Effect of Melamine-Formaldehyde Structure on Cure Response of Thermoset Coatings

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Reactivity of etherified melamine-formaldehyde (MF) resins with polyol binders depends on the pattern of substitution on off-ring nitrogen atoms. These sites can be doubly substituted [$-N(CH_2OCH_3)_2$] or singly substituted [$-N(H)(CH_2OCH_3)$]. The (N–H) portion of singly substituted sites is referred to as an imino group. The main finding of this work is that acid catalyzed cure response is improved greatly when the imino content is reduced to very low levels. The effect of degree of substitution on MF basicity and the site of protonation, ring, or side chain are key elements in the explanation of this cure response behavior.

Properties were determined for films cured for 30 min at various temperatures with constant catalyst level and type (0.5 phr para-toluenesulfonic acid). Resins of varying imino content were used. With the MF resin of lowest imino content, extensive cure of acrylic and polyester polyols was observed at cure temperatures as low as 180°F (82°C).

Paint tests of hardness and solvent resistance were useful for determining cure response. Dynamic mechanical analysis (DMA) on free films also indicated cure response differences. Storage modulus values from DMA were used to calculate crosslink densities of the thermoset films.

INTRODUCTION

Etherified melamine-formaldehyde (MF) resins have been used for crosslinking thermoset coatings for over 60 years,[1,2] but coatings chemists are still learning more about cure response. Wicks et al.[1] report that with 0.5 to 1.0 wt% sulfonic acid as catalyst, typical Class I (high solids, hexamethoxy methylmelamine (HMMM) type) MF resins give cured films in 10 to 30 min at 110° to 130°C (230° to 266°F). This paper describes 30 min cure studies at 71° to 104°C (160° to 220°F). The structural feature that has been changed to achieve low temperature cure is the content of imino groups. The purpose of this paper is to show that in the presence of strong acid catalysts reducing imino group content improves cure response.

Vaughn et al.[3] reported commercial production of a low imino MF resin that contained just enough butoxymethyl groups to prevent crystallization. Jones et al.[4,5] reported laboratory preparation of low imino MF resins by purification of commercial resins using a combination of hexane extraction and adsorption on alumina. Our results on enhanced cure response are consistent with previous reports.[3-5]

EXPERIMENTAL

Materials

Three methylated MF resins that differ in imino content were included in this study. A developmental crosslinker designed to have very low imino content and a very low level of oligomerization was included and coded as MF1. MF1 is a waxy solid that dissolves readily in typical coatings solvents. Most commercial high solids MF resins are viscous liquids, but if the structure approaches that of pure HMMM, the resin tends to crystallize. The other methylated MF resins used here are commercial products from Solutia Inc.: Resimene™ 747 (coded MF2) and Resimene 717 (coded MF3).

The functional group content in MF resins is determined mainly by high performance liquid chromatography (HPLC) and ^{13}C NMR spectroscopy.[1] Extent of bridg-

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Table 1—Effect of MF on Cure of Acrylic Films
Cure Time—30 min; Catalyst—0.5 phr pTSA

MF Resin	Cure Temp.		Tukon Hardness		Acetone Resis.
			1 Day	7 Days	
	°F	°C	KHN		D. Rubs
MF1	220	104	13	14	>200
	200	93	11	13	>200
	180	82	11	11	>200
	160	71	8	8	170
MF2	220	104	12	13	>200
	200	93	10	11	>200
	180	82	6	7	90
	160	71	—	—	—
MF3	220	104	13	15	>200
	200	93	7	9	30
	180	82	(1)	(1)	(3)
	160	71	—	—	—

ACR/MF = 2/1 by equivalents

ing or oligomerization is estimated from molecular weight as determined by size exclusion chromatography (SEC). The imino content can be estimated from NMR and SEC, but some assumptions must be made about types of bridges. We estimate (with assumptions) that the equivalents of imino groups expressed per triazine ring are <0.20, 0.42, and 2.3 for MF1, MF2, and MF3, respectively.

Equivalent weights of MF resins for co-condensation with polyol co-reactants were calculated by including methoxymethyl groups (=N–CH_2OCH_3) and methylol groups (=N–CH_2OH) as reactive groups. Once again assumptions were made concerning types of bridging. Equivalent weights based on these assumptions are 68, 78, and 91 g/eq. for MF1, MF2, and MF3, respectively.

The co-reactants used in this study included a high-solids acrylic polyol from SC Johnson Polymer (Joncryl™ 500, coded ACR) and a high-solids polyester polyol from McWhorter Technologies (Polymac™ HS 57-5776, coded PE). ACR is reported to have low molecular weight (M_n = 1700 gm/mole), a narrow molecular weight distribution (M_w/M_n = 1.7), and a hydroxyl equivalent weight of 400 g/eq.[6] The equivalent weight of PE is reported to be 315 g/eq.[7]

Table 2—Effect of MF on Cure of Polyester Films
Cure Time—30 min; Catalyst—0.5 phr pTSA

MF Resin	Cure Temp.		Tukon Hardness		Acetone Resis.
			1 Day	7 Days	
	°F	°C	KHN		D. Rubs
MF1	220	104	16	17	>200
	200	93	15	16	>200
	180	82	13	16	140
	160	71	7	9	60
MF2	220	104	16	17	190
	200	93	10	13	60
	180	82	(2)	(2)	(7)
	160	71	—	—	—
MF3	220	104	16	17	130
	200	93	6	7	(5)
	180	82	(<1)	(<1)	(1)
	160	71	—	—	—

PE/MF = 2/1 by equivalents

Film Preparation and Cure

Formulations were prepared at a 2:1 ratio of methoxymethyl to hydroxyl groups. Butyl acetate was used to reduce viscosity for drawdown application. Films were prepared using a bar having a 4 mil gap. Dry film thickness was 0.9 to 1.2 mil (22 to 30 µm). The substrates were 3 in. × 6 in. tin-plated steel panels from Q-Panel Company. Films were cured 30 min with para-toluenesulfonic acid (pTSA) as catalyst at 0.5 parts per 100 parts binder solids. Temperature was the main cure variable. The oven settings used were 220°F (104°C), 200°F (93°C), 180°F (82°C), and 160°F (71°C).

Test Methods

Penetration of a diamond-tipped indenter was used to determine film hardness. The length of the imprint of a Knoop diamond was measured microscopically and converted to Knoop hardness number (KHN, Tukon hardness, ASTM D 1474). Solvent resistance was determined by counting the number of back and forth strokes (double rubs) required to remove the coating down to the substrate. Rubs were carried out with a cheese cloth saturated with acetone in a modification of ASTM D 4752. Flexibility of films was determined by bending the coated tin-plated panels around rods of various diameters (cylindrical mandrel bend test, ASTM D 522B).

Cured free films for dynamic mechanical analysis (DMA) were obtained by mercury amalgamation.[8] DMA was carried out on 0.6 cm × 2.5 cm samples at 10 Hz oscillating frequency on a Rheometrics Solids Analyzer (RSA™, Rheometric Scientific, Inc.). Tensile storage modulus (E′), tensile loss modulus (E″), and loss tangent (Tan δ = E″/E′) were determined from 20° to 190°C at a scan rate of 3°C/min. The glass transition temperature (T_g), was taken as the temperature at the maximum in the plot of Tan δ versus scan temperature.[8]

RESULTS

Paint Test Results—Acrylic Films

Properties of acrylic films cured with three MF crosslinkers are compiled in *Table* 1. Tukon hardness values are reported for determinations made one day and seven days after bake. Acetone rub values in *Table* 1 were determined seven days after bake. Hardness increased moderately with time after baking.

Hardness and acetone resistance indicate that the acrylic films were well cured regardless of the MF resin at 220°F bake temperature. As cure temperature is decreased, MF1 retains good cure response down to 180°F and significant cure response down to 160°F. In contrast, MF2 retains good cure response only down to 200°F, and response is clearly marginal at 180°F bake. For MF3, the film baked at 220°F is well cured, but the decrease in cure is already very strong at 200°F. Properties could hardly be measured below 200°F when MF3 was used as the crosslinker.

Results of *Table* 1 make it very evident that the order of cure response is:

MF1 > MF2 > MF3

This is reverse order to imino content of these MF resins. This finding, therefore, is in agreement with earlier reports[3-5] that for catalyzed cure, low imino content gives good cure response.

Previous reports[1] state that with 0.5 to 1.0 wt% sulfonic acid as catalyst, typical high-solids MF resins give cured films in 10 to 30 min at 230° to 266°F. The highest cure temperature in *Table* 1 is below the low end of this guide line, and the lowest bake temperatures are very far below this guide line with MF1 still giving a cured film.

Mandrel bend flexibility results were all either "pass 1/2 inch" or "pass 1/4 inch." The values did not change much with MF selected or with cure temperature. Therefore, flexibility was not useful for determining extent of cure in this study.

Paint Test Results—Polyester Films

Properties of polyester films cured with the same three MF crosslinkers are compiled in *Table* 2. Tukon hardness values indicate that the polyester films were all quite well cured regardless of MF at 220°F bake temperature. Hardness and acetone resistance of polyester films (*Table* 2) decreased as expected with decreasing cure temperature. The MF1 film begins to show the effects of decreasing cure temperature at 180°F, but even at 160°F the film still has some hardness and acetone resistance. In contrast, MF2 and MF3 films show large property decreases even at 200°F. There is very little cure with MF2 at 180°F or with MF3 at 200°F. Once again it is very evident that the order of cure response is:

MF1 > MF2 > MF3

DMA Results—Acrylic Films

DMA results for acrylic films cured with MF1 are shown in *Figure* 1. Storage modulus (E′) and loss tangent (Tan δ) values for 220°F cure are plotted versus temperature in *Figure* 1a. The temperature scan covers the full range of polymer behavior from glassy (left) to transition (center) to rubbery plateau (right). E′ is related to the stiffness of the sample. It is evident that the sample is very stiff in the glass region, softens throughout the transition region, and levels out at a low value in the rubbery plateau. The value of E′ in the rubbery plateau region is proportional to crosslink density of the sample.[8] The value at the minimum, E′ (min), is believed to be characteristic of the sample as originally cured. As the scan temperature is increased above the cure temperature (220°F = 104°C), additional crosslinking takes place during the scan.[8] The rise in E′ at high temperatures (far right in *Figure* 1a) is attributed largely to this additional crosslinking.

The loss tangent is related to the liquid-like or viscoelastic response of the sample. Tan δ goes through a maximum in the middle of the transition region. The position on the temperature scale where the maximum occurs is taken as the glass transition temperature, T_g. As extent of cure increases, the value of T_g also increases.

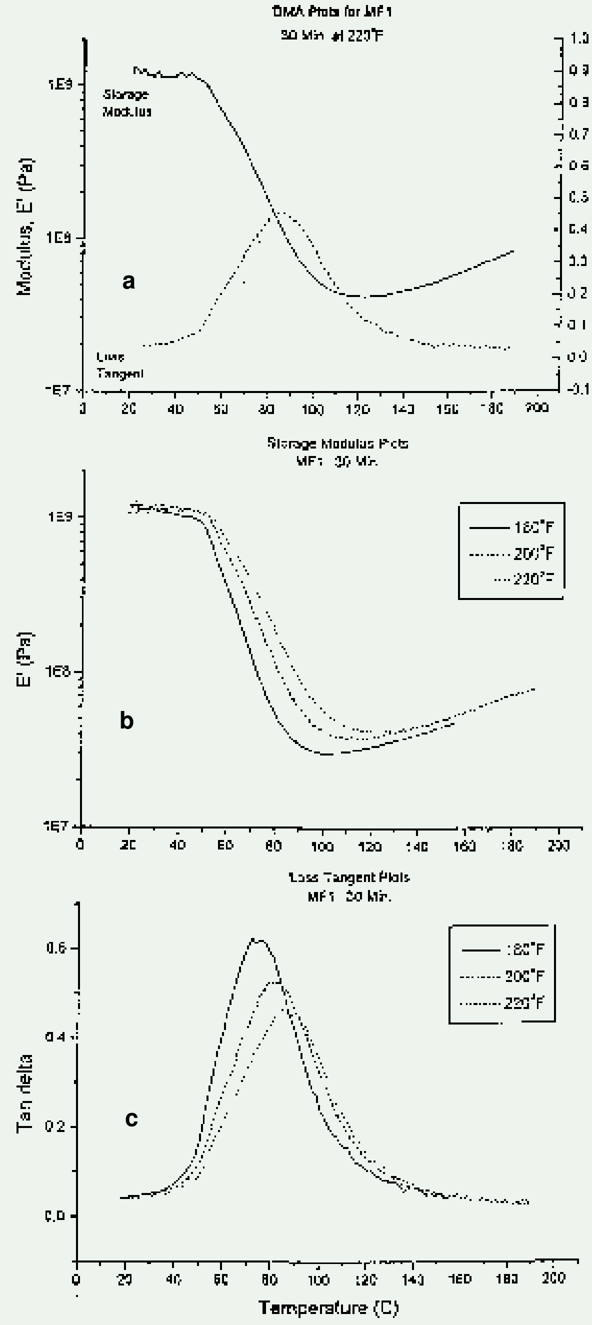

Figure 1—Dynamic mechanical analysis of ACR/MF1 films: (a) DMA plots at 220°F cure temperature; (b) effect of cure temperature on storage modulus; and (c) effect of cure temperature on loss tangent.

However, since liquid-like response is suppressed when crosslink density increases, the height of the loss tangent peak, called Tan δ (max), decreases with increasing extent of cure.[8]

The E′ plot from *Figure* 1a is repeated in *Figure* 1b, and two additional E′ plots obtained at lower cure temperatures are plotted on the same axes to facilitate comparison. It is evident that the value of E′ (min) decreases and the temperature of the minimum also decreases as the cure temperature is decreased. These changes are not very large, which suggests that good cure response persists down to the lowest cure temperature of 180°F.

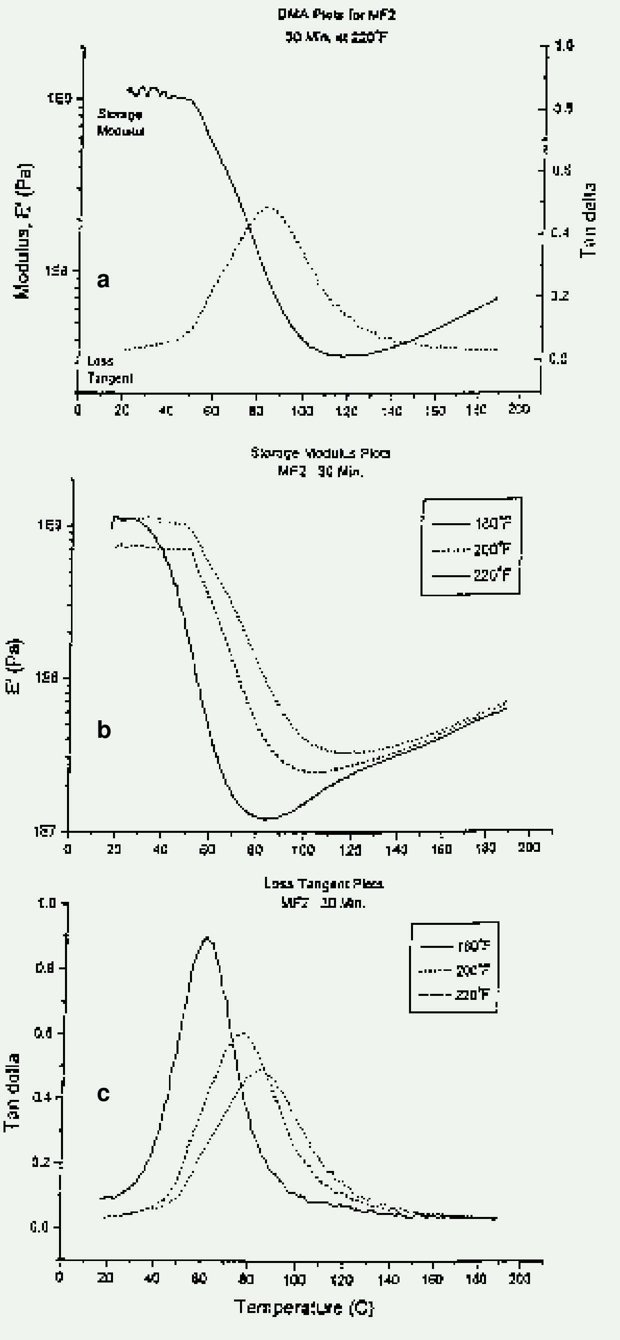

Figure 2— Dynamic mechanical analysis of ACR/MF2 films: (a) DMA plots at 220°F cure temperature; (b) effect of cure temperature on storage modulus; and (c) effect of cure temperature on loss tangent.

The Tan δ plot from *Figure* 1a is repeated in *Figure* 1c, and two additional Tan δ plots obtained at lower cure temperatures are plotted on the same axes to facilitate comparison. It is evident that the temperature at the maximum (T_g) decreases and the value of Tan δ (max) increases as the cure temperature is decreased. These changes are also not very large, which further suggests that good cure response persists down to the lowest cure temperature of 180°F.

DMA results for acrylic films cured with MF2 are shown in *Figure* 2. Storage modulus (E′) and loss tangent (Tan δ) values for 220°F cure are plotted versus temperature in *Figure* 2a. *Figure* 2b shows a comparison plot of E′ for three films cured at different temperatures. The effect of cure temperature on E′ is much stronger for MF2 (*Figure* 2b) than for MF1 (*Figure* 1b). *Figure* 2c shows a comparison plot of Tan δ for three films cured with MF2 at three different temperatures. The effect of cure temperature on Tan δ is much stronger for MF2 (*Figure* 2c) than for MF1 (*Figure* 1c). Note that the highest value on the Tan δ scale had to be increased from 0.6 in *Figure* 1c to 1.0 in *Figure* 2c to show the value of Tan δ (max) with MF2 as crosslinker.

Comparisons of *Figures* 1 and 2 indicate that films cured with MF1 give a much smaller decrease in cure response with decreasing cure temperature than observed with MF2 as crosslinker. This difference is attributed to the lower imino content of MF1. Both DMA and paint tests show that low imino content gives good catalyzed cure response.

Dynamic property values from *Figures* 1 and 2 are compiled in *Table* 3. At 220°F cure, values of T_g and Tan δ (max) are similar for MF1 and MF2, but crosslink density is significantly lower for MF2 based on E′ (min). MF2 shows a more rapid drop off in properties with decreasing temperature. Property values for MF2 at 200°F cure are very similar to those observed at 180°F cure for MF1.

DMA has been used extensively to determine extent of cure of thermoset coatings.[8] The equation for calculating crosslink density from E′ (min) is rather simple for short chain networks[9]

$$\nu_e = E'(\text{min})/3\,RT \qquad (1)$$

where ν_e is crosslink density expressed in moles of elastically effective network chains per cubic meter of film, R is the gas constant (8.314 Joules/°K•m^3 in the mks system of units), and T is the temperature (in degrees Kelvin) at which the minimum in E′ occurs. From *Figures* 1a and 2a it is evident that the needed T values are (125 + 273) and (117 + 273) for MF1 and MF2, respectively. Inserting these T values and E′ (min) values in (Pascals) from *Table* 3 into equation (1) gives ν_e values of 4.23×10^3 and 3.36×10^3 moles/meter^3 for the MF1 and MF2 cured films, respectively.

Based on comparison with DMA results for many films,[8] these crosslink density values are known to be

Table 3—DMA of Acrylic Films
Cure Time—30 min; Catalyst—0.5 phr pTSA

MF Resin	Cure Temp.		T_g	Tan δ (max)	10^{-7} x E' (min)
	°F	°C	°C		Pascals
MF1	220	104	87	0.46	4.2
	200	93	82	0.52	3.8
	180	82	75	0.62	3.0
MF2	220	104	85	0.49	3.2
	200	93	76	0.61	2.4
	180	82	60	0.90	1.2

characteristic of very highly cured films. In previous work ν_e was usually expressed in the cgs system for units. Because the conversion factor from cubic meters to cubic centimeters is 10^{-6}, the ν_e values above expressed in cgs units are 4.23×10^{-3} and 3.36×10^{-3} moles/cm^3.

DMA Results—Polyester Films

DMA results for polyester films cured with MF1 and MF2 are given in *Table* 4. The DMA plots (not shown) are similar to those described for acrylic films. At 220°F cure, T_g is higher and Tan δ (max) is lower for MF1 than for MF2. The difference in E′ (min) values for MF1 and MF2 is small at 220°F, but larger at lower cure temperatures. These comparisons indicate that MF1 has better cure response than MF2. As noted previously, better cure response for MF1 is attributed to the lower imino content.

As the cure temperature is decreased, the property changes noted with MF1 are less extreme than those observed with MF2. A significant level of cure is maintained down to a cure temperature of 180°F with MF1, but T_g and E′ (min) are very low for the MF2 film cured at 180°F. At 160°F, DMA was possible for the MF1 film, but the MF2 was too soft.

Comparison of *Tables* 3 and 4 shows that ACR has a higher T_g than PE. Cure of ACR results in a considerably higher crosslink density than obtained with PE. The difference in crosslink density may be related to a low molecular weight for PE (not revealed by supplier). Based on equivalent weights alone, PE would be expected to give a higher crosslink density. When a co-reactant has low molecular weight, many of the functional groups are used up for chain extension, and fewer are left for crosslinking.[8] Acrylic films cured at 160°F are not included in *Figure* 3 because they broke early in the run.

Table 4—DMA of Polyester Films
Cure Time—30 min; Catalyst—0.5 phr pTSA

MF Resin	Cure Temp.		T_g	Tan δ (max)	10^{-7} x E' (min)
	°F	°C	°C		Pascals
MF1	220	104	74	0.75	1.60
	200	93	66	0.91	1.22
	180	82	60	1.06	0.96
	160	71	57	1.32	0.84
MF2	220	104	67	0.97	1.57
	200	93	55	1.39	0.72
	180	82	43	1.86	0.34
	160	71	—	—	—

DISCUSSION

Basicity and Ring Protonation

The large effect on cure response of rather small differences in imino content is surprising. An explanation can be offered in terms of basicity and position of protonation. The discussion is simplified by consideration of a crosslinker molecule that has no imino groups (HMMM) and one that has one imino group (pentamethoxymethylmelamine, PMMM). The structures of HMMM and PMMM are shown in *Figure* 3. Competition between HMMM and PMMM for protons is depicted in *Figure* 3a.

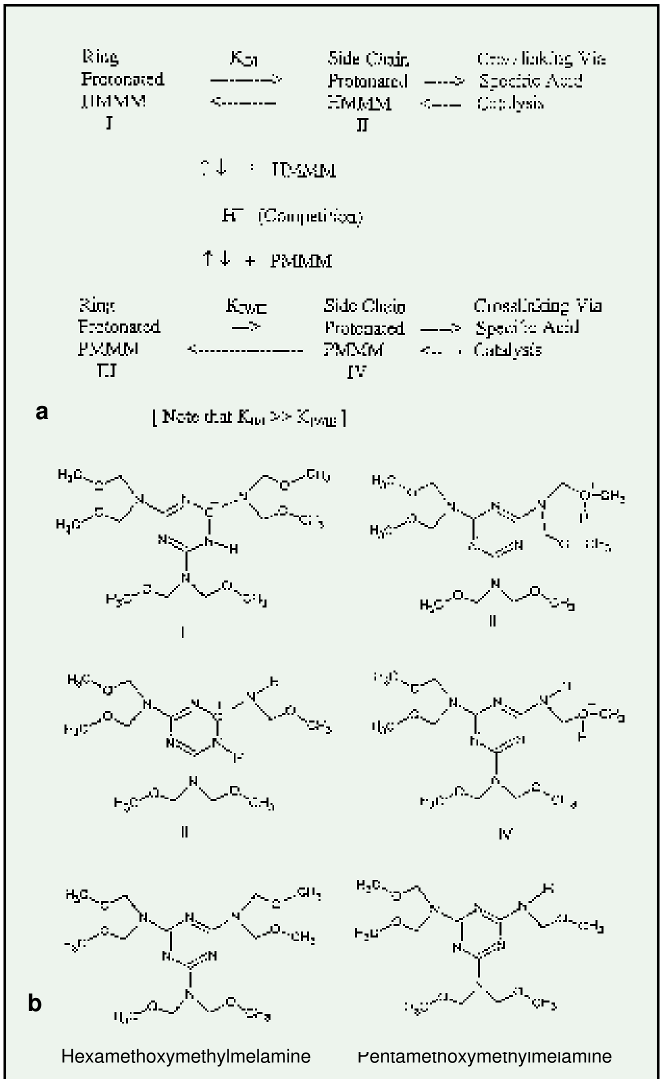

Figure 3—Ring protonation versus side chain protonation of MF resins: (a) reaction scheme, (b) structures.

It is well documented that MF basicity decreases as the degree of substitution increases.[10] PMMM is more basic, and it will win the competition unless its concentration is reduced to very low levels.

When PMMM gets a proton, a question remains as to where it goes. Berge et al.[11] discuss protonation of ring nitrogens during hydrolysis of MF resins of low degree of substitution. To form crosslinks by accepted mechanisms,[12,13] off-ring protonation is needed (*Figure* 3b, II and IV). Ring protonation is likely to cause deactivation for either hydrolysis or crosslinking. By hyperconjugation arguments, the ring protonated form of PMMM (*Figure* 3b, III) is more favored than the ring protonated form of HMMM (*Figure* 3b, I).

In conclusion, if the imino content is greatly reduced, HMMM can compete for protons. When it gets a proton, it is just about as likely to put it in a useful place (II) as in a dead end (I). If imino content is not greatly reduced, PMMM will get nearly all of the protons and such protons are likely to go to the dead end form (III).

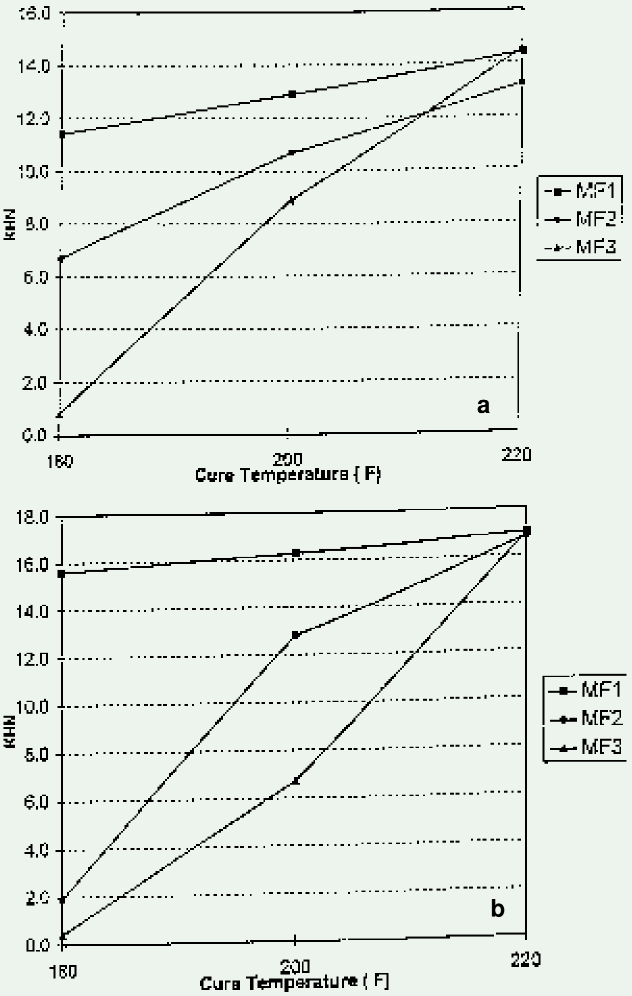

Figure 4—Tukon hardness versus cure temperature, 30 min cure (a) acrylic films, (b) polyester films.

Co-Condensation and Self-Condensation

In general, the balance of co-condensation and self-condensation in MF cure is believed to vary with the MF resin selected and with cure temperature. The term co-condensation is applied to reactions between the –OH group of the acrylic (or polyester) polyol and functional groups on the MF resin.[1,2] The term self-condensation refers to the reactions between functional groups attached to different MF molecules.[1,2] Film hardness is reported to increase with both types of condensation reaction.[8]

The shape of Tukon hardness plots of *Figure* 4 can be well understood by considering both co- and self-condensation. We believe hardness of MF1 films is generated entirely by co-condensation. The MF1 plots are very flat for both acrylic (*Figure* 4a) and polyester (*Figure* 4b) films. The absence of a strong drop off at the left suggests that co-condensation proceeds to a rather high level of completion even at the lower cure temperatures. In contrast, the drop off in hardness of the MF2 and MF3 plots suggests that these higher imino MF resins cannot reach high levels of co-condensation at lower cure temperatures. MF2, and especially MF3, have some ability to self-condense, but the low hardness values at the left in *Figure* 4 suggest that self-condensation does not occur at such low temperatures.

As cure temperature is increased, the changes in cure chemistry for MF2 and MF3 are somewhat complicated. When moving to the right in *Figure* 4a or 4b, the extent of co-condensation increases, and eventually self-condensation becomes possible. The trajectories of the MF3 hardness plots at the 220°F points in *Figure*s 4a and 4b suggest that at higher cure temperatures MF3 will give harder films than MF1. This is logical if both co-condensation and self-condensation contribute to hardness with MF3 whereas with MF1 only co-condensation takes place.

Cure Response with Weak Catalyst or No Catalyst

This paper emphasizes low temperature cure with strong acid catalysts. When a weak acid catalyst is used, high imino resins such as MF3 are more reactive than low imino resins such as MF1. Blank[14] has explained this finding in terms of a general acid catalysis mechanism. Weak acids catalyze cure of mono-substituted sites [$–N(H)(CH_2OCH_3)$], through formation of an imino intermediate of type $–N{=}CH_2$. Di-substituted sites cannot form this intermediate.

Often MF resins are used to cure polyols at higher cure temperatures with no catalyst at all. High imino resins such as MF3 are more reactive than low imino resins such as MF1 for uncatalyzed cure.[1,14] Both self-condensation and co-condensation are believed to occur during high temperature uncatalyzed cure.

SUMMARY

Tukon hardness and acetone double rub resistance indicate that MF resins with low imino content have better catalyzed cure response than commercial resins currently available. Crosslink densities and glass transition temperatures of cured films determined by DMA confirm the good cure response of low imino MF resins.

A low imino, methylated MF resin (called MF1 here) was used to prepare sulfonic acid catalyzed formulations with acrylic polyol and polyester polyol co-reactants. Films from these formulations were highly cured in 30 min at bake temperatures of 220°F (104°C), 200°F (93°C), and even 180°F (82°C). These cure temperatures will permit use of MF-cured coatings on heat sensitive substrates.

A possible explanation is given for the effect of imino groups on cure response based mainly on the early work of Berg et al.[11] Ring protonation as distinguished from side chain protonation and the effect of degree of substitution on MF basicity are important elements of this explanation. Low imino content strongly disfavors MF self-condensation.

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