

## MELAMINE–FORMALDEHYDE RESINS

### Introduction

Melamine-based resins represent an important class of aminoplastic resins (1–6) and are made by the reaction of formaldehyde with mainly melamine, using urea, phenol, or other components as comonomers. The raw material and the basic chemistry of melamine–formaldehyde (MF) resins, their history, their basic industrial manufacturing procedures, as well as their use as laminating resins, molding compounds, coatings, textile finishes, and other applications have been described earlier (7,8) (see AMINO RESINS). This article concentrates on melamine-based resins used as wood adhesives, which is by far the biggest area of application, as well as on various special chemical aspects such as cocondensation and analysis (see also WOOD COMPOSITES). SciFinder (1960–2003) comprises approximately 2500 citations for MF resins (all types), implying the still high significance of research in this area.

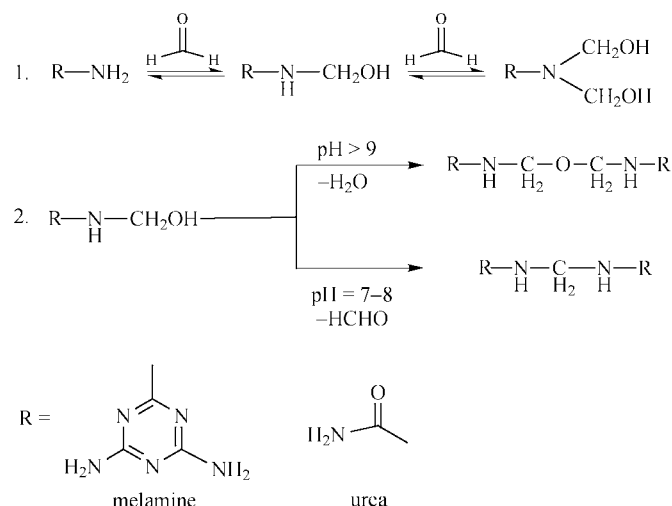
For most applications as wood adhesives, the melamine resins are in liquid form; for special applications powdered (spray dried) types are used. The resins consist of linear or branched oligomeric and polymeric molecules in an aqueous solution, and sometimes partly as a dispersion of molecules in an aqueous phase. The resins show duroplastic hardening behavior, leading to three-dimensional cross-linking and hence to insoluble and nonmeltable networks. The resins, however, always contain some residual monomers, especially free formaldehyde, even in the hardened state.

Even with only the three monomers melamine, formaldehyde, and urea, a variety of different types of resins exists which can fulfill nearly all requirements given in the wood-based panels industry. This field of application involves the production of wood-based panels like particleboards, medium density fiberboard (MDF), oriented strand board (OSB), plywood, blockboards, and others. In rare cases the resins and panels are also used in the furniture industry. According to the raw materials used, various types of melamine resins are possible:

MF	melamine–formaldehyde resin
MUF	melamine–urea–formaldehyde cocondensation resin
mUF	melamine-fortified UF resins
MF + UF	mixture of a MF and an UF resin
PMF	phenol–melamine–formaldehyde cocondensation resin
MUPF, PMUF	melamine–urea–phenol–formaldehyde cocondensation resin

### Composition of the Resins and Basic Reactions

The generation of melamine–formaldehyde resins usually follows a two-step mechanism (Fig. 1). The first step (methylolation step) leads to the formation of



**Fig. 1.** Reaction mechanism for the formation of formaldehyde-based amino resins. 1, methylation; 2, condensation.

methylolated melamine species by reaction with formaldehyde. The second step (bridging) forms ether or methylene bridges by condensation, either water or free formaldehyde is generated depending on pH. Both steps can be either base- or acid-catalyzed and are equilibrium reactions.

The most important parameters for the melamine-formaldehyde resins are

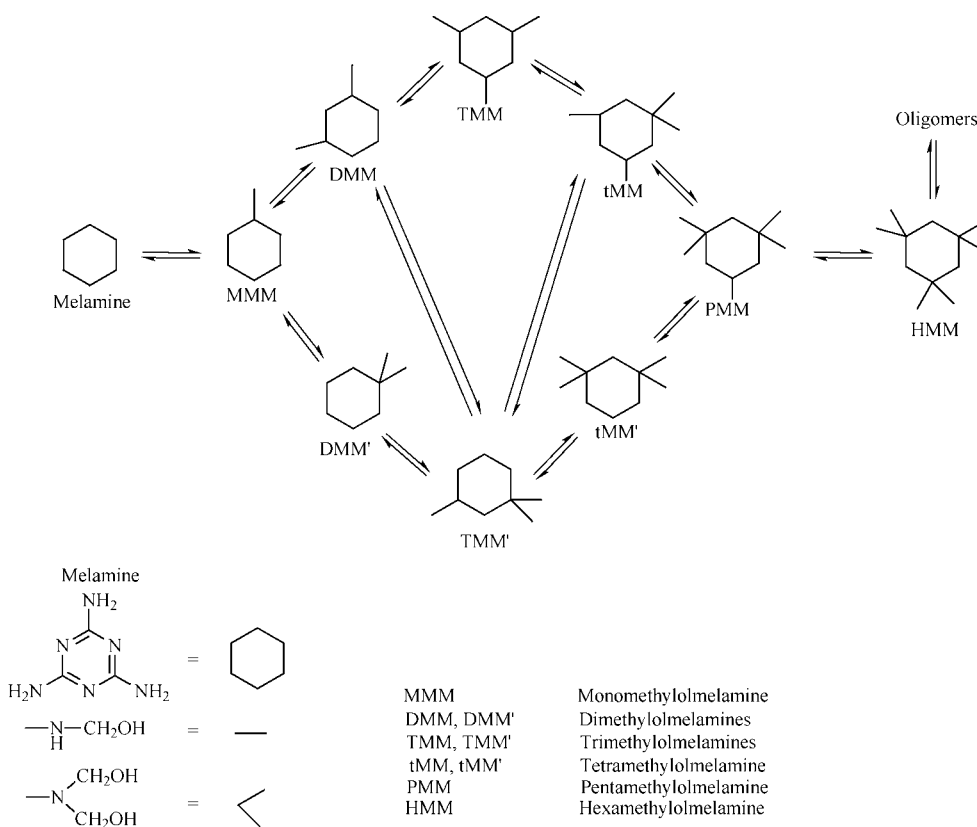
- (1) the type of the monomers (melamine, urea, phenol)
- (2) the molar ratio or mass ratio of the various monomers in the resin:

F/M	Molar ratio of formaldehyde to melamine
F/(NH <sub>2</sub> ) <sub>2</sub>	Molar ratio of formaldehyde to amide groups, whereby urea counts for two NH <sub>2</sub> groups, and melamine for three NH <sub>2</sub> groups
M/U	Molar ratio of melamine to urea
F/U/M	Triple molar ratio
% melamine	Mass portion of melamine in the resin: (a) based on the liquid resin, (b) based on the resin solids content, or (c) based on the sum of urea and melamine in the resin

- (3) the purity of the different raw materials, eg residual methanol or formic acid in formaldehyde or ammeline/ammelide in melamine (9,10), with ammeline-melamine-formaldehyde resins described in the literature (11,12)
- (4) the “cooking” procedure, which usually is a multi step procedure with both alkaline and acidic steps:
  - a. pH-program
  - b. temperature program
  - c. types and amounts of alkaline and acidic catalysts
  - d. sequence of addition of the different raw materials
  - e. duration of the different steps of the cooking procedure

The melamine molecule contains three primary amine groups, each of which has the potential of reacting with two moles of formaldehyde forming up to a hexa-substituted product if the molar ratio F/M is high enough. Because of the significant higher reactivity of these melamine amine groups towards substitution with formaldehyde than urea, the melamine resins show the ability to form polymer structures with a much higher cross-link density compared to UF resins.

The production of pure MF resins is usually performed by the reaction of melamine with formaldehyde in an aqueous solution yielding a precondensate mixture of different monomeric as well as short linear and branched oligomeric melamine-formaldehyde compounds; all these reactions are determined mainly by temperature, length of condensation, pH of condensation, as well as the order and time course of heating and reagent addition (13). Usually all types of methylolated melamine species together with oligomeric parts (usually more than six melamine residues are linked from the beginning of the reaction) are present in the reaction mixture (see Fig. 2). Kinetic investigations (14–17) indicate the following order of reactivity towards methylation of functional groups : (a) the rate of the methylation decreases with increasing number of methylol groups/melamine; (b) the methylation of secondary nitrogens is favored over tertiary nitrogens; and (c) secondary nitrogens (ie, already methylolated  $\text{-NH}_2$  moieties) deactivate the methylation of neighbored nitrogen atoms. Further important parameters



**Fig. 2.** Formation pathways of methylolated melamines.

are changes in the pH due to parallel running Canizarro reactions and the grain size of the melamine used (18,19).

The obtained liquid resins are colorless and normally of low viscosity. Such MF solutions are cured in a second stage by the application of heat, pressure, or an acid catalyst to give an insoluble, highly cross-linked resin. The long-term storage stability of the resins mainly requires stable rheological properties. Possible thixotropic behavior during storage at room temperature and chemical cross-linking or alterations due to further condensation are the drawbacks (20,21).

The molar mass distributions of melamine-based condensation and cocondensation resins are much broader than for other synthetic polymers. The low molar mass monomers comprise free formaldehyde ( $M = 30$  g/mol) as well as residual and nonreacted post-added urea ( $M = 60$  g/mol). Monomeric methylols are generated, eg, in the case of MUF resins, by the reaction of this post-added urea with the free formaldehyde. The oligomeric compounds with two to five molecules of melamine are linked by methylene or methylene ether bridges. Free formaldehyde in the resin has positive and negative effects: on the one hand it induces the hardening reaction by reaction with the aminoplastic hardener and functions as an additional cross-linker; on the other hand it causes formaldehyde emission during the press cycle. Additionally the residual formaldehyde leads to the displeasing subsequent formaldehyde emission from the pressed boards. Because of the stringent formaldehyde emission regulations worldwide, especially Germany/Austria and Japan ["E1"; "E Zero"; "Super E Zero"/"Four star" (22)] and hence the necessity to limit the subsequent formaldehyde emission, the molar ratio  $F/(NH_2)_2$  has been decreased drastically within the last two decades.

The molar ratio of formaldehyde/reactive amino groups  $[F/(NH_2)_2]$  distinctly determines reactivity, the possible degree of cross-linking, and hence the bonding strength. If the molar ratio is decreased in order to lower the formaldehyde emission, the reactivity as well as the degree of hardening (degree of cross-linking) decreases (see Table 1).

An increase in the M/U molar ratio at a fixed  $F/(M + U)$  molar ratio enhances the bond performance. MUF resins with high melamine content have a more highly branched cross-linked structure and free melamine compared to

**Table 1.  $F/(NH_2)_2$  Molar Ratio of Melamine-Based Resins<sup>a</sup>**

1.20 to 1.35	Resins for water-resistant plywood; addition of a formaldehyde catcher is necessary
0.98 to 1.15	E1-particleboard- and E1-MDF-resin for water-resistant boards (PB: EN 312-5 and 312-7; MDF: EN 622-5). Especially for MDF production, formaldehyde catchers are added.
Distinctly below 1.00	Special resins for boards with a very low subsequent formaldehyde emission

<sup>a</sup>(mUF, MUF, MUPF, and others) currently in use in the wood-based panels industry.

resins with low melamine content even if there is no significant difference in the linkage structure (23).

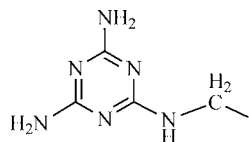
**Influence of the Degree of Condensation.** The higher the degree of condensation (higher molar masses), the higher is the viscosity at the same solid content. Besides a reduced water dilutibility of the resin, the flowing ability and the penetration into the wood surface are diminished. Additional effects are a decreased wetting behavior of a wood surface and a reduced distribution of the resin on the wood surface (particles, fibers). For mixtures MF + UF the degrees of condensation of the two components determine the viscosity of the mix according to the composition.

Correlations between the molar mass distribution (degree of condensation) and mechanical and hygroscopic properties of the produced boards are rather uncertain. The influence of the degree of condensation shows itself during the application and the hardening reaction (wetting behavior, penetration into the wood surface in dependence of the degree of condensation, drying out behavior after the application of the resin onto the surface).

**Hydrolysis Resistance.** The deterioration of a bond line, and hence its durability under the conditions of weathering, is determined essentially by

- (1) failure of the resin (low hydrolysis resistance, degradation of the hardened resin causing loss of bonding strength);
- (2) failure of the interface between the resin and wood surface due to the replacement of physical bonds between resin and reactive wood surface sites by water or other nonresin chemicals; and
- (3) breaking of bonds due to mechanical forces and stresses: the influence of water causes swelling, and therefore movement of the structural components of the wood-based panels (cyclic stresses due to swelling and shrinking, including stress rupture).

The different behavior and resistance against hydrolysis depends on the type of the formaldehyde based resin and is determined at the molecular level. The aminomethylene links in urea-formaldehyde resins (UF) are susceptible to hydrolysis and therefore not stable at higher relative humidity or increased moisture contents, especially at elevated temperatures (24,25). A higher hydrolysis resistance can be achieved by incorporating melamine into the resin (melamine fortified UF resins, MUF, PMF, MUPF, PMUF), whereby the bonding between the nitrogen of the melamine and the carbon of the methylol group shows an increased stability against hydrolysis. The stabilization of the C-N bond arises from the conjugated double bonds of the aromatic ring structure of the melamine. An additional stabilization effect is exerted by the slower decrease of the pH in the bond line due to the buffering capacity of melamine (26).



Higher hydrolysis resistance compared to UF

Because of the high costs of melamine as raw material, the costs for melamine-based resins are, however, much higher than for UF resins. Therefore the content of melamine in these resins is always as high as necessary but as low as possible. Pure melamine-formaldehyde resins are found mainly in mixtures with UF resins. The possible higher hydrolysis resistance as the most important advantage of these pure MF resins is counteracted by their low storage stability in liquid form and their exceedingly high price. The melamine content in the resins can vary between a few percent in melamine-fortified UF glue resins and more than 30%. Additionally, the mode of incorporation of the melamine can be very different. This knowledge is usually proprietary, and therefore description in the literature is rare (27,28). The higher the content of melamine, the higher is the stability (hydrolysis resistance) of the hardened resin against the influence of humidity and water (2, 29, 30). The stability of a resin against hydrolysis can be evaluated by monitoring the formaldehyde emanation during hydrolysis caused by boiling water or the influence of diluted acids at higher temperatures (31).

The reaction progress and end point can be monitored *in situ* under actual reaction conditions using FTIR spectroscopy for functional groups in real time, whereby the concentration of key reaction species can be followed directly using their isolated IR bands (32).

Melamine-fortified resins with a melamine content of up to approximately 10% based on liquid resin are used for various applications where straight UF resins cannot provide the desired combination of processing tolerance, formaldehyde emission, and specific board properties such as a low thickness swelling. MUF resins with higher content of melamine (up to 30% based on liquid resin) find applications in enhanced performance grade boards for use in humid conditions (moisture-resistant application).

**Cocondensation Resins.** Cocondensation of MF resins with urea, phenols, and other components is possible in many ways. One of the most interesting tasks is to clarify whether there is a real cocondensation within these resins or rather whether two independent, interpenetrating networks are formed (see INTERPENETRATING POLYMER NETWORKS). Cocondensation between urea and melamine via methylene bridges and methylene ether bridges has been strongly suggested or proven (33), but precise analysis cannot always be attained (34).

The production of MUF resins of various content of melamine can follow various paths:

- (1) Direct cocondensation of melamine, urea, and formaldehyde in a multi-step reaction with varying sequences of addition of the components (35–41), in particular of melamine and urea (27). Subsequent partial etherification leads to improved storage stability of the MUF resins with a low content of formaldehyde (42) and an improved reactivity (43).
- (2) Direct mixing of an MF resin with a UF resin (28,44–46).
- (3) Addition of melamine in various forms (pure melamine, MF/MUF-powder resin) to a UF resin during the application of the resin. In the case of the addition of pure melamine, the UF resin must have a rather high molar ratio of at least  $F/U = 1.5$  approximately. Otherwise there is not enough formaldehyde available to react with the melamine in order to incorporate it into the resin.

- (4) Melamine can also be added in the form of melamine salts, such as acetates, formiates, or oxalates (47–53), which decompose in the aqueous resin mix at higher temperatures. The melamine is then incorporated into the UF resin, forming an MUF resin and generating acids as latent hardeners. Furthermore it has been reported that using this procedure with melamine salts, the amount of melamine needed is much lower than in other MUF resins (47–52). MUF resins can also contain various other compounds that can react with formaldehyde such as urea derivatives, guanamines, or amides (54,55).

MUPF resins (PMUF resins) are mainly used for the production of particle-boards according to DIN 68763 and EN 312 (quality P5 and P7, option 2 “V100”), as well as of OSB (quality type OSB3 and OSB4 according to EN 300). They usually contain small amounts of a phenol component. Production procedures are described in patents and in the literature (56–66). Newly developed MUPF resins enable a distinct reduction of the necessary resin consumption in the OSB face layers (67,68).

PMF/PMUF resins usually contain little or no urea. The analysis of the molecular structure of these resins has shown that there is no cocondensation between the phenol and the melamine, but that there exist two separate networks (69–72). This can be explained on the basis of a different reactivity of the phenol methylols and the melamine methylols, depending on the existing pH.

Under acidic conditions there are two steps in the hardening of a PMF resin (73): in the first, quick step, the condensation of the melamine dominates; in the second, rather slow step, the phenol is incorporated into the network. Under alkaline conditions a cocondensation between phenol and melamine could be detected (74,75). A PMUF resin with a distinctly higher portion of phenol and also a high content of melamine can be produced by starting with a PF condensation, followed by addition of melamine and further formaldehyde; urea is then added at the end of the procedure to decrease the molar content of free formaldehyde (76).

There are interesting niche markets for resins with very low content of formaldehyde and hence boards with extremely low subsequent formaldehyde emission. Since pure UF resins are too weak to be used for this purpose (low mechanical strength, high thickness swelling), melamine-fortified resins or MUF resins are used. The necessary content of melamine in these resins can vary distinctly and depends on the level of subsequent formaldehyde emission, on the board type as well as on other board requirements; eg, a certain thickness swelling (77–80).

Melamine-based resins with extreme low molar ratios  $[F/(NH_2)_2 < 0.5]$  can be used as so-called formaldehyde scavenger resins (81). They are mixed mainly with UF resins during the application for the production of wood-based panels with low subsequent formaldehyde emission.

MUF honeymoon adhesive systems for bonding of timber of high moisture content (wet gluing) to produce laminated wood (glulam) and finger-jointing are composed of two components: (1) a MUF resin at a pH of approximately 10 with no fillers added, and (2) a low pH aqueous solution of carboxymethylcellulose and formic acid lacking resorcinol in the system (82–85).

### Correlations Between the Composition of Melamine Resins and Properties of Hardened Glue Lines and Wood-Based Panels

Only a few investigations have been done concerning the prediction of adhesive bond strengths and other properties based on the composition of the resin. Equations for evaluating a possible correlation between the chemical structures in various MUF resins with different molar ratios  $[F/(NH_2)_2]$  and different types of preparation and the achievable internal bond together with the subsequent formaldehyde emission have been investigated. For this purpose, various structural components have been determined by means of NMR, and several ratios of the amounts of the various structural components have been calculated, eg,

- (1) for MF resins (86):
  - a. unreacted melamine to monosubstituted melamine
  - b. unreacted melamine to total melamine
  - c. methylene bridges related to methylol groups
  - d. degree of branching: number of branching sites at methylene bridges related to total number of bondings at methylene bridges
- (2) for MUF-resins (87,88) typical ratios determined are
  - a. sum of unreacted melamine and urea to the sum of substituted melamine and urea
  - b. methylene bridges related to methylols or to the sum of methylene bridges and methylols.

### Applications

Depending on the various requirements different resin types are selected for use. Boards with low requirements (interior use) are usually UF-bonded. The incorporation of melamine (MUF, MF + UF), and sometimes phenol (MUPF), improves the low resistance of UF bonds to the influence of humidity, water, and weather. Fields of application for the various melamine-based wood adhesives resins are boards with reduced thickness swelling; eg, as laminate flooring cores and boards for use in humid conditions [according to EN 312 for particleboard, EN 300 for OSB, EN 622-5 for MDF, EN 314 for plywood and prEN 12775, prEN 13353, prEN 13017, and prEN 13354 for blockboard (solid wood panels)].

Impregnation of wood with MF impregnating resins has shown considerable potential to improve various wood properties such as surface hardness and weathering resistance. Using UV micro spectroscopy, it has been shown that water-soluble MF resins diffused well into the secondary cell wall and the middle lamella of wood (89–92).

Laminate floorings require a very low long-term (24 h) thickness swelling of the MDF/HDF- or particleboard cores. Requirements usually are less than 8% or 10%, respectively, sometimes less than 6% or even lower. Such a low thickness swelling usually cannot be obtained with UF resins; the incorporation of melamine is a suitable way to achieve the desired results. The necessary melamine content



**Table 2. MUF–Glue Resin Mixes for Particleboard, MDF, and Plywood**

Components/resin mixes	A <sup>a</sup>	B <sup>b</sup>	C <sup>c</sup>	D <sup>d</sup>
MUF resin <sup>e</sup>	100	100	—	—
MUF resin <sup>f</sup>	—	—	100	—
MUF resin <sup>g</sup>	—	—	—	100
Extender <sup>h</sup>	—	—	—	10
Water	—	10–20	20–50	up to 10
Urea solution <sup>i</sup>	up to 5	up to 5	up to 10	—
Hardener solution <sup>j</sup>	15	6	up to 4	—
Powder hardener <sup>k</sup>	—	—	—	3

<sup>a</sup>Glue mix A: particleboard for use in humid conditions (core layer).

<sup>b</sup>Glue mix B: particleboard for use in humid conditions (face layer).

<sup>c</sup>Glue mix C: MDF board for use in humid conditions.

<sup>d</sup>Glue mix D: plywood, class 2 or class 3 (EN 314).

<sup>e</sup>MUF resin with F/(NH<sub>2</sub>)<sub>2</sub> ≈ 1.03–1.08.

<sup>f</sup>MUF resin with F/(NH<sub>2</sub>)<sub>2</sub> ≈ 0.95–1.03.

<sup>g</sup>MUF plywood resin with F/(NH<sub>2</sub>)<sub>2</sub> ≈ 1.2–1.4.

<sup>h</sup>Extender: rye or wheat flour, containing in case some inorganic fraction.

<sup>i</sup>Urea solution (40%).

<sup>j</sup>eg, Ammonium sulfate solution (20%).

<sup>k</sup>eg, Ammonium sulfate in powder form.

in the resin depends on various parameters; eg, the type of wood furnish, the pressing parameters (pressure profile, density profile), and the resin consumption. Another important parameter is the cooking procedure of the resin, which considerably influences the thickness swelling of the boards even at the same gluing factor and the same content of melamine. It is especially important to use the formaldehyde present in the system as efficiently as possible by maximizing the content of methylene bridges compared to methylene ether bridges.

**Combination of Melamine Resins with Other Adhesives.** PMDI can be used as an accelerator and as a special cross-linker for MUF resins, with additions of approximately 1–2% based on dry particles (46,93–95).

For the purpose of special effects, combinations of adhesives or glue resins might be used; eg, the combination of adhesives in the particleboard or OSB production with PMDI in the core layer and a MU(P)F resin in the face layer.

**Glue Resin Mixes for the Application of Melamine Resins.** Table 2 summarizes some glue resin mixes for different applications in the production of particleboard, MDF, and plywood.

## Hardening of Melamine Resins

During the curing process of a thermosetting adhesive resin, a three-dimensional network is built up. This yields an insoluble resin which is no longer thermoformable. The acid hardening conditions can be adjusted (1) by the addition of a so-called latent hardener (eg, ammonium sulfate or ammonium nitrate), or (2) by the direct addition of acids (maleic acid anhydride, formic acid, phosphoric acid and others) or of acidic substances, which dissociate in water (eg aluminium

sulfate). Ammonium sulfate reacts with the free formaldehyde in the resin to generate sulfuric acid, which decreases the pH. These acidic conditions hence enable the condensation reaction to restart, and finally the gelling and hardening of the resin. The rate of decrease of the pH during the hardening process depends upon the amount of available free formaldehyde and on the amount of hardener. An acceleration of the hardening process is achieved by heat (26,96), whereas the addition of melamine to a UF resin slows down the pH drop after the addition of the hardener (26) and thus yields an increase in the gel time.

The mechanism of the hardening reaction of MUPF/PMUF resins is not entirely clear. Such resins harden under similar acid conditions as MUF resins, whereas phenolic resins have a minimum of reactivity under these conditions; hence the phenolic portion of the resin might not really be incorporated into the aminoplastic portion of the resin during hardening (66).

During the hardening of PMF resins, no cocondensation reaction occurs. Therefore in the hardened state, two independent interpenetrating networks exist (69–72,97). Indications for a cocondensation via methylene bridges between the phenolic nucleus and the amido group of the melamine have been found by  $^1\text{H}$  NMR only in model reactions between methylolated phenols and melamine (97).

The hardening of MUF resins can be enhanced by the addition of formaldehyde-based accelerator mixtures and monitored via rheology, gel time measurements, as well as the so-called ABES tests (98,99). Analyses indicate that cured MUF resins are mainly composed of separate MF and UF networks. Thus particleboards glued with an MUF/accelerator mixture exhibit improved mechanical properties compared to boards produced with commercially used MUF adhesives. The swelling properties of particleboards glued with an MUF/accelerator mixture are comparable to boards made from a commercial MUF resin (100).

Imino-amino methylene base intermediates obtained by the decomposition of hexamethylenetetramine (hexamine) stabilized by the presence of strong anions (hexamine sulfate) have been shown to markedly improve the water and weather resistance of hardened MUF resins used as wood adhesives (101–105). Even with only small additions between 1% and 5% the use of MUF resins of much lower melamine content with constant performance of the boards is possible.

### Analytical Chemistry of MF Resins

The analytical chemistry of MF resins requires modern and sophisticated analytical methods because of the chemical complexity of the resin mixture. Several tens of components, ranging from defined low molecular component to oligomeric and polymeric components, can be identified within the resin mixture. Usually analytical methods are performed to achieve information on the following points: (1) the detailed composition (structure and amount) of low molecular components, (2) the estimation of the amount of characteristic functional moieties, and (3) the structure of the hardened thermoplastic networks. A complete overview of analytical methods concerning MF resins can be found in the literature (1).

Nuclear Magnetic Resonance (qv) (86,106) in the liquid state has proven one of the most efficient and valuable tools for analyzing the composition of MF and related resin materials. Besides  $^1\text{H}$  NMR (16,107) spectroscopy, whose




**Table 3.**  $^{13}\text{C}$  Chemical Shifts for Selected Functional Groups in MF Resins

Assignment	$^{13}\text{C}$ Chemical shift (ppm) <sup>a</sup>
$-\text{NHCH}_2\text{NH}-$	47
$=\text{NCH}_2\text{NH}-$	52
$=\text{NCH}_2\text{OCH}_3/-\text{N}(\text{CH}_2\text{OCH}_3)_2$	58
$=\text{NCH}_2\text{N}=\text{}$	64
$=\text{NHCH}_2\text{OH}$	68–69
$-\text{N}(\text{CH}_2\text{OH})_2$	68–69
$-\text{NHCH}_2\text{OCH}_2\text{NH}-$	73
$=\text{NCH}_2\text{OCH}_2\text{NH}-$	73
$-\text{NHCH}_2\text{OCH}_3$	77.3
$-\text{N}(\text{CH}_2\text{OCH}_3)_2$	77
$\text{HOCH}_2\text{OH}$	82
$(\text{CH}_2\text{O})_n$ oligomers	85.2

<sup>a</sup>Chemical shift in ppm relative to TMS in DMSO.

resolution is limited by the small spectral range ( $\sim 15$  ppm),  $^{13}\text{C}$  NMR spectroscopy (15,108,109) (spectral range  $\sim 200$  ppm) is very effective for the analysis of hydrated or lyophilized samples in dimethyl sulfoxide (DMSO) or aqueous solution. Table 3 and Table 4 show the relevant resonances together with the assignment to the corresponding structural units (17,110). Values are shown for methylolated as well as methoxylated MF resins. Additional information on MUF (87) and M(U)PF resins (69–71,111) is reported in the literature. Degrees of branching as well as distinct molecular species can be identified with this method. The molecular mobility of resins components can be analyzed by gel-phase NMR spectroscopy on native MF resins (13). The changes of the concentration of various structural elements during the condensation of an MF resin can be followed by  $^{13}\text{C}$  NMR (112).

**Table 4.**  $^{13}\text{C}$  Chemical Shifts of the Triazine Region

Assignment		$^{13}\text{C}$ Chemical shift (ppm) <sup>a</sup>	
		R = H	R = $\text{CH}_3$
	Melamine	167,4	167,4
	MMM	167,2	overlapped
	<i>N,N'</i> -DMM	167,0	overlapped
	MMM	166,3	166,7
	<i>N,N'</i> -DMM	166,0	166,7
	<i>N,N',N''</i> -TMM	165,8	166,7
	<i>N,N,N',N''</i> -TMM	165,2	167,4
	PMM	165,2	167,4
	HMM	165,2	167,4

<sup>a</sup> $^{13}\text{C}$  Chemical shift in 40% DMSO/60%  $\text{H}_2\text{O}$ .

The lower the pH during the condensation, the higher is the portion of methylene bridges compared to ether linkages.

Hardened MF resins can be analyzed by solid-state NMR spectroscopy (113,114) detecting  $^{13}\text{C}$  NMR and  $^{15}\text{N}$  nuclei (requiring  $^{15}\text{N}$ -enriched material). The chemical shift values from Table 3 and Table 4 are valid because of the equivalence between chemical shifts in solution and solid-state NMR spectra. The usual limited resolution of these spectra, however, limits the detailed analysis possible by liquid NMR spectroscopy. An analysis of molecular mobility within the hardened networks can be achieved by  $^{13}\text{C}$  solid-state NMR spectroscopy.

IR spectroscopy is used frequently for the analysis of MF-type resin materials. Despite its broad use and availability, the information is quite limited for the analysis of distinct chemical species because of broad bands and overlap with water signals (see VIBRATIONAL SPECTROSCOPY). Information on cocondensation between phenolic resins and melamine (72,115), the structural analysis of hydroxymethylated melamines (116,117), as well as the chemistry of hardening (118) can be followed.

The analysis of MF resins as well as alkoxyalted MF resins by chromatographic methods has been described vastly in the literature (119,120) and allows the separation and identification of oligomeric methylolated melamines by conventional UV- or refractive index based detection. The most direct method for the determination of methylolated melamines within a MF resin is the coupling between HPLC methods and Mass Spectrometry (qv), enabling the direct structural analysis by HPLC-MS methods on methoxylated (121–124) and butoxylated MF resins (see CHROMATOGRAPHY, HPLC) (125). Favored ionization methods use ESI-MS ionization methods to achieve an efficient ionization process. The detection of up to pentameric melamine units can be achieved by this method.

High pressure DSC coupled with both HPLC and GPC can characterize the polymerization or cure of MF resins (126). DSC was used to calculate the kinetics of the reaction resin during curing, and GPC monitored the change in molar masses.

The effects of cure temperature and amount of catalyst on the rheokinetic behavior of an MF resin can be followed using dynamical mechanical techniques (127), and time–temperature–transformation (TTT) cure diagrams can be constructed using the results of these methods (127–129) (see DYNAMIC MECHANICAL ANALYSIS).

Other, more historic methods for analyzing the chemical composition of MF resins rely on size-exclusion chromatography (SEC) (130,131) and thin-layer chromatography (132) (see CHROMATOGRAPHY, SIZE EXCLUSION).

## Economic Aspects

Out of the approximately 6.5 million ton of formaldehyde-based resins (in dry form) used as adhesives in the wood-based panels industry, more than 900,000 ton are based on melamine (133). The resins are produced mainly by the chemical industry itself, as well as partly by the wood-based panels industry on its so-called megasites. In 1999 approximately 28%, or 196,000 ton, of the melamine that was produced worldwide was converted into wood adhesives (133).

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