New Melamine–Formaldehyde–Ketone Polymers. V. Coatings from Melamine and MEK-Based Reactive Solvents

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ABSTRACT: Preparation and curing conditions of melamine–formaldehyde–butanone coatings are described. The coatings were prepared from melamine solutions in reactive solvents. The latter were obtained from ethyl-methyl ketone and formaldehyde reacted at different molar rations. Most of the coating had good appearance and good resistance against boiling water. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 2156–2168, 2008

Key words: heteroatom-containing polymers; coatings; resins; curing of polymers; thermosets

INTRODUCTION

The presence of 1,3,5-trizine ring in melamine molecule provides the materials prepared from this monomer with outstanding chemical and thermal resistance.[1] Literature data, on the other hand, on application of melamine monomer for preparation of new materials are scarce, except for the classical melamine–formaldehyde resins. The reason seems to be the lack of organic solvents of melamine to carry out reactions with its presence.

In the recently prepared, so-called reactive solvents (RSs) of melamine,[2–6] the solubility of this monomer exceeds the value of 100 g per 100 g of the solvent obtained from cyclohexanone[5] or ethyl-methyl ketone (MEK)[6] and formaldehyde. Mechanistic studies revealed that melamine dissolved in this solvent by reacting with it and forming a resin-like solution.[2,3] The resulting solutions could be cured with acidic catalysts to yield new melamine–formaldehyde–ketone polymers suitable for preparation of expanded materials[7] or coatings[8,9] of high water resistance.[10]

In this report, we concentrate on the possibility of applying melamine–formaldehyde–butanone (Mel-F-MEK) resins, i.e., the resins prepared by dissolving melamine in formaldehyde-MEK RSs[6] as materials for coatings of high hot water resistance.

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EXPERIMENTAL

Chemicals

Methyl-ethyl ketone [analytically pure (p.a.)], Chempur, Piekary Slaskie, Poland; Formalin p.a., Standard, Lublin, Poland; Triethylamine p.a., Fluka, Buchs, Switzerland; Melamine p.a., Fluka; Formic acid (80%), POCH, Gliwice, Poland; Acetic acid (80%), POCH; Hydrochloric acid (36%), Chempur, Aekany Slaskie, Poland.

Preparation of RSs

The RSs were prepared from methyl-ethyl ketone and 5–12-fold molar excess of formaldehyde as described in detail in Refs. 4 and 6. The products of reactions were coded with explicit information on the molar excess of formaldehyde used in the preparation stage. Thus, the solvent *n*-HMMEK (e.g., 5-HMMEK,..., 12-HMMEK) contains *n* moles of formaldehyde reacted with 1 mol of methyl-ethyl ketone (HMMEK stands for hydroxy-methylbutanone). The reaction between methyl-ethyl ketone and formalin was carried out at 80°C for 6–7 h in the presence of triethylamine as catalyst. Water and catalyst were then removed by distillation under reduced pressure (9–15 mmHg) while keeping the mixture at below 50°C. Anhydrous RSs were obtained. The RSs 5-HMMEK were also prepared at low temperature of 25, 40, or 60°C using appropriately longer time 7.5–9.5 h.

Determination of melamine dissolution in RSs

The solubility of melamine in the anhydrous RSs, in which 20–30 wt % of water was introduced, was

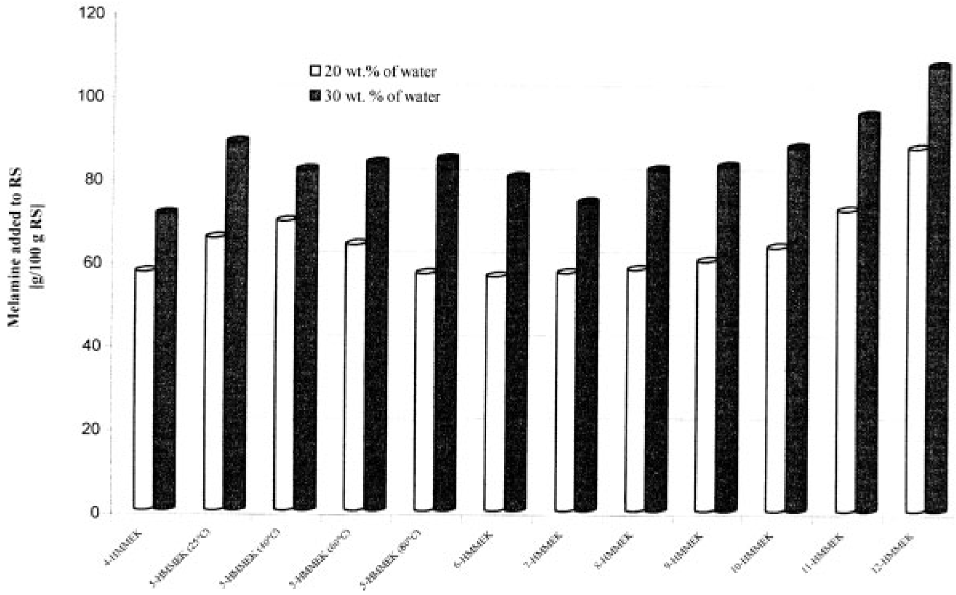

Figure 1 The highest solubility of melamine in reactive solvents containing 20 or 30 wt % of water.

determined as described previously.[4,9] Melamine was introduced into the RSs in the amounts just sufficient to obtain liquid mixtures that could easily be homogenized with catalyst at room temperature. The amounts were established in our previous experiments.[6,10] In fact, the solutions used in curing experiments contained almost the highest possible amounts of melamine that could be dissolved in a given RS diluted with water. These highest amounts of melamine dissolved in RS containing 20–30% of water are shown in Figure 1.

Curing of melamine solutions in RSs

The melamine solutions in RSs were cured in the same way as described previously,[4,10] i.e., without catalyst or with concentrated acids: hydrochloric acid (36%), formic acid (80%), or acetic acid (80%) used in the amounts of 0.5, 1.0, or 2.0 wt % (with respect to RS). The catalysts were introduced at a temperature that was somewhat lower (~ 80°C) than the dissolution temperature (90–110°C). The solutions were prepared by stirring melamine in RSs with a glass rod and poured over a glass plate just before gelation experiment. The glass plate was then heated at 120°C for 30–240 min.

Gelation time

The gelation time (in seconds) was determined by the method of broken filament as described in Ref. 1. The time was measured until the solution gelled while continuously stirred with glass rod. It was the time when filament could not be formed anymore by withdrawing the rod from solution. The gelation time for Mel-F-MEK resins ranged from 90 to 120 s in the presence of 1 wt % to 180–220 s in the presence of 0.5 wt % of catalyst with respect of anhydrous RS, respectively.

Resistance of Mel-F-MEK coatings against water

The stability of Mel-F-MEK against water was determined as described previously.[10] Cured sample of Mel-F-MEK resin (~ 0.3 g) was carefully weighed (to within 0.0001 g) and exposed to ~ 50 cm^3 of boiling (distilled) water for 30 min. Then the sample was withdrawn, examined visually, and placed in oven at 105°C for 30 min. Then the sample was weighed again.

The stability was defined as the loss of mass of cured Mel-F-MEK resin after exposition to boiling water. The appearance of resin after exposition to water (i), amount of formaldehyde transferred (as determined in water by sulfite method[11]) (ii), and mass loss (iii) of the samples were determined. The samples for which the mass loss after exposition to boiling water did not exceed 1 wt % were considered as water resistant.

RESULTS AND DISCUSSION

While seeking applications for the RSs of melamine,[4–6,9,10] we have tested their potential as sources of water-resistant polymer coatings. The coatings were obtained by pouring melamine solutions in RS over glass plates. The RSs were prepared by reacting 1 mol of butanone (MEK) with 5 through 12 mol of formaldehyde, in the presence of triethylamine, to obtain RS coded as 5-HMMEK through 12-HMMEK,

TABLE I
The Best Resistance Against Boiling Water (as Measured by Mass Loss) of Mel-F-MEK Coatings Cured at 120°C (Without Catalyst)

Reactive solvent, RS[a]	Water added (wt %)	Melamine added (g/100g RS)	Curing time (min)	Mass loss Δm (wt %)	Sample appearance after curing
5-HMMEK (25°C)	20	63.2	30	−1.0	Transparent, smooth
			90	−0.9	
	30	83.2	90	−0.6	Transparent, some blisters
			120	−0.3	
5-HMMEK (40°C)	20	59.4	30	−3.8	Transparent, smooth
			60	−2.6	
5-HMMEK (60°C)	20	63.2	60	−3.5	Transparent, some blisters
			90	−2.0	
	30	86.5	90	−2.9	Transparent, some blisters
			120	−1.1	
5-HMMEK (80°C)	20	56.8	90	−3.2	Transparent, hard, some blisters
			120	−2.0	
	30	69.6	90	−1.7	Transparent, some brittle, slightly rough
			120	−0.1	
6-HMMEK	20	55.4	150	−0.8	Transparent, hard, smooth
			180	−0.6	
			210	−0.7	
			240	0.0	
	30	68.9	90	−1.9	Transparent, hard, slightly rough
			120	−1.1	
7-HMMEK	20	56.8	120	−1.0	Transparent, hard, smooth
			150	−0.5	
			180	−0.3	
	30	69.4	90	−1.0	Transparent, hard, smooth
			120	−0.5	
			150	−0.1	
			180	−0.4	
			210	−0.1	
8-HMMEK	20	56.4	90	−0.6	Hard, transparent, smooth
			120	−0.6	
			180	0.0	
			210	0.0	
			240	0.0	
	30	72.5	120	−0.7	Slightly opalescent, slightly rough
			150	−0.6	
			180	−0.5	
			240	−0.4	
9-HMMEK	20	60.2	180	−0.1	Hard, slightly opalescent, smooth
			240	0.0	
	30	77.0	210	−0.3	Hard, slightly opalescent, smooth
			240	−0.5	
10-HMMEK	20	63.2	120	−0.9	Transparent, some blisters
			150	−0.6	
			180	−0.1	
			210	−0.4	
			240	−0.7	
	30	78.9	150	−0.8	Transparent, slightly rough
			180	−0.8	
			210	−0.1	
11-HMMEK	20	58.1	30	−1.2	Brittle, transparent, smooth
			60	−0.9	
			120	−0.9	
	20	66.7	30	−0.6	Transparent, slightly rough
			60	−0.8	
			90	−0.5	
			120	−0.2	
			150	−0.2	
			180	−0.1	
			210	−0.1	
			240	0.0	

TABLE I *Continued*

Reactive solvent, RS[a]	Water added (wt %)	Melamine added (g/100g RS)	Curing time (min)	Mass loss Δm (wt %)	Sample appearance after curing
11-HMMEK	30	65.7	60	−0.9	Transparent, hard, smooth
			90	−0.1	
			120	0.0	
			150	−0.1	
			180	−0.7	
			210	−0.2	
			240	−0.2	
	30	85.5	30	−1.0	Transparent. hard, smooth
			60	−0.5	
			90	−0.1	
			120	0.0	
			150	−0.5	
			180	−0.3	
			210	−0.9	
			240	−0.1	
12-HMMEK	20	78.7	60	−0.5	Transparent, hard, smooth
			90	−0.1	
			120	0.0	
			150	−0.7	Transparent, hard, smooth
			180	−0.4	
			210	−0.5	
			240	0.0	
	30	78.7	60	−1.5	Transparent, hard, smooth
			90	−1.0	
			120	0.0	
		99.9	90	−0.7	Transparent, roughish, opalescent
			120	−0.5	
			150	−0.3	
			180	−0.7	
			210	−0.4	

[a]In Column 1, under RS code, temperature is specified at which solvent was prepared. Preparation temperature is not specified if it was 80°C.

respectively. The curing tests (and subsequently the water resistance tests) were carried out for the RS of the highest capacity of melamine dissolution (Fig. 1). All RS-melamine solutions contained water to improve melamine solubility.[6]

As found in the preliminary experiment, the coatings that had the best properties were those prepared from melamine solutions in RS containing 20–30 wt % of water. We therefore concentrated our attention on these compositions. The presence of water improved the solubility of melamine and facilitated catalyst homogenization. The solutions of melamine in RS not containing water did not produce coatings because of low melamine content and difficulties with curing. To maximize the amount of melamine dissolved in RS was essential because the curing time was significantly reduced.

Water resistance tests were carried out taking into account the effects of (i) amount of dissolved melamine, (ii) proportion of water in the system (usually 20–30 wt % with respect to RS), (iii) type of acid catalyst (HCl, HCOOH, or CH_3COOH), (iv) amount of catalyst (0, 0.5, 1.0, or 2.0 wt % relative to RS), (v) curing temperature, and (vi) curing time. The curing catalysts chosen are typical in curing classical melamine-formaldehyde resins.

The melamine solutions in RSs were found to cure thermally (without catalyst) just upon heating to 120°C for 30–240 min. Literature data suggested much higher temperature to be required,[2] up to 200°C. Such a high temperature was found inconvenient, because the coatings became blistered and too brittle just after few minutes of curing.

The typical curing time was 30–120 min; it was prolonged to 150–240 min in the cases in which the coating had insufficient water resistance.

The samples were prepared from RS containing 0, 20, or 30 wt % of water. The samples prepared from RS containing 40 wt % of water gave blistered coatings.

Coatings cured without catalyst

The coatings prepared from solutions of melamine in RS containing no extra water and cured without catalyst had very poor water resistance. The reason

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

Reactive solvent, RS	Water added (wt %)	Melamine added (g/100g RS)	Catalyst added (wt %)	Curing time (min)	Mass loss Δ*m* (wt %)	Sample appearance after curing
5-HMMEK (25°C)	20	63.3	0.5	90	−1.6	Transparent, smooth
				120	−1.3	
		63.3	1.0	150	−0.4	Transparent, smooth
				180	−0.9	
		63.3	2.0	150	−0.1	Transparent, smooth
				180	−0.5	
	30	82.3	0.5	90	−0.6	Transparent, some blisters
				240	−1.0	
		82.3	1.0	180	2.1	Opalescent, some blisters
				210	1.7	
		82.3	2.0	150	−0.7	Smooth, slightly opalescent
				180	−0.9	
				210	−0.5	
5-HMMEK (40°C)	20	59.4	0.5	60	−2.5	Transparent, smooth
				90	−0.9	
	30	70.1	0.5	60	−0.5	Transparent, smooth, slightly opalescent
				90	−1.0	
				120	−1.0	
5-HMMEK (60°C)	20	63.2	0.5	90	−3.5	Smooth, slightly opalescent
				120	−2.1	
	30	87.2	0.5	60	−2.1	Smooth, opalescent
				90	−1.8	
5-HMMEK (80°C)	20	63.2	0.5	60	−2.4	Transparent, slightly opalescent
				90	−1.4	
		63.2	1	90	−1.6	Transparent, opalescent
				120	−1.0	
		63.2	2	90	−1.8	Transparent, opalescent
				120	−1.0	
	30	98.5	2	90	−1.8	Transparent, some brittle, opalescent
				120	−0.9	
6-HMMEK	30	69.8	0.5	90	−4.3	Transparent, hard, smooth
				120	−0.6	
				150	−0.4	
				180	−0.6	
8-HMMEK	20	56.8	0.5	90	−1.6	Transparent, hard, slightly rough
				120	−0.7	
	30	73.0	0.5	60	−2.4	Transparent, hard, roughish
				90	−1.8	
				120	−0.9	
10-HMMEK	20	63.2	0.5	90	−1.6	Transparent, brittle, roughish
				120	−1.2	
11-HMMEK	20	66.7	0.5	60	−1.4	Rather transparent, blisters, brittle
				90	−1.2	
				120	−1.0	
	30	64.6	0.5	30	−1.1	Transparent, brittle, roughish
				60	−0.9	
				90	−0.8	
		86.2	0.5	60	−0.9	Transparent, hard, slightly rough
				90	0.0	
				120	−0.1	
				150	0.0	Transparent, brittle, roughish
				180	−0.1	
12-HMMEK	20	78.7	0.5	90	−1.0	Transparent, hard, smooth
				120	−0.6	
				150	−0.7	Transparent, brittle, slightly rough
				180	−1.0	
				210	−0.3	
	30	100.3	0.5	30	−0.5	Transparent, hard, opalescent
				60	−0.5	
				120	0.0	
				150	−0.3	Transparent, brittle, slightly rough
				180	−0.1	
				210	−0.1	

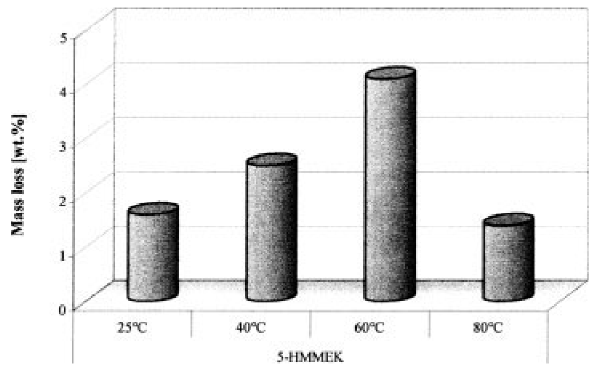

Figure 2 Resistance against boiling water (as measured by mass loss) of a Mel-F-MEK coating obtained from 5-HMMEK (63.2 g of melamine/100 g of RS, 20 wt % of water) cured at 120°C for 90 min, in the presence of 0.5 wt % of HCl.

was that the solution of melamine in RS had high viscosity which prevented good homogenization of catalyst. The presence of water in RS, in the amount of 20–30 wt %, substantially improved the water resistance of coatings (Table I).

In general, the coatings prepared from melamine solutions in RS containing more formaldehyde per MEK molecule (7-HMMEK through 12-HMMEK) had better stability against boiling water. The coatings prepared from these RS had excellent stability (mass loss below 1 wt %). The coatings prepared from 5-HMMEK had also good water resistance, but they contained occasional blisters developed upon curing.

The time of curing was found to increase with synthesis temperature in the case of 5-HMMEK. At elevated temperature, the reaction between MEK and formaldehyde is accompanied by condensation of hydroxymethyl groups. Their concentration decreases and hence the curing time becomes longer.

The coatings prepared from 11-HMMEK or 12-HMMEK RSs had outstanding water stability. The stability was practically independent of the amount of melamine that was dissolved in these RS. The best appearance and total water resistance was exhibited by the coating prepared from melamine solutions in (i) 8-HMMEK cured for 210–240 min, (ii) 11-HMMEK (120 min), and (iii) 12-HMMEK (120 or 240 min).

Coatings cured with 36% hydrochloric acid

The coatings prepared using this catalyst had good water stability, but some of them were brittle (Table II). The samples of Mel-M-MEK (except of those prepared from 5-HMMEK) were cured with 0.5 wt % of HCl, only. Higher amounts of catalyst led to too fast curing reaction.

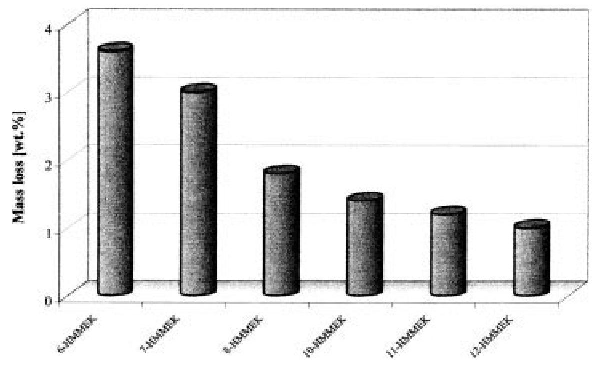

Figure 3 Resistance against boiling water (as measured by mass loss) of a Mel-F-MEK coating (56.8 g of melamine/100 g of RS, 20 wt % of water) cured at 120°C for 90 min, in the presence of 0.5 wt % of HCl.

Excellent water resistance (usually below 1 wt % of mass loss) was exhibited by the coatings prepared from 5-HMMEK with melamine dissolved at different temperatures and cured for 90–120 min at 120°C. Melamine in nearly highest possible amount dissolved in this RS diluted with 20–30 wt % of water (Table II, Fig. 2). Further increase of curing time improved the water resistance, but the coatings were less smooth and slightly blistered. In general, the curing time affected the appearance of coating surface, particularly at relatively large amount (1–2 wt %) of catalyst (Table II) (Fig. 2).

The materials obtained from melamine solutions in 6-HMMEK through 10-HMMEK had different water resistances. For the RS prepared from high proportion of formaldehyde (11-HMMEK, 12-HMMEK), the resistance against boiling water improved, but the quality of surface became poor (Table II). Superb water resistance was exhibited by the coatings prepared from melamine solutions in 11-HMMEK, cured for 90 or 150 min, and those prepared from 12-HMMEK and cured for 120 min (Table II).

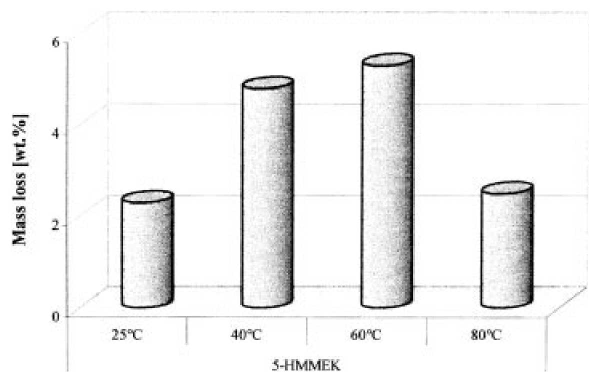

Figure 4 Resistance against boiling water (as measured by mass loss) of a Mel-F-MEK coating (69.5 g of melamine/100 g of RS, 30 wt % of water) cured at 120°C for 90 min, in the presence of 0.5 wt % of HCl.

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

Reactive solvent, RS	Water added (wt %)	Melamine added (g/100g RS)	Catalyst added (wt %)	Curing time (min)	Mass loss Δm (wt %)	Sample appearance after curing
5-HMMEK (25°C)	20	63.2	0.5	150	−0.5	Transparent, smooth
				180	−0.8	
				210	−0.7	
			1.0	150	−0.4	Transparent, smooth
				180	−0.4	
				210	−0.7	
			2.0	150	−0.8	Transparent, smooth
				210	−0.9	
				240	−0.6	
	30	83.2	0.5	60	−1.0	Transparent, some blisters
				90	−0.9	
				120	−0.3	
5-HMMEK (80°C)	20	52.1	0.5	120	−0.9	Transparent, smooth
				150	−0.9	
				180	−1.0	
	30	82.1	0.5	60	−1.8	Transparent, some blisters
				90	−1.0	
				120	−1.0	
6-HMMEK	20	57.2	0.5	90	−3.8	Transparent, smooth
				120	−2.4	
	30	68.5	0.5	30	−3.9	Transparent, slightly rough
				120	−0.3	
7-HMMEK	20	56.8	0.5	60	−3.4	Transparent, smooth
				120	−1.8	
	30	69.9	0.5	90	−3.2	Transparent, slightly rough
				120	−0.9	
			2	90	−1.2	Rather transparent, slightly rough
				120	−0.7	
8-HMMEK	20	56.4	0.5	60	−2.6	Transparent, smooth
				90	−2.3	
		56.4	1	60	−0.9	Transparent, rather smooth
				120	−0.4	
9-HMMEK	30	77.0	0.5	150	−0.1	Transparent, slightly rough
				210	−0.3	
			1	60	−1.7	Transparent, rather brittle, slightly rough
				90	−1.1	
				120	−0.9	
10-HMMEK	20	63.2	0.5	90	−1.4	Transparent, rather smooth
				120	−0.3	
			1	120	−0.6	Rather transparent, some roughish
				150	−0.2	
				180	−0.3	
	30	81.0	0.5	150	−0.5	Transparent, rather smooth
				180	−0.4	
				240	0.0	
11-HMMEK	20	66.7	0.5	60	−1.7	Transparent, rather smooth
				90	−1.0	
	30	86.3	0.5	90	−0.5	Transparent, slightly rough
				120	−0.5	
				150	−0.7	
12-HMMEK	20	78.7	0.5	30	−0.6	Transparent, rather smooth
				60	−0.5	
				90	−0.6	
				120	−0.5	
	30	97.7	0.5	90	−0.4	Transparent, some roughish
				120	0.0	
				150	0.0	Transparent, opalescent
				180	−0.3	
				210	0.0	

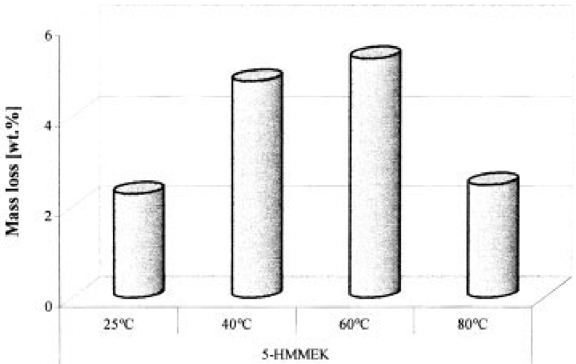

Figure 5 Resistance against boiling water (as measured by mass loss) of a Mel-F-MEK coating obtained from 5-HMMEK (63.2 g of melamine/100 g of RS, 20 wt % of water) cured at 120°C for 90 min, in the presence of 0.5 wt % of HCOOH.

The presence of 20 wt % of water in the RS prior to melamine dissolution improved both the water resistance and quality of surface (Fig. 3). More water in RS (30 wt %) improved water stability (Fig. 4), but reduced the elasticity of the coatings and resulted in poor surface quality (Table II).

Coatings cured with 80% formic acid

Similarly as for hydrochloric acid catalyst, in the presence of formic acid, the coatings prepared from melamine solutions in RS which contained high proportion of melamine had the best water resistance. In this case, the gelation time was longer than for HCl, and hence, experiments were performed with higher amount of catalyst (1 or 2 wt %) as well.

Excellent water resistance was exhibited by the coatings prepared from melamine solutions in 5-HMMEK prepared at room temperature or at 80°C (Table III, Fig. 5). The coatings were colorless, transparent, and usually smooth (RS diluted with 20 wt % of water) or transparent, but slightly blistered (RS diluted with 30 wt % of water). The presence of blisters might have been caused by released formaldehyde from unreacted hydroxymethyl groups in RS or in hydroxymethylmelamines. High viscosity of the curing coating facilitates such a blistering.

As before, the best water resistance was exhibited by the coatings prepared from RS with high formaldehyde content (10-HMMEK – 12-HMMEK) (Table III, Fig. 6). The coatings prepared from RS diluted with 20 wt % of water were transparent, hard, and smooth; more diluting water or prolonged curing time reduced the coating quality (rough surface), though improved water stability.

The catalyst concentration seemed not to affect the appearance or water stability of the coatings.

The coatings of excellent water resistance were obtained from melamine solutions in 10-HMMEK or 12-HMMEK containing 30 wt % of water, cured with 0.5 wt % of catalyst for 240 min (10-HMMEK) or for 120–210 min (12-HMMEK) (Table III).

Coatings cured with 80% acetic acid

Acetic acid was found to be an outstanding catalyst for curing Mel-F-MEK coatings. The coatings prepared from melamine solutions in 5-HMMEK and cured for 150 min or more exhibited excellent water stability (Table IV, Fig. 7). The coatings prepared at the same system, but with more water diluting RS (30 wt %) or with more catalyst (1–2 wt %) had poorer quality. They started to be opaque, sometimes blistered, and became brittle (Table IV). Too much water introduced into the composition increases the chance of trapping it within the resin. The trapped water is then washed away by boiling water. Similarly, too much of catalyst (80% aqueous solution of acetic amid) results in faulty coating.

Fully water resistant ($\Delta m = 0\%$) was exhibited by the coatings prepared from melamine solutions in 5-HMMEK under different conditions (cf. Table IV).

As in previous cases, among the coatings prepared by dissolving melamine in RS, obtained by reacting 1 mol of MEK with 6–12 mol of formaldehyde, the best resistance against boiling water was exhibited by the solutions in RS containing large proportion of formaldehyde and diluted with 20 wt % of water (Table IV, Fig. 8). The coatings prepared from RS diluted with more than 20 wt % of water had somewhat better water resistance, but poor appearance, and blisters showed up and the material became brittle, although remained transparent.

With more catalyst used, the coatings were more water resistant, but less nice-looking; prolonged curing time improved both these properties. When exposed to boiling water, no weight reduction was exhibited by the coatings prepared from RS contain-

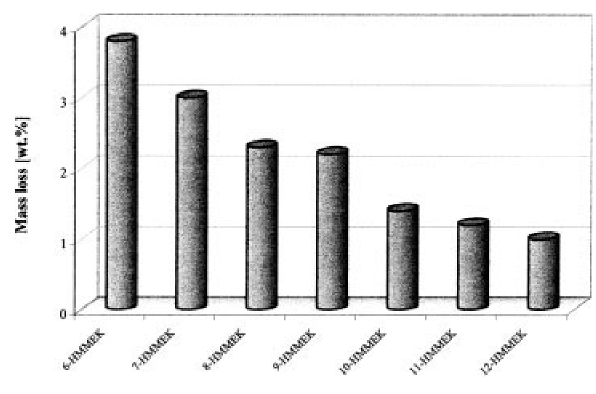

Figure 6 Resistance against boiling water (as measured by mass loss) of a Mel-F-MEK coating (52.1 g of melamine/100 g of RS, 20 wt % of water) cured at 120°C for 90 min, in the presence of 0.5 wt % of HCOOH.

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

Reactive solvent, RS	Water added (wt %)	Melamine added (g/100g RS)	Catalyst added (wt %)	Curing time (min)	Mass loss Δm (wt %)	Sample appearance after curing
5-HMMEK (25°C)	20	63.2	0.5	150	−1.2	Transparent, smooth
				180	−0.2	
				240	−0.6	
		63.2	1.0	150	−0.5	Transparent, smooth
				180	−0.2	
				210	−0.2	
				240	−0.3	
	30	83.2	0.5	150	−0.3	Smooth, slightly opalescent
				180	0.0	
				210	−0.3	
				240	−0.5	
		83.2	1.0	150	−0.9	Smooth, slightly opalescent
				210	−0.7	
				240	−0.6	
		83.2	2.0	150	−0.9	Smooth, opalescent
				180	−0.3	
				240	−0.6	
5-HMMEK (40°C)	20	59.4	0.5	90	−1.3	Transparent, some blisters
				120	−1.0	
				150	−0.8	
	30	73.1	0.5	60	0.0	Transparent, rather smooth
				90	−0.4	
				120	−0.6	
		73.1	1.0	90	−0.6	Transparent, some blisters
				120	−1.0	
		73.1	2.0	90	0.5	Transparent, blisters
				120	0.9	
5-HMMEK (60°C)	20	63.2	0.5	150	−0.5	Transparent, smooth
				180	−0.3	
				210	−0.2	
		63.2	1.0	180	0.0	Smooth, transparent
				210	0.0	
				240	0.0	
		63.2	2.0	150	−0.1	Smooth, opalescent
				180	−0.1	
				210	−0.1	
				240	−0.2	
	30	82.0	0.5	180	−0.6	Opalescent, some blisters
				240	−0.8	
		82.0	1.0	180	−0.7	Opalescent, some blisters
				240	−1.7	
		82.0	2.0	150	−0.2	Opalescent, rather smooth, brittle
				180	−1.0	
				210	−0.9	
5-HMMEK (80°C)	20	56.8	0.5	120	−0.2	Transparent, hard, smooth
				150	0.0	
				180	0.0	
				210	−0.2	
				240	−0.3	
	30	70.0	0.5	120	−0.8	Transparent, hard, smooth
				150	−0.4	
				180	−0.8	
				210	−0.8	
		70.0	1.0	90	−1.2	Transparent, brittle, smooth
				120	−0.7	
		70.0	2.0	30	−0.7	Transparent, brittle, smooth
				60	−0.9	
				90	−1.0	

TABLE IV *Continued*

Reactive solvent, RS	Water added (wt %)	Melamine added (g/100g RS)	Catalyst added (wt %)	Curing time (min)	Mass loss Δm (wt %)	Sample appearance after curing
6-HMMEK	30	69.6	0.5	60	−2.9	Hard, some blisters
				90	−1.2	
			1.0	90	−1.0	Hard, some blisters
				120	−0.9	
7-HMMEK	20	56.8	0.5	90	−1.0	Transparent, rather hard, smooth
				150	−0.6	
				180	−0.5	
8-HMMEK	20	56.8	0.5	120	−1.0	Transparent, hard, smooth
				150	−0.5	
			1.0	90	−2.4	Transparent, slightly rough
				120	−1.8	
			2.0	60	−3.7	Transparent, slightly rough
				120	−0.9	
	30	73.3	0.5	30	−1.0	Transparent, some blisters
				60	−1.0	
9-HMMEK	20	59.4	0.5	120	−0.3	Transparent, hard, smooth
				150	0.0	
				180	−0.2	
				240	0.0	
10-HMMEK	20	63.2	0.5	90	−0.8	Transparent, hard, smooth
				120	−0.4	
				150	−0.2	Transparent, hard, smooth
				180	0.0	
				210	0.0	
				240	0.0	
			1.0	90	−1.1	Transparent, hard, slightly rough
				120	−0.8	
			2.0	90	−1.5	Transparent, hard, slightly rough
				120	−0.7	
	30	80.8	0.5	120	−0.6	Transparent, hard, smooth
				180	0.0	
				210	−0.2	
				240	0.0	
11-HMMEK	20	66.7	0.5	60	−0.5	Transparent, hard, smooth
				90	−0.3	
				120	0.0	
				150	0.0	
		66.7	1.0	90	−1.0	Rather transparent, hard, slightly rough
				120	0.0	
		66.7	2.0	30	−0.2	Rather transparent, hard, slightly rough
				90	−0.9	
	30	72.6	0.5	150	−0.3	Transparent, hard, smooth
				180	−0.2	
				210	−0.1	
		86.5	0.5	30	−0.8	Transparent, hard, smooth
				90	−0.8	
12-HMMEK	20	72.2	0.5	90	−0.2	Transparent, hard, smooth
				120	0.0	
				150	0.0	Transparent, hard, smooth
				180	−0.4	
		72.2	1.0	90	−1.0	Transparent, rather hard, some roughish
				120	−1.0	
				150	−1.0	
	30	96.1	0.5	150	−0.8	opalescent, hard, smooth
				180	−0.4	
				210	−0.3	
		96.1	1.0	30	−0.9	opalescent, rather hard, smooth
				90	−1.4	

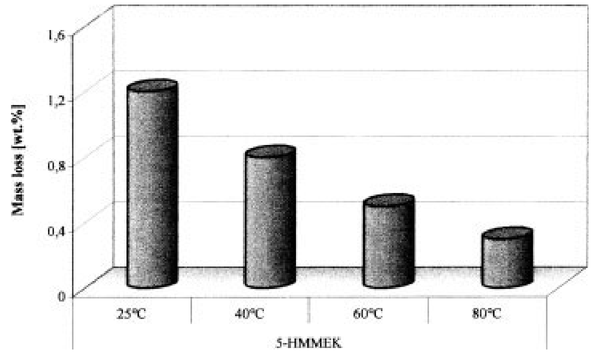

Figure 7 Resistance against boiling water (as measured by mass loss) of a Mel-F-MEK coating obtained from 5-HMMEK (63.2 g of melamine/100 g of RS, 20 wt % of water) cured at 120°C for 90 min, in the presence of 0.5 wt % of CH_3COOH.

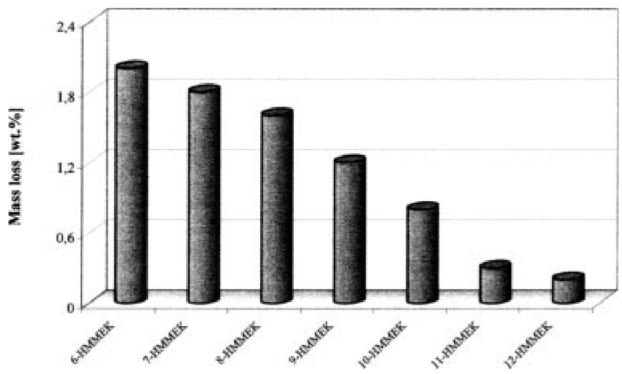

Figure 8 Resistance against boiling water (as measured by mass loss) of a Mel-F-MEK coating (63.2 g of melamine/100 g of RS, 20 wt % of water) cured at 120°C for 90 min, in the presence of 0.5 wt % of CH_3COOH.

TABLE V
Mel-F-MEK-Based Coatings of Best Water Resistance Cured for Relatively Short Time in the Presence Various Catalysts (Compiled from Tables I–IV)

Reactive solvent, RS	Water added (wt %)	Melamine added (g/100g RS)	Catalyst		Curing time (min)	Mass loss Δm (wt %)	Sample appearance after curing
			Type	Type			
5-HMMEK (25°C)	20	63.2	HCl	1.0	150	−0.4	Transparent, smooth
				2.0	150	−0.1	
	20	63.2	HCOOH	0.5	150	−0.5	Transparent, smooth
				1.0	150	−0.4	
			CH_3COOH	1.0	150	−0.5	Transparent, smooth
	30	70.1	HCl	2.0	120	−0.5	Smooth, some opalescent
5-HMMEK (40°C)	30	59.4	HCl	0.5	90	−0.2	Transparent, smooth
		70.1		0.5	60	−0.5	Transparent, smooth, opalescent
5-HMMEK (60°C)	20	63.2	CH_3COOH	0.5	150	−0.2	Transparent, smooth
				1.0	180	0.0	
5-HMMEK (80°C)	20	56.8	CH_3COOH	0.5	150	0.0	Transparent, hard, smooth
	30	70.0	CH_3COOH	0.5	120	−0.6	Transparent, hard, smooth
				1.0	120	−0.6	
				2.0	30	−0.6	
					60	−0.6	
6-HMMEK	20	65.8	Without	Without	210	−0.6	Transparent, hard, smooth
					240	0.0	
	30	70.0	HCl	0.5	150	−0.4	Transparent, hard, smooth
7-HMMEK	20	56.8	Without	Without	150	−0.5	Transparent, hard, smooth
	30	69.4	Without	Without	120	−0.5	
8-HMMEK	20	56.8	Without	Without	180	0.0	Transparent, hard, smooth
			HCOOH	1.0	90	−0.5	Transparent, hard, smooth
			CH_3COOH	0.5	120	−0.5	Transparent, hard
	30	72.5	Without	Without	180	−0.5	Transparent, hard, smooth
9-HMMEK	20	59.4	CH_3COOH	0.5	120	−0.3	Transparent, hard, smooth
					150	0.0	
10-HMMEK	20	63.2	CH_3COOH	0.5	120	−0.4	Transparent, hard, smooth
					180	0.0	
	30	80.1	CH_3COOH	0.5	180	0.0	Transparent hard, rather smooth
11-HMMEK	20	66.7	CH_3COOH	0.5	60	−0.5	Transparent, hard, smooth
					120	0.0	
	30	65.7	Without	Without	90	−0.1	Transparent, hard, smooth
					120	0.0	
		85.5			90	−0.1	Transparent, hard, smooth
					120	0.0	
		96.1	CH_3COOH	0.5	180	−0.4	Transparent, hard, smooth
12-HMMEK	20	78.7	Without	Without	90	−0.1	Transparent, hard, smooth
					120	0.0	
		72.2	CH_3COOH	0.5	90	−0.2	Transparent, hard, smooth
					120	0.0	
	30	78.7	Without	Without	120	0.0	Transparent, hard, smooth

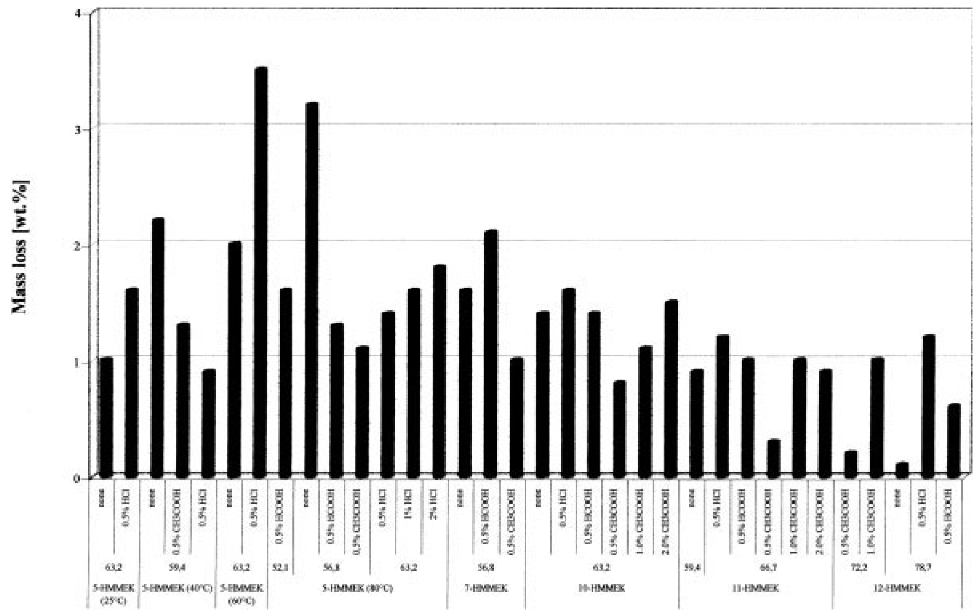

Figure 9 Resistance against boiling water (as measured by mass loss) of various Mel-F-MEK coatings (containing 20 wt % of water) cured in the presence of different catalysts. Cure conditions: 120°C and 90 min.

ing high proportion of formaldehyde (9-HMMEK through 12-HMMEK, cf. Table IV).

Comparison of water resistances of coatings cured in the presence of different catalysts

By comparing the stabilities against boiling water of coatings prepared in the presence of different catalysts, one can note that the best properties was exhibited by those cured with acetic acid. The coatings were transparent, hard, and smooth (Tables IV and V). The materials cured thermally (without catalyst) or in the presence of hydrochloric acid or formic acid had slightly worse stability against water (Fig. 9, Tables II and III).

The majority of coatings prepared in this work were transparent. As the proportion of melamine increased in the composition comprising RS, the water resistance of coatings prepared from these compositions also increased. An important effect on the appearance and properties of coatings had water introduced to RS prior to melamine dissolution. As the amount of water introduced into RS exceeded ∼ 30 wt %, the water resistance of resulting coatings decreased. The optimal amount of water providing sufficiently high melamine dissolution (56.0 g of melamine in 100 g of RS) and at the same time good water resistance was 20 wt % of water. As the amount of melamine dissolved in RS exceeded 97.0 per 100 g (11-HMMEK and 12-HMMEK), the coating were slightly opalescent, but their water resistance was still very good. Clearly opalescent were Mel-F-MEK coatings cured with hydrochloric acid.

The amount of melamine dissolved in RS, as well as the amount of water added, determined the gelation time and viscosity of solutions. The solutions containing little water and a high proportion of melamine were very viscous in temperature below 100°C. Uniform distribution of catalyst in such viscous media was often difficult or even impossible. The solution temperature had to be increased and hence the gelation time became too short to cast the solution evenly over the glass plate. Reduction of temperature, and hence lengthening the gelation time, on the other hand, made it difficult to remove air bubbles, and the resulting water resistance became determined smaller than for the same sample (i.e., containing the same amount of water and melamine) cured in higher temperature.

As the molar ratio of formaldehyde to MEK in the Mel-F-MEK resin increased, the gelation time also slightly increased. On the contrary, higher amount of water added to RS reduced the gelation time; water reduced the solution viscosity and facilitated uniform mixing of catalyst. Gelation time was also reduced with increasing amount of curing agent.

One of the methods of assessing the quality of coatings was the amount of free formaldehyde released during boiling in water. This was measured by determining the concentration of formaldehyde in water after exposition. The analysis was limited to the samples that (i) exhibited no changes in their appearance and (ii) the solution after exposition was clear. The analysis revealed that no formaldehyde was released from Mel-F-MEK resins exposed to boiling water.

The summary of results is collected in Table V. The compositions and properties of coatings are presented, which exhibit excellent boiling water resistance (expressed as the lack of mass reduction after exposition in boiling water), have excellent appearance (transparent and smooth), hardness, and exhibit a short curing time. The coatings that were brittle, had rough surface, and required long curing time were omitted.

The best results ($\Delta m = 0\%$) were obtained in the case of Mel-F-MEK resins prepared from melamine solutions in RS after curing for 120 min.

CONCLUSIONS

1. The water stability of coatings prepared from melamine solutions in RSs is high when they contain more melamine, have longer curing time, high water content in the RS (below 30 wt %, though) before melamine dissolution, and high formaldehyde/MEK molar ratio in the RS.
2. In most cases, the optimal curing catalyst concentration is 0.5 wt % with respect to anhydrous RS. A quantity smaller than this extends the time of curing needed to achieve the best water resistance. A higher amount of catalyst (1–2 wt %) usually reduces the stability of a coating against boiling water. The best curing catalyst is concentrated (80%) acetic acid and the optimal amount of water diluting RS prior to melamine dissolution is 20 wt %.
3. Unlike the classical bulk melamine–formaldehyde resins, the new melamine–formaldehyde–butanone resins are transparent and hard and do not release formaldehyde when exposed to boiling water.

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