

# Formaldehyde-Free Aminoresin Wood Adhesives Based on Dimethoxyethanal

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**ABSTRACT:** Aminoresin precursors prepared by the addition of a new, colorless, nonvolatile and nontoxic aldehyde, dimethoxyethanal (DME), to melamine or urea gave resins for boards that were able to harden, however they were underperforming because of the lower reactivity of DME in relation to formaldehyde. Melamine and urea reacts with one and two (melamine up to three) molecules of DME to form M-DME and U-DME (called DU), but the subsequent cross-linking reaction to form bridges does not occur unless the reaction is catalyzed during resin preparation by the addition of glyoxylic acid. Such bridges between two melamine molecules form only up to the formation of dimers and no more. The use of glyoxylic acid during the reaction has allowed the formation of different oligomers formed by both aldol condensation and condensation of melamine and glyoxylic acid with two molecules of melamine to form dimers. These were observed by <sup>13</sup>C NMR and MALDI-TOF (matrix-assisted laser desorption/ionization mass

spectroscopy). However, the addition of 20% isocyanate (pMDI) was necessary to satisfy the relevant mechanical strength standards of panels prepared with these resins. pMDI contributed to cross-linking of M-DME and DU by its reaction to form urethane bridges according to reactions already described. The adhesive resins so formed had excellent performance and were colorless, and they produced boards that well satisfied the requirements of the relevant standards for interior panels. Formaldehyde emission was down to what would be expected obtained by just heating the wood chips in absence of adhesives. The panels emission was sufficiently low to even satisfy the most severe relevant F\*\*\*\* JIS A 5908 Japanese standard. These adhesives are colorless as MUF and UF resins. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3908–3916, 2008

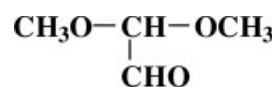
**Key words:** urea-dimethoxyethanal resins; synthetic resins; adhesives; panels; boards; formaldehyde-free

## INTRODUCTION

Aminoresins based on melamine-formaldehyde, melamine-urea-formaldehyde, and urea-formaldehyde condensation are the major binders for wood composite boards such as plywood, medium density fiberboards, and particleboards. However, the main drawback of these resins is formaldehyde, which is their principal component. Formaldehyde has been classified as dangerous to health. Approximately, 11 million tons of urea-formaldehyde resins are produced and used yearly in the world, the greater proportion of these as binders for wood products. The ever decreasing formaldehyde emission limits, hence formaldehyde resin content, imposed by ever stricter standard regulations have induced considerable research not only in the engineering of all aminoresins to yield ever decreasing formaldehyde content

but also in the development of all sorts of alternative resins to urea-formaldehyde.<sup>1–10</sup> One route that has not been much explored is the use of alternative, nontoxic, nonvolatile aldehydes to produce urea-based resins. Alternative aldehydes also have problems, i.e., either they are colored (furfural)<sup>11</sup> rendering the resin unsuitable for a number of board applications or they are also toxic to some level, or they are also volatile,<sup>12,13</sup> or they present potential problems of solubility,<sup>12,13</sup> or they present some reactional problems with urea such as glyoxal.<sup>14</sup>

Recently, a newly conceived aldehyde that is not colored, is water clear, nontoxic, and nonvolatile has been developed and produced,<sup>15</sup> namely dimethoxy ethanal (DME), a derivative of glyoxal.



Its only problem is its level of reactivity with urea, phenols, and melamine that is considerably slower

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than formaldehyde, and this is the only relatively grave problem it presents.

As melamine is more reactive with aldehydes than urea, this article deals with a study to produce melamine-DME (called MDME) resins in which cross-linking and reactivities are enhanced to produce adhesives suitable for particleboard and other wood panels of no to very low formaldehyde emission. It must be pointed out that the aim of this research was the preparation of colorless interior grade aminoresins for wood panels such as particleboard. Glyoxylic acid was used as the catalyst for the reaction, as it was shown to present some advantages both during the reaction as well over more traditional aminoresin hardeners.<sup>14</sup>

## EXPERIMENTAL

### Preparation of the resins

The melamine-dimethoxyethanal-glyoxylic acid (M-DME-AG) (M : DME : AG = 1 : 2 : 0.31) resin was prepared by adding 1034 g of melamine (8.2 mol) under continuous mechanical stirring to a reactor containing 2844.95 g (16.4 mol) of a 60% dimethoxyethanal solution in water and 341 g of water. The pH was adjusted and kept at 9.0–9.5 with 25% NaOH (31 g) and the mix heated at 60°C for 2 h. Then, 366.32 g of 50% glyoxylic acid (2.47 mol) was added and the mix was heated at 60°C for 4 h. The yellow resin was then cooled and stored at ambient temperature. Nine samples were taken from this resin every 30 min, the first one just before adding the glyoxylic acid and the last one just before cooling the resin. These samples were stored in the fridge at 1°C. The M-DME resin without AG was prepared according to the same procedure but without the addition of glyoxylic acid.

For the M-DME-AG resin in which pMDI (polymeric 4,4'-diphenylmethane diisocyanate) was used, two different types of isocyanate were used: the first one is DESMODUR VKS20 (ex Bayer). The second one is a water-dispersible emulsified polyisocyanate, MONDUR 1441 (ex Bayer). When the pMDI used is not indicated in the tables it is always the first that was used. When MONDUR was used it is clearly indicated in the tables.

In the complex adhesive system comprising the M-DME-AG resins, both with and without pMDI, a latex was added to improve the results. The latex used was APPRETAN N 9213 (Clariant) an acrylic ester copolymer of predominantly ethyl acrylate, and in minority styrene and methacrylic acid,<sup>16</sup> having a latex solids content of 45% and pH = 6.

The urea-DME (U-DME) resin, 147 g of urea (2.45 mol), was added in a stirred reactor to 849.3 g (4.9 mol) of a 60% dimethoxyethanal solution in water.

The pH was adjusted and kept at 9.0–9.5 with 30% NaOH solution and the mix heated at 45°C for 2 h. Then, the yellow resin was cooled and stored at ambient temperature.

### Gel permeation chromatography

The samples of the M-DME-AG resin described earlier were also analyzed by gel permeation chromatography (GPC) at different stages of their preparation. A Waters 600 E pump and GPC system was used, and the resins were analyzed through a Polymer Lab Mixed E column (for determination of  $M_w$  between 500 and 20,000) at the elution rate of 1 mL/min, after polyethylene glycol (PEG) calibration of the column. The PEG samples used for calibration had  $M_w$  of 194, 400, 620, 1080, 1470, 4120, 7100, 12,600, 22,800. A waters 410 refractometer was used as the detector.

### Nuclear magnetic resonance

The liquid <sup>13</sup>C NMR spectrum of the MDME used was obtained on a Bruker Avance 400 FT NMR spectrometer. Chemical shifts were calculated relative to (CH<sub>3</sub>)<sub>3</sub>Si(CH<sub>2</sub>)<sub>3</sub>SO<sub>3</sub>Na dissolved in D<sub>2</sub>O for NMR shifts control. The spectrum was done at 100 MHz for a number of transients of approximately 3000. All the spectra were run with a relaxation delay of 2 s and the chemical shifts were accurate to 1 ppm.

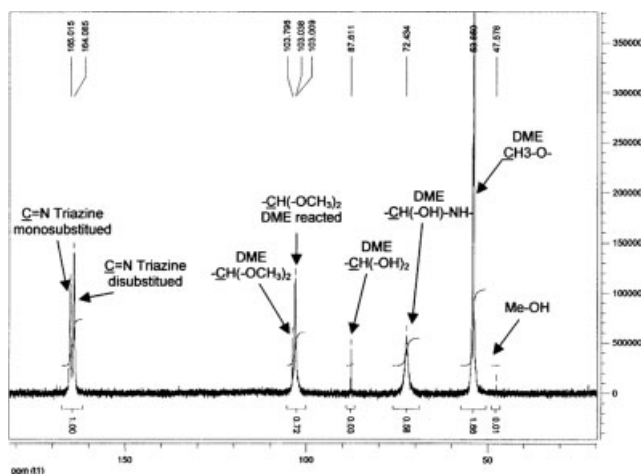
### Maldi-TOF-MS

The spectra were recorded on a KRATOS Kompact MALDI 4 instrument. The irradiation source was a pulsed nitrogen laser with a wavelength of 337 nm. The length of one laser pulse was 3 ns. The measurements were carried out using the following conditions: polarity-positive, flight path-linear, mass-high (20 kV acceleration voltage), 100–150 pulses per spectrum. The delayed extraction technique was used applying delay times of 200–800 ns.

The samples were dissolved in acetone (4 mg/mL). The sample solutions were mixed with an acetone solution (10 mg/mL acetone) of the matrix, as the matrix 2,5-dihydroxy benzoic acid was used. For the enhancement of ion formation, NaCl was added to the matrix. The solutions of the sample and the matrix were mixed in equal amounts and 0.5 to 1 μL of the resulting solution were placed on the MALDI target. After evaporation of the solvent, the MALDI target was introduced into the spectrometer.

### Preparation and testing particleboards

Single-layer boards were made using 2% moisture core wood particles. A mix 70/30 of hardwood



**Figure 1** Quantitative  $^{13}\text{C}$  NMR spectrum of M-DME resin.

[mostly beech (*Fagus sylvatica*)] and softwood [Norway spruce (*Picea abies*)] species was used for wood particles. A rotary drum blender and an automated hot press were used to make the laboratory panels. Resins were hardened by 5% glyoxylic acid as a 50% water solution based on the solid resin, and the resin solids load was 10% and 7% based on oven dry wood mass. The hot-pressing time was 10 min at  $193^\circ\text{C}$ . Three to five panels ( $350\text{ mm} \times 300\text{ mm} \times 14\text{ mm}$ ) were made for each resin and glue mix used. The target density of the panels was about  $700\text{ kg/m}^3$ . For each panel, the formaldehyde emission was measured with the perforator method.<sup>17</sup>

## RESULTS AND DISCUSSION

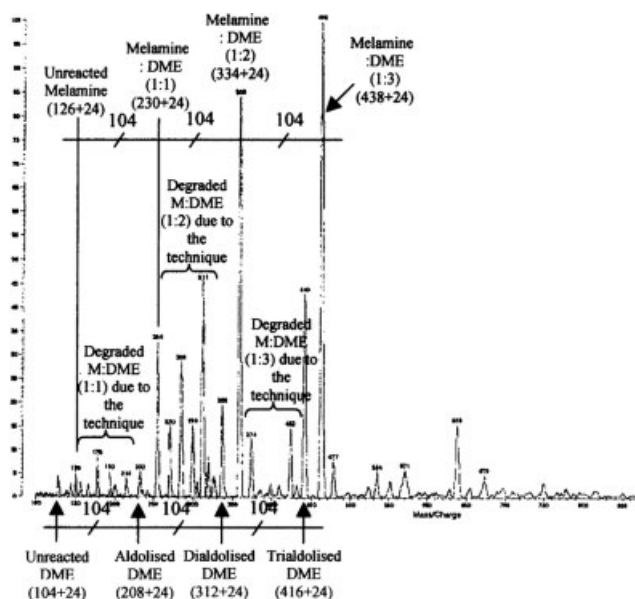
The  $^{13}\text{C}$  NMR spectrum of the M-DME resin of molar ratio M : DME 1 : 2 is shown in Figure 1. The interpretation of the different groups represented by the various bands show the C=N groups of the triazine ring of reacted melamine, namely, at 164.99 ppm band of  $-\text{N}=\text{C}(-\text{N})-\text{NH}_2$  and at 164.07 ppm the band of  $-\text{N}=\text{C}(-\text{N})-\text{NH}-\text{C}^*\text{H}(-\text{OH})-\text{C}^{**}\text{H}(\text{O}-\text{C}^{***}\text{H}_3)_2$ , in which the three carbons  $\text{C}^*$ ,  $\text{C}^{**}$ , and  $\text{C}^{***}$  present bands at 72.39, 102.99, and 54.09 ppm, respectively.

With respect to melamine, the ratio of the integrated areas of the two bands at 164.07 and  $(164.99 + 164.07)$  ppm in Figure 1 indicates that 60%  $(1.49 / (1.49 + 1))$  of the melamine carbons are linked to amine groups which have reacted with DME. As melamine presents three reactive amine groups for each mole of melamine, and the molar ratio of M : DME being 1 : 2, indicates that the great majority of DME has reacted. The proportion of DME that has not reacted can be accurately calculated by the ratio of the integrated areas of the 87.65 ppm band and the 72.4 ppm band, respectively, representing the carbon of the aldehyde (in the form of glycol)

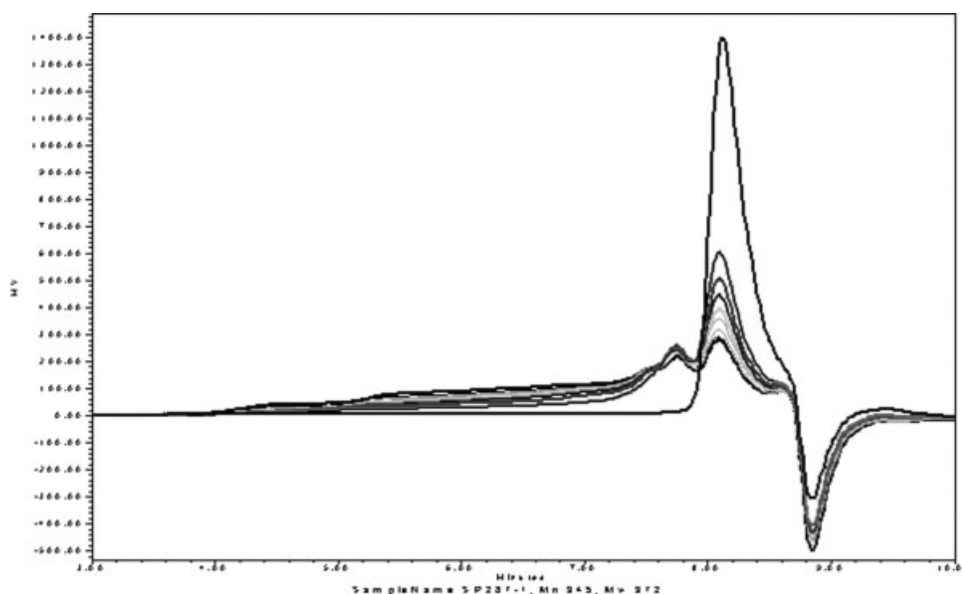
unreacted or reacted only once. This indicates that approximately 7% of the DME is still free in the M-DME resin. Last, the band indicating the formation of an alkyl methine ( $-\text{CHR}-$ ) bridge due to the reaction of the aldehyde with two melamine molecules to form a M-DME-M dimer, which should occur at 49–50 ppm, is absent. This indicates that the reactivity of the DME aldehyde is very low, and therefore, only the addition phase to melamine occurs but not the consequent condensation reaction.

The MALDI-TOF analysis shown in Figure 2 of the same M-DME resin supports the findings by  $^{13}\text{C}$  NMR. To the peak of the melamine ( $126 + 24\text{ Da}$  of the  $\text{Na}^+$  matrix used) follow three peaks separated by a 104 Da repeating motive representing the reaction products of M and DME in the relative molar ratios M : DME 1 : 1 (254 Da), 1 : 2 (358 Da), and 1 : 3 (463 Da). The peak of unreacted DME at 128 Da is as small as that forecasted from the  $^{13}\text{C}$  NMR spectrum in Figure 1. The peaks characteristic of DME molecules, which have undergone aldol condensation, such as those at 232 Da [two DME joined by aldol condensation, 336 Da (3 DMEs joined, dialdol condensation)] and 440 Da (4 DMEs joined, trialdol condensation) are also visible. Their relative intensity in Figure 6 indicate that notwithstanding aldol condensation is in a minority in relation to DME reaction with melamine it is nonetheless a reaction still noticeable under the preparation conditions used.

The distribution of the reaction products and mainly of their molecular weight becomes rather



**Figure 2** MALDI-TOF mass spectrum of the melamine : dimethoxyethanal (1 : 2) resin with the indication of the repeating mass patterns. Note that the difference of 24 g/mol noted everywhere between the Maldi-tof answer and the real molecular mass of the molecules are due to the use of the sodium during the analysis.



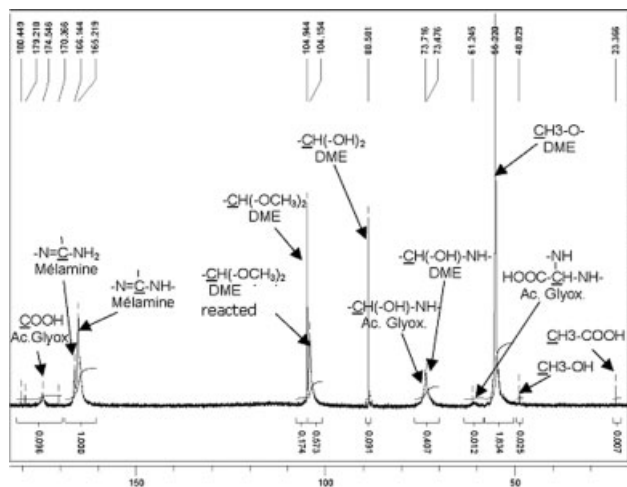
**Figure 3** Gel permeation chromatograms (GPC) of the M-DME-AG resin samples taken each 30 min during the resin manufacture.

different in the case of M-DME-AG resins, thus glycolic acid (AG) has been used as a catalyst of reaction during resin preparation. In this case, GPC analysis of samples of the M-DME-AG resin collected at 30-min intervals after the addition of glycolic acid for 240 min during its preparation, when compared with the chromatogram of the M-DME resin without glycolic acid catalyst, shows a change of pattern and a shift to compounds with higher molecular weights (Fig. 3). Thus in Figure 3 the resin without AG presents a very pronounced peak at 8.15 min elution time and have  $M_n$  and  $M_w$  of 345 and 372, respectively. Such peak corresponds to an average addition product of melamine: DME = 1 : 2 as shown by NMR and MALDI-TOF (Figs. 1 and 2). This peak decreases rapidly and steadily, once AG is added, and higher molecular weight peaks appear at shorter elution times and increase in time. Four hours of reaction after the addition of AG, the  $M_n$  has increased to 938. This clearly indicates that some sort of condensation appears to have occurred.

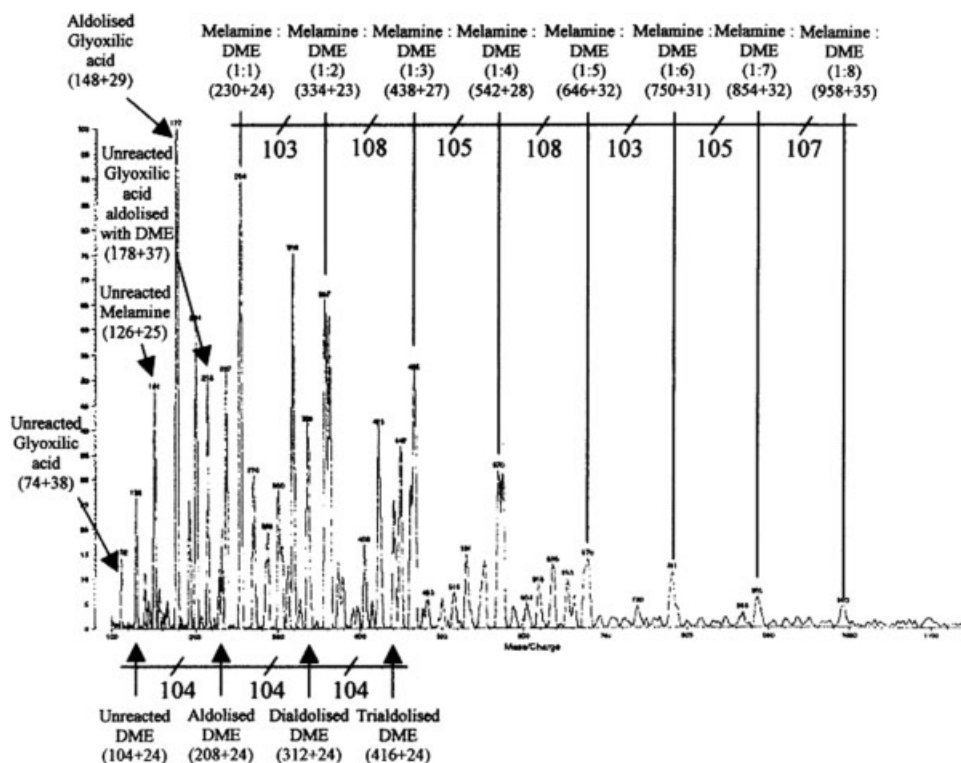
The products obtained were analyzed by  $^{13}\text{C}$  NMR and MALDI-TOF to define the reaction (Figs. 4 and 5). In Figure 5, the  $^{13}\text{C}$  NMR spectrum of the M-DME-AG resin is similar to the spectrum of a M-DME resin in Figure 1, with the exception of what concerns the reaction of glycolic acid. Thus, the carboxyl group of AG appears at 174.55 ppm, and as a shoulder of the DME peak at 73.48 ppm, a small shoulder appeared at 73.72 ppm corresponding to the carbon of the aldehyde of AG after one single reaction with melamine. Last, a small peak appeared at 61.25 ppm corresponding to the carbon of the group of AG or of DME after two reactions with melamine, hence forming an alkylmethine bridge

between two melamines. This weak peak appears to indicate that dimers or higher oligomers start to form once AG is present. Which one is the aldehyde that causes oligomerization, AG or DME, need to be defined. This is because either the increased acidity of the system caused by the AG presence could induce DME to finally give a condensation reaction or because the aldehyde function of AG is more reactive than that of DME. The MALDI-TOF analysis in Figure 5 allows to glean the types of oligomers that are formed.

A rather complex picture of the products mix emerges in Figure 5 from the MALDI-TOF analysis. Unreacted glyoxylic acid at 112 Da, unreacted protonated DME at 128 Da, and unreacted diprotonated



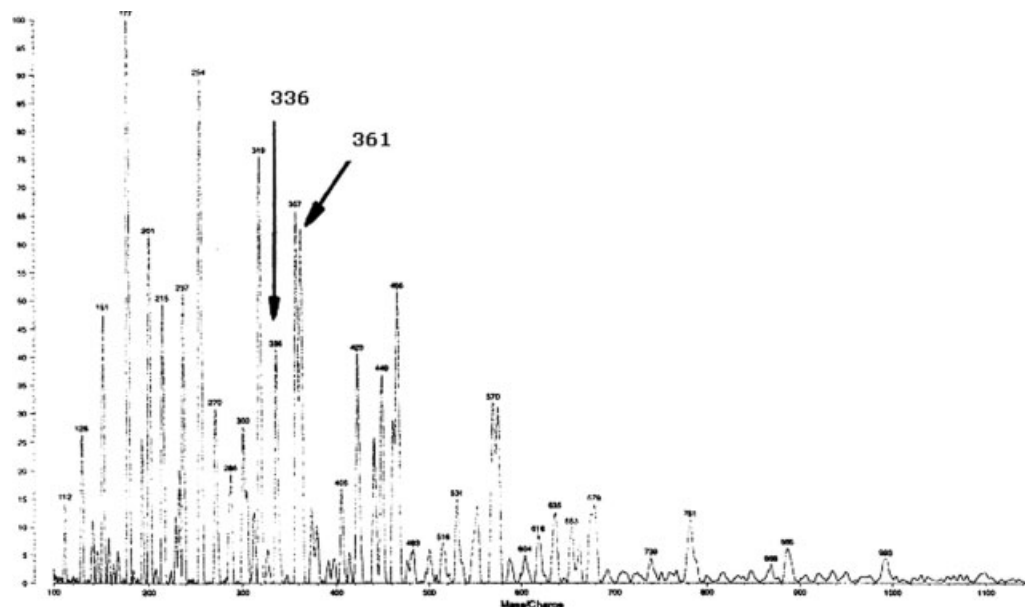
**Figure 4** Quantitative  $^{13}\text{C}$  NMR spectrum of M-DME-AG resin.



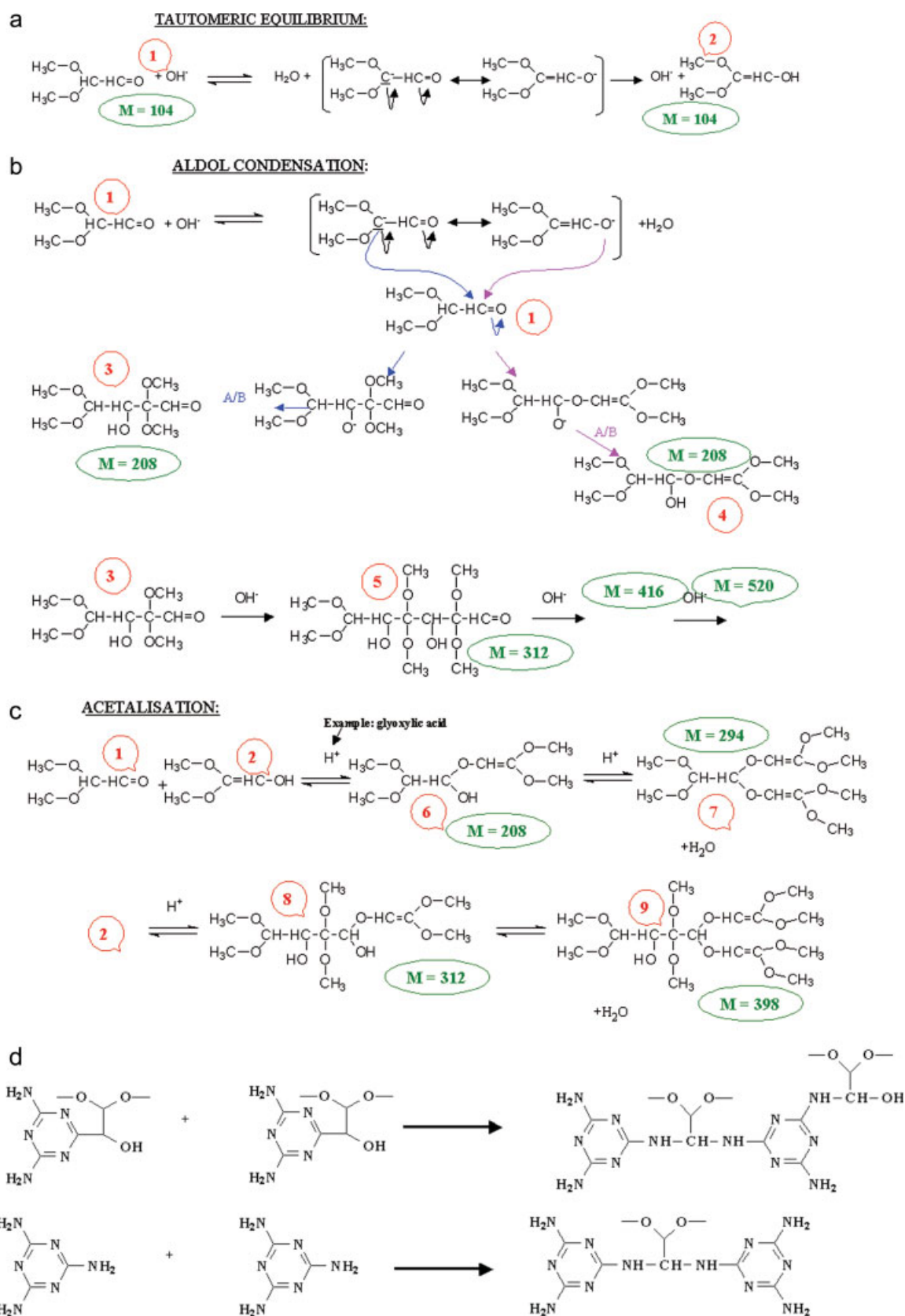
**Figure 5** MALDI-TOF mass spectrum of the M-DME-AG melamine : dimethoxyethanal: glyoxylic acid (1 : 2 : 0.31) resin with the indication of the repeating mass patterns.

melamine at 151 Da are all observed. Peaks at 177 Da and 215 Da appear to indicate the presence of protonated products of the aldol condensation of glyoxylic acid with itself and with DME, respectively. Two, three, and four DME joined through aldol condensation are identified with the 232 Da (two DME

joined), 336 Da (3 DMEs joined), and 440 Da (4 DMEs joined) as in the case of the resin without AG addition. Aldol condensation appears to greatly dominate the formation of oligomers, although an alternate explanation is also possible (see later). Thus, the dominant series of M-DME, M-(DME)<sub>2</sub>,



**Figure 6** MALDI-TOF mass spectrum of the M-DME- (1 : 2 : 0.31) resin with the indication of the peaks corresponding to the two dimers M-AG-M and M-DME-M.

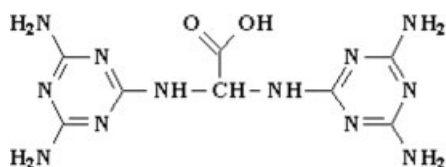


**Figure 7** Schematic representation of the reaction routes through which (a) tautomeric equilibria, (b1, b2) aldol condensation, (c) acetalisation, and (d) condensation products observed by the MALDI-TOF spectrum of the M-DME-AG resin are formed. The numbers indicated with an M correspond to the mass of the different compounds that are or should be found in the MALDI-TOF spectra. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

**TABLE I**  
**Influence of the Use of the Latex 9213 on M-DME:**  
**Quantities of Materials Used to Make the Laboratory**  
**Particle Boards**

	1	2	3	4
Dry wood	1,000	1,000	1,000	1,000
Dry M/DME (1/2) resin	120		82	82
Dry latex 9213		120	38	38
Dry hardener: Glyoxylic acid CHO—COOH				6
Dry hardener: (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	6		6	

and M-(DME)<sub>3</sub> peaks at 254, 357, and 465 Da, respectively, is continued by the dominant pattern of peaks at 570, 678, 781, 886, and 993 Da, each in turn separated by a DME 104 Da (or slightly more, if protonated) repeating unit. This series can only be

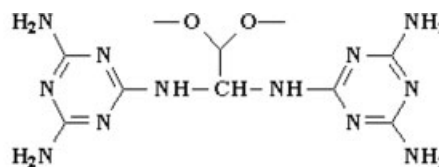


Their relative abundance is 41% (M-AG-M) and 63% (M-DME-M), respectively. This indicates that it is the acidity of AG that is likely to play the major role in promoting the condensation to dimers, otherwise only the compound M-AG-M would be the one formed, and this is not the case. It must also be noted that only condensation oligomers up to dimers are observed, no trimers being present during the 5-h M-DME-AG resin preparation time. Then, the reactivity appears to drop considerably once the dimer is formed. This does not exclude that extending considerably the reaction time some trimers may eventually form. This hypothesis stem from a possible and different interpretation than aldol multicondensation of the series of peaks at 466, 570, 678, and 781 Da. These correspond to the series of compounds M-DME-M-DME, DME-M-DME-M-DME, (DME)<sub>2</sub>-M-DME-M-DME, and (DME)<sub>2</sub>-M-DME-M-(DME)<sub>2</sub>.

An indication that both types of compounds are present, if not for all peaks, namely, these latter

explained in three ways: either (i) a series of M-(DME)<sub>1-6</sub> compounds in which some of the 6 DME linked to a single melamine have also undergone aldol condensation giving rise to compounds such as M-(DME)<sub>5</sub>(DME-DME), M-(DME)<sub>4</sub>(DME-DME)<sub>2</sub>, M-(DME)<sub>2</sub>(DME-DME)<sub>3</sub>, M-(DME-DME)<sub>4</sub>, etc., or (ii) a series of M-[(DME)<sub>n</sub>]<sub>m</sub> compounds in which to a melamine is joined one or two DME longer chains obtained by aldol condensation of the type such as M-(DME-DME-DME-DME) or M-(DME-DME-DME)<sub>2</sub>, or (iii) a mix of the two cases.

However, even if aldol condensation appears to dominate the formation of oligomers, it is not the only reaction occurring. Thus in Figure 6 the two peaks at 336 and 361 Da are representative of the two condensation dimers M-AG-M and M-DME-M, already predicted by NMR.



obtained by condensation, and those obtained by aldol multicondensation is the double peak at 570–572 Da indicating that two different compound of similar mass are present.

Furthermore, reaction of acetalisation, as shown in Figure 7, also do occur as shown by the presence in the MALDI-TOF spectrum in Figure 6 of the two peaks at 336 Da (312 + 24) and 422 Da (398 + 24) corresponding to the molecular weights 312 and 398 of the structures in Figure 7.

A summary scheme of the reactions involved in the condensation phase to oligomers of the initial addition products of melamine and DME in the M-DME-AG resin are shown in Figure 7.

The results in Tables 1–4 show the performance of wood particleboard prepared by using some of these resins. The resin by themselves are relatively weak and they were upgraded by addition of polymeric 4,4'-diphenylmethane diisocyanate (pMDI) to achieve cross-linking and hardening through the formation of

**TABLE II**  
**Influence of the Use of the Latex 9213 on M-DME: Results**

Sample number	Resin load on dry wood (%)	Pressing time (min)	Board density (kg/m <sup>3</sup> )	Internal bond (MPa)
1. M-DME	12	10	721	0.13
2. Latex 9213	12	10	698	0.18
3. M-DME+Latex+(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	12	10	722	0.28
4. M-DME+Latex+glyoxylic acid	12	10	722	0.48

**TABLE III**  
**Influence of the Use of an Isocyanate on U-DME+Latex and M-DME+Latex Resins: Quantities of Materials Used to Make the Laboratory Particle Boards**

	Sample number					
	5	6	7	8	9	10
Dry wood	1,000	1,000	1,000	1,000	1,000	1,000
Dry M-DME (1/2) resin	82	68.5	68.5			
Dry U-DME (1/2) resin				82	68.5	68.5
Dry latex 9213	38	31.5	31.5	38	31.5	31.5
Dry hardener: Glyoxylic acid	6	5	5	6	5	5
Water dispersible isocyanate: (Mondur)		20			20	
pMDI			20			20

urethane bridges with the —CHR—OH groups present on the M-DME resin precursors according to reactions already described.<sup>18,19</sup>

Table 1 shows the first series of glue-mixes used. The results of the particleboards bonded with these are shown in Table 2. The result of boards prepared with a M-DME resin alone are relatively poor at an internal bond (IB) strength of 0.13 MPa against a requirement of 0.35 MPa, the relevant European Norm EN 312<sup>19</sup> for interior panels. Acrylic latex was added to improve the performance of the resin,<sup>20</sup> but when alone this too gives a poor IB strength at 0.18 MPa. Combining the two materials and adding ammonium sulfate, a traditional hardener for aldehyde-based resins improved the results at 0.28 MPa, but the standard requirements were not reached. The M-DME+Latex+glyoxylic acid, this was only added later in the hardener and not during resin preparation, improved sufficiently the IB strength results to satisfy at 0.48 MPa, the relevant European Norm EN 312<sup>20</sup> for interior wood particleboard.

Table 3 shows the second series of glue-mixes used. The results of the particleboards bonded with these are shown in Table 4. Both M-(DME)<sub>2</sub> resins and U-(DME)<sub>2</sub> (called DU) condensation products were prepared and mixed with latex, glyoxylic acid hardener, and either pMDI or a water dispersible pMDI isocyanate.<sup>18–23</sup> The results improve when passing from the addition of only latex to the latex+water dispersible isocyanate (MONDUR) to the pMDI, the IB strength passing from 0.48 to 0.58,

respectively, and finally 0.89 MPa. The same trend is observed for the U-DME (DU) resin with the IB strength passing from 0.24 to 0.41, respectively, and finally 0.66 MPa in the case of the M%-DME resin. These results are well in excess of the European Norm EN 312 0.35 MPa requirement for P2 interior fitment boards (including furniture) and indicate that clear (transparent) aminoresins giving panels of acceptable results can be produced. Of interest are also the results obtained by perforator method (European Norm EN 120<sup>17</sup>) for formaldehyde emission obtained from the panels (Table 4). These are all the same as they correspond just to the formaldehyde emitted by the wood when heated, thus no formaldehyde is emitted from the adhesive itself. All of these are much lower than the limit of 6.5 mg/100 g oven dry board imposed by the European Norm, and they correspond to emission values even lower than those required by the more severe JIS A 5908 F\*\*\*\* standard.<sup>24</sup>

## CONCLUSIONS

In conclusion, the reaction of 20% isocyanate (pMDI) with M-DME and U-DME (DU) condensation products, thus melamine-DME and urea-DME aminoresin precursors containing no formaldehyde, allows the preparation of particleboards of excellent properties. DME is a nontoxic and nonvolatile aldehyde. The panels prepared have very weak formaldehyde emission, only the proportion emitted in heating the

**TABLE IV**  
**Influence of the Use of an Isocyanate on U-DME+Latex and M-DME+Latex Resins: Results**

Sample number	Resin load (%)	Pressing time (min)	Board density (kg/m <sup>3</sup> )	Internal bond (MPa)	Formaldehyde content <sup>17</sup> (mg/100 g)
5. M-DME+Latex	12	10	729	0.48	0.8
6. M-DME+Latex+Mondur	12	10	729	0.58	0.8
7. M-DME+Latex+pMDI	12	10	722	0.89	0.8
8. U-DME+Latex	12	10	696	0.20	0.8
9. U-DME+Latex+Mondur	12	10	704	0.41	0.8
10. U-DME+Latex+pMDI	12	10	716	0.66	0.8



wood chips and no formaldehyde emitted from the adhesive as no formaldehyde was used. The panel properties satisfy well the European Norm for formaldehyde emission and correspond to the F\*\*\*\* requirement according to Japanese standard JIS A 5908. The use of water-emulsified pMDI still gives good results but lower than what obtained with non-emulsified pMDI. It must also be pointed out that the formulations described are clear transparent ones, an important commercial consideration, and can be mixed in any proportion with urea-formaldehyde resins, the cases reported here being the ones in which no formaldehyde has been used.

MALDI-TOF and  $^{13}\text{C}$  NMR analysis have allowed to determine the considerable mix of species present in the M-DME reaction products. The use of glyoxylic acid during the reaction has allowed the formation of different oligomers formed by both aldol condensation and condensation of melamine and glyoxylic acid with two molecules of melamine to form dimers.

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