the ratios investigated. The area of the spectra which gave the best correlations with the physical properties of the resins were the 160–170 ppm region, where the very sensitive peaks of the triazine nucleus of melamine, urea, and their substituted counterparts are located. The interpretation of the ^{13}C-NMR bands were taken from the literature.[13–16] Peak assignments are reported in Table II. Potentially significant peak intensity ratios are reported in Table III. Correlation of the relevant NMR peak ratios with the I.B. strength and HCHO emission of the boards was carried out by an iterative Levenby–Marquardt polynomial approximation method.

Table VI Correlation Equations of Particleboard I.B. Strength and HCHO Emission as a Function of the ¹³C-NMR Peak Ratios of Different Liquid MUF Resin Systems

Resin series A: MUF resin + UF accelerator + UF scavenger

I.B. dry (MPa) = $-0.409Y_1 + 0.633Y_2 + 0.795$	s.d. = 0.083
I.B. boil/dry (MPa) = $-0.888Y_1 + 1.429Y_2 + 0.393$	s.d. = 0.088
ln HCHO emission (mg/100 g) = $-1.0554Y_1 - 2.4584Y_2 + 4.8511$	s.d. = 0.118

Resin series B: MUF resin + MF accelerator + MF scavenger

I.B. dry (MPa) = $-0.473Y_1 - 0.060Y_2 + 0.887$	s.d. = 0.057
I.B. boil/dry (MPa) = $-0.522Y_1 - 0.063Y_2 + 0.505$	s.d. = 0.052
ln HCHO emission (mg/100 g) = $-0.945Y_1 + 0.0940Y_2 + 4.564$	s.d. = 0.153
ln HCHO emission (mg/100 g) = $-0.752Y_1 - 0.165Y_2$	
$+ 0.531(F/Me) + 4.366$	s.d. = 0.144*

Resin series C: MUF resin + MF accelerator + UF scavenger

I.B. dry (MPa) = $-0.199Y_1 - 0.222Y_2 + 0.811$	s.d. = 0.053
I.B. boil/dry (MPa) = $-0.273Y_1 - 0.370Y_2 + 0.414$	s.d. = 0.060
ln HCHO emission (mg/100 g) = $-1.312Y_1 + 0.004Y_2 + 4.735$	s.d. = 0.189

Resin series D: MUF resin + UF accelerator + MF scavenger

I.B. dry (MPa) = $-0.081Y_1 - 0.733Y_2 + 0.750$	s.d. = 0.073
I.B. boil/dry (MPa) = $-0.076Y_1 - 1.144Y_2 + 0.262$	s.d. = 0.086
ln HCHO emission (mg/100 g) = $-0.923Y_1 + 3.798Y_2 + 4.161$	s.d. = 0.263

Resin series E: MUF resin + MUF accelerator + MUF scavenger

I.B. dry (MPa) = $-0.397Y_1 + 0.221Y_2 + 0.847$	s.d. = 0.074
I.B. boil/dry (MPa) = $-0.348Y_1 + 0.316Y_2 + 0.351$	s.d. = 0.072
ln HCHO emission (mg/100 g) = $-0.520Y_1 - 3.760Y_2 + 4.690$	s.d. = 0.150

ª Free formaldehyde/methylenes ratio taken into consideration.

DISCUSSION

The absolute intensities of ¹³C-NMR peaks can never be taken as a measure of the abundance of a particular chemical group. Recent work on the correlation between liquid UF[4,5] and PF[6] resin ¹³C-NMR with the physical characteristics of the hardened network produced indicated that the ratios of the integrated areas of peaks characteristic of chemical groups known to contribute to the cured strength and formaldehyde emission of the resin appear to indicate excellent correlation with the experimental reality.[4-6]

Furthermore, MUF copolymers are generally prepared at fairly constant mass ratios of melamine to urea (50 : 50 to 40 : 60), near to the optimum applied performance of the resin. Variation of the relative proportions of the materials then often relies on the addition of cure accelerators and formaldehyde scavengers. These are both, in general, UF or MF prepolymers—hence, methylolated monomeric and dimeric species of urea or melamine. The correlation of MUF resin ¹³C-NMR spectra with the physical characteristics of the cured resin network is complicated by having to take into account this peculiarity in the application of these resins as adhesives. Thus, five series of mixes based on the same MUF basic resin were studied: (i) MUF resin + UF accelerator + UF scavenger, (ii) MUF resin + MF accelerator + MF scavenger, (iii) MUF resin + UF accelerator + MF scavenger, (iv) MUF resin + MF accelerator + UF scavenger, and (v) MUF resin + MUF accelerator + MUF scavenger, in each of which the relative proportions of resin, accelerator, and scavenger supplied the differences in mass and molar ratio of the adhesive mix. As a consequence, the use of this approach for a MUF resin appears, then, more complicated than for the UF and PF resin cases where a direct variation of the molar ratio of the

Table VII   Strengths, NMR Unsubstituted/ Substituted Y_1 and Y_2 Peak Ratios, and Correlation Equations for MUF Resins in Which the Relative Proportion of (M + U) : F Are Changed Directly During the Preparation of the Resin

(M + U) : F Molar Ratio	Y_1	Y_2	I.B. Dry (MPa)	I.B. 0.5 h Boil/Dry (MPa)
1 : 1.24	0.658	2.083	0.49	0.18
1 : 1.39	0.862	2.564	0.55	0.23
1 : 1.82	1.695	6.250	0.82	0.58
1 : 2.00	2.083	8.333	0.94	0.55

I.B. dry (MPa) = $0.165Y_1 + 0.034Y_2 + 0.316$, s.d. = 0.013; I.B. 0.5 h boil/dry (MPa) = $0.793Y_1 - 0.113Y_2 - 0.124$, s.d. = 0.087.

components was carried out directly at the resin preparation level.

In Table I, the experimental results for I.B. strength and formaldehyde emission for each combination of proportions of each resin system are reported (in total 76 different combinations). The ^{13}C-NMR peak assignments to different chemical groups are reported in Table II. The experimental ^{13}C-NMR peaks integrated areas of species which were found to contribute to the hardened strength of an MUF resin are reported in Table III: The data for other groups which contributed to other resin systems[4–6] but which did not contribute to the MUF resin case are also available[17] but are not reported here. Table IV shows the ratios of the integrated areas of the peaks reported in Table III.

Table V shows the ^{13}C-NMR species ratio correlation to the I.B. strength, formaldehyde emission, and percentage scavenger content for all the five series of resins. Correlations for each series, with higher correlation coefficients, were also obtained, but these additional values are available elsewhere.[17] While other groups such as methylol content, methylene content, and free formaldehyde can sometime also correlate well with one or other physical property within a single series of resins and have been checked,[17] this is not the case for the total of the resin combinations. The heterogeneity of the system chosen achieves an acceptable correlation with physical properties only through the very sensitive band ratios of nonsubstituted/substituted triazine (at around 170 ppm)[1,7,17,19] and the nonsubstituted/ substituted urea (at around 160–165 ppm).[1,7,17,19] The correlation coefficients are better for I.B. strength after boiling and drying (rather than for dry I.B.

strength) due to the expected flattening out of the results in this type of test and for formaldehyde emission.

Contrary to the UF and PF resin cases, the combination of just two variables (Y_1 = triazine/substituted triazine; Y_2 = urea/substituted urea) already appear to explain to an acceptable level the behavior of an MUF system. The equations correlating the two variables Y_1 and Y_2 to resin crosslinking, hence, to experimental I.B. strength, and to formaldehyde emission are shown in Table VI. The standard deviations obtained are acceptable for both I.B. strength and formaldehyde emission.

One of the most interesting findings is that differently from UF and PF resins the influence on formaldehyde emission of the free formaldehyde left in the resin does not need to be taken into account in the correlation equations for MUF resins. The free formaldehyde peak intensity in different ratios has been found to have little or no correlation with, and, hence, little or no bearing on, MUF resin (and by inference MF resins) formaldehyde emission from the cured network. To illustrate this point, in Table VI (B resins), an equation in which the free formaldehyde/methylene peak ratio has been included as a variable in the correlation equation is also presented as an example: The very similar values of the standard deviations for the two equations indicate that taking into account the free formaldehyde present does not help in explaining the phenomenon to a higher level of significance. This is an unusual finding, as free formaldehyde always contributes to a greater or lesser extent to both UF and PF resin emission. There are two reasons why free formaldehyde might not appear to contribute in the equation: The first is because the amount of free formaldehyde is reflected in the lower or higher substitution of the amino groups on the triazine ring of melamine and the amido groups of urea: The more substituted are such groups, the lower the amount of free formaldehyde, and the less substituted, the higher the amount of free formaldehyde. A term based on the free formaldehyde signal is redundant as already represented by Y_1 and Y_2. The second reason is that considering the high reactivity toward formaldehyde of melamine, and that crosslinking to hardening in MUF resins occurs almost exclusively through the melamine moieties, all the free formaldehyde is mopped up during hardening. The additional equation for formaldehyde emission in Table VI (resin series B) shows that both reasons are valid. The balance of the coefficients of the equation changes with the introduction of the free formaldehyde term, with the apparent contribution of Y_1

and Y_2 decreasing $(-0.94 + 0.09 + 4.56 = 3.71; -0.75 -0.16 + 0.53 + 4.37 = 3.99)$, indicating that approximately half of the lack of influence of free formaldehyde on the correlation is due to reactions with melamine and urea during hardening and approximately half to the redundancy of the term. It must be pointed out that the coefficients of the equations in Table VI are unique for each homologous series of resins. The coefficients would change for resins synthesized and boards prepared under different conditions.

An important conclusion which can be deduced from the results in Table VI is that the physical properties of a hardened resin can be related to the ratio of species in the liquid resin before curing. In the equation in Table VI, it is important to note that the Y_1 and Y_2 terms are the ratios of nonsubstituted/substituted species. When the amount of unsubstituted urea and triazine are greater, the resin is less reacted and, thus, the results of I.B. strength will be lower: The term in this form then subtracts from the I.B. strength of the resin. This means that, within the limits and under the conditions used, the more advanced is the resin—hence, the more substituted are the triazine and urea nuclei—the higher is the strength of the cured resin. It is easy to see then that the addition of a scavenger or an accelerator, in both cases monomeric and dimeric methylolated species of different amine/formaldehyde molar ratio, does always reduce the I.B. strength of the total resin system. The accelerator then has just the function of accelerating resin curing and in reality does not improve the ultimate cured strength of the resin.

The situation is different for the HCHO emission equations (Table VI), from which it appears that in the melamine part of the resin accelerators and scavengers always contribute to diminish formaldehyde emission (the Y_1 coefficient is always negative) of the finished product. The urea part of the resin instead contributes to increase the formaldehyde emission (i) considerably in the case in which a UF accelerator (high F : U molar ratio) is used (D resins series) and (ii) minimally when a UF scavenger (low F : U molar ratio) is used (C resins series) or no UF additives are used (B resins series) or (iii) does not contribute or, better, it scavenges formaldehyde when the MUF accelerator and scavenger are used (E resins series) and when the UF scavenger and accelerator are used (A resins series).

The above indicates again that a three-part system is not very useful as regards formaldehyde emission, as better results can be obtained by just using an MUF resin + a scavenger only. However, a better balance of overall properties, both strength and emission, can be obtained by using a three-part system. In this respect, from the results it becomes evident that an efficient accelerator should have a higher molar ratio than used here and be used in smaller proportions.

Correlation of the ¹³C-NMR spectra by variation of the molar ratio (M + U) : F directly in the preparation of the MUF resin, without additives, as already reported for UF and PF resins, is also possible[1,18] (Table VII). From this, it appears that in the case of just the MUF resin, without additives, the contribution to crosslinking during resin hardening is due mostly to melamine moieties if one compares the relative proportions of the Y_1 and Y_2 coefficients, this being even more evident for the I.B. strength after boiling and drying. This confirms in a different manner results already reported showing that hardening is almost exclusively through the melamine moieties of an MUF resin.[19,20] This is not the case when the variation in different proportions of M : U : F is achieved through addition of scavengers and accelerators. The latter is then a method to address, along a different route, the hardening of MUF resins. Of equal interest is that the standard deviation in the dry I.B. correlations is smaller when the M : U : F molar ratio is varied directly during preparation of the resin than if postadditives are used, indicating that the former method of preparation tends to give resins of better consistency and performance.

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