Macromol. Symp. **2004**, *217*, 417-429

Adhesives Based on Formaldehyde Condensation Resins

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Summary: Formaldehyde based resins are by far the most important adhesives for the production of wood based panels. This paper reviews in compact form the main application near features of these products including their composition, their molar mass distribution as well as their hardening behaviour, which all three parameters have decisive influence on the properties of the resins themselves and their performance as wood adhesives.

Keywords: adhesives; crosslinking; formaldehyde based resins; molar ratio; molecular weight distribution/molar mass distribution

Introduction

The quality of a bond line and hence the properties of the wood based panels depend on the three main parameters (i) wood, especially the wood surface, including the interface between the wood surface and the bond line, (ii) the adhesive or glue resin and (iii) the working conditions and process parameters. Hence, the adhesive plays an important role in wood gluing.

Adhesives for wood are based on various chemical compositions, like formaldehyde condensation resins, isocyanates, thermoplastic adhesives (e.g. PVAc), hot melts, adhesives based on natural resources like tannins, lignins and carbohydrates or traditional adhesives based on natural resources, e.g. protein adhesives.

Formaldehyde based glue resins

Formaldehyde based glue resins represent the by far the biggest volumes within the wood adhesives.[1] They are built up by the reaction of formaldehyde with mainly urea, melamine or phenol, resp., also combinations of these three substances can be used. The application is given mainly in liquid form, even for special applications also powdered (spray dried) types are sold. The resins consist of linear or branched oligomeric and polymeric molecules in an aqueous solution and partly as a dispersion of molecules in these aqueous solutions. They show a duroplastic hardening behaviour, which leads to a three dimensionally crosslinking and hence to

DOI: 10.1002/masy.200451338

unsoluble and nonmeltable networks. Resins contain always some amount of residual monomers, even in the hardened state.

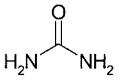
About formaldehyde based resins a big number of papers can be found in the literature. The SciFinder® (1960 – 2003) comprises approx. 12.000 for all formaldehyde resins, among them 4.000 dealing with UF resins, 2.500 with MF resins (all types) and 5.500 with PF resins.

Table 1 gives an overview on the various formaldehyde based glue resins.

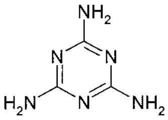
Table 1. Overview on formaldehyde based glue resins.

UF	urea-formaldehyde-resin
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
MUPF, PMUF	melamine-urea-phenol-formaldehyde resin
PF	phenol-formaldehyde resin
PUF	phenol-urea-formaldehyde resin

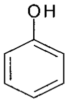
The following main raw materials are in use:



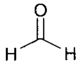
urea



melamine



phenol



formaldehyde

Production volumes and fields of application

On global basis approx. 15 million tons of formaldehyde based resins in liquid form are used annually. In Europe approx. 6 million tons in this liquid form are sold, whereby UF resins sum up to approx. 80% of this volume, MUF/MUPF to approx. 10 % and PF to approx. 5 %. Worldwide

UF resins climax to approx. 6 million tons per year, based on a usual solid content of 66% of mass (= approx. 10 mill. tons in liquid form).

Table 2 summarizes the fields of application for the various formaldehyde based wood adhesives resins. Table 3 evaluates several partly competing adhesives concerning various application parameters.

Table 2. Fields of application for the various formaldehyde based wood adhesives resins.

Type	V20[a]	V100[b]	V313[c]	HB[d]	MDF[e]	PLW[f]	BB[g]	ven.[h]	furn.[i]
UF	x				x	x	X	x[j]	x[j]
MUF	x[k]				x				
MF/MUF		x[l]	X		x	x	X		
MUPF		x			x	x			
PF/PUF		x		x	x	x			

[a] particleboard according to DIN 68761 (part 1 und 4), DIN 68763 (V20) and EN 312-2 to 4 and –6

[b] particleboard according to DIN 68763 and EN 312-5 and 7, option 2 (internal bond after boil test according to EN 1087-1)

[c] particleboard according to EN 312-5 and 7, option 1 (cycle test according to EN 321)

[d] hardboard (wet process) according to EN 622-2

[e] medium density fiberboard according to EN 622-5

[f] plywood according to EN 636 with various resistance against influenceof moisture and water

[g] blockboard: solid wood panels according to OeNORM B 3021 to B 3023 (prEN 12775, prEN 13353 part 1 to 3, prEN 13017-1 and 2, prEN 13354)

[h] veneering and covering with foils

[i] production of furnitures

[j] partly powder resins

[k] boards with reduced thickness swelling, e.g. for laminate flooring

[l] only possible as MUF+PMDI

Table 3. Evaluation of various adhesive types concerning various parameters.

Property	UF	MUF	PF	PMDI
Price	low	medium to high	medium	high
Necessary hardening temperature	low	medium	high	low
Press time	short	medium	medium to long	medium
Susceptibility against wood species	high	medium	low	low
Efficiency	low	medium to high	medium to high	high
Manipulation	easy	Easy	easy	difficult
Resistance against hydrolysis	no	medium to high	high	high
Use in humid conditions	no	partly yes	yes	yes
Formaldehyde emission	E1[a]	E1[a] E0 possible[b]	more or less no	no

[a] emission class for low subsequent formaldehyde emission

[b] for the Japanese market

The most important parameters for formaldehyde based resins are:

the type of monomers

the molar ratio of the various monomers in the resin:

F/U	molar ratio of formaldehyde to urea
$F/(NH_2)_2$	molar ratio of formaldehyde to amide groups
F/P/NaOH	molar ratio of formaldehyde to phenol and alkaline

the cooking procedure: e.g. the pH-program, the temperature program, types and amounts of alkaline and acidic catalysts, the sequence of addition of the different raw materials and the duration of the different steps of the cooking procedure.

The molar mass distributions of formaldehyde condensation resins are much broader than for other polymers. The low molar mass monomers comprise free formaldehyde (M = 30) as well as residual and non reacted species like urea (M = 60), melamine (M = 126) or phenol (M = 94), resp. Monomeric methylols are generated e.g. by the reaction of post added urea with the free formaldehyde or with monomeric methylolphenols. The oligomeric compounds with two to five molecules of urea or melamine or phenol, resp., are linked by methylene or methylene ether bridges. The more or less polymeric structures with higher molar masses are the resin molecules in the closer sense of the word and mainly responsible to build up the glue line. The highest molar masses in formaldehyde resins are a still highly disputed question.[2]

Due to the equilibrium reactions within all formaldehyde based resins always some small amounts of residual monomers can be present. Aminoplastic resins for particleboard and MDF usually contain less than 0.1 % free formaldehyde.[3] Monomer concentrations for PF resins are in the range of < 0.3 to 0.5 mass% for the free formaldehyde and < 0.1 to 0.3 mass% for free phenol. The content of monomers always should be minimized by the proper cooking procedure due to environmental and health concerns. On the other hand the free formaldehyde is necessary to induce the hardening reaction via the reaction with the aminoplastic hardener; it is an additional crosslinker beside of methylol groups, however it also causes a certain formaldehyde emission during the press cycle and some residual formaldehyde leads to the displeasing subsequent formaldehyde emission from the pressed boards.[1] Due to the stringent formaldehyde emission regulations worldwide, especially Germany/Austria and Japan ("E1"; "E Zero") and hence the necessity to limit the subsequent formaldehyde emission, the molar ratios F/U or $F/(NH_2)_2$ had been decreased thoroughly within the last two decades. No problems occur with phenolic resins due to the strong C-C-bondings in the resin (no hydrolysis and hence no liberation of formaldehyde).

Resistance against humidity and water

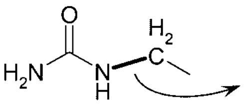
The deterioration of a bond line under humid conditions can have several reasons:

failure of the resin: low hydrolysis resistance, degradation of the hardened resin leading to the loss of bonding strength failure of the interface between resin and wood surface: replacement of physical bondings between resin and reactive wood surface sites by water or other non resin chemicals

breaking of bondings due to mechnical forces and stresses: influence of water will cause swelling and therefore movement of the structural components of wood based panels, like particles

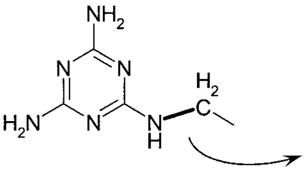
Differences in the hydrolysis behaviour of resins are based on molecular level:

UF resin: low resistance



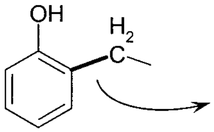
easily to split

MUF resin: increased stability against hydrolysis, due to the stabilisation of the C-N-bonding due to the quasi aromatic ring structure of the melamine and to the slower decrease of the pH in the bond line due to the buffer capacity of melamine



higher hydrolysis resistance (compared to UF)

PF resins: the C-C bonding is very stable against hydrolytic attack.



hydrolytically stable C-C bonding

The amelioration of the hygroscopic behaviour of boards bonded with aminoplastic resin for application in humid conditions can be done in various ways:

Incorporation of melamine in various forms into an aminoplastic resin like melamine fortified UF resins, MUF, MUPF or PMUF: the limitation is the high price of melamine as raw material; so always as much melamine as necessary should be used but also as low as possible. The melamine content varies from very few percent (melamine fortified UF glue resins) up to 25% and sometimes even more, numbers always based on liquid resin.

A neutral aminoplastic glue line should show a distinct better hydrolysis resistance. The neutralization, however, must not take place as long as the acidic hardening reaction has not yet finished, otherwise it would delay or even prevent curing. Laboratory experiments up to now have promised quite good success, but this procedure is not yet industrially approved.

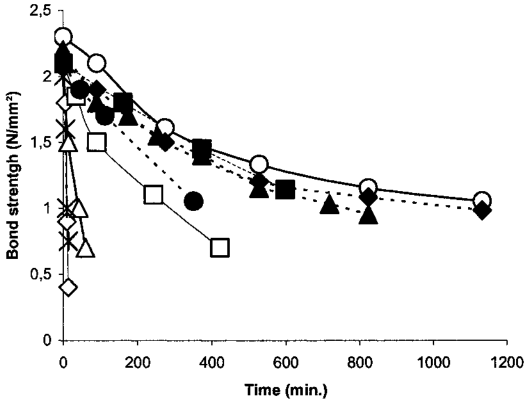
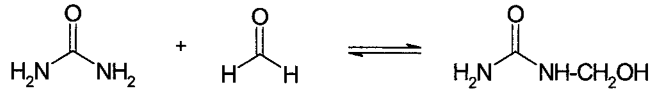


Figure 1: Decrease of the bonding strength in UF-bonded plywood, when samples are stored in various aqueous buffer solutions.[4]

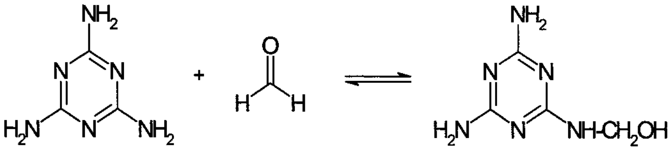
The cooking procedure of formaldehyde condensation resins mainly contains two steps:

(i) methylolation: strongly exothermic reaction, mainly monomeric methylols are formed, in most cases in alkaline conditions

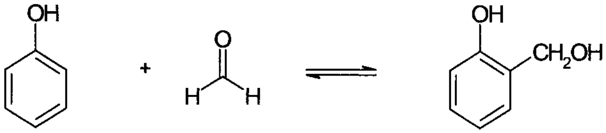
UF resin:



MF resin:



PF resin:



(ii) condensation: forming of methylene- and ether linkages in acidic (aminoplastic resins) or alkaline conditions (PF resins). The reaction has to be stopped when the resin is still liquid (pH ⇒ alkaline conditions or by cooling), whereby the determination of the proper endpoint of the reaction is essential.

Methylenebridges:

$$R{-}CH_2OH \quad + \quad H_2N{-}R' \quad \xrightarrow[-H_2O]{} \quad R{-}CH_2\text{-}NH\text{-}R'$$

Ether bridges with further reaction to methylene bridges:

$$R{-}CH_2OH \quad + \quad OHCH_2\text{-}R'' \quad \xrightarrow[\substack{-CH_2O \\ -H_2O}]{} \quad R{-}CH_2\text{-}R''$$

The final urea addition as the deciding step for the reactivity of aminoplastic resins enables the adjustment of the usual low molar ratio of the final aminoplastic resin and is done in one or several steps, including in case also maturing times.[5] The addition of urea to a phenolic resin (i) decreases the content of free formaldehyde and the viscosity of the glue resin by cleveage of hydrogen bondings and the dilution effect and (ii) accelerates the hardening reaction via the possible higher degree of condensation of the resin; however, rather no cocondensation of this postadded urea with the phenolic resin occurs.

Cocondensation is theoretically possible in many ways, like (i) urea + melamine[6], (ii) urea + melamine + phenol[7], (iii) melamine + phenol[8-12] or (iv) phenol + urea[13-15]. Still questions are open if and how cocondensation really occurs.

Reactivity, hardening and curing reactions

The hardening process is the continuation of the resin condensation process. For aminoplastic resins it occurs in acidic conditions, caused by the addition of ammonium salts or acids; the acceleration of this hardening process is possible by addition of free formaldehyde sources.[16] Phenolic resins predominantly harden thermally under alkaline conditions; the higher the degree of condensation, the shorter is the necessary gelling time. Limits of the increase of the degree of condensation is pumping of the resin (viscosity), the storage stability, a proper distribution of the resin on the particles during blending and the flow behaviour of the resin under heat (wetting and penetration behaviour). The post curing during hot stacking is very important for PF resins to achieve full curing.

During hardening elongation of the resin molecule chains, branching and crosslinking to a more or less threedimensional network with a theoretical endless high molar mass occurs, generating an unsoluble resin which is not longer thermoformable (thermoplastic). Heat generally accelerates the curing reaction obeying Arrhenius' law.

During hot pressing two processes take place:

(i) chemical curing of the thermosetting resin: building up of the threedimensional network; monitoring is possible by DTA, DSC, (solid state) NMR and in case IR

(ii) mechanical forming of the bonding strength between the two adherends (mechanical hardening): monitoring is possible by DMA, the so-called ABES-method[17], TMA and TBA.

Plots of the degree of chemical hardening versus the degree of mechanical hardening can describe the different hardening behaviour of various resins[18], as shown in Figure 2.

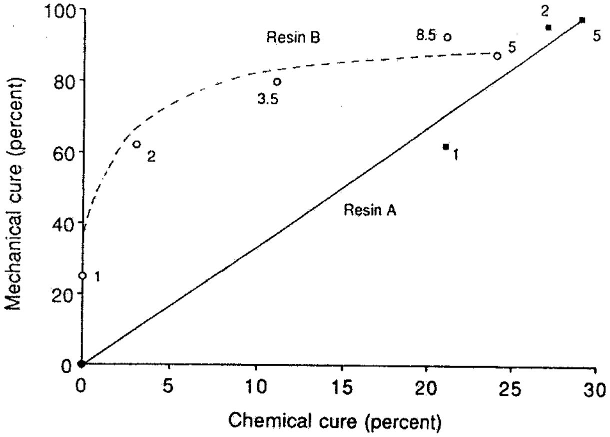


Figure 2: Chemical-mechanical hardening plot for two different PF resins; prehardening temperature 140 deg C, times in minutes.[18]

Shorter press times are important due to a permanent pressure on costs and prices and hence the necessity for an increased production rate to reduce production costs. This means (i) high reactive adhesive resins with a steep increase in bonding strength even at a low degree of chemical curing, (ii) high reactive glue resin mixes (accelerators or special hardeners), (iii) the optimization of the pressing process, e.g. by an increased steam shock and (iv) the temporary constancy of the production process.

Figure 3 shows the ABES comparison of two UF-resins with the same molar ratio F/U = 1.08, but with different reactivities, due to different cooking procedures. UF-resin A: special cooking procedure for high reactivity; UF-resin B: traditional UF-resin. This test was done using the so-called Automatic Bonding Evaluation System as shown in Figure 4.[17,19]

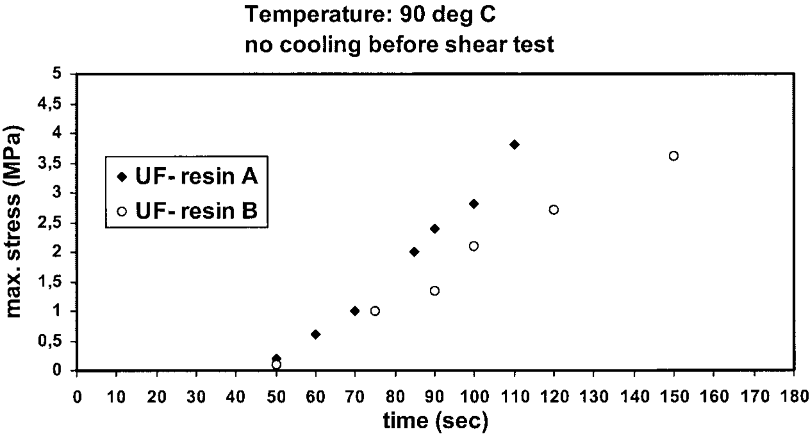


Figure 3: ABES comparison of two UF-resins with F/U = 1.08:
UF-resin A: special cooking procedure for high reactivity;
UF-resin B: traditional UF-resin.

Influence of the molar ratio for aminoplastic resins

Decreasing the molar ratios F/U or F/$(NH_2)_2$ of aminoplastic resins means a decrease of the reactivity of the resin due to the higher content of free formaldehyde and the degree of crosslinking in the cured network. Additionally the formaldehyde emission during the production of the wood based panels, the subsequent formaldehyde emission, the mechanical properties and the degree of hardening decrease; the thickness swelling and the water absorption as well as the susceptibility for hydrolysis will increase.

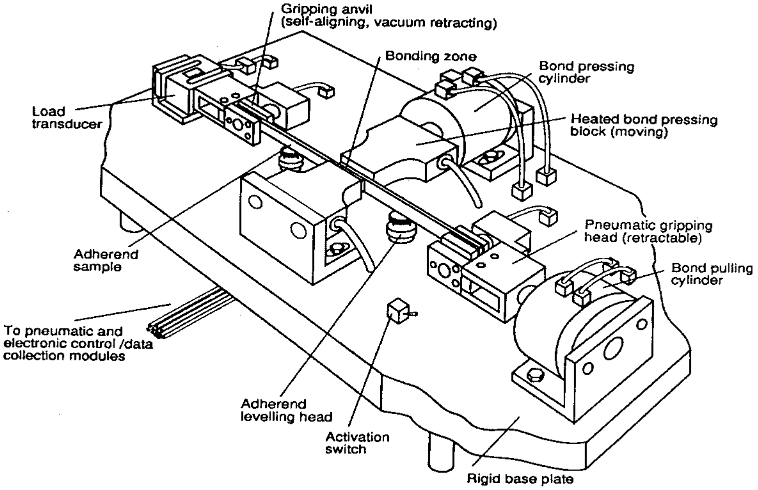


Figure 4: Automatic Bonding Evaluation System (ABES).[17,19]

Molar ratios F/U and $F/(NH_2)_2$, resp., of aminoplastic resins are in the range of 1.20 to 1.85 for plywood resins with partly cold setting behaviour of UF resins; these resins usually need special hardeners and additives and partly the addition of formaldehyde catchers 0.90 to 1.10 for particleboard and MDF resins, where partly further addition of formaldehyde catchers is necessary. In case a modification or fortification with melamine can be given.

Below 0.90 for special aminoplastic glue resins for boards with a very low formaldehyde emission ("E zero", "Super E zero"[20]).

Influence of the degree of condensation and of the molar mass distribution on the properties of the resins

With higher condensated structures (higher molar masses) the viscosity at a given solid content increases, the flowing ability is reduced, the wetting behaviour of a wood surface becomes worse, the penetration into the wood surface is reduced, the distribution of the resin on the furnish (particles, fibers) becomes worse and the water dilutability of the resin decreases. Phenoplastic resins show a higher hardening reactivity with higher molar masses. 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 mainly is given during the application and the hardening reaction (wetting behaviour, penetration into the wood surface in dependence of the degree of condensation).

Molecular characterisation of formaldehyde based resins

The molecular characterisation of resins comprises the determination of:
the concentration and the molar ratios of the main components, e.g. F/U, $F/(NH_2)_2$, F/P/NaOH
the content of reactive sites and functional groups and their distribution in the resin, including the type of bridges between the aromatic rings of the phenol molecule as well as branching sites and others, analysis done by IR, ^{1}H-NMR, ^{13}C-NMR or ^{15}N-NMR
the degree of condensation and the molar mass distribution by GPC/SEC[2, 21, 22]
and the monitoring of the condensation process by water dilutibility, water tolerance or the increase in molar masses (shift of the molar mass distribution).
Still unsolved is the prediction of board properties based on the analysis results of the used resins. Some few correlation equations between chemical structures in various resins with different composition and the various board properties (dry or wet IB, subsequent formaldehyde emission) have been described in the literature[23-29], but a general correlation for various resins and various panels rather will not exist. The definition of main parameters, however, is valuable, even the numbers within the individual correlation equations might differ.

Conclusions

Also in future formaldehyde based resins will be the most important adhesive system for wood based panels, considering the different advantages of these resins but also keeping in mind their limits and disadvantages. A huge progress within the last twenty years in knowledge and technology has been gained, but still a fruitful soil for research and development is given. Main driving forces in the development of adhesive resins are the key words “cheaper” (e.g. less melamine or lower resin consumption), “quicker” (e.g. shorter press times) and “more complex” (“How to cook the resins?” or „How to formulate an optimal adhesive mix“).

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