

Melamine Salts as Hardeners for Urea Formaldehyde Resins

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ABSTRACT: Various salts derived from melamine and organic acids were prepared and used as melamine substitutes for melamine urea formaldehyde (MUF) resins. The synthesis of these melamine salts and a detailed characterization of their stoichiometry are described. All salts form 1 : 1 or 1 : 2 stoichiometries in a homogeneous reaction. They crystallize during cooling of the hot and diluted reaction mixture. Both ¹³C-NMR and ¹⁵N-NMR data are reported and point toward the formation of real ionic structures. Most salts have higher water solubility than that of pure melamine and are tested for their ability to substitute melamine in MUF resins. The mechanical and chemical properties of plywood panels made up of traditional MUF resins and mixtures of UF resins with melamine salts are investigated. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 1654–1661, 2001

Key words: melamine urea formaldehyde resin; melamine salt; melamine substitute; NMR spectroscopy; plywood panels

INTRODUCTION

Urea-formaldehyde (UF) resins^{1–3} constitute the most widely used materials for wood adhesives. Despite their good mechanical and chemical abilities, they suffer from two major drawbacks that result from their brittleness and lack of water resistance,⁴ which reduce their spectrum of applicability. To overcome these disadvantages melamine has been shown to be a powerful additive, leading to the class of melamine-urea-formaldehyde (MUF) resins. Wood panels produced with these resins show increased mechanical and water resistance. Melamine is condensed into these resins via the formation of precondensates with formaldehyde and urea, thus leading to highly crosslinked structures after curing reactions.⁵ However, because of the usual distribution of melamine in the resin during precondensation and

curing, only a minor quantity of its initial amount leads to efficient crosslinking inside the resin, thus wasting a major part of the cost-intensive melamine.⁶ One solution to this problem was formulated by Pizzi et al.^{7–9} in applying the melamine in the form of its organic salts, which show increased solubility in water. Pizzi expected that this leads to an improved distribution of the melamine in the three-dimensional network after curing. Together with the advantage of a lower melamine content, the organic acid acts as hardener during the curing process, thus eliminating the need for an external hardener such as ammonium salts.

Our investigation focused on the preparation and characterization of new melamin salts, derived from the reaction of melamine with various organic acids as well as on their incorporation into UF resins, which leads to an extension of the repertoire of the preparation of MUF resins. The mechanical bond strength as well as the water resistance and the formaldehyde emissions of these boards are reported, the characteristics of

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Table I Reaction Parameters and Analysis Data of Melamine Salts

Entry	Acid	Product	Reaction Parameters ^a				Elemental Analysis			
			Melamine (mmol)	Acid (mmol)	Washing Fluid	Yield (%)	Formula	% C	% H	% N
1	Formic	1	79.3	84.9	Ether	79	C ₄ H ₁₈ N ₆ O ₇	27.96	4.65	49.70
2	Glycolic	2	79.3	85.6	Acetone	91	C ₅ H ₁₀ N ₆ O ₃ · $\frac{1}{2}$ H ₂ O	28.42	5.22	39.77
3	Lactic	3	79.3	79.3	Acetone	74	C ₆ H ₁₂ N ₆ O ₃ · $\frac{1}{2}$ H ₂ O	31.25	6.14	38.75
4	Fumaric	4a	79.3	79.3	Acetone	98	C ₇ H ₁₀ N ₆ O ₄ · H ₂ O	32.45	5.03	31.77
		4b	79.3	39.7	Acetone	99	C ₁₀ H ₁₆ N ₁₂ O ₄	33.08	4.47	45.11
5	Maleic	5	79.3	79.3	Methanol	99	C ₇ H ₁₀ N ₆ O ₄ · H ₂ O	32.32	5.38	32.42
6	Succinic	6	79.3	79.3	Acetone	97	C ₇ H ₁₂ N ₆ O ₄ · H ₂ O	32.13	5.50	31.93
7	Malic	7	79.3	100	Ether	96	C ₇ H ₁₈ N ₁₂ O ₅ · 4H ₂ O	26.54	5.61	36.27
8	Tartric	8	79.3	100	Methanol	91	C ₁₀ H ₁₈ N ₁₂ O ₆ · $\frac{1}{2}$ H ₂ O	29.62	4.65	40.90
9	Citric	9	79.3	100	Acetone	98	C ₉ H ₁₄ N ₆ O ₇	43.15	4.31	26.18
10	Gluconic	10	79.3	79.3	Acetone	71	C ₉ H ₁₈ N ₆ O ₇ · H ₂ O	31.90	5.90	26.14
11	Glucaric	11	79.3	79.3	Acetone	89	C ₁₂ H ₂₂ N ₁₂ O ₈ · $\frac{1}{2}$ H ₂ O	29.79	5.30	35.84
12	Aspartic	12	79.3	79.3	Acetone	99	C ₇ H ₁₃ N ₇ O ₄ · $\frac{1}{2}$ H ₂ O	31.57	5.60	36.46
13	Glutamic	13	79.3	79.3	Acetone	98	C ₈ H ₁₅ N ₇ O ₄	34.29	5.86	32.50

^a Reaction was performed in 200 mL of water.

which are superior compared to those of traditional MUF resins. Because of the fact that very few melamine salts with organic acids have been characterized chemically, a major focus was directed on the detailed chemical characterization of the melamine salts by means of NMR spectroscopy and HPLC analysis, as well as by data on their thermal stability. The thermal characteristic is important in that the salt is assumed to decompose during the thermal curing process, thus leading to homogeneously distributed melamine and free organic acid, which catalyzes the hardening process of forming insoluble three-dimensional networks with the UF resin.

EXPERIMENTAL

General Procedure for the Synthesis of Melamine Salts

A 10-g (79.3-mmol) sample of melamine was weighed into a three-neck flask equipped with a reflux condenser, dropping funnel, and a thermometer, and 200 mL of water was added. This mixture was stirred with a magnetic stirrer while heating to 100°C until all of the melamine had been dissolved. To this hot solution the acid (see Table I) was added within 5 min, after which the mixture was refluxed for 10 min and then cooled to room temperature. The resulting precipitate

that formed on cooling was isolated by filtration and washed with a solvent in which the acid was very soluble (see Table I). The crystalline products were then dried in vacuum at 40–50°C.

Characterization of the Melamine Salts

Titration with NaOH

A 0.2-g sample of the melamine salt was dissolved in 25 mL of dimethylsulfoxide with warming and titrated against 0.1N NaOH using phenolphthalein as indicator.

HPLC Analysis

A 0.005% solution of the melamine salt was prepared containing 5 g/L *N,N*-dimethylformamide as an internal standard. A 20- μ L aliquot of this solution was used for the analysis with a RP-Select B column (125 \times 3 mm) and RP 18e (125 \times 3 mm). A UV detector was used (235 nm) together with a Spectra Physics P 4000 HPLC. The solvent flux was 0.67 mL/min and the oven temperature was 30°C.

NMR Spectroscopy

Both ¹H-NMR and ¹³C-NMR spectra were measured on a Bruker AC-E-200 FT-NMR spectrometer (Bruker Instruments, Billerica, MA) at frequencies of 200.13 and 50.32 MHz, respectively.

The gated decoupling pulse sequence was used together with a relaxation delay of 5 s to obtain quantitative ^{13}C -NMR spectra. ^{15}N -NMR spectra were acquired on a Bruker Avance DRX 400 and measured according to the INEPT Sequence using inverse detection. The number of scans was between 1000 and 5000 for each sample using a relaxation delay of 2.0 s.

DSC Analysis

DSC analyses were performed on a Shimadzu DSC-50 differential scanning calorimeter (Shimadzu, Japan) using a heating rate of $1^\circ\text{C}/\text{min}$.

Determination of Gel Times

Two different sets of resins with a molar ratio of formaldehyde to urea of $F/U = 1:1.52$ and $1:1.21$, respectively, were used. The melamine salt (10% by weight calculated as free melamine based on liquid resin) was added and 2 g of the mixture was weighed into an eproutette and heated to the temperature indicated (100, 70, or 30°C). The time until solidification occurred was measured and constituted the gel time.

Preparation of Plywood Panels

Beech veneers of 2.1 mm thickness were glued with a glue spread of $250\text{ g}/\text{m}^2$ of glue mix to produce three-layer plywood panels. The veneers were pressed at a temperature of 120°C for 6–7 min and a specific pressure of $1.5\text{ N}/\text{mm}^2$. The resulting plywood panels were then tested for water resistance, tensile strength, and formaldehyde emission.

RESULTS AND DISCUSSION

Synthesis and Characterization of Melamine Salts

Inorganic salts^{10–14} such as the melamine hydrochloride, -sulfate, -phosphate, and -nitrate have been extensively described in the literature and have been thoroughly characterized by elemental analysis, spectroscopic methods, and even X-ray crystallography. Depending on the acids' valency and strength mono- and disalts are formed by simply heating the reaction components. Nearly all inorganic salts formed in this manner do not show increased solubilities in water when compared to that of pure melamine and can thus be

regarded as improper additives for the preparation of MUF resins.

One major focus was dedicated toward the synthesis and the exact characterization of melamine salts derived from organic acids. Few salts of this kind have been reported to date, including some carboxylic and sulfonic acids.^{15,16} However, organic salts such as the melamine acetate, -formate, -adipate, and -propionate have significantly higher solubility in water and are thus promising additives for UF resins. This prompted us to prepare melamine salts derived from hydrophilic organic acids to further improve water solubility.

Melamine is a weak base¹⁷ with three different pK_a values that decline with increasing protonation status. The first ($\text{pK}_{a1} = 5.10$) is slightly above the pK_a of acetic acid (4.76), and the second and third (0.20 and -2.10 , respectively) are significantly below that of most organic carboxylic acids. Because the difference between the pK_a values during an acid–base reaction corresponds to the free energy of reaction, stable products can be expected only for acids with a pK_a value significantly below 5.10, whereas organic acids with acidities in the range of 5.10 or above can be expected to yield mixtures of unreacted melamine, free acid, and melamine salt.

Common preparations of melamine salts use heterogeneous reaction mixtures with subsequent heating of the components using water as the reaction solvent. When applying this method to the synthesis of melamine salts using various molar mixtures of melamine versus acid, formation of products with varying stoichiometric contents of acid were obtained as judged by elemental analysis. Because the heterogeneity of the reaction mixture was assumed to yield undefined product compositions,⁸ a homogeneous method was developed to prepare the melamine salts. Thus, the organic acid was added to a boiling, homogeneous (5%) solution of melamine in water, either as solution or in solid form. Heating was then continued for 10 min and the solution was cooled to room temperature, which led to precipitation of the melamine salt. Table II lists the carboxylic acids and their pK_a values as well as analytical data on the salt composition. Table I gives information on reaction parameters and elemental analysis data.

To establish the stoichiometry of the melamine salts formed, four different methods were applied: (1) titration with base, (2) integration of ^{13}C -NMR-spectra, (3) HPLC analysis, and (4) elemental analysis.

Table II Melamine Salts Derived from Organic Acids

Entry	Acid	pK _{a1}	pK _{a2} (pK _{a3})	Molar Ratio [Melamine]/[Acid]	Product	Molar Ratio [Melamine]/[Acid] in Product			
						Titration	¹³ C–NMR	HPLC	CHN Analysis
1	Formic	3.77		1 : 0.93	1	1 : 1.00	1 : 1	1 : 1.02	1 : 0.94
2	Glycolic	3.83		1 : 0.93	2	1 : 0.99	1 : 1	1 : 1.06	1 : 1.00
3	Lactic	3.86		1 : 1	3	^a	1 : 1	1 : 0.89	1 : 0.88
4	Fumaric	3.02	4.38	1 : 1	4a	1 : 0.94	1 : 1	1 : 1.07	1 : 1.03
				1 : 0.5	4b	1 : 0.47	1 : 0.5	^b	1 : 0.53
5	Maleic	1.94	6.22	1 : 1	5	1 : 0.60	1 : 1 ^c	1 : 0.99	1 : 0.99
6	Succinic	4.21	5.72	1 : 1	6	1 : 1.01	1 : 1	1 : 1.03	1 : 1.00
7	Malic	3.46	5.10	1 : 0.79	7	1 : 0.43	1 : 0.5	1 : 0.58	1 : 0.53
8	Tartric	3.01	4.53	1 : 0.79	8	1 : 0.52	1 : 0.5	1 : 0.55	1 : 0.52
9	Citric	3.13	4.74 (5.40)	1 : 0.79	9	1 : 1.05	1 : 1	1 : 1.00	1 : 1.02
10	Gluconic	3.70		1 : 1	10	1 : 0.89	1 : 1	1 : 1.01	1 : 0.92
11	Glucaric	3.01	3.94	1 : 1	11	1 : 0.41	1 : 0.5	1 : 0.49	1 : 0.47
12	Aspartic	2.10	3.86	1 : 1	12	^a	^d	1 : 1.00	1 : 0.96
13	Glutamic	2.10	4.07	1 : 1	13	^a	1 : 1	1 : 1.31	1 : 1.32

^a Titration did not yield reproducible results.

^b Because of the extremely low solubility, detection was not feasible.

^c This value is based on integration of ¹H–NMR spectra.

^d Strongly differing values in various solvents (i.e., D₂O, 1 : 2.40; DMSO, 1 : 0.30).

1. Titration was based on the reaction of melamine salts with sodium hydroxide solution and involved titration up to the color change of added phenolphthalein in DMSO solution. This method was highly reproducible in most cases but failed when applied to lactic acid (entry 3), aspartic acid (entry 12), and glutamic acid (entry 13).
 2. Integration of NMR spectra was a powerful tool to establish the composition of the melamine salts. In the first instance ¹H–NMR spectroscopy was investigated for determination of the melamine-to-acid ratio. However most ¹H–NMR spectra were difficult to quantify because of unresolved resonances and residual water. In contrast ¹³C–NMR spectroscopy showed good resolution and allowed integration of quaternary carbonyls of the acid moieties versus the melamine carbon signals. Details of the ¹³C–NMR spectra are shown in Table III, which lists all of the ¹³C resonances. Care was taken to ensure quantification of these spectra¹⁸ by use of long relaxation delays and the inverse gated technique to eliminate NOE effects. Because aspartic acid (entry 12) did not yield a reasonably resolved spectrum, integration was not feasible. All other salts gave results that were in good agreement with those of the other analytical methods.
 3. HPLC analysis allowed a separate determination of the melamine and acid contents. The ratio indicated in Table II is thus the direct value of two independent measurements. All gave reasonable results, except the disalt of fumaric acid (**4b**), for which the solubility in water was too low to perform a good analysis.
 4. Elemental analysis yielded another method to determine the ratio of melamine to acid. Because most salts were crystallized or precipitated from aqueous solution, the existence of residual water can be assumed even after extensive drying *in vacuo*. To eliminate the influence of water in the calculation of the stoichiometry, the carbon-to-nitrogen ratio was used to calculate the salt composition. This value is independent of crystal water or residual moisture.
- The different analytical methods are in good agreement when applied to the same melamine salt and yield molar salt compositions of either 1 : 1 or 1 : 0.5, despite the fact that the starting molar ratio of [acid]/[melamine] is not necessarily equal to the final stoichiometry. All monovalent

Table III ^{13}C - and ^{15}N -NMR Parameters of Melamine Salts

Entry	Acid	Product	^{13}C -NMR Data (ppm) ^a						^{15}N -NMR Data ^b		
			COOH	Melamine		Other					
1	Formic	1	165.53	165.22					84.09		
2	Glycolic	2	175.63	164.77	60.35				84.20		
3	Lactic	3	177.71	165.30	66.41	20.96			83.96		
4	Fumaric	4a	168.18	163.67	135.14				85.57		
		4b	168.38	165.41	135.19				83.19		
5	Maleic	5	167.94	160.44	135.98				89.71		
6	Succinic	6	174.57	166.58	29.51				83.11		
7	Malic	7	177.32	173.58	165.3	67.91	40.83			84.48	
8	Tartric	8	175.78	164.62	72.89				84.96		
9	Citric	9	177.32	173.58 (2C)	163.09	72.74	43.99			86.54	
10	Gluconic	10	176.17	165.29	73.41	72.73	71.83	70.76	63.64	84.17	
11	Glucaric	11	176.54	176.20	165.33	73.83	72.74	71.73	71.35	^c	
12	Aspartic	12	205.70	202.73	189.46	80.56	64.84 ^d			83.20	
13	Glutamic	13	177.30	175.22	166.67	55.33	29.45	24.94			82.66

^a In DMSO relative to 39.7 ppm.

^b In DMSO relative to $\text{NH}_{3(\text{g})} = 0$ ppm.

^c No resonance because of extremely low solubility in DMSO.

^d In D_2O relative to dioxane (60.6 ppm).

acids (entries 1–3, entry 10) form salts with a 1 : 1 ratio of acid/melamine. In contrast the divalent acids show rather ambiguous behavior: malic acid (entry 7), tartic acid (entry 8), and glucaric acid (entry 11) clearly form salts with two melamine residues per acid moiety, whereas all other divalent and even trivalent acids (citric acid, entry 9) form salts with one melamine residue per acid moiety. Fumaric acid (entry 4) is an exception, in that the stoichiometry of the final salt can be controlled by the initial molar ratio of melamine to acid. In this way both of its salts can be prepared.

When taking a look at the second acidities ($\text{pK}_{\text{a}2}$ values) of the starting acids it is rather obvious why maleic and succinic acid ($\text{pK}_{\text{a}2} = 6.22$ and 5.72 , respectively) are not able to react with two melamine residues, because their acidity is well below that of melamine ($\text{pK}_{\text{a}2} = 5.10$). However, it cannot be explained why malic acid ($\text{pK}_{\text{a}2} = 5.10$) is able to yield a dimelamine salt and citric acid ($\text{pK}_{\text{a}2} = 4.74$), aspartic acid ($\text{pK}_{\text{a}2} = 3.86$), and glutamic acid ($\text{pK}_{\text{a}2} = 4.07$) yield only monomelamine salts. Additional factors such as crystallization energy and aggregation phenomena might be responsible for this kind of reaction behavior.

To judge the salt characteristics, extensive ^{13}C - and ^{15}N -NMR spectroscopic measurements were performed (Table III). The ^{13}C resonances of

the melamine carbon showed a small but significant shift of 0.5 to 2.0 ppm when compared to that of pure melamine. This can be regarded as an indication of salt formation.

Additional information can be derived from the ^{15}N resonances of the melamine nitrogen. Because it is well documented that ^{15}N resonances can be very sensitive toward their protonation status¹⁹ we performed ^{15}N spectroscopy on all of the melamine salts. Because of the very low solubility, even in dimethylsulfoxide, both the INEPT technique and the inverse detection technique were used to obtain a significant signal-to-noise ratio. In only one case (glucaric acid, entry 11) could no resonance be detected as a result of the extremely low solubility of this salt in dimethylsulfoxide. Figure 1 correlates the differences of the ^{15}N shifts [$\delta_{(\text{salt})} - \delta_{(\text{melamine})}$] to the $\text{pK}_{\text{a}1}$ values of the corresponding acids. There is a clear correlation that is, the higher the acidity, the more positive the difference in chemical shift. Two melamine salts, those derived from aspartic acid (**12**) and glutamic acid (**13**), do not follow this correlation. In this case aggregation and thus irregular behavior can be assumed. In general the trend follows the results known from the protonation of amino acids and thus forms a strong indication of real salt formation resulting from protonation of the melamine–amino moiety by the organic acid.

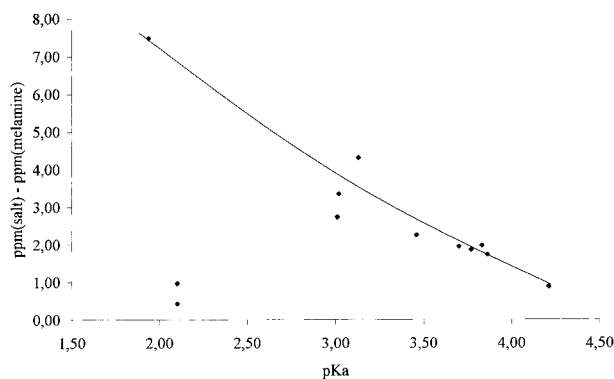


Figure 1 Difference of ^{15}N chemical shifts of melamine salts in relation to the pK_a of the corresponding acid. The line is a guide for the eye only.

Condensation of Melamine Salts into UF Resins

The condensation of selected melamine salts into UF resins and the resulting mechanical properties of resulting plywood panels were investigated. Two main criteria were chosen to select melamine salts: (1) solubility in water and (2) the decomposition temperature.

Because pure melamine is assumed to show insufficient crosslinking reaction into the UF resin, a higher aqueous solubility of the melamine salts was assumed to lead to better distribution of the melamine within the UF matrix and thus to more efficient crosslinking reaction. This should lead to comparable internal bond strength of the resulting panels compared to that of those glued with a conventional MUF resin at higher melamine content.

The decomposition temperature forms the second criterion for the selection of the appropriate

melamine salt. Because on decomposition free acid and melamine are liberated, the former will act as an acid catalyst for the crosslinking reaction and thus be a substitute for the normally used ammonium salts.

Table IV shows the selected melamine salts, their solubility in water at the indicated temperature, and their decomposition temperature. The maximum temperature in the glue line during the production of panels is usually below 120°C . Taking into consideration the vapor pressure and the shifting of the equilibrium of the decomposition reaction, we chose those salts with decomposition temperatures around 150°C or below. The solubility in water of all salts is far better than that of pure melamine, although the solubility and stability at the pressing temperature may be quite different under these conditions.

To evaluate the reactivity of the resulting mixtures of UF resins and melamine salts, the gelling times at different temperatures were determined using glue mixtures with two different [urea] : [formaldehyde] molar ratios. For industrial applications the pot life at a temperature of 30°C should be well above 2 h, to prevent early gelling, and the gelling time at 100°C in the range of 1 min to ensure complete hardening within the press time usually applied. Except for melamine maleate (**5**), for which the gelling times at 100 and 70°C , respectively, were not available as a result of an instant viscosity increase of the reaction mixture, all other melamine salts show usable gelling times and thus reactivities within the glue mixture as well as sufficient pot lives. However, the reactivities did not depend on the decomposi-

Table IV Properties of Selected Melamine Salts in UF Resins

Salt	Acid	Solubility (wt %) (Temperature)	Decomposition Temperature (DSC)	U : F Molar Ratio = 1 : 1.52			U : F Molar Ratio = 1 : 1.21		
				Gel Time ^a			Gel Time ^a		
				100°C	70°C	30°C	100°C	70°C	30°C
1	Formic	5% (45°C)	155.4	52 s	5 m	4 h	60 s	7 m	4 h
3	Lactic	6% (30°C)	153.2	54 s	7 m	> 5 h	74 s	10 m	7 h
5	Maleic	9% (75°C)	91.4	^b	^b	5 h	^b	^b	6 h
7	Malic	7% (80°C)	80.0	52 s	8 m	6 h	76 s	10 m	6 h
10	Gluconic	8% (30°C)	116.6	45 s	5 m	4 h	65 s	8 m	5 h
13	Glutamic	11% (40°C)	81.7	52 s	6 m	4 h	77 s	10 m	4 h

^a Gel time without external hardener in seconds (s), minutes (m), and hours (h).

^b This value could not be obtained because of the very high viscosity of the glue mixture.

Table V Composition and Mechanical Parameters of Plywood Panels Condensed with Melamine Glutamate (13) and Melamine Formate (1)

Entry	Melamine Salt	UF Resin Composition				Tensile Strength Dry (N/mm ²)	Formaldehyde Emission (mg h ⁻¹ m ⁻²)	Knife Test Dry ^c
		% Melamine ^a	% Melamine ^b	% Flour ^a	% NH ₄ Cl _(s) ^a			
1	Glutamate	10	14.9	—	—	2.0	^d	+3
2	Glutamate	10	14.9	—	3	1.9	^d	4
3	Glutamate	10	14.9	15	3	1.7	^d	3–4
4	Glutamate	6.5	9.7	15	3	2.6	^d	2–3
5	Glutamate	6.5	9.7	15	—	2.1	^d	2–3
6	Formate	10	14.9	7	—	3.2	4.55	3
7	Formate	10	14.9	7	3	2.4	1.61	4
8	Formate	6.7	10	7	3	2.2	1.94	+3
9	Formate	6.7	10	7	—	3.0	5.06	+3
10	MUF resin	23	32.9	10	3	3.6	0.73	—

^a Based on liquid UF resin.^b Based on solid UF resin.^c Evaluation: 1, excellent bonding; 2, good bonding; 3, sufficient bonding; 4, insufficient bonding.^d Because these panels were destroyed in the wet test no emission values were obtained.

tion temperatures of the investigated melamine salts.

All salts were subjected to a preliminary test using laboratory plywood boards for checking the resistance of the bonding in aqueous solution (data not shown). Only the boards with UF–melamine salt mixtures derived from glutamate (**13**) and formate (**1**) showed appropriate mechanical and chemical stability. These two salt mixtures were then used for manufacturing additional plywood panels. The amount of melamine salt and thus the melamine content of the whole mixture was varied as well as the further addition of ammonium chloride as hardener. Table V shows the different resin compositions together with the tensile strength and the formaldehyde emission values for the resulting panels. Panels derived from melamine glutamate (entries 1–5) showed good mechanical values compared to those of a glue mixture derived from a commercially available MUF resin (entry 10). The panels did not show appropriate resistance toward boiling water (data not shown).

Melamine formate (entries 6–9), however, yielded panels with excellent mechanical resistance at melamine contents far below that of panels bonded with a conventional MUF resin (compare entries 6–9 with entry 10). Even at half the amount of melamine salt in the resin (10%) the panels showed good tensile strength together with reasonable formaldehyde emission values. This stresses the fact that melamine formate is an

extremely good substitute for the melamine condensed traditionally to a MUF resin. Another important feature is the possibility of the production of panels with high tensile strength without the use of ammonium chloride as external hardener (entries 7 and 8 compared to entries 6 and 9). It can be assumed that the liberated formic acid acts as catalyst during the pressing process. Whereas the dry strength properties look even better without external catalyst, for these boards we found by far the highest formaldehyde emissions. Concerning the wet strength tests, we got results that were similar to those for the dry tests (entry 6 without external catalyst showed the best properties, with a tensile strength of 1.8 N/mm²).

CONCLUSIONS

The synthesis of salts derived from the reaction of melamine with organic acids is reported. All salts form 1 : 1 or 1 : 2 stoichiometries in a homogeneous reaction. They crystallize during cooling of the hot and diluted reaction mixture. These salts were characterized by elemental analysis as well as by titration-based methods, HPLC, and NMR spectroscopy. Most salts have higher water solubility than that of pure melamine and are thus tested for their ability to substitute melamine in MUF resins. In particular, use of melamine formate leads to plywood panels with good mechanical properties at much lower amounts of addition

when compared to melamine within a traditional MUF resin. Ammonium salts used as catalyst can be also substituted by melamine formate.

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