MELAMINE RESINS

1. 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) (see AMINO RESINS AND PLASTICS). 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-BASED COMPOSITES AND LAMINATES). SciFinder (1960–2003) comprises approximately 2500 citations for MF resins (all types), implying the still high significance of research in this area. A section on investigations of hardening MF resins for other uses, however, is also included.

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

2. 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 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
$F/(NH_2)_2$	Molar ratio of formaldehyde to amide groups, whereby urea counts for two NH_2 groups, and melamine for three NH_2 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 (8,9), with ammeline–melamine–formaldehyde resins described in the literature (10,11)
4. The “cooking” procedure, which usually is a multi step procedure with both alkaline and acidic steps:
   (*1*) pH-program;
   (*2*) temperature program;
   (*3*) types and amounts of alkaline and acidic catalysts;
   (*4*) sequence of addition of the different raw materials; and
   (*5*) 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 (12). 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 (13–16) indicate the following order of reactivity towards methylolation of functional groups : (a) the rate of the methylolation decreases with increasing number of methylol groups/melamine; (b) the methylolation of secondary nitrogens is favored over tertiary nitrogens; and (c) secondary nitrogens (ie, already methylolated $-NH_2$ moieties) deactivate the methylolation of neighbored nitrogen atoms. Further important parameters are changes in the pH due to parallel running Canizarro reactions and the grain size of the melamine used (17,18).

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 (19,20).

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” (21)] 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 resins with low melamine content even if there is no significant difference in the linkage structure (22).

2.1. 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.

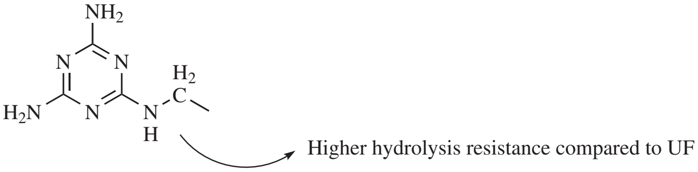
Correlations between the molar mass distribution (degree of condensation) and mechanical and hygroscopic properties of the produced boards are rather uncertain. The influence of the degree of condensation shows itself during the application and the hardening reaction (wetting behavior, penetration into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

2.2. 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 (23,24). 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 (25).



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 (26,27). The higher the content of melamine, the higher is the stability (hydrolysis resistance) of the hardened resin against the influence of humidity and water (2,28,29). 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 (30).

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 (31).

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).

2.3. 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 (32), but precise analysis cannot always be attained (33).

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

1. Direct cocondensation of melamine, urea, and formaldehyde in a multistep reaction with varying sequences of addition of the components (34–40), in particular of melamine and urea (26). Subsequent partial etherification leads to improved storage stability of the MUF resins with a low content of formaldehyde (41) and an improved reactivity (42).
2. Direct mixing of an MF resin with a UF resin (27,43–45).
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 (46–52), 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 (46–51). MUF resins can also contain various other compounds that can react with formaldehyde such as urea derivatives, guanamines, or amides (53,54).

MUPF resins (PMUF resins) are mainly used for the production of particleboards 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 (55–65). Newly developed MUPF resins enable a distinct reduction of the necessary resin consumption in the OSB face layers (66,67).

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 (68–70). 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 (71): 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 (72,73). 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 (74).

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 (75–78).

Melamine-based resins with extreme low molar ratios $[F/(NH_2)_2 < 0.5]$ can be used as so-called formaldehyde scavenger resins (79). 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 (80–83).

2.4. 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, For MF resins (84): Unreacted melamine to monosubstituted melamine; unreacted melamine to total melamine; methylene bridges related to methylol groups; and degree of branching: number of branching sites at methylene bridges related to total number of bondings at methylene bridges.

For MUF-resins (85,86) typical ratios determined are sum of unreacted melamine and urea to the sum of substituted melamine and urea; and methylene bridges related to methylols or to the sum of methylene bridges and methylols.

3. Hardening of Melamine Resins

3.1. For Wood Panel Use.

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 thermo-formable. 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 (25,87), whereas the addition of melamine to a UF resin slows down the pH drop after the addition of the hardener (25) 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 (65).

During the hardening of PMF resins, no cocondensation reaction occurs. Therefore in the hardened state, two independent interpenetrating networks exist (68–70,88). Indications for a cocondensation via methylene bridges between the phenolic nucleus and the amido group of the melamine have been found by ^{1}H NMR only in model reactions between methylolated phenols and melamine (88).

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 (89,90). 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 (91).

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 (92–96). 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.

3.2. An Investigation of Hardening for Other MF Uses. If the impact strength of MF resins could be increased without seriously compromising the high modulus, these materials may become suitable for application as engineering plastics in the automotive industry, for example. Despite the potentially high reward, not much work has been reported in the literature on the toughening of MF resins. There is some patent literature, which deals with mixing MF resins with various thermoplastic polymers such as polyamides and polyesters. Although the shrinkage during curing was decreased, the impact strength of MF systems was barely affected. The control of morphology during mixing at elevated temperatures is expected to be difficult because of highly reactive character of MF resins.

An alternative approach that is based on mixing an aqueous MF resin solution with an emulsion of a certain impact modifier at room temperature. After spray drying, a homogeneous powder is produced that can be compression molded at the desired temperature, ie, 140°C. Since a number of practical applications of MF resins, such as paper impregnation, are also carried out from solution, this approach has the additional advantage that it can easily be incorporated in existing production lines. The approach was tested on acrylic core/shell rubber particle resins.

Modeling. In order to obtain a general idea about the flexibility of an MF network, a model of an idealized segment of the network was developed.

The size of the modeled structure was of course limited, primarily because of experimental restrictions. The structures were constructed by starting with a melamine molecule in which each amine group is chemically linked to only one melamine molecule. By repeating this operation, a dendritic structure is formed with a single melamine molecule positioned in the core of the dendritic structure. By changing the contribution of attractive and repulsive forces, the radius of gyration (R_g) of simulated segments in both poor and good solvents was calculated. This procedure was applied previously to dendritic polymers, and proved to be quite reliable. The simulated structures are shown in Figure 3. To study the effect of chemistry, the structures were built either exclusively from methylene or ether bridges. Obviously the MF structures of both types are sufficiently flexible to expand in good solvent and contract in a poor environment. This can also be concluded from the R_g values shown in Table 2.

On the basis of simulated R_g values the volume of the system in solvents of different quality was determined. The ratio of the volumes in poor and good solvents (V^{good}/V^{poor}) could be seen as a measure of the swelling behavior. It should be noted, however, that the experimental networks would not have the ability to expand as much as the limited modelling structures do. Furthermore, in the modeled structures each amine group has reacted only once. In principle, a real MF network can have a more dense structure due to the high functionality of melamine. ie, 6. Nevertheless, based on the V^{good}/V^{poor} values, it was deduced that the local mobility of MF networks should sufficiently high to permit a toughening effect to be induced using the standard approaches, such as rubber toughening technology. Interestingly, it can be seen that the V^{good}/V^{poor} value is higher for structures with ether bridges when compared with MF segments consisting of methylene linkages. Apparently, ether bridges result in a more flexible MF network.

Morphological Characterization. A homogenous dispersion of rubber particles is a requirement for increasing the toughness and at the same time maintaining the good mechanical properties of MF resins. As can be seen in Figure 4**a**, a fairly good dispersion of rubber particles is achieved using EF-AR emulsions. For comparison, the dispersion of standard ABS particles, processed under similar conditions in MF resins, is shown in Figure 4**b**. Apparently, grafting with epoxy groups improves both the dispersion and interfacial strength of rubber particles to MF matrix. The best homogenous dispersion of rubber particles is achieved using MF/EF-AR emulsions with a pH of 7–8. The spray drying the emulsions with a pH above 8 and subsequent curing resulted in a poor dispersion of rubber particles. These results indicate that improved dispersion of rubber particles is probably due to the chemical reaction between epoxy groups and amine and/or methylol functionalities of MF resins, taking place preferably below a pH of 8. It is difficult, if not impossible, to provide direct evidence of chemical reaction between epoxy groups and MF resins, using spectroscopic techniques for example, because of the very low concentration of epoxy groups grafted on the surface of rubber particles ($<2\%$).

As can be seen in Figure 4**a**, the diameter of EF-AR particles is about 350 nm. Although one might expect a real effect of particle size in the rubber toughening of glassy polymers (97), however, it was necessary to study whether there is any improvement in toughness using present EF-AR particles. The amount of rubber in MF resins was varied. It appears that the particles start to percolate above a loading of 15 wt%. It has been suggested that this transition is important for rubber toughening of polymers (98). Interestingly a rather interesting morphology is formed at a loading of 50 wt%. It seems that rubber particles start to cluster in regions of about 2–8 μm.

Figure 5 shows the dynamic mechanical analysis (DMA) runs of cured MF resins with and without rubber particles. Because of vitrification phenomenon (99) and the fact that the curing reaction was carried out at 140°C, heating above this temperature should result in a slight decrease of the modulus and continuation of reaction (see Figure 5**a**). The second heating run for virgin MF resin indicated that the glass transition (T_g) should lie above 300°C. Since it quite difficult to establish, or even define, full chemical conversion for MF resins, it is not a trivial task to determine the glass transition of a fully cured system (Tg^{∞}). It is, however, clear that the structure of MF network is so rigid that Tg^{∞} must be located above the degradation temperature of the system. The inclusion of ABS and EF-AR particles results in a slight decrease of glass modulus. The transitions observed at -75°C and -50°C correspond to the Tgs of ABS and EF-AR particles respectively. Although, as indicated by TEM experiments, the level of dispersion of both types of impact modifiers in MF matrix differs strongly, the DMA runs suggest that these rubber particles have a similar effect on mechanical properties.

Toughness and Mechanical Characterization. The results of three point flexural tests on and Izod impact strength data from virgin and rubber modified (20 wt% loading) cured MF resins are shown in Table 3.

The inclusion of 20 wt% rubber has a significant effect on the modulus. The elongation at break also decreases slightly upon addition of rubber particles. Although there is no significant effect of the type of impact modifiers, the ABS rubber particles appear to make the mechanical properties deteriorate somewhat more strongly. This may be attributed to the poor dispersion of ABS particles when compared with the distribution of the EF-AR system in MF matrix. The margin of error for Izod impact strength measurements on virgin MF resins is rather large due to the difficulty of producing crack-free test bars. Nevertheless, it appears that 20 wt% rubber of either type also has a negative effect on Izod impact strength. Since the Izod measurements are rather crude and are not expected to discriminate between the performance of the various impact modifiers under investigation here, the critical values for the stress intensity factor (K_{ic}) for MF resins modified with different concentrations of EF-AR particles were determined. For the present systems, mode of failure was expected to be sufficiently brittle to process raw data using the linear elastic fracture mechanics (LEFM) theory (100).

Figure 6 shows the K_{ic} values as a function of EF-AR loading in cured MF resins. It appears that K_{ic} tends to decrease as a function of rubber concentration, with a minimum being reached at 15 wt% EF-AR. A further increase of the rubber loading causes the K_{ic} to increase, but the value at 35 wt% is still lower than the impact strength of unmodified MF resins. In fact at 50 wt% EF-AR, the material was so soft that a determination of a valid K_{ic} value was not possible.

The fracture surface of virgin cured MF resins and resins modified with different types of rubber. As can be expected, the unmodified MF resin breaks in a very brittle manner leaving a highly smooth surface. The inclusion of ABS particles leads to some roughening of the fracture surface, therefore increasing the fracture energy. According to TEM images, however, the structure is rather inhomogeneous. The most homogenous and regular structure is achieved using the EF-AR system. It is, however, clear from toughness measurements that even this improvement of the morphology does not lead to an increase of the fracture toughness of MF resins. The SEM image of the MF/EF-AR system at higher magnifications suggests that the MF matrix still breaks in a brittle manner. There is no evidence of formation of shear bands. The shear deformation is believed to be the mechanism of rubber toughening for cross-linked polymers such as epoxies (101).

The flexural modulus decreases linearly with loading up to 20 wt% EF-AR. It appears that the decrease of the modulus at higher loading is slowed down drastically. Interestingly, the strain at break (ϵ) shows a different trend—ϵ decreases slightly up to 20 wt% loading, but then ϵ starts to increase steadily with rubber concentration. Above a loading of 20 wt% EF-AR, the system apparently starts to toughen without a further major decrease in the modulus. On the whole it is, however, apparent that the toughening effect is not significant enough to allow for practical application of rubber modified MF resins as composite materials. This behavior can be attributed to the highly rigid character of cured MF matrix with intrinsically high yield stress.

Summary. Molecular modeling experiments on an idealized segment of MF resins both in good and poor solvents have revealed that, despite the rigid structure, MF resins have the remarkable ability to significantly expand and contract depending on the type of solvent. Apparently there is sufficient local modality in the MF systems to allow some toughening effect to be induced. Some results suggest that ether bridges result in a more flexible structure compared with MF segments consisting of only ether bridges. The addition of chemically inert impact modifiers, such as ABS, does not lead to a homogenous distribution of rubber particles in MF matrix. A rather good dispersion of rubber particles is achieved by using epoxy functionalized acrylic based emulsions. Some indirect evidence indicates that chemical reaction between MF resin and epoxy groups is responsible for the good dispersion and interfacial strength of acrylic rubber particles. Despite the good morphology, the impact strength of EF-AR modified MF resins does not increase. On the contrary, the toughness decreased up to a loading of 20 wt% rubber. There is a slight toughening effect above a loading of 20 wt%, but it is clear that this is achieved after a serious loss of modulus. The inability of rubber inclusion technology to toughen MF resin can be attributed to the intrinsically high yield stress of the matrix.

4. 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 (102). 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 (102).

After experiencing strong demand in 1998 and most of 2000, melamine markets declined or remained stagnant in most regions in 2001. In the United States, consumption of melamine declined by nearly 8% between 2000 and 2001 as a result of the economic slowdown; consumption declined by nearly 10% in Western Europe. High natural gas costs, lower margins, depressed demand and significant capacity additions during 1998–2001 forced many melamine producers to curtail production in 2001.

The United States, Europe and Southeast Asia are the largest markets for melamine. Demand for melamine in the United States and Western Europe is expected to recover and grow at nearly 3% per year during 2001–2006. Demand in Southeast Asia is expected to experience much higher growth rates, because of increasing production of laminates for both domestic use and exports. Consumption of melamine in Japan is expected to continue to fall because of weak construction activity and increasing competition from low-cost imported wood-based products and laminates (103).

Global melamine capacity is forecast to grow at an average annual rate of 4.5% between 2001 and 2006.

5. Analytical Methods

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 (84,104) 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}H nmr (15,105) spectroscopy, whose resolution is limited by the small spectral range (~15 ppm), ^{13}C nmr spectroscopy (14,106,107) (spectral range ~200 ppm) is very effective for the analysis of hydrated or lyophilized samples in dimethyl sulfoxide (DMSO) or aqueous solution. Table 4 and Table 5 show the relevant resonances together with the assignment to the corresponding structural units (16,108). Values are shown for methylolated as well as methoxylated MF resins. Additional information on MUF (85) and M(U)PF resins (68–70,109) 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 (12). The changes of the concentration of various structural elements during the condensation of an MF resin can be followed by ^{13}C nmr (110). 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 (111,112) detecting ^{13}C nmr and ^{15}N nuclei (requiring ^{15}N-enriched material). The chemical shift values from Table 4 and Table 5 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}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 (113), the structural analysis of hydroxymethylated melamines (114,115), as well as the chemistry of hardening (116) can be followed.

The analysis of MF resins as well as alkoxylated MF resins by chromatographic methods has been described vastly in the literature (117,118) 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, enabling the direct structural analysis by hplc-ms methods on methoxylated (119–122) and butoxylated MF resins (123). 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 (124). 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 rheokinetical behavior of an MF resin can be followed using dynamical mechanical techniques (125), and time–temperature–transformation (TTT) cure diagrams can be constructed using the results of these methods (125–127).

Other, more historic methods for analyzing the chemical composition of MF resins rely on size-exclusion chromatography (sec) (128,129) and thin-layer chromatography (130) (see CHROMATOGRAPHY, SIZE EXCLUSION).

6. Uses

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 (131–134).

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 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.

6.1. 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 (45,135–137).

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.

6.2. Glue Resin Mixes for the Application of Melamine Resins.

Table 6 summarizes some glue resin mixes for different applications in the production of particleboard, MDF, and plywood.

BIBLIOGRAPHY

1. M. Dunky and P. Niemz, *Wood Based Panels and Glue Resins: Technology and Influence Parameters*, Springer, Heidelberg, 2002, p. 978.
2. A. Pizzi, *Advanced Wood Adhesives Technology*, Marcel Dekker, Inc., New York, 1994, pp. 67–88.
3. M. Dunky and A. Pizzi, in D. A. Dillard and A. V. Pocius, eds., *Adhesion Science and Engineering, Vol. 2: Issue Surfaces, Chemistry and Applications*, Elsevier Science B.V., Amsterdam, 2003, pp. 1039–1103.
4. M. Dunky, in A. Pizzi and K. L. Mittal, eds., *Handbook of Adhesive Technology*, 2nd ed., Marcel Dekker, Inc., New York, 2003, pp. 887–956.
5. A. Pizzi, in A. Pizzi and K. L. Mittal, eds., *Handbook of Adhesive Technology*, 2nd ed., Marcel Dekker, Inc., New York, 2003, pp. 653–680.
6. B. Broline, in Proceedings of Wood Adhesives 2000, Lake Tahoe, Nev., June 22–23, 2000, pp. 469–473.
7. H. Diem and G. Matthias, *Ullmann's Encyclopedia of Industrial Chemistry*, 6th ed., Electronic Release, Wiley-VCH, Weinheim, 1998.
8. J. Shen and G. M. Crews, *Polym. Prepr.* **74**, 238–239 (1996).
9. S. Ono, T. Funato, Y. Inoue, T. Munechika, T. Yoshimura, H. Morita, S.-I. Rengakuji, and C. Shimasaki, *J. Chromatogr.* **A 815**, 197–204 (1998).
10. J. Shen, G.-M. Crews, C. U. Pittman Jr., Y. Wang, and R. Ran, *J. Polym. Sci: Part A: Polym. Chem.* **34**, 2543–2561 (1996).
11. C. U. Pittman Jr., M. G. Kim, D. D. Nicholas, L. Wang, F. R. A. Kabir, T. P. Schultz, and L. L. Ingram Jr., *J. Wood Chem. Technol.* **14**, 577–603 (1994).
12. J. Mijatovic, W. H. Binder, F. Kubel, and W. Kantner, *Macromol. Symp.* **181**, 373–382 (2002).
13. B. Tomita, *J. Appl. Polym. Sci., Polym. Chem. Ed.* **15**, 2347–2365 (1977).
14. B. Tomita and H. Ono, *J. Appl. Polym. Sci., Polym. Chem. Ed.* **17**, 3205–3215 (1979).
15. J. R. Ebdon, J. E. B. Hunt, and W. T. S. O'Rourke, *Br. Polym. J.* **19**, 197–203 (1987).
16. J. R. Ebdon, J. E. B. Hunt, W. T. S. O'Rourke, and J. Parkin, *Br. Polym. J.* **20**, 327–334 (1988).
17. D. Braun and V. Legradic, *Angew. Makromol. Chem.* **25**, 193–196 (1972).
18. D. Braun and V. Legradic, *Angew. Makromol. Chem.* **34**, 35–53 (1973).
19. T. Gebregiorgis and M. Gordo, *J. Chem. Soc. Faraday Trans.* **180**, 359–382 (1984).
20. S. Jahromi, *Macromol. Chem. Phys.* **200**, 2230–2239 (1999).
21. JIS A 5905 (May 2003), Fiberboards; JIS A 5908 (2003), Particleboards.

22. S. Tohmura, A. Inoue, and S. H. Sahari, *J. Wood Sci.* **47**, 451–457 (2001).
23. H. Yamaguchi, M. Higuchi, and I. Sakata, *Mokuzai Gakkaishi* **26**, 199–204 (1980).
24. H. Yamaguchi, M. Higuchi, and I. Sakata, *Mokuzai Gakkaishi* **35**, 801–806 (1989).
25. M. Higuchi, H. Shimokawa, and I. Sakata, *Mokuzai Gakkaishi* **25**, 630–635 (1979).
26. T. A. Mercer and A. Pizzi, *Holzforsch. Holzverwert.* **46**, 51–54 (1994).
27. R. Maylor, in Proceedings of Wood Adhesives 1995, Portland, Oreg., June 29–30, 1995, pp. 115–121.
28. S. Chow and K. J. Pickles, *Wood Sci.* **9**, 80–83 (1976).
29. H. Neusser and W. Schall, *Holzforsch. Holzverwert.* **24**, 108–116 (1972).
30. H. G. Freeman and R. E. Kreibich, *For. Prod. J.* **18**(7), 39–43 (1968).
31. M. Pavlovsky, R. Ferwerda, M. Scheepers, and J. J. Nusselder, in TAPPI Plastics Laminates Symposium, Atlanta, Ga., Aug. 21–23, 2000, pp. 43–45.
32. B. Tomita and C.-Y. Hse, *Mokuzai Gakkaishi* **41**, 349–354 (1995).
33. B. Tomita and C.-Y. Hse, *Mokuzai Gakkaishi* **41**, 490–497 (1995).
34. Ger. Pat. DE 2,455,420 (Nov. 22, 1974), H. Czepel (to Lentia GmbH.).
35. Eur. Pat. EP 62,389 (Apr. 7, 1982), J. J. Hoetjer (to Methanol Chemie Nederland V.o.F.).
36. U.S. Pat. 4,123,579 (Mar. 30, 1977), H. O. McCaskey Jr. (to Westinghouse Electric Corp.).
37. U.S. Pat. 5,681,917 (Mar. 26, 1996), R. A. Breyer, S. G. Hollis, and J. J. Jural (to Georgia-Pacific Resins, Inc.).
38. Eur. Pat. EP 185,205 (Nov. 16, 1985), H. Etling, H. Diem, W. Eisele, and M. Siegler (to BASF AG).
39. Eur. Pat. EP 913,411 (Oct. 28, 1998), J. Lalo and R. Garrigue (to Elf Atochem S.A.).
40. Eur. Pat EP 1,088,838 (Sept. 29, 2000), J. Lalo (to Atofina).
41. Eur. Pat. EP 864,603 (Feb. 17, 1998) O. Wittmann, M. Kummer, and H. Schatz (to BASF AG).
42. Ger. Pat. DE 4,011,159 (Apr. 6, 1990), G. Matthias, E. Weber, and H. Diem (to BASF AG).
43. Ger. Pat. DE 3,116,547 (Apr. 25, 1981), F. Kaesbauer and W. Bolz (to BASF AG).
44. Eur. Pat. EP 52,212 (Oct. 3, 1981), H. Etling, C. Dudeck, H. Diem, and M. Siegler (to BASF AG).
45. Eur. Pat. EP 107,260 (Oct. 25, 1983), A. Tinkelenburg, H. W. L. M. Vaessen, and J. G. J. Dirix (to Methanol Chemie Nederland V.o.F.).
46. C. Cremonini and A. Pizzi, *Holzforsch. Holzverwert.* **49**, 11–15 (1997).
47. C. Cremonini and A. Pizzi, *Holz Roh. Werkst.* **57**, 318 (1999).
48. C. Kamoun and A. Pizzi, *Holz Roh. Werkst.* **56**, 86 (1998).
49. M. Prestifilippo, A. Pizzi, H. Norback, and P. Lavisci, *Holz Roh. Werkst.* **54**, 393–398 (1996).
50. M. Zanetti and A. Pizzi, *J. Appl. Polym. Sci.* **88**, 287–292 (2003).
51. A. Pizzi, in Proceedings of Wood Adhesives 2000, Lake Tahoe, Nev., June 22–23, 2000, pp. 219–239.
52. A. Weinstabl, W. H. Binder, H. Gruber, and W. Kantner, *J. Appl. Polym. Sci.* **81**, 1654–1661 (2001).
53. Ger. Pat. DE 19,532,719 (Sept. 5, 1995), A. Meier, C. Hittinger, H. Schatz, G. Lehmann, T. Reiner, and M. Niessner (to BASF AG).
54. U.S. Pat. 6,566,459 (Apr. 29, 2002), P. G. Dopico, S. L. Wertz, J. C. Phillips, and G. E. Mirous (to Georgia-Pacific Resins, Inc.).
55. Ger. Pat. DE 2,020,481 (Apr. 27, 1970), J. Mayer and C. Schmidt-Hellerau (to BASF AG).
56. Eur. Pat. EP 69,267 (June 19, 1982), H. Diem, R. Fritsch, H. Lehnert, G. Matthias, H. Schatz, and O. Wittmann (to BASF AG).

57. Ger. Pat. DE 3,145,328 (Nov. 14, 1981), H. Diem, R. Fritsch, H. Lehnert, G. Matthias, H. Schatz, and O. Wittmann (to BASF AG).
58. U.S. Pat. 4,285,848 (July 31, 1978), C. H. Hickson (to Borden, Inc.).
59. Ger. Pat. DE 3,807,403 (Mar. 7, 1988), C. Schmidt-Hellerau, E. Weber, and G. Matthias (to BASF AG).
60. Eur. Pat. EP 31,533 (Dec. 13, 1980), H. Schatz, C. Dudeck, H. Diem, J. Mayer, and C. Schmidt-Hellerau (to BASF AG).
61. Eur. Pat. EP 337,093 (Feb. 28, 1989), C. Schmidt-Hellerau, E. Weber, and G. Matthias (to BASF AG).
62. U.S. Pat. 4,285,848 (Aug. 25, 1981), C. H. Hickson (to Borden, Inc.).
63. Ger. Pat. DE 3,027,203 (July 18, 1980), H. Schittek (to Deutsche Texaco AG).
64. M. Prestifilippo and A. Pizzi, *Holz Roh. Werkst.* **54**, 272 (1996).
65. C. Cremonini, A. Pizzi, and P. Tekely, *Holz Roh. Werkst.* **54**, 85–88 (1996).
66. J. Gomez-Bueso, J. Mattheij, L. Evers, W. Kantner, and M. Dunky, in Proceedings of the Seventh European Panel Products Symposium, Llandudno, North Wales, U.K., 2003, pp. 75–81.
67. J. Gomez-Bueso, J. Mattheij, L. Evers, W. Kantner, and M. Dunky, *Holz Zentr. Bl.* **129**, 1226 (2003).
68. D. Braun and W. Krausse, *Angew. Makromol. Chem.* **108**, 141–159 (1982).
69. D. Braun and W. Krausse, *Angew. Makromol. Chem.* **118**, 165–182 (1983).
70. D. Braun and H.-J. Ritzert, *Angew. Makromol. Chem.* **125**, 9–26, 27–36 (1984).
71. J.-K. Roh, M. Higuchi, and I. Sakata, *Mokuzai Gakkaishi* **35**, 320–327 (1989).
72. J.-K. Roh, M. Higuchi, and I. Sakata, *Mokuzai Gakkaishi* **36**, 36–41 (1990).
73. J.-K. Roh, M. Higuchi, and I. Sakata, *Mokuzai Gakkaishi* **36**, 42–48 (1990).
74. Eur. Pat. EP 915,141 (Oct. 21, 1998), M. Paventi (to Arc Resin Corp.)
75. M. Dunky, unpublished results, 2001.
76. F. Wolf, in Proceedings of the First European Panel Products Symposium, Llandudno, North Wales, U.K. 1997, pp. 243–249.
77. G. Lehmann, in Proceedings of Adhesives for Wood Based Panels and Fiber Form Parts (Klebstoffe für Holzwerkstoffe und Faserformteile), Braunschweig, Germany, 1997.
78. R. M. Rammon, in Proceedings of the 31st Washington State University International Particleboard/Composite Materials Symposium, Pullmann, Wash. 1997, pp. 177–181.
79. U.S. Pat. 5,684,118 (Mar. 26, 1996), R. A. Breyer, B. R. Arndell, and S. Stompel (to Georgia-Pacific Resins, Inc.).
80. M. Properzi, A. Pizzi, and L. Uzielli, *Holz Roh. Werkst.* **61**, 77–78 (2003).
81. M. Properzi, A. Pizzi, and L. Uzielli, *Holzforschung Holzverwert.* **53**, 73–77 (2001).
82. M. Properzi, A. Pizzi, and L. Uzielli, *Holz Roh. Werkst.* **59**, 413–421 (2001).
83. M. Properzi, C. Simon, A. Pizzi, B. George, L. Uzielli, and G. Elbez, *Holzforschung Holzverwert.* **54**, 18–20 (2002).
84. T. A. Mercer and A. Pizzi, *J. Appl. Polym. Sci.* **61**, 1697–1702 (1996).
85. T. A. Mercer and A. Pizzi, *J. Appl. Polym. Sci.* **61**, 1687–1695 (1996).
86. L. A. Panangama and A. Pizzi, *J. Appl. Polym. Sci.* **59**, 2055–2068 (1996).
87. M. Higuchi and I. Sakata, *Mokuzai Gakkaishi* **25**, 496–502 (1979).
88. M. Higuchi, S. Tohmura, and I. Sakata, *Mokuzai Gakkaishi* **40**, 604–611 (1994).
89. P. E. Humphrey, in Proceedings of the Third Pacific Rim Bio-Based Composites Symposium, Kyoto, Japan, 1996, pp. 366–373.
90. U.S. Pat. 5,176,028 (Oct. 1, 1990), P. E. Humphrey (to The State of Oregon, Oregon State University).

91. J. Mijatovic, M. Dunky, and W. Kantner, in Proceedings of the Seventh European Panel Products Symposium, Poster Session, Llandudno, North Wales, U.K., 2003, pp. T15–T19.
92. M. Zanetti, A. Pizzi, and C. Kamoun, *Holz Roh. Werkst.* **61**, 55–65 (2003).
93. A. Pizzi, P. Tekely, and L. A. Panamgama, *Holzforschung* **50**, 481–485 (1996).
94. M. Zanetti and A. Pizzi, in Proceedings of the Sixth European Panel Products Symposium, Llandudno, North Wales, U.K., 2002, pp. 231–248.
95. M. Zanetti and A. Pizzi, *J. Appl. Polym. Sci.* **90**, 215–226 (2003).
96. C. Kamoun, A. Pizzi, and M. Zanetti, *J. Appl. Polym. Sci.* **90**, 203–214 (2003).
97. See for example: C. B. Bucknall, P. Davis, and I. K. Partridge, *J. Mat. Sci.* **22**, 1341 (1987); M. E. Fowler, H. Keskkula, and D. R. Paul, *Polymer* **28**, 1703 (1987).
98. A. Margolina and S. Wu, *Polymer* **29**, 2170 (1988).
99. E. F. Oleinik, *Adv. Polym. Sci.* **80**, 49 (1986).
100. J. G. Williams, *Fracture Mechanics of Polymers*, Ellis Horwood, Chichester, 1984.
101. See for example: J. Kyung, and R.E. Robertson, *J. Mat. Sci.* **27**, 161 (1992).
102. A. C. L. M. van der Waals, J. J. H. Nusselder, and T. Bacon, in Proceedings of Wood Adhesives 2000, Portland, Oreg., 2000, pp. 193–195.
103. S. Bizzari and K. Yokose, "Melamine," *Chemical Economics Handbook*, SRI Consulting, Menlo Park, Calif., 2002.
104. R. P. Subrayan and F. N. Jones, *J. Appl. Polym. Sci.* **62**, 1237–1251 (1996).
105. H. Schindlbauer and J. Anderer, *Fresenius Z. Anal. Chem.* **301**, 210–214 (1980).
106. B. Tomita, *J. Polym. Sci.* **15**, 2347–2365 (1977).
107. A. J. J. de Breet, W. Dankelman, W. G. B. Huysmans, and J. de Wit, *Angew. Makromol. Chem.* **62**, 7–31 (1977).
108. M. Dawbarn, J. R. Ebdon, S. J. Hewitt, J. E. B. Hunt, I. E. Williams, and A. R. Westwood, *Polymer* **19**, 1309–1312 (1978).
109. D. Braun and R. Unvericht, *Angew. Markomol. Chem.* **226**, 183–195 (1995).
110. V. M. L. J. Aarts, M. L. Scheepers, and P. M. Brandts, in Proceedings of the European Plastic Laminates Forum, Heidelberg, Germany, 1995, pp. 17–25.
111. M. Andreis, J. L. Koenig, M. Gupta, and S. Ramesh, *J. Polym. Sci. Part B: Polym. Physics* **33**, 1449–1460 (1995).
112. J. R. Ebdon, P. E. Heaton, T. N. Huckerby, W. T. S. O'Rourke, and J. Parkin, *Polymer* **25**, 821–825 (1984).
113. D. Braun and V. Vargha, *Angew. Markomol. Chem.* **163**, 169–193 (1988).
114. D. Braun and V. Legradic, *Angew. Markomol. Chem.* **36**, 41–55 (1974).
115. D. Braun and V. Legradic, *Angew. Makromol. Chem.* **34**, 35–53 (1973).
116. K. Umemura, S. Kawai, H. Sasaki, R. Hamada, and Y. Mizuno, *J. Adhes.* **59**, 87–100 (1996).
117. S. Kawai, H. Nagano, and T. Maji, *J. Chromatogr.* **477**, 467–470 (1989).
118. T. T. Chang, *Progr. Org. Coat.* **29**, 45–53 (1996).
119. A. Marcelli, D. Favretto, and P. Traldi, *Rapid. Commun. Mass. Spectram* **11**, 1321–1328 (1997).
120. T. T. Chang, *Anal. Chem.* **66**, 3267–3273 (1994).
121. T. T. Chang, *Polym. Prepr.* **37**(1), 292–293 (1996).
122. E. Longordo, L. A. Papazian, T. L. Chang, *J. Liq. Chromatogr.* **14**(11), 2043–2063 (1991).
123. D. Favretto, P. Traldi, and A. Marcelli, *Eur. Mass Spectrom.* **4**, 371–378 (1998).
124. E. W. Kendall, L. D. Benton, and B. R. Trethewey Jr., Proc. TAPPI Plast. Laminates Symp. 117–132 (2000).
125. P.-O. Hagstrand, C. Klason, L. Svensson, and S. Lundmark, in Proceedings of the XIIIth International Congress on Rheology, Cambridge, U.K., 2000, Vol. 1, pp. 157–159.

126. P.-O. Hagstrand and C. Klason, *Polym. Eng. Sci.* **39**, 2019–2029 (1999).
127. M. Properzi, A. Pizzi, and L. Uzielli, *J. Appl. Polym. Sci.* **81**, 2821–2825 (2001).
128. D. Braun and W. Pandjojo, *Angew. Makromol. Chem.* **80**, 195–205 (1979).
129. K. Dietrich, J. Moskalenko, K. Wiener, and W. Teige, *Acta Polym.* **37**(4), 252–253 (1986).
130. D. Braun and W. Pandjojo, *Fresenius Z. Anal. Chem.* **294**, 375–378 (1979).
131. W. Gindl, F. Zargar-Yaghubi, and R. Wimmer, *Bioresour. Technol.* **87**, 325–330 (2003).
132. W. Gindl, E. Dessipri, and R. Wimmer, *Holzforschung* **56**, 103–107 (2002).
133. D. Lukowsky, *Holz Roh. Werkst.* **60**, 349–355 (2002).
134. W. Gindl, H. S. Gupta, *Compos. Part A: Appl. Sci. Manufact.* **33**, 1141–1145 (2002).
135. A. Tinkelenberg, H. W. L. M. Vassen, K. W. Suen, and P. G. J. Leusink, *J. Adhesi.* **14**, 219–231 (1982).
136. Eur. Pat. EP 25,245 (Aug. 28, 1980), A. Tinkelenberg, H. W. L. M. Vassen, and K. W. Suen (to Methanol Chemie Nederland V.o.F.)
137. H.-J. Deppe, *Holz Zentr. Bl.* **111**, 1433–1435 (1985).

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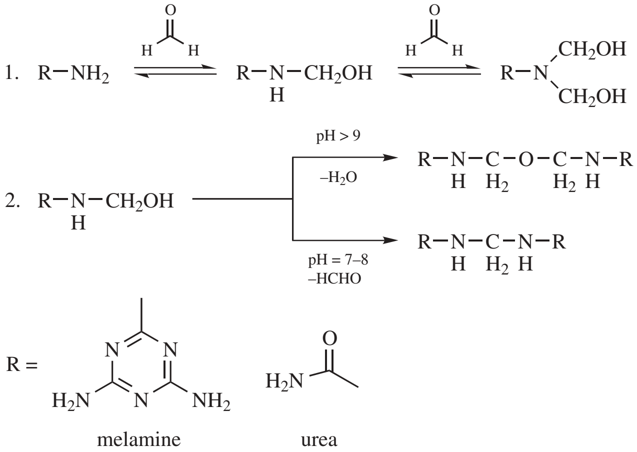


Fig. 1. Reaction mechanism for the formation of formaldehyde-based amino resins. 1, methylolation; 2, condensation.

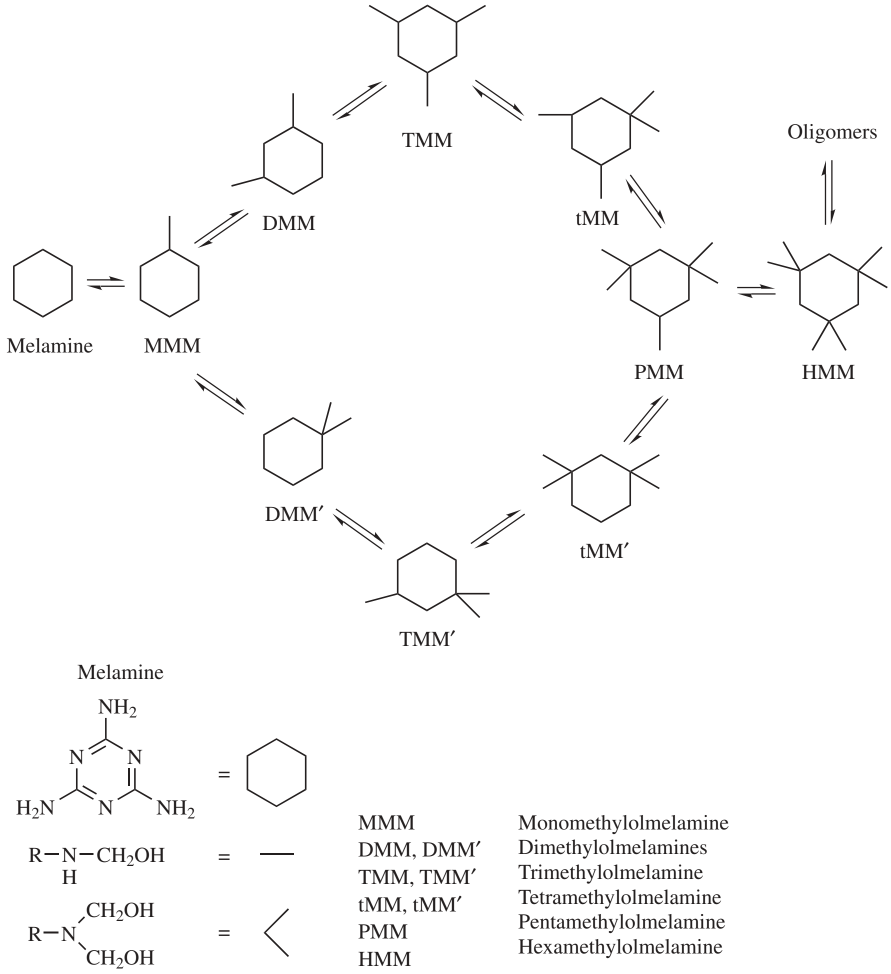


Fig. 2. Formation pathways of methylolated melamines.

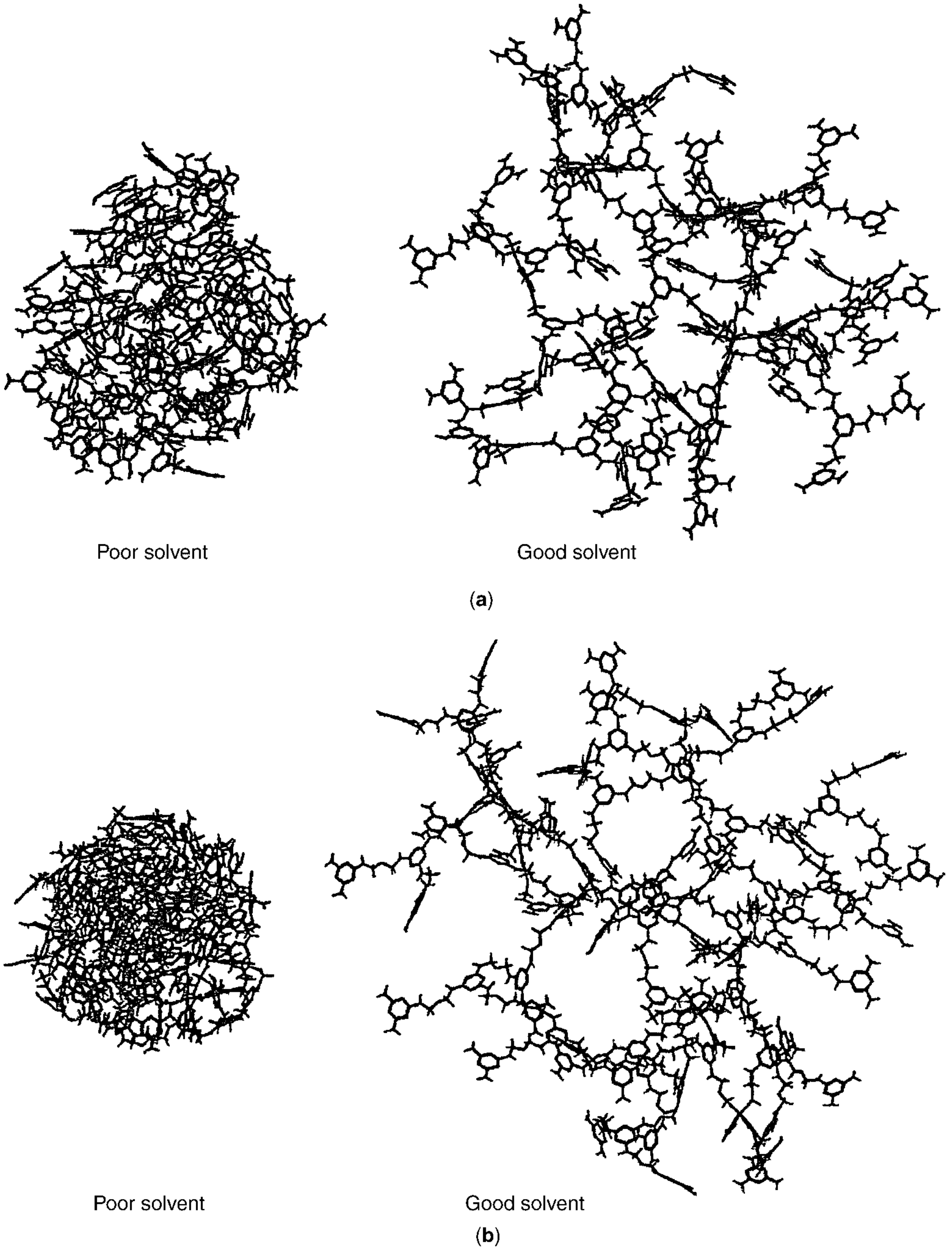


Fig. 3. Average molecular configuration of an MF resins from molecular dynamics simulations with a poor as well as a good solvent. The structures are built from either (**a**) methylene bridges or (**b**) ether linkages. Various segments are coloured differently for the sake of clarity.

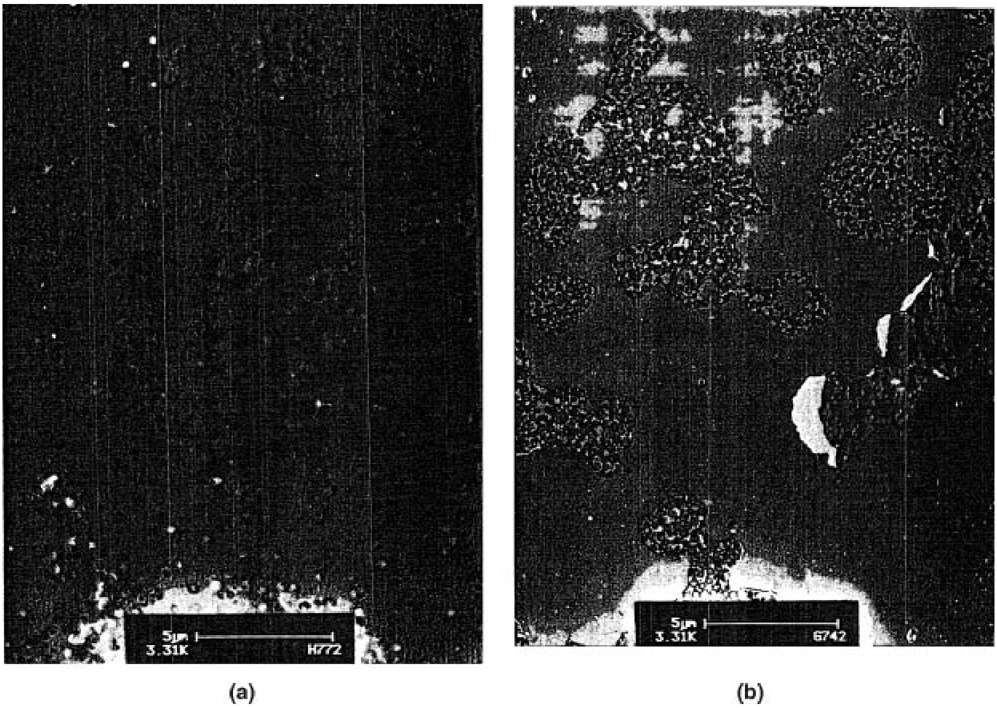
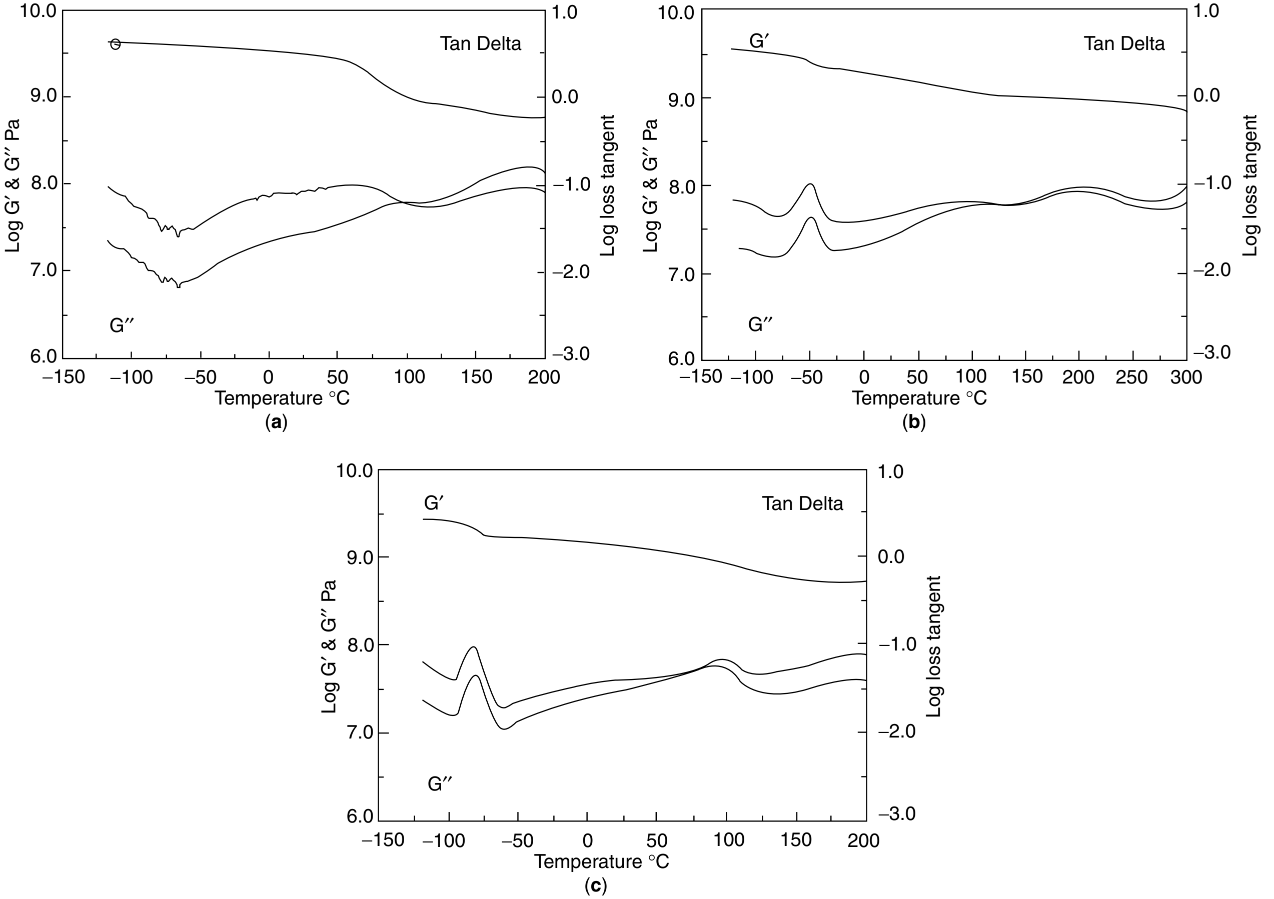


Fig. 4. TEM images of cured MF resins with 20 wt% of EF-AR (**a**) and ABS (**b**) particles.



(a)

(b)

(c)

Fig. 5. The dynamic mechanical analysis runs of cured MF resins modified with different types of rubber particles: (**a**) virgin MF resin; (**b**) 20 wt% EF-AR; (**c**) 20 wt% ABS. The first heating runs are shown.

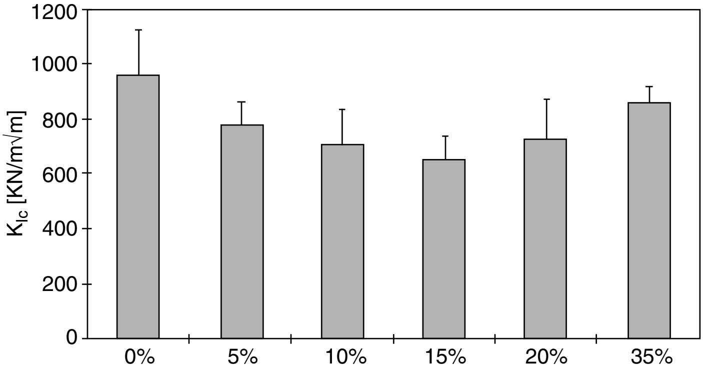


Fig. 6. Critical values for the stress intensity factor (K_{ic}) for MF resins at different weight percentages of EF-AR particles.

Table 1. **$F/(NH_2)_2$ Molar Ratio of Melamine-Based Resins**[a]

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

[a] (mUF, MUF, MUPF, and others) currently in use in the wood-based panels industry.

Table 2. **Data Obtained from Molecular Dynamics Simulations of MF Resins**

	R_g(A)		V(A^3)[a]		
Type of bridge	*Poor*	*Good*	*Poor*	*Good*	V^{good}/V^{poor}
methylene	12.70	22.00	18476	95949	5.2
ether	26.60	13.40	21686	169625	7.8

[a] V stands for volume calculated from V=4/3 π R^3 where R = $\sqrt{5/3\mathrm{Rg}}$.

Table 3. **Mechanical Test Results on Rubber Modified Cured MF Resins**

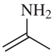
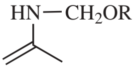
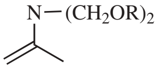
Sample	Flexural Modulus, *E*, GPa	Elongation at break, ϵ, %	Izod impact strength, kJ/m^2
MF	7.9	2.3	2.5±1.5
MF/ABS (20 wt%)	2.3	1.4	1.3±0.1
MF/EF-AR (20 wt%)	2.9	1.9	1.3±0.1

Table 4. **^{13}C Chemical Shifts for Selected Functional Groups in MF Resins**

Assignment	^{13}C Chemical shift (ppm)[a]
$-NHCH_2NH-$	47
$=NCH_2NH-$	52
$=NCH_2OCH_3/-N(CH_2OCH_3)$	58
$=NCH_2N=$	64
$=NHCH_2OH$	68–69
$-N(CH_2OH)_2$	68–69
$-NHCH_2OCH_2NH-$	73
$=NCH_2OCH_2NH-$	73
$-NHCH_2OCH_3$	77.3
$-N(CH_2OCH_3)_2$	77
$HOCH_2OH$	82
$(CH_2O)_n$ oligomers	85.2

[a] Chemical shift in ppm relative to TMS in DMSO.

Table 5. **^{13}C Chemical Shifts of the Triazine Region**

		^{13}C Chemical shift (ppm)[a]	
Assignment		R = H	R = CH_3
	melamine	167,4	167,4
	MMM	167,2	overlapped
	N,N′-DMM	167,0	overlapped
	MMM	166,3	166,7
	*N,N′*DMM	166,0	166,7
	N,N′,N″-TMM	165,8	166,7
	*N,N,N′*,N′-TMM	165,2	167,4
	PMM	165,2	167,4
	HMM	165,2	167,4

[a] ^{13}C Chemical shift in 40% DMSO/60% H_2O.

Table 6. **MUF−Glue Resin Mixes for Particleboard, MDF, and Plywood**

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

[a] Glue mix A: particleboard for use in humid conditions (core layer).

[b] Glue mix B: particleboard for use in humid conditions (face layer).

[c] Glue mix C: MDF board for use in humid conditions.

[d] Glue mix D: plywood, class 2 or class 3 (EN 314).

[e] MUF resin with $F/(NH_2)_2 \approx 1.03–1.08$.

[f] MUF resin with $F/(NH_2)_2 \approx 0.95–1.03$.

[g] MUF plywood resin with $F/(NH_2)_2 \approx 1.2–1.4$.

[h] Extender: rye or wheat flour, containing in case some inorganic fraction.

[i] Urea solution (40%).

[j] eg, Ammonium sulfate solution (20%).

[k] eg, Ammonium sulfate in powder form.