A ^{13}C-NMR Analysis Method for MF and MUF Resins Strength and Formaldehyde Emission from Wood Particleboard. II. MF 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-formaldehyde (MF) resins strength is presented. The method relates results obtained by NMR analysis of liquid MF resins with their strength 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 MF resin from the ^{13}C-NMR spectrum of the liquid MF resin. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Melamine-formaldehyde (MF) 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 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]

This article then presents for pure MF resins, as was done for melamine-urea-formaldehyde (MUF) resins in the preceding article of this series,[3] a method to identify which of the main chemical groups in liquid MF resins prepared in two different manners contribute to their hardened strength, as well as to correlate their ^{13}C-NMR signal ratios to both the IB (tensile internal bond) strength of the particleboard bonded with them. The method is intended to be exclusively comparative and not absolute.

EXPERIMENTAL

Resin Preparation—One-step Route

By this procedure, all the reactants are added at the beginning of the reaction.[4,5] An MF resin of the M : F molar ratio = 1 : 1.8 was prepared as follows: 60.4 parts by mass of melamine, 50 parts water, and 70 parts 37% formalin solution and 1.2 parts dimethylformamide were mixed in a reactor equipped with a reflux condenser and mechanical stirring and the pH was adjusted between 9.6 and 10.2 with 40% NaOH water solution. The reaction mixture was the heated at 90–95°C and the pH monitored to maintain it at 9–10. After reaching the turbidity point, the pH was slowly lowered while monitoring the water tolerance point of the resin. When the water tolerance point became lower than 160%, the reaction was immediately stopped by increasing the pH to 9.8–10 and rapidly cooling the resin to ambient temperature. Resins of an M : F molar ratio of 1 : 2.1,

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Journal of Applied Polymer Science, Vol. 61, 1697–1702 (1996)

CCC 0021-8995/96/101697-06

Table I Particleboard IB Strength and Other MF Resins Characteristics

Resin	Ave. Density (g cm^{-3})	IB Dry (MPa)	IB Aged (MPa)	Resin Viscosity (Centipoises)	Gel Time (s)	Water Tolerance (%)	Final pH	Swelling 2 h Boil Wet (%)
1 : 2.1	0.684	0.616	0.280	48	—	180	9.67	18.6
1 : 1.8(A)	0.699	0.692	0.364	30	—	100	9.52	19.3
1 : 1.8(B)	0.687	0.568	0.184	114	68	100	9.51	18.9
1 : 1.5(A)	0.689	0.612	0.324	87	76	80	9.35	19.8
1 : 1.5(B)	0.688	0.544	0.156	95	66	160	9.62	22.9
1 : 1.3(A)	0.698	0.595	0.060	70	102	50	8.33	26.4
1 : 1.3(B)	0.687	0.392	0.024	40	142	150	9.69	42.6
1 : 1.1(A)	0.688	0.104	0.020	< 10	100	90	9.06	> 43
1 : 1.1(B)	0.680	0.080	0.006	36	101	80	10.07	> 43

1 : 1.8, 1 : 1.5, 1 : 1.3, and 1 : 1.1 were prepared by this route (series B).

Resin Preparation—Stepwise Route

This method of preparation was added in stages, the number depending on the resin being prepared.[4,5] The basic resin was a 1 : 2.1 M : U molar ratio resin prepared according to the procedure set out for the concerted route. The basic resin procedure used to prepare the lower molar ratio resins by addition of melamine was according to the following scheme:

1 : 2.1
1 : 2.1 > 1 : 1.8
1 : 2.1 > 1 : 1.8 > 1 : 1.5
1 : 2.1 > 1 : 1.8 > 1 : 1.5 > 1 : 1.3
1 : 2.1 > 1 : 1.8 > 1 : 1.5 > 1 : 1.3 > 1 : 1.1.

The preparation of the resins is illustrated by the following description of the preparation of the 1 : 1.3 molar ratio resin: Sixty grams water and 135 g of a 37% formalin solution were placed in a glass reactor equipped with thermometer and mechanical stirrer and the pH adjusted between 9.6 and 10.1 with a 40% sodium hydroxide water solution. Melamine, 102 g, was then added and the reaction mixture was heated to 95°C under continuous mechanical stirring. After complete dissolution of the melamine, the reaction was continued for 15 min when 21 g of a second melamine was added: It was usually necessary to add bis(hydroxyethyl)ether either alone or with dimethylformamide to ensure complete melamine dissolution. As little water as possible was added in order not to alter the resin solids content to an undue extent. As the water tolerance point of the resin reached a value of 160%, a third amount of 22 g melamine was added, and the reaction continued under continuous monitoring of pH and the water tolerance point. As soon as the water tolerance was found to have fallen again to 160%, then a fourth amount of 15 g melamine in dimethylformamide was added. The total amount of dimethylformamide used during the reaction was 20 mL. As soon as the water tolerance was found to have fallen to approximately 100%, the reaction was stopped by cooling rapidly to ambient temperature and increasing the pH over 10 by addition of a sodium hydroxide solution. The resins solids content was maintained at 55% throughout the resin series. The results obtained are shown in Table I.

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 MF 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% MF resin solids content on dry wood, and 3.3% NH_4Cl hardener were used as a 20% water solution based on the resin solids content; the boards' pressing time was of 7.5 min at a temperature of 180°C and with a pressing cycle of 2 min from pressplaten contact time to high pressure and high-pressure maintenance (23 kg/cm^2) followed by 2.5 min at an intermediate pressure of 11 kg/cm^2, followed, finally, by a holding period of 3 min at 4.5 kg/cm^2 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

Table II ^{13}C-NMR Spectra Peak Integrated Areas for MF Resins in the Molar Ratio Range 1 : 2.1 to 1 : 1.1 Prepared by the Stepwise (A Series) and the One-Step Route

	Molar Ratio (M : U)								
Functional Group	1 : 2.1	1 : 1.8A	1 : 1.8B	1 : 1.5A	1 : 1.5B	1 : 1.3A	1 : 1.3B	1 : 1.1A	1 : 1.1B
Triazine rings									
Unsubstituted (1°)									
167 ppm	12.023	13.189	21.939	10.196	7.985	4.067	18.863	22.860	21.939
Monosubstituted (2°)									
166 ppm	13.561	11.159	19.102	7.267	11.663	1.653	4.086	8.799	4.583
Disubstituted (3°)									
165 ppm	—	—	—	3.797	—	2.311	—	15.481	6.261
Others									
$N(CH_2)\underline{C}H_2OCH_2NH$									
72 ppm	6.731	3.361	14.103	7.491	11.937	13.702	15.043	18.577	20.667
$-N(CH_2)\underline{C}H_2OH$ {*Mo*}									
71 ppm	2.341	1.791	7.698	0.125	5.599	1.489	0.625	2.040	0.263
$-NH\underline{C}H_2OCH_2NH-$									
68 ppm	1.147	—	3.646	—	—	—	—	—	—
$-NH\underline{C}H_2OH$ {*Mo*}									
65 ppm	10.415	9.457	8.209	2.663	6.553	2.773	3.775	12.900	5.709
$-N(CH_2)\underline{C}H_2N(CH_2)$									
61 {*Me*}	6.683	3.734	15.853	7.711	12.531	12.209	15.389	18.601	21.553
$-N(CH_2)\underline{C}H_2NH-$									
{*Me*} 53 ppm	0.878	0.820	0.854	0.390	0.902	0.229	0.099	1.432	1.103
$-NH\underline{C}H_2NH-$ {*Me*}									
47 ppm	3.878	1.362	0.810	0.560	0.722	0.322	0.214	1.520	2.344

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 were compared with the requirements of standard specifications for MF and MUF-bonded particleboard.[1,2] 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.[6,7] The results were too low and irregular for correlation and were disregarded.

^{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 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 dimethyl sulfoxide (DMSO), run separately, and the signals for the four signals were set. About 1 mL of the 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.[8-10] Tomita and Hatono[8] 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 the reported shifts were accurate to 1 ppm. The spectra were run with nOe enhancement, the spectral width was 15,000, and 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.[8-16] Identification of the NMR peaks is as reported in previous articles.[3,17,18] Potentially significant peak integrated areas ratios are reported in Table III. The ^{13}C-NMR spectra of MUF resins

Table III ^{13}C-NMR Peak Integrated Area Ratios for MF Resins

Resin	1°/ (2° + 3°)	Me/Mo	(C + 2E)/ (A + C + E)[a]	Me/ (Me + Mo)	1° : (1° + 2° + 3°)	(Me + Ether)/ (Me + Mo + Ether)	(Me + Ether)/ Mo
1 : 2.1	0.886	0.894	0.184	0.452	0.482	0.556	1.307
1 : 1.8A	1.182	0.525	0.375	0.345	0.541	0.452	0.824
1 : 1.8B	1.148	1.239	0.513	0.473	0.514	0.618	1.617
1 : 1.5A	0.921	3.106	0.411	0.597	0.479	0.852	5.793
1 : 1.5B	0.684	1.623	0.555	0.538	0.618	0.682	2.147
1 : 1.3A	1.026	2.994	0.415	0.749	0.506	0.861	5.692
1 : 1.3B	4.616	3.568	0.316	0.781	0.710	0.874	6.988
1 : 1.1A	0.940	1.442	0.485	0.590	0.485	0.729	2.686
1 : 1.1B	2.023	4.186	0.320	0.807	0.670	0.884	7.647

[a] $A = —NHCH_2NH—$; $C = —N(CH_2)CH_2NH—$; $E = —N(CH_2)CH_2N(CH_2)—$.

can be split into four main areas of importance to the analysis at hand[3,5]:

1. The substituted and unsubstituted melamine's triazine groups with their very sensitive signals in the 160–170 ppm region.
2. Methylene groups with signals from 45 to 60 ppm.
3. Methylol groups with signals from 65 to 72 ppm.
4. Methylene–ether groups with signals from 69 to 90 ppm.

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.[17,18]

DISCUSSION

The absolute intensities of ^{13}C-NMR peaks can never be taken as a measure of the abundance of a particular chemical group. In resins such as the melamine–formaldehydes (MF) in which all the chemical groups are closely interrelated, ratios of the intensities of peaks characteristic of chemical groups known or suspected to contribute to the cured strength of the resin and to its formaldehyde emission appear to indicate excellent correlation with the experimental reality. The two series of resins prepared, of M : F molar ratios 1 : 2.1, 1 : 1.8, 1 : 1.5, 1 : 1.3, and 1 : 1.1, were prepared by two different methods. The MF resins in one series were prepared starting at a 1 : 2.1 molar ratio and were brought to their final molar ratio by the addition of melamine in several steps (series A). The MF resins in the second series instead were prepared by using the desired ratio of melamine to formaldehyde directly at the start of the reaction (series B). Both methods are used for the preparation of MF resins.

In Table I are reported the results for the resins' characteristics, tensile internal bond (IB) strength, and formaldehyde emission of the laboratory particleboard bonded with them, while the experimental ^{13}C-NMR results are reported in Table II. Table III shows, instead, the values of the peaks' integrated area ratios of species known or suspected to contribute or to potentially contribute to the hardened strength of the resin. While most of the resins prepared by the single-step preparation method (series B) present group ratios which correlate well with the particleboard IB strength, this does not appear to be the case for the resins prepared by the stepwise route (series A). In this latter series (series A), the only two ratios which appear to bear good correlation were those of the different types of methylene bridges[19,20] and the ratio (Me + ethers)/(Me + Mo + ethers). What is of interest is that the ratio of primary/secondary substituted triazine signals which has been found to relate reasonably for the MF resins prepared by the one-step route does not appear to work well in the case of MF resins prepared stepwise. This is the only case in which such a behavior is observed, since for MUF resins prepared by any route[3,20] and even by glue-mix addition of accelerator and scavenger resins,[18] this ratio or related ones always show an excellent correlation with the IB strength results.

As regards the one-step resin series, several ^{13}C-NMR intensity ratios can be used. Of these, the ratio of primary/secondary substituted triazines, although again presenting a lower correlation with the IB strength than other ratios, has also been considered in the final equations. For the other resins used, the choice was made on the basis of the best mathematical correlation among ratios which might represent similar structural characteristics in the resin makeup. Thus, for the dry IB results, the Me/Mo and the (Me + ethers)/Mo ratios were the ones used, while for the IB strength after accelerated aging, the Me/(Me + Mo) and the (Me + ether)/Mo terms were the ones used instead. The physical reasons why these ratios are of significance are the same as exposed for MUF resins.[3,20]

Due to the contribution of several terms, a composite equation correlating and explaining the greater part of the phenomenon in a conceptually correct manner as regards the expected contribution of chemical species to crosslinking can be presented. Thus, for resin series B,

$$\mathrm{IB_{dry}(MPa)} = -0.338(1^\circ/2^\circ) + 0.063\ \mathrm{Me/Mo} + 1.664(\mathrm{Me} + \mathrm{ethers})/\mathrm{Mo}$$

in which the standard deviation = 0.019. As in this equation methylene (Me) and methylol (Mo) groups might be counted twice, a conceptually more correct equation to describe the phenomenon is

$$\mathrm{IB_{dry}(MPa)} = -0.155(1^\circ/2^\circ) + 1.266\ (\mathrm{Me} + \mathrm{ethers})/(\mathrm{Me} + \mathrm{Mo} + \mathrm{ethers})$$

with the standard deviation = 0.051. Again, for the aged series B resins,

$$\mathrm{IB_{aged}(MPa)} = -0.181(1^\circ/2^\circ) + 1.063\ \mathrm{Me/Mo} + 0.053\ (\mathrm{Me} + \mathrm{ethers})/\mathrm{Mo}$$

in which the standard deviation = 0.04. Again, a more conceptually correct equation in which the fact that after boiling the methylene ether groups have in effect disappeared is

$$\mathrm{IB_{aged}(MPa)} = -0.305[1^\circ/(1^\circ + 2^\circ + 3^\circ)] + 0.517\ \mathrm{Me/Mo}$$

with the standard deviation = 0.004. From these equations, it is possible to deduce that both in the dry and aged samples the proportion of unreacted melamine exerts a negative effect upon the IB strength, while the amount of bridging groups as a proportion of the sum of all bridges and methylol groups exerts a positive effect on the strength of the cured resin. This means that the larger is the proportion of unreacted melamine in the resin the lower will be the strength of the cured resin of the particleboard bonded with it, a confirmation of what is already known.[5,21] The greatest contribution to the strength comes from the presence of the bridging species, both methylene and methylene ether groups in the case of the dry resin. It is known that in MF resins the relative proportion of methylene ether groups tends to be rather higher than in other resins.[21] In the first equation, it is interesting to note the effect of the Me/Mo ratio. This ratio when alone has a very high correlation with the IB strength (Table III). Methylene bridges are already of importance at the resin stage in which the NMR analysis is done, thus at the stage of the resin having been built up. In the case of the aged resins, the two equations presented bring enough evidence that ether bridges do not contribute, or contribute very little, to the resin strength after the aging process, a clear indication that their rearrangement to methylene bridges is extensive during aging. Thus, while in the freshly cured MF resin a rather high proportion of methylene ether bridges contribute to the network strength, this is not anymore the case after the process of accelerated aging. This does not mean to say that in ambient temperature, naturally aged MF resins the proportion of methylene ether bridges is much lower: It might just be a peculiarity of the accelerated aging test which uses an elevated temperature. It would be interesting to test the proportion of methylene ether bridges in naturally aged resins to check if such a finding is only a peculiarity of the standard test method used.[1,2] It might put into question, at least for melamine-based resins, the suitability of current standard specifications.

For the series of resins prepared in a stepwise manner (series A), only an equation correlating dry IB strength to NMR results could be obtained, and this is as follows:

$$\mathrm{IB_{dry}\ (MPa)} = 2.360(C + 2E)/(A + C + E) - 0.423(\mathrm{Me} + \mathrm{ethers})/(\mathrm{Me} + \mathrm{Mo} + \mathrm{ethers})$$

in which the standard deviation = 0.035 and where $A = -\mathrm{NHCH_2NH}-$, $C = -\mathrm{N(CH_2)CH_2NH}-$, and $E = -\mathrm{N(CH_2)CH_2N(CH_2)}-$. An equally acceptable and conceptually correct equation was also found to be

$$\mathrm{IB_{dry}}\ (\mathrm{MPa}) = 0.274\ \mathrm{Me/Mo} - 0.603[(C + 2E)/(A + C + E)]$$

with the standard deviation = 0.011. These equations show that there are some important differences between stepwise (series A) and one-step (series B) resins. It is surprising to find in the second of these equations that branched methylene bridges are already a threat to the efficiency of resin curing. It would be expected that the branched methylenes exert a positive effect upon cured strength by acting as a nucleus for the growth of the polymer network. Instead, it becomes clear from the equations that these units act as hoarders of the relatively scarce methylol groups and therefore disrupt the efficiency of the curing process. The equations also show that the linear methylene bridge is the mainstay of the strength of the future cured resin. This means that for a stepwise resin the importance of the methylol group is even less than for one-step resins and that of linear methylene bridges is greater. Methylene ether bridges do not appear to be important because they do not give good correlation and are, hence, not expected to be as numerous under the stepwise manufacturing conditions (they have time to rearrange to methylenes already during resin preparation). The aged results for the stepwise set of resins were much less enlightening, with only one definite correlation [with the (Me + ethers)/Mo ratio].[20] This indicates that in these resins the effect of aging is too complex to be described by the simple method used, possibly due to the greater mixture of products in the reaction mixture, which makes interpretation of the NMR spectra more difficult. Formaldehyde emission was found to be rather low in pure MF resins and meaningful correlation was not possible.

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Received January 11, 1996
Accepted March 30, 1996