New Melamine–Formaldehyde–Ketone Polymers. III. Coatings from Melamine and Reactive Solvents Based on Cyclohexanone

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Received 25 January 2005; accepted 8 May 2005
DOI 10.1002/app.22622
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The conditions and methods of preparing novel melamine–formaldehyde–cyclohexanone coatings are presented. The coatings were prepared by dissolving melamine in reactive solvents based on formaldehyde and cyclohexanone. The latter were prepared at different molar ratios of the components. The water resistance of the resulting coatings was measured. J Appl Polym Sci 99: 1083–1092, 2006

Key words: heteroatom-containing polymers; thermosets; coatings; water resistance; reactive solvents; melamine

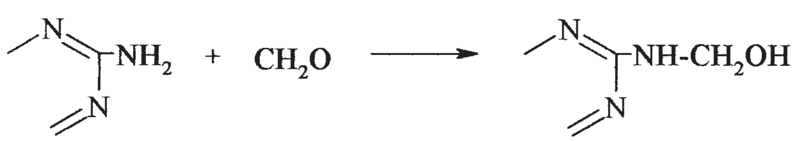
INTRODUCTION

The major disadvantage of melamine is its poor solubility in typical organic solvents.[1] This property undoubtedly limits its potential application range. The best among poor solvents are multihydroxyl alcohols (e.g., 10 g melamine dissolves in 100 g of glycerin).[2] In recently discovered the so-called reactive solvents (RS),[2–7] the solubility of melamine exceeds 100 g in 100 g of the RS prepared from cyclohexanone.[8] The solubility studies have shown that melamine not only dissolves physically in the solvents but also reacts, yielding resinous reactive system,[3–5] with polycondensation taking place at elevated temperature and in the presence of acidic compounds. The polycondensation products are the melamine–formaldehyde–ketone resins. Melamine dissolution involves the following chemical transformations.

a. Dissociation of *O*-hydroxymethyl groups of the RS, with liberation of formaldehyde.

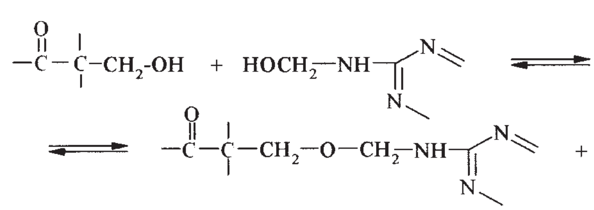
(1)

b. Addition of melamine amino groups to formaldehyde, with formation of *N*-hydroxymethyl groups.



(2)

c. Condensation of *N*-hydroxymethyl groups of melamine and *C*-hydroxymethyl groups of the RS.



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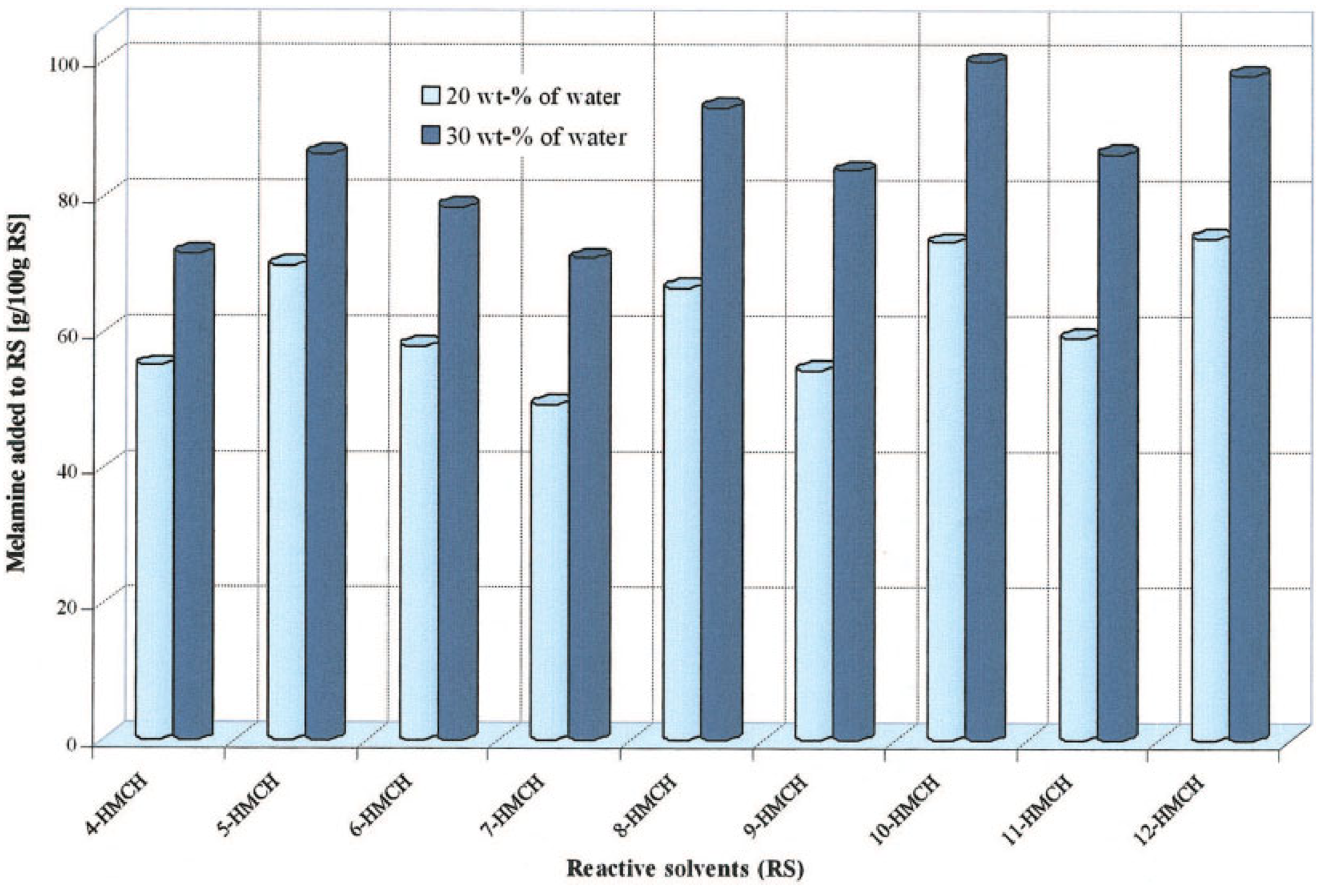

Figure 1 The highest solubility of melamine in reactive solvents containing 20 or 30 wt % of water. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

In this article, we report on potential applications of melamine–formaldehyde–ketone resins[1,8] as coatings resistant against boiling water.

EXPERIMENTAL

Chemicals

Cyclohexanone, Chempur, Poland; formalin, Standard, Poland; melamine, Fluka, Switzerland; formic acid (80%), POCH, Poland; acetic acid (80%), POCH, Poland; hydrochloric acid (36%), Chempur, Poland.

Preparation of RS

The RS were prepared from cyclohexanone and 1–12-fold molar excess of formaldehyde, as described in detail in ref 1.[1] The products of reactions were coded with explicit information on the molar excess of formaldehyde used in the preparation stage. Thus, the solvent *n*-HMCH (e.g., 4-HMCH, 6-HMCH) contains *n* moles of formaldehyde reacted with 1 mol of cyclohexanone (HMCH stands for hydroxymethylcyclohexanone). The reaction between cyclohexanone and formalin was carried out at 80°C for 5–6 h in the presence of triethylamine as catalyst. Water and catalyst were then removed by distillation under reduced pressure (12–24 hPa) while keeping the mixture at below 50°C.

Determination of melamine dissolution in RS

The amounts of melamine dissolved in anhydrous RS or in the solvents containing 20–30 wt % of water were determined, as described elsewhere.[5]

By using the results established previously,[1,5,8] a calculated amount of melamine was introduced to a solvent, so that the solution was sufficiently liquid to homogenize easily with the catalyst. In fact, the melamine content in the solutions were close to those of the upper solubility limit for a given type of solvent as obtained by gradual adding of melamine to the RS containing water.[1,5] The solutions of the highest possible melamine content were found to cure too rapidly.

Gelation and curing of melamine solutions

The gelation time of different solutions of melamine in RS was estimated in preliminary experiments. The

TABLE I
Resistance against Boiling Water (as Measured by Mass Loss) of Mel-F-CH Coatings Cured at 120°C without Catalyst

RS	Water added (wt %)	Melamine added (g/100g RS)	Curing time (min)	Mass loss, Δm (wt %)	Sample appearance
4-HMCH	20	43.4	90	−2.9	Transparent, smooth, brittle
			120	−1.8	Transparent, smooth, brittle
	30	65.5	30	−1.6	Transparent, some blisters
			90	−0.4	Transparent, some blisters
			120	−0.7	Transparent, some blisters
5-HMCH	20	60.0	60	−3.5	Roughish, brittle
			90	−1.5	Roughish, brittle
	30	66.6	30	−0.1	Transparent, smooth, hard
			60	−0.7	Transparent, smooth, hard
7-HMCH	20	45.2	120	−1.0	Hard, transparent
			150	−0.8	Hard, transparent
			180	−0.6	Hard, transparent
			210	−0.4	Hard, transparent
	30	66.3	90	−1.8	Hard, transparent
			120	−1.2	Hard, transparent
		66.3	150	−0.9	Hard, transparent
			180	−0.6	Hard, transparent
			210	−0.4	Hard, transparent
			240	−0.6	Hard, transparent
9-HMCH	20	53.8	30	−3.9	Slightly blistered, glossy, transparent
			60	−4.4	Slightly blistered, glossy, transparent
11-HMCH	20	50.0	90	−2.3	Slightly blistered, glossy, transparent
			120	−1.6	Slightly blistered, glossy, transparent
12-HMCH	30	84.9	90	−2.1	Hard, slightly blistered, glossy
			120	−1.3	Hard, slightly blistered, glossy
			150	−1.0	Hard, slightly blistered, glossy

solution was kept at ~90°C and its viscosity observed by mixing with a glass road and withdrawing a filament from time to time. The moment at which the filament broke while being withdrawn was taken as the gelation time. The gelation time ranged from 1, 5 to 3, 5 min. Only those solution/catalyst systems for which the gelation time was sufficiently long to form a coating were taken into consideration.

To melamine solutions in RS, 0.5, 1.0, or 2.0 wt % of concentrated solutions of hydrochloric (36%), formic (80%), or acetic acid (80%) were introduced at a temperature ~10–20°C lower than the temperature of melamine dissolution (80–90°C, depending on solution composition). The amount of different acids was selected after preliminary experiments with gelation time of melamine solutions in RS. Blank reference samples containing no catalyst were also prepared. A test solution was heated to ~90°C while stirring with glass stick and poured onto glass plates just before gelation. The plates were then cured at 120°C for 30–240 min.

Determination of resistance against water of melamine–formaldehyde–cyclohexanone (Mel–F–CH) resins

A cured sample of Mel–F–CH resin (~0.3 g) was taken off the glass plate, carefully weighed to within 0.0001 g, and exposed to 50 cm^3 of boiling distilled water for 30 min. Then the sample appearance was examined. Finally, the sample was placed in an oven at 105°C for 30 min to dry out and then weighed again. The water resistance was defined as the mass loss during the exposition in boiling water. Furthermore, (1) appearance of the sample was described and (2) the traces of formaldehyde released by the sample to boiling water was determined by sulfite method.[9] The sample was considered water resistant when the mass loss in boiling water was less 1 wt %.

RESULTS AND DISCUSSION

Polymer coatings were obtained by curing melamine solutions in RS poured onto glass plates. The RS were obtained by reacting 1 mol of cyclohexanone with 4–12 mol of formaldehyde (codes 4-HMCH.. 12-HMCH) in the presence of triethylamine catalyst. The solvents selected featured the highest melamine solubility (Fig. 1). For that reason, the solvents containing water were used in preparation of melamine coatings.

The water resistance measurements were carried out taking into account (1) the effect of melamine dissolved, (2) the amount of water in starting solution (20–30 wt % with respect to the mass of RS), (3) the

TABLE II
Resistance against Boiling Water (as Measured by Mass Loss) of Mel-F-CH Coatings Cured at 120°C in the Presence of Concentrated HCl (36%)

RS	Water added (wt %)	Catalyst added (wt %)	Melamine added (g/100g RS)	Curing time (min)	Mass loss, Δm (wt %)	Sample appearance
4-HMCH	20	0.5	43.5	90	−0.9	Transparent, smooth
				120	−0.1	Transparent, smooth
			43.5	150	−0.3	Transparent, smooth
				180	−0.1	Transparent, smooth
				210	−0.2	Transparent, smooth
	30	0.5	68.1	90	−1.8	Few blisters
				120	−1.6	Few blisters
5-HMCH	20	0.5	60.0	60	−2.9	Brittle
				90	−1.2	Brittle
	30	0.5	89.9	60	−2.0	Brittle
				90	−1.6	Brittle
	30	1	89.9	60	−2.7	Brittle, slightly rough
				90	−1.5	Brittle, slightly rough
		2	89.9	60	−3.1	Brittle, transparent
				90	−3.0	Brittle, transparent
7-HMCH	20	1	43.4	60	−4.0	Hard, few blisters
				90	−3.3	Hard, few blisters
	30	2	71.2	30	−4.1	Slightly rough, opalescent
				60	−4.0	Slightly rough, opalescent
9-HMCH	20	2	49.7	90	−2.5	Blisters
				120	−1.2	Blisters
10-HMCH	20	2	80.1	90	−0.7	Brittle, slightly rough
				120	−1.7	Brittle, slightly rough
11-HMCH	20	0.5	49.9	30	−1.5	Slightly rough, glossy
				60	−0.9	Slightly rough, glossy
				90	−0.9	Slightly rough, glossy
12-HMCH	20	0.5	56.8	60	−0.1	Transparent, few blisters
				90	−0.9	Transparent, few blisters
				120	−0.9	Transparent, few blisters

kind of catalyst (concentrated HCl, HCOOH, and CH_3COOH), (4) the amount of catalyst (0.0, 0.5, 1.0, or 2.0 wt % with respect to RS), (5) cure temperature, and (6) time of cure.

The solution of melamine in RS were thermally cured at 120°C. This temperature was found optimal for most of the samples prepared, although literature data suggested higher temperature reaching even 200°C.[2] Curing experiments were also performed at 100–110°C and 130–140°C. An increase of curing temperature above the optimal temperature (120°C) resulted in cracked and blistered coatings just after few minutes, whereas its reduction below 120°C excessively prolonged the curing time. The times tested were 30, 60, 90, or 120 min. The longer was the curing time the better was the water resistance of coatings; the curing time was also extended to 150, 180, 210, and 240 min. Some compositions were still elastic (they yielded under stress); hence, the time of their cure was increased by extra 30 min. This procedure assured the highest possible degree of curing (i.e., the samples did not react visibly on stress, anymore) and eliminated formaldehyde release in boiling water.

The resistance against water was tested for the compositions obtained from RS containing 20–30 wt % of water. Some experiments were also made for RS containing 40 wt % of water. The resulting coatings, however, were blistered; hence, these RS were eliminated from further experiments.

Coating cured without catalyst

The coatings from Mel–F–CH resins cured without a catalyst were in most cases resistant against boiling water (less than 1 wt % of mass reduction, *cf*. Table I). The best water resistance had the coatings prepared from melamine solutions in the RS obtained by reacting 1 mol of cyclohexanone with 7 mol of formaldehyde (7-HMCH). The loss of mass was small and independent of the amount of water used. It ranged from 0.4 to 1.8 wt % for resins cured for 210 and 90 min, respectively. The coats were hard and transparent. The longer was the cure time the better was the water resistance of coatings.

For the coatings prepared from RS of a lower excess of formaldehyde (4-HMCH, 5-HMCH), the presence of water in the resin (30 wt %) was advantageous; the mass loss in boiling water became smaller (Δm = 0.4 wt % after cure) and surface quality was very good. The coatings were transparent, smooth, and hard (5-HMCH) or transparent and with some blisters (4-

TABLE III
Resistance against Boiling Water (as Measured by Mass Loss) of Mel-F-CH Coatings Cured at 120°C in the Presence of 80% Formic Acid

RS	Water added (wt %)	Catalyst added (wt %)	Melamine added (g/100g RS)	Curing time (min)	Mass loss, Δm (wt %)	Sample appearance
5-HMCH	20	0.5	68.0	60	−2.1	Hard, smooth
				90	−1.0	Hard, smooth
				120	−1.0	Hard, smooth
	30	0.5	87.9	60	−1.0	Hard, smooth
				90	−1.0	Hard, smooth
				180	−0.4	Hard, smooth
				210	0.0	Hard, smooth
		1	87.9	60	−4.2	Brittle, roughish
				90	−2.9	Brittle, roughish
		2	87.9	60	−2.6	Brittle, roughish
				90	−1.9	Brittle, roughish
6-HMCH	20	0.5	53.1	90	−2.2	Transparent, smooth
				120	−1.0	Transparent, smooth
	30	1	75.8	90	−1.5	Transparent, smooth
				120	−1.2	Transparent, smooth
7-HMCH	20	0.5	49.7	30	−2.1	Smooth, opalescent
				60	−0.9	Smooth, opalescent
				120	−1.0	Smooth, opalescent
				150	−0.3	Hard, transparent
				180	0.0	Hard, transparent
8-HMCH	20	0.5	49.7	90	−2.0	Transparent, some blisters
				120	−0.5	Transparent, some blisters
	20	0.5	67.5	30	−1.8	Transparent, some blisters
				90	−0.4	Transparent, some blisters
10-HMCH	20	0.5	73.3	30	−2.5	Transparent, some blisters
				90	−1.0	Transparent, some blisters
				120	−0.4	Transparent, some blisters
	20	2	73.3	30	−1.8	Brittle, some blisters
				60	−1.0	Brittle, some blisters
				90	−0.9	Brittle, some blisters
11-HMCH	20	0.5	55.8	90	−1.0	Transparent, some blisters
				120	−1.0	Transparent, some blisters
12-HMCH	20	0.5	70.0	60	−1.6	Transparent, smooth, hard
				90	−0.8	Transparent, smooth, hard
	30	0.5	96.1	60	−1.9	Brittle, some blisters
				90	−1.0	Brittle, some blisters
				120	−1.2	Brittle, some blisters

HMCH). Similar observations were made for the coatings prepared from the higher hydroxymethyl derivatives of cyclohexanone (9-HMCH . . . 12-HMCH).

Coatings cured with 36% hydrochloric acid

The curing catalysts typical for the classical melamine–formaldehyde resins were used, i.e., hydrochloric, formic, and acetic acid. The coatings obtained in the presence of hydrochloric acid had a good water resistance, but they were too brittle (Table II). Among the coatings prepared from the lower hydroxymethyl derivatives of cyclohexanone, the smallest mass losses were recorded for those prepared from 4-HMCH, containing 20 wt % of water, and cured at 90–210 min. The coatings were smooth and transparent. The best water resistance had the layers cured with 0.5 wt % of catalyst. The presence of more than 1% of catalyst resulted in higher mass losses in boiling water. For the RS's 7-, 8-, 9-, or 10-HMCH, the best boiling water resistance was observed after using 2 wt % of HCl; the surfaces, however, were blistered. The smaller mass losses were observed for the coatings prepared from RS containing less water (20% wag.).

Among coatings prepared from solution of melamine in the higher hydroxymethyl derivatives of cyclohexanone (11-, 12-HMCH), the best resistance against boiling water had those containing almost the highest amount of dissolved melamine (cf. Ref. 1) and cured in the presence of 0.5 wt % of catalyst. They were, however, slightly blistered and rough.

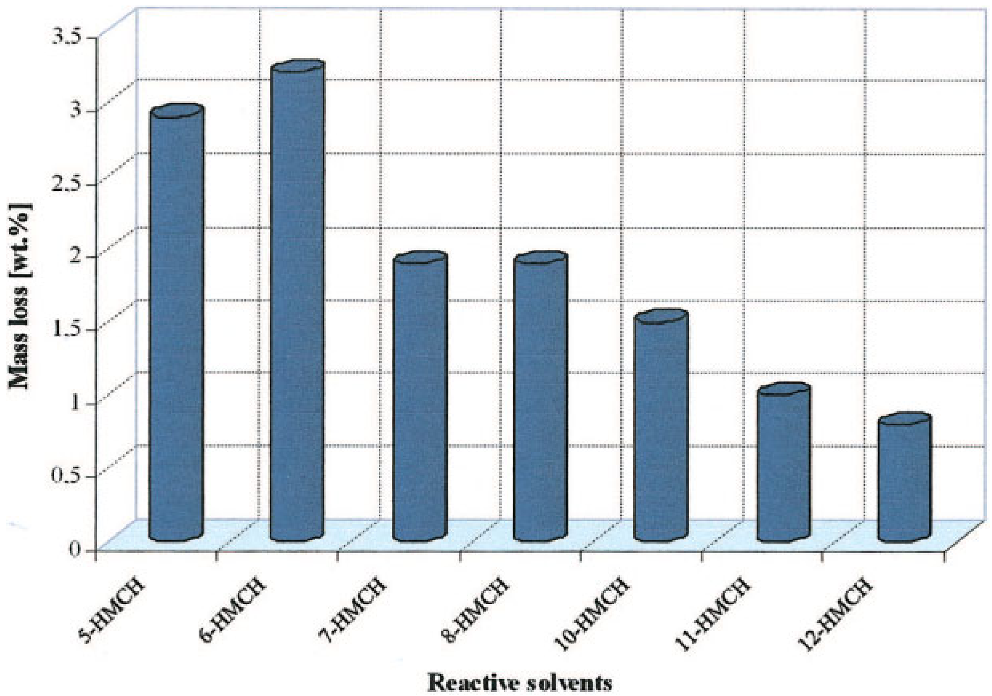

Figure 2 Resistance against boiling water (as measured by mass loss) of a Mel–F–CH coating (53.1 g of melamine/100 g of RS; 20 wt % of water) cured at 120°C for 90 min in the presence of 0.5 wt % of HCOOH. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Mel–F–CH coatings of an improved water resistance were obtained by extending the time of cure beyond 90–120 min. The products, however, became more and more brittle. The presence of 20 wt % of water in an RS was found advantageous for both the water resistance and the appearance of the coatings. Further increase of water content (to 30 wt %) improved the water resistance, but the coating became rough and blistered (Table II).

To summarize, one could state that in the presence of HCl catalyst, the best were the coatings cured for 90–120 min. By extending this time, one could obtain coating of a better resistance against water, but of worse appearance. A particularly well-pronounced effect of cure time on the water resistance was observed for the resins obtained with a large (1–2 wt %) amount of catalyst (cf. Table II).

Coatings cured with 80% formic acid

Generally, the Mel–F–CH coatings cured with formic acid had a good resistance against boiling water (cf. Table III). Similarly as for other catalysts, somewhat better resistance had the coatings prepared from the solution of melamine in RS containing possibly the highest amount of melamine and extra 20 wt % of water. The presence of 30 wt % of water improved the water resistance, but in the expense of coating elasticity and surface smoothness.

Along with extended curing time, the water resistance improved (for coatings prepared from 5-, 7-, and 10-HMCH) independently of the amount of water present in RS. The resulting coatings were hard and smooth (5-HMCH), smooth and opalescent or hard and transparent (7-HMCH), or transparent with some blisters (10-HMCH). In the case of higher derivatives (11-, 12-HMCH), the substantial amount of water (30 wt %) made the coatings brittle and blistered (cf. Table III). Again, the use of more catalyst improved water resistance, but yielded inhomogeneous surfaces. On the other hand, the presence of more water in RS yielded more brittle layers.

A good resistance against boiling water had the coatings prepared from Mel–F–CH resins based on the "higher" hydroxymethyl derivatives of cyclohexanone (Fig. 2), containing 20 wt % of water and cured with 0.5 wt % HCOOH. They were hard and smooth (Table III). Further increase of both water content in RS or curing time made the coatings rough, but improved its water resistance.

The best resistance against boiling water had the coatings prepared from solutions of melamine in 5- and 7-HMCH cured for 210 and 180 min, respectively. The coatings had smooth, transparent sur-

TABLE IV
Resistance against Boiling Water (as Measured by Mass Loss) of Mel-F-CH Coatings Cured at 120°C in the Presence of 80% Acetic Acid

RS	Water added (wt %)	Catalyst added (wt %)	Melamine added (g/100g RS)	Curing time (min)	Mass loss, Δm (wt %)	Sample appearance
4-HMCH	20	0.5	43.7	120	−1.3	Transparent, crazes
				150	−0.4	Transparent, crazes
				180	−0.1	Transparent, crazes
				210	−0.3	Transparent, crazes
				240	−0.2	Transparent, crazes
		1	43.7	150	−0.3	Transparent, some blisters
				180	−0.4	Transparent, some blisters
				210	−0.7	Transparent, some blisters
				240	−0.5	Transparent, some blisters
		2	43.7	210	−0.1	Transparent, some blisters
				240	−0.4	Transparent, some blisters
	30	0.5	71.4	180	−0.4	Transparent, some blisters
				210	−0.3	Transparent, some blisters
				240	−0.1	Transparent, some blisters
5-HMCH	20	0.5	67.7	90	−1.8	Transparent, smooth
				120	−1.2	Transparent, smooth
				150	−1.0	Transparent, smooth
		1	67.7	60	−1.2	Transparent, smooth
				90	−1.0	Transparent, smooth
				90	−1.4	Transparent, smooth
				120	−1.0	Transparent, smooth
	30	0.5	86.5	60	−2.0	Transparent, smooth
				90	−1.5	Transparent, smooth
		1	86.5	30	−2.0	Transparent, smooth
				60	−1.5	Transparent, smooth
6-HMCH	20	0.5	56.1	90	−2.2	Some blisters, glossy
				120	−1.7	Some blisters, glossy
	30	1	56.1	60	−1.5	Blisters, glossy
				90	−1.1	Blisters, glossy
				120	−1.0	Blisters, glossy
7-HMCH	20	0.5	47.2	90	−1.5	Hard, transparent
				120	−0.9	Hard, transparent
		1	47.2	90	−1.8	Hard, some blisters
				120	−1.3	Hard, some blisters
	30	0.5	68.8	90	−2.3	Brittle, many blisters
				120	−1.9	Brittle, many blisters
8-HMCH	20	0.5	63.0	120	−1.4	Hard, transparent
				150	−1.2	Hard, transparent
		1	63.0	90	−1.2	Hard, few crazes
				120	−1.0	Hard, few crazes
	30	0.5	91.1	90	−2.2	Brittle, blisters
				120	−1.3	Brittle, blisters
9-HMCH	20	0.5	52.2	90	−2.0	Hard, roughish
				120	−1.3	Hard, roughish
	30	0.5	82.1	90	−2.8	Brittle, blisters
				120	−2.9	Brittle, blisters
10-HMCH	20	0.5	73.4	60	−1.9	Hard, transparent
				90	−1.8	Hard, transparent
				120	−1.0	Hard, transparent
	30	0.5	96.0	120	−3.0	Brittle, blisters
				150	−2.4	Brittle, blisters
11-HMCH	20	0.5	56.8	90	−1.6	Hard, transparent
				120	−0.6	Hard, transparent
		1	56.8	90	−2.3	Hard, some blisters
				120	−2.0	Hard, some blisters
	30	0.5	84.0	90	−2.4	Brittle, crazes
				120	−2.0	Brittle, crazes
12-HMCH	20	0.5	72.7	90	−1.3	Hard, some blisters
				120	−1.0	Hard, some blisters
		1	72.7	60	−2.1	Hard, some blisters
				90	−1.9	Hard, some blisters
	30	0.5	97.1	90	−2.2	Brittle, blisters
				120	−2.0	Brittle, blisters

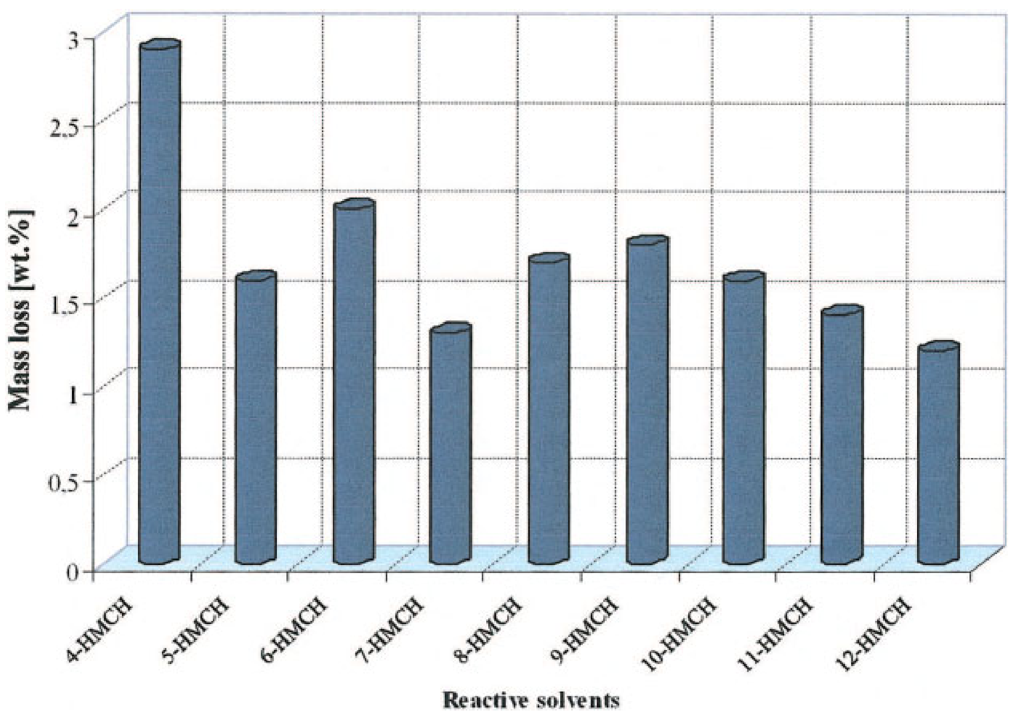

Figure 3 Resistance against boiling water (as measured by mass loss) of a Mel–F–CH coating (56.8 g of melamine/100 g of RS; 20 wt % of water) cured at 120°C for 90 min in the presence of 0.5 wt % of CH_3COOH. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

faces, with no mass loss when boiled in water ($\Delta m = 0\%$, cf. Table III).

Coatings cured with 80% acetic acid

The Mel–F–CH coatings cured with acetic acid catalyst had excellent water resistance and appearance; they were smooth and transparent (Table IV). The best were the coatings prepared with 4-, 5-, or 7-HMCH, containing 20 wt % of water and cured for at least 120–150 min (cf. Fig. 3). As for the other curing systems, the amount of water in RS exceeding 20 wt % slightly reduced the water resistance (the only exception were the samples cured with formic acid) and worsen the appearance of coatings; occasional blisters developed and increased brittleness. The coatings, however, remained transparent.

Acetic acid, as an acid of somewhat lower ionization constant than hydrochloric or formic acids, turned out to be a worse catalyst for curing Mel–F–CH coatings. It also had poorer miscibility with Mel–F–CH resins.

Comparison of boiling water resistance for coatings prepared using different catalysts

By comparing the properties of Mel–F–CH coatings cured in the presence of various catalysts, one could state that the least advantageous was the use of acetic acid; even better boiling water resistance had the samples prepared without any catalyst (cf. Fig. 4). Somewhat better a catalyst was hydrochloric acid. The coatings prepared in the presence of 0.5 wt % of this acid had a good water resistance. The resistance of coatings cured with more HCl, however, became less and less resistant. Moreover, HCl catalyst made the coatings brittle.

The best were the coatings cured with 80% formic acid; they were transparent, smooth, and resistant against boiling water (cf. Fig. 4 and Table III). Hence, strong acids, such as HCOOH or HCl, seem to be better curing catalysts for Mel–F–CH resins than acetic acid. The best was formic acid, probably because of its higher affinity to organic substances. Hydrochloric acid required longer gelation time, by several seconds, in average. Moreover, the gelation time depended on the amount water in RS and the amount of dissolved melamine. The solutions containing little water and a large amount of melamine (cf. Table IV) were very viscous even above 100°C. The high viscosity was a serious disadvantage from the point of view of homogenizing the resin–catalyst system and its uniform application onto glass plate. Hence, the solutions had to be prepared at elevated temperature; thus, considerably reducing curing time. In some cases (particularly with the higher hydroxymethyl derivative solutions), uneven coating layers were obtained, or layers could not be

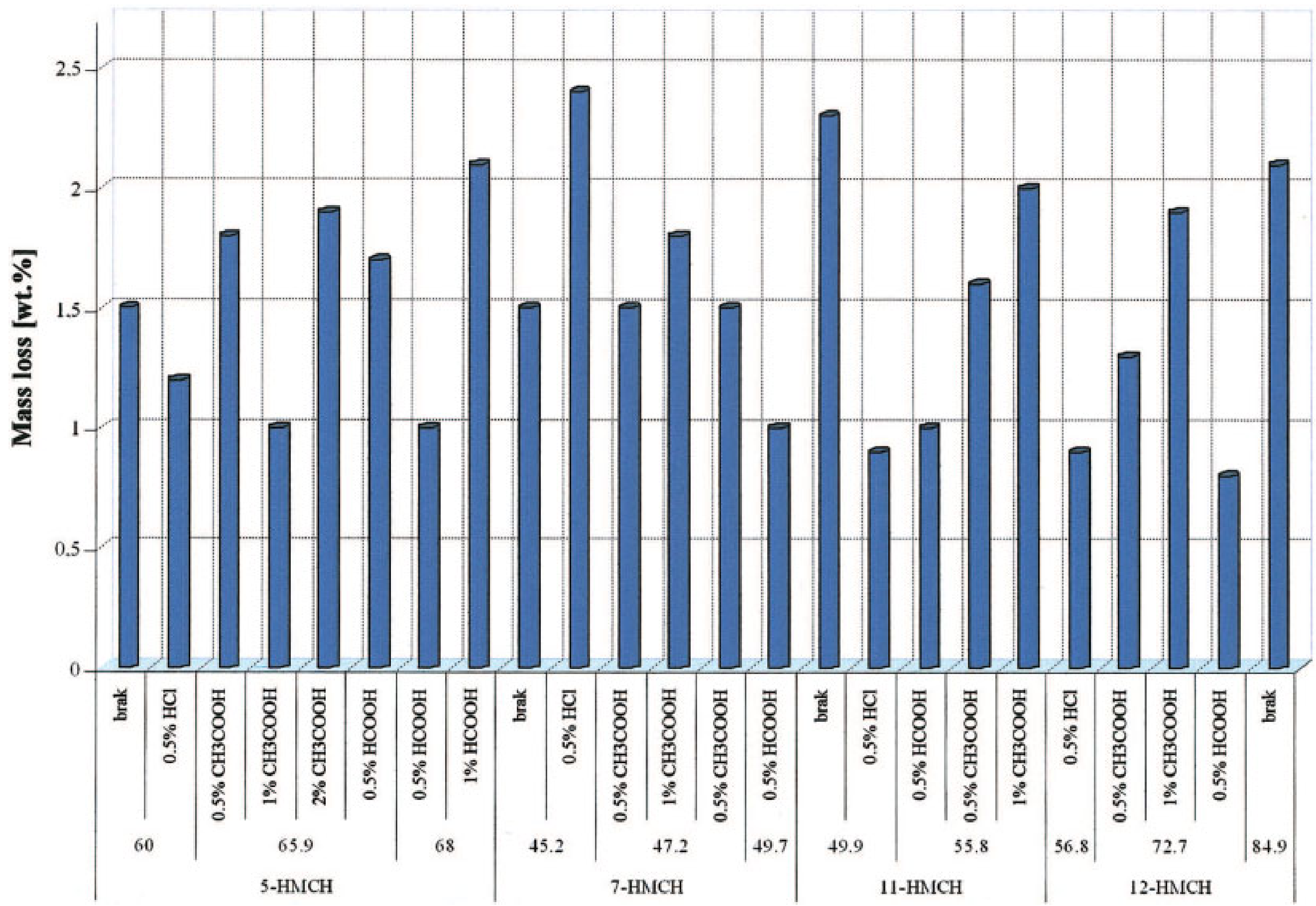

Figure 4 Resistance against boiling water of various Mel–F–CH coatings cured in the presence of different catalysts. Cure conditions: 120°C and 90 min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

obtained at all. At reduced temperature of homogenization, on the other hand, the viscosity prevented all air bubbles to be removed, and the measured boiling water resistances were inconsistent (too low).

An effective method of quality evaluation for coatings is the lack of formaldehyde release from a resin exposed to boiling water. We have measured the amount of formaldehyde in water after resistance experiments. The analyses were made only for the samples in which (1) no change of appearance was evident and (2) the postexposition solution was clear. The results have shown that Mel–F–CH coatings do not release measurable quantities of formaldehyde when boiled in water.

To clarify, the results are again summarized in Table V for those coatings that exhibit excellent water resistance (expressed as the zero mass loss upon exposition to boiling water), have an excellent appearance (transparent, clear and of smooth surface), and sufficient hardness. The coatings that are brittle and/or rough are disregarded despite their good boiling water resistance.

CONCLUSIONS

1. By dissolving melamine in RS prepared from cyclohexanone, one obtains a resin-like reactive composition suitable for the preparation of water resistant polymer coatings.
2. Their water resistance is generally the higher, the longer is curing time, the more melamine is dissolved, and the higher molar ratio of formaldehyde to cyclohexanone in reacting solvent.
3. The best curing agent for the compositions is formic acid used in the amount of 0.5 wt % with respect to the mass of RS.
4. The best resistance against boiling water along with the best appearance of coatings was obtained by curing melamine solutions in RS diluted with 20 wt % of water for 150–210 min at 120°C. The coatings prepared from solutions in 5-HMCH or 7-HMCH exhibited no measurable mass loss after exposure to boiling water for 30 min.

TABLE V
Specification of Resins Cured by Various Systems and Exhibiting the Best Resistance against Boiling Water (Data from Tables 1 through 4).

RS	Water added (wt %)	Catalyst Type	Catalyst Amount (wt %)	Melamine added (g/100g RS)	Curing time (min)	Mass loss, Δm (wt %)	Sample appearance
5-HMCH	30	without	without	66.6	30	−0.1	Transparent, smooth
					60	−0.7	Transparent, smooth
7-HMCH	20	without	without	45.2	120	−1.0	Hard, transparent
					150	−0.8	Hard, transparent
					180	−0.6	Hard, transparent
					210	−0.4	Hard, transparent
	30	without	without	66.3	150	−0.9	Hard, transparent
					180	−0.6	Hard, transparent
					210	−0.4	Hard, transparent
					240	−0.6	Hard, transparent
4-HMCH	20	HCl	0.5	43.5	90	−0.9	Transparent, smooth
					120	−0.1	Transparent, smooth
					150	−0.3	Transparent, smooth
					180	−0.1	Transparent, smooth
					210	−0.2	Transparent, smooth
5-HMCH	20	HCOOH	0.5	68.0	90	−1.0	Hard, smooth
					120	−1.0	Hard, smooth
					180	−0.4	Hard, transparent
					210	0.0	Hard, transparent
	30	HCOOH	0.5	87.9	60	−1.0	Hard, smooth
					90	−1.0	Hard, smooth
7-HMCH	20	HCOOH	0.5	49.7	60	−0.9	Transparent, smooth, opalescent
					120	−1.0	Transparent, smooth, opalescent
					90	−1.0	Transparent, smooth, opalescent
					120	−1.0	Transparent, smooth, opalescent
					150	−0.3	Hard, transparent
					180	0.0	Hard, transparent

5. Unlike the classical, unmodified melamine–formaldehyde resins, the new Mel–F–CH resins are transparent, hard, and do not release formaldehyde after exposure to boiling water.

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