

# Viscoelastic Properties and Coating Performance of Water-Soluble Acrylic Copolymers Crosslinked with Melamine Resin

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## SYNOPSIS

Acrylic copolymers with different amounts of carboxyl and hydroxyl groups for obtaining practical performance of melamine-cured acrylic coatings was investigated. Property testing results indicated that glass transition temperature ( $T_g$ ) and shear modulus increased, and molecular weight between crosslinks ( $M_c$ ) decreased with the increase of hydroxyl and carboxyl number in the acrylic copolymers. The degree of crosslinks influenced the resistance to solvent and chemicals at a lower baking temperature. Compared with acrylic acid, itaconic acid as a carboxyl monomer was more effective in inducing a lower baking schedule. The water-soluble acrylic copolymer, which is neutralized with triethylamine, consists of 20 wt % methylmethacrylate, 55 wt % butylacrylate, 15 wt % hydroxyethyl methacrylate, and 10 wt % itaconic acid. The copolymer showed higher crosslinks when cured with methoxymethyl melamine formaldehyde resin under a relatively lower baking schedule at 135°C for 30 min. It also has excellent solvent and chemical resistance. This coating film has a  $T_g$  value of 39°C, modulus of  $2 \times 10^8$  dyne/cm<sup>2</sup> in the rubbery state, and  $M_c$  value of 464. Also the acrylic copolymer films with  $M_c < 900$  have good properties for solvent, acid, and alkali resistance. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

Water-soluble coatings are considered to be one of the promising coatings of the future that may solve the solvent-pollution problem. The main intention is to replace organic solvents with certain environmentally favorable solvents such as water. Many efforts have been made to apply these usages in water-soluble thermosetting acrylic coatings.

In general, these crosslinked coatings can be characterized as polymers obtained by polymerizing derivatives of acrylic and methacrylic acid. The effects of the functional groups of acrylic monomer derivatives on the basic reactions have been discussed by many workers.<sup>1-15</sup>

It is evident that the most commonly used functional groups are hydroxyl and carboxyl. Hydroxyl-type acrylics are usually crosslinked with amino resins. In the course of this research, acrylic copolymers

with different amounts of pendant functional groups, and the effects of the carboxyl and hydroxyl groups on the cure chemistry proper, for obtaining practical performance of the melamine-cured acrylic coatings was investigated.

The dynamic mechanical behavior and film performance of the crosslinked coating films obtained by the reaction of water-soluble acrylic copolymers with methoxymethylated melamine formaldehyde resin are discussed in terms of acrylic copolymer compositions.

## EXPERIMENTAL

### Materials

#### *Water-Soluble Acrylic Copolymers*

Various kinds of acrylic copolymers with pendant functional groups were synthesized. A three-necked flask fitted with a stirrer, inert gas ( $N_2$ ) inlet, and a thermometer was charged with isopropanol as me-

**Table I Monomers Used in Preparation of Acrylic Copolymers**

Monomers
Methyl methacrylate (MMA) (50 ppm MEHQ) <sup>a</sup>
Styrene (St) (50 ppm <i>p-t</i> -butyl catecol) <sup>b</sup>
Ethyl acrylate (EA) (20 ppm MEHQ) <sup>a</sup>
Butyl acrylate (BA) (20 ppm MEHQ) <sup>a</sup>
Hydroxyethyl methacrylate (100 ppm MEHQ) <sup>a</sup>
Acrylic acid (AA) (100 ppm MEHQ) <sup>c</sup>
Itaconic acid (IA) <sup>d</sup>

<sup>a</sup> Mitsubishi Rayon Co., Ltd.<sup>b</sup> Mitubishi Petrochemical Co., Ltd.<sup>c</sup> Osaka Organic Chemical Industry Ltd.<sup>d</sup> Iwata Chemical Co., Ltd.

dium. This solvent was gradually brought to 93°C and refluxed by using a hot water bath. The premixed monomers and initiator (1.5% benzoyl peroxide of weight of monomers) were added by dropping into the refluxing solvent. The reaction was continued until getting high conversion was accomplished. The values of conversion were more than 98%. These values were determined by measuring the weight percent of the nonvolatile matter in the copolymer solution. The monomers used for this experiment are shown in Table I.

These acrylic copolymer solutions were mixed with methoxymethylated melamine formaldehyde resin and neutralized with triethylamine corresponding with an equivalent weight of carboxy functionality to be water soluble. Finally the solutions were diluted with distilled water.

The total monomer mixture content in the initial

charge was 50 wt %. The compositions and properties of acrylic copolymers are given in Table II.

Each sample has a specific functionality. Acrylic copolymer A has a carboxyl group only, and acrylic copolymers B and C have the hydroxyl group only. The copolymers D–J have both the carboxyl and hydroxyl group as functional groups. The carboxyl group originates from acrylic acid and itaconic acid; the hydroxyl group in the acrylic copolymer originates from  $\beta$ -hydroxyethyl acrylate. The content of carboxyl and hydroxyl groups in the copolymers of the samples is shown in Table III. The content of these functional groups in the copolymers was calculated from the functional monomer concentration in the initial charge.

The Gardner–Holdt bubble viscosity of these solutions is in the range of S to X. The molecular weights ( $M_n$ ) of these acrylic copolymers are approximately the same and in the range of 5000 to 8000.

### Melamine Resin

The melamine resin used in this study is industrial grade Nikalac MW-22. This grade is mainly methoxymethyl and partially polymerized methyl melamine formaldehyde resin. The weight average and number average molecular weight ( $M_w$  and  $M_n$ ) of this melamine were 550 and 500.  $M_w$  and  $M_n$  were determined by gel permeation chromatography (GPC), and styrene molecular weight standard samples were used to calibrate the chromatographic system. The composition and the physical properties of the melamine resin are given in Table IV.

**Table II Composition and Physical Properties of Acrylic Copolymers**

Samples	Composition (wt %)						Solid Content (wt %)	Gardner Viscosity
	MMA	EA	BA	HEMA	AA	IA		
A	25	50	10	—	5	10	49.6	U-T
B	40	—	50	10	—	—	49.9	S-T
C	30	—	50	20	—	—	49.8	T-U
D	30	—	50	10	10	—	49.7	V
E	35	—	50	10	—	5	49.8	X
F	30	—	50	15	—	5	49.8	V
G	20	40	15	10	10	5	49.9	S-T
H	25	50	10	5	—	10	49.6	X
I	30	—	50	10	—	10	49.6	V-W
J	20	—	55	15	—	10	49.5	U-V

**Table III** Content of Functional Groups in Acrylic Copolymers

Samples	Carboxyl Group (mol/g)	Hydroxyl Group (mol/g)
A	$22.3 \times 10^{-4}$	0
B	0	$7.7 \times 10^{-4}$
C	0	$15.4 \times 10^{-4}$
D	$13.9 \times 10^{-4}$	$7.7 \times 10^{-4}$
E	$7.7 \times 10^{-4}$	$7.7 \times 10^{-4}$
F	$7.7 \times 10^{-4}$	$11.5 \times 10^{-4}$
G	$21.6 \times 10^{-4}$	$7.7 \times 10^{-4}$
H	$15.4 \times 10^{-4}$	$3.9 \times 10^{-4}$
I	$15.4 \times 10^{-4}$	$7.7 \times 10^{-4}$
J	$15.4 \times 10^{-4}$	$11.5 \times 10^{-4}$

## Methods

### Preparation of Acrylic Copolymer Melamine Resin Coatings and Films

The typical compositions for the preparation of the clear coatings and pigmented enamel capable of crosslinking is given in Table V. This enamel consists of a crosslinking acrylic solution copolymer, melamine formaldehyde crosslinking agent, and pigment.

The clear films for testing viscoelastic properties were cast on a tinned mild steel panel ( $150 \times 50 \times 0.3$  mm). Crosslinking was accomplished by baking about 40- $\mu$ m thick coatings for 30 min at 120, 135, and 150°C in an air-circulating oven. The film properties of thermosetting acrylic white baking enamels were tested after conditioning at room temperature for 48 h. The films were removed from the cast panels by using the amargamatic method. The sample name of the clear film is represented by acrylic copolymer.

The films for practical properties testing were coated by spraying on the steel coated primer. The

**Table IV** Physical Properties of Melamine Resin

Items	Results
Monomer	55 wt %
Dimer, trimer, and others	45 wt %
$M_w$	Average 550
$M_n$	Average 500
Number of groups/mol triagine	
—CH <sub>2</sub> —O—CH <sub>3</sub>	4.8 mol
—CH <sub>2</sub> —OH	1.2 mol

**Table V** Preparation of Clear and Pigmented Acrylic Enamel

Component	Parts by wt
Clear enamel	
Water soluble acrylic copolymer solution <sup>a</sup>	87.5
Methoxymethylol melamine <sup>b</sup>	15.0
Distilled water	47.5
White enamel	
Water soluble-acrylic copolymer solution <sup>a</sup>	87.5
Methoxymethylol melamine <sup>b</sup>	15.0
Rutile titanium dioxide <sup>c</sup>	50.0
Distilled water	47.5

Nonvolatile, 50%; pigment weight concentration, 50%.

<sup>a</sup> 40% solid content

<sup>b</sup> Nikalac MW-22 manufactured by Sanwa Chemical Co., Ltd.

<sup>c</sup> Rutile type R-820 manufactured by Ishiharasangyo Co., Ltd.

pigmented enamels were allowed to dry for 30 min to minimize solvent popping, and then the coated panels were heated for 30 min at 135°C and 30 min at 150°C. The baked dry film thickness was about 40  $\mu$ m.

The curing films of white enamels are termed E (acrylic copolymer). The solvent and chemical resistance of the film were determined by dipping in methyl ethyl ketone (MEK) to test solvent resistance, in 1% HCl aqueous solution for acid resistance, and in 1% NaOH aqueous solution for alkali resistance. Coating resistance was tested for period of a day at room temperature, and then examined for evidence of color changes or softening.

### Measurement of Molecular Weight

The number average molecular weights of acrylic copolymers were determined by using a Vapor Pressure Osmometer 301A (Mechrolab, Inc.) according to the following equation,

$$\Delta R/C = K/M_n$$

where  $\Delta R$  is changes in resistant values measured by the Thermister apparatus,  $C$  is the concentration of chloroform solution of the acrylic copolymer, and  $K$  is an apparatus constant number.

### Measurement of Dynamic Viscoelasticity

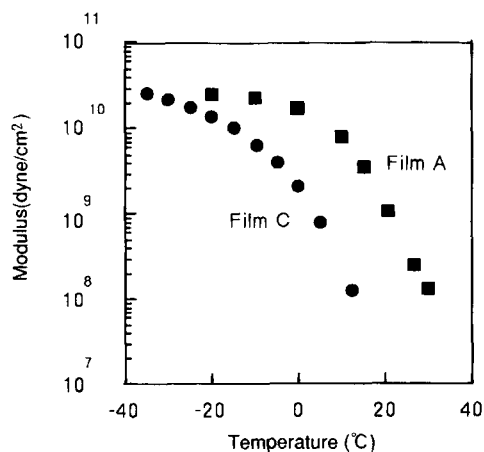
The dynamic mechanical measurements were performed by a schematic diagram of torsional braid

analysis (TBA). The method followed ASTM D-1053-58T.

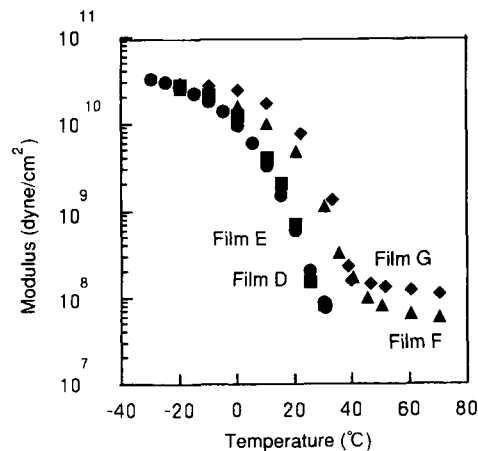
## RESULTS AND DISCUSSION

The plots of the dynamic shear modulus  $3G$  as a function of temperature for the various clear water-soluble acrylic copolymer films crosslinked with melamine resin are shown in Figures 1–3. The difference of the patterns in modulus dispersions for the acrylic copolymer films changes relatively according to the amount of functional groups. There is a plateau region at temperature above  $T_g$  for some samples such as the copolymer films F, G, I, and J. These films show rubber elasticity. However, there is no plateau region in the measured temperature range for the films A, C, E, D, and H as shown in Figures 1–3. At low temperatures the coating films are in the glasslike region where the modulus is on the order of  $10^9$  dyne/cm<sup>2</sup>. In the glass transition region the modulus decreases drastically. In the adjacent entanglement network range, the modulus falls off more gradually and is on the order of  $10^7$ – $10^8$  dyne/cm<sup>2</sup> for the samples with rubbery elasticity.

The influence of functional groups in the acrylic copolymer on the modulus as a function of temperature is demonstrated in Figures 4 and 5. For comparison coating films E versus I and F versus J, which were crosslinked to different degrees by changing the baking temperature, are included. The dispersion of the modulus in the glass transition region is shifted to higher temperatures with elevated



**Figure 1** Shear modulus of acrylic copolymer films A and C crosslinked with melamine resin at 135°C for 30 min.



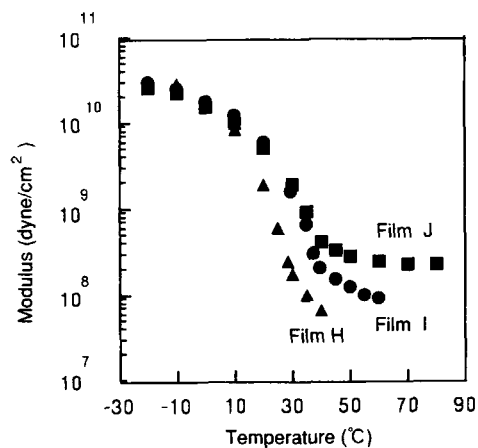
**Figure 2** Shear modulus of acrylic copolymer films D, E, F, and G crosslinked with melamine resin at 135°C for 30 min.

baking temperature. In addition the modulus in the rubber state increases with higher content of the carboxyl group in the acrylic copolymer.

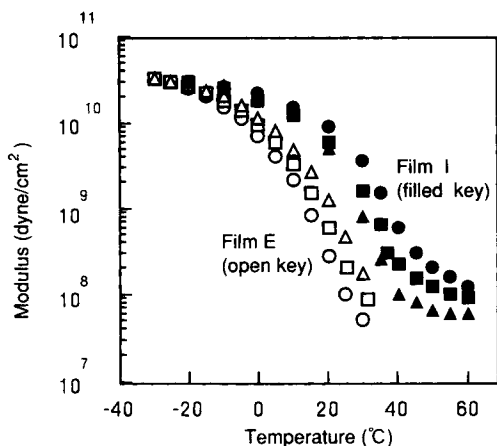
The number average molecular weight between crosslinks,  $M_c$ , is calculated by using the following equation.

$$M_c = 3\rho RT/E,$$

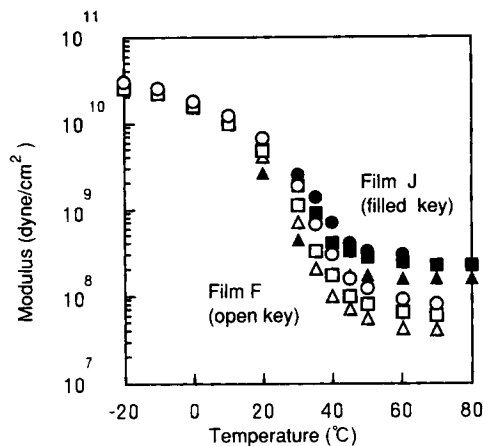
where  $E$  is the storage elastic modulus at temperature above the transition region and can be calculated by setting  $E = 3G$ .  $R$  is a gas constant,  $\rho$  is polymer density, and  $T$  is an absolute temperature.  $M_c$  can be obtained by measuring a modulus of the sample, although the restrictions of the above equation result from ideal behavior.



**Figure 3** Shear modulus of acrylic copolymer films H, I, and J crosslinked with melamine resin at 135°C for 30 min.



**Figure 4** Shear modulus of acrylic copolymer films E and I crosslinked with melamine resin at (▲, △) 120°C, (■, □) 135°C, and (●, ○) 150°C for 30 min.



**Figure 5** Shear modulus of acrylic copolymer films F and J crosslinked with melamine resin at (▲, △) 120°C, (■, □) 135°C, and (●, ○) 150°C for 30 min.

The glass transition temperature can be determined from the point of inflection of the modulus dispersion in the glass transition. The values for  $T_g$ , shear modulus,  $E_h$ , at a high temperature,  $\rho$ , and  $M_c$  for crosslinked coating films are summarized in Table VI. The properties of resistance to solvents, acid, and alkali for the various cured films of the water-soluble acrylic white enamels are also shown in Tables VII and VIII.

It is evident that the degree of crosslinks influences film properties and is related to functional group content of the water-soluble acrylic white enamels. There is an optimum amount of hydroxyl and carboxyl groups to achieve superior resistance to solvent and chemicals.

The dispersion of the modulus against the temperature is closely interrelated with the structure and mobility of the macromolecule. The influence of various molecular parameters on the curable functional groups in the acrylic copolymer is subsequently discussed.

#### Effects of Acrylic Carboxyl Group or Hydroxyl Group on Crosslinking Reaction

Acrylic copolymer A has a carboxyl group only and acrylic copolymers B and C have hydroxyl functional groups. Coating film A was compared with films B and C to discuss the effects of functional groups in acrylic copolymers on the crosslinking reactions. In

**Table VI** Values for Crosslinked Coating Films

Samples	$T_g$ (°C)	$E_h$ (dyne/cm <sup>2</sup> )		$\rho$ (g/mL)	$M_c$
		20°C	Rubbery State		
EA	22	$1.0 \times 10^9$		1.15	
EB	—	$< 1.0 \times 10^8$		1.16	
EC	—	$< 1.0 \times 10^8$		1.15	
ED	25	$7.0 \times 10^8$		1.16	
EE	—	$6.0 \times 10^9$		1.15	
EF	36	$4.8 \times 10^9$	$0.6 \times 10^8$	1.16	1610
EG	34	$7.2 \times 10^9$	$1.1 \times 10^8$	1.14	884
EH	27	$1.9 \times 10^9$		1.14	
EI	37	$6.0 \times 10^9$	$0.9 \times 10^8$	1.15	1125
EJ	39	$5.0 \times 10^9$	$2.2 \times 10^8$	1.15	464

Glass transition ( $T_g$ ) dynamic shear modulus at 20°C and in rubbery state ( $E_h$ ), densities ( $\rho$ ), and molecular weight between crosslinks ( $M_c$ ) for acrylic copolymers crosslinked with melamine formaldehyde resin baked at 135°C for 30 min.

**Table VII Solvent Resistance of Thermosetting Acryl/Melamine White Baking Films**

Sample No.	Baking Schedule		
	120°C × 30 min	135°C × 30 min	150°C × 30 min
EA	Poor	Poor	Fair
EB	Poor	Poor	Poor
EC	Poor	Poor	Poor
ED	Poor	Poor	Fair
EE	Poor	Poor	Poor
EF	Poor	Fair	Good
EG	Poor	Fair	Excellent
EH	Poor	Poor	Fair
EI	Poor	Fair	Good
EJ	Good	Excellent	Excellent

Figure 1, both moduli of films A and C fall off drastically on the order of  $10^7$ . Coating films A and C show almost no rubberlike behavior. This is a result of too few crosslinks under the baking schedule at 120–150°C for 30 min.

Network formation in water-soluble acrylic copolymer-melamine resin is dominated by two reactions. The first is the condensation of acrylic hydroxyl and carboxyl groups with methoxymethyl and methylol groups on the melamine to form acrylic-melamine crosslinks. The second is the condensation of methylol groups on different melamine molecules to form melamine-melamine crosslinks. The addition of acid catalysts greatly enhances the crosslinking reactions at lower temperature and favors

melamine-melamine formation.<sup>4</sup> Although the carboxyl group of the water-soluble coating enamels is neutralized with triethylamine, the modulus in the adjacent glasslike region of film A is higher than that of film C because of being associated with the acid effect. This is a result of easy release of triethylamine from carboxylic acid salt during baking.

#### Effects of Acrylic Carboxyl Group and Hydroxyl Group on Crosslinking Reaction

A carboxyl-functional monomer of the acrylic copolymer D is an acrylic acid, whereas that of the acrylic copolymers E, F, H, I, and J is itaconic acid. That of the acrylic copolymer G is an acrylic copolymer and itaconic acid.

On the other hand, a hydroxyl-functional monomer is  $\beta$ -hydroxyethyl methacrylate for all samples of the copolymers B–J. The concentration of the hydroxyl group increases in the order of copolymers  $E < F$  or  $H < I < J$ .

There is a plateau region for copolymer films F, G, I, and J cured at the lower baking schedule at 135°C for 30 min shown in Figures 2 and 3.

Judging from the viscoelastic properties of films D and I, whose acrylic copolymers use different acid-functional monomer, itaconic acid has been shown to be preferable to acrylic acid, and is effective as the acid-functional monomer on water-soluble coatings under a lower baking schedule. This might be attributed to the difference of acid strength and the better distribution of itaconic acid units into the copolymer due to their copolymerizable reactivity<sup>16</sup>

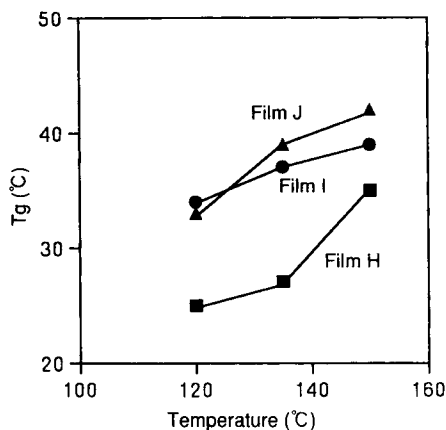
**Table VIII Chemical Resistance of Thermosetting Acryl/Melamine White Baking Films**

Sample	Acid Resistance <sup>a</sup> Baking Schedule <sup>c</sup>			Alkali Resistance <sup>b</sup> Baking Schedule <sup>c</sup>		
	120°C	135°C	150°C	120°C	135°C	150°C
EA	Poor	Poor	Poor	Poor	Poor	Poor
EB	Poor	Poor	Poor	Poor	Poor	Fair
EC	Poor	Poor	Poor	Poor	Poor	Fair
ED	Poor	Poor	Poor	Poor	Poor	Fair
EE	Poor	Poor	Fair	Poor	Fair	Fair
EF	Poor	Poor	Fair	Poor	Poor	Fair
EG	Poor	Fair	Fair	Poor	Poor	Fair
EH	Poor	Poor	Fair	Poor	Poor	Fair
EI	Poor	Fair	Good	Poor	Fair	Good
EJ	Good	Excellent	Excellent	Excellent	Excellent	Excellent

<sup>a</sup> Dipping in 1% HCl aq soln for 24 h.

<sup>b</sup> Dipping in 1% NaOH aq soln for 24 h.

<sup>c</sup> Baking time 30 min.



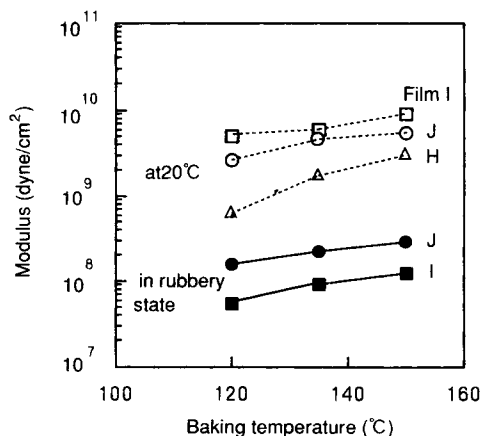
**Figure 6** Influence of baking temperature on  $T_g$  of acrylic copolymer films H, I, and J crosslinked with melamine resin.

or their lower solubility in most of the organic solvents as compared with acrylic acid.

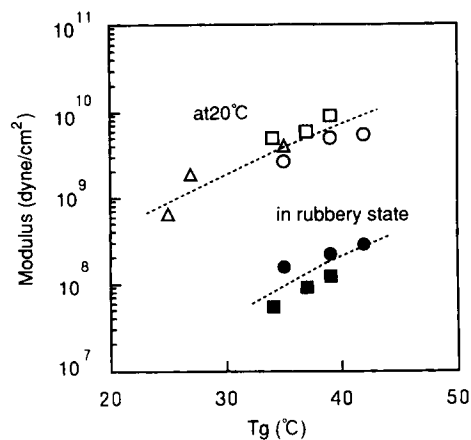
The influence of baking temperature on  $T_g$  of the copolymer films H, I, and J is demonstrated in Figure 6.  $T_g$  value increases in the order of film  $J > I > H$  with raising baking temperature.

A similar correlation between the modulus and baking temperature was observed for copolymer films H, I, and J with a different amount of hydroxyl group, as shown in Figure 7.

The relation between modulus and  $T_g$  is shown in Figure 8 and  $M_c$  and  $T_g$  in Figure 9.  $T_g$  tends to increase almost linearly with increasing modulus at 20°C or in a rubbery state, and with decreasing  $M_c$  value.



**Figure 7** Modulus at 20°C and in rubbery state for acrylic copolymer films ( $\Delta$ ) H, ( $\square$ ,  $\blacksquare$ ) I, and ( $\circ$ ,  $\bullet$ ) J crosslinked with melamine resin at 120, 135, and 150°C for 30 min.



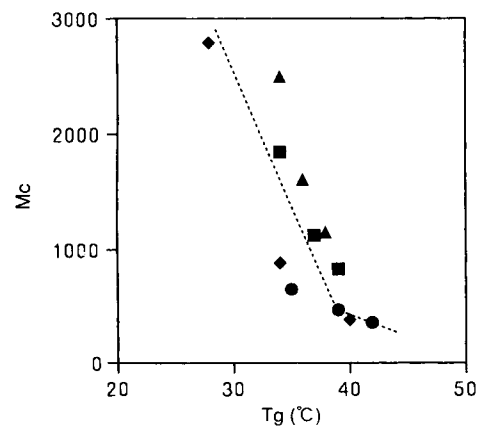
**Figure 8** Modulus at 20°C and in rubbery state vs.  $T_g$  for acrylic copolymer films ( $\Delta$ ) H, ( $\square$ ,  $\blacksquare$ ) I, and ( $\circ$ ,  $\bullet$ ) J baked at 120, 135, and 150°C for 30 min.

A deviation of  $T_g$  for the coating films baked at 120 and 135°C is associated with a shift of temperature from 3 to 7°C.

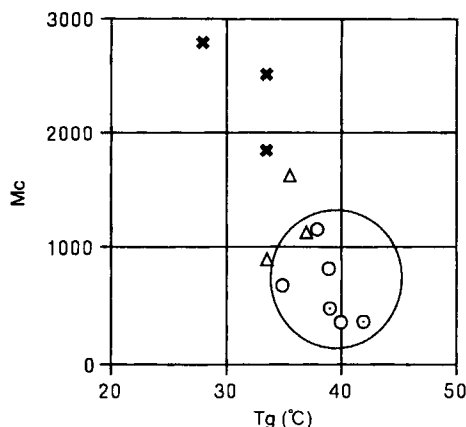
Above all, the copolymer film J prepared from the acrylic copolymer using  $\beta$ -hydroxyethyl methacrylate (15 wt %) and acrylic acid (10 wt %) as a hydroxyl-functional monomer has lower  $M_c$  of 400, the same as the available alkyd resin coatings.

### Performance of Coating Films

In general mechanical behavior of the coating film highly influences coating performance. The resistance toward solvent, acid, and alkali for the various coating films were evaluated in accordance with the test method matching requirements of the paint in-



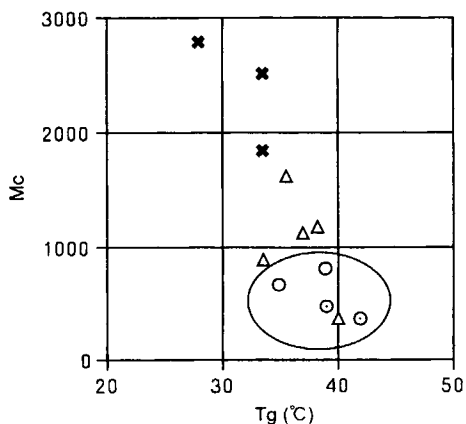
**Figure 9**  $M_c$  vs.  $T_g$  for acrylic copolymer films ( $\blacktriangle$ ) F, ( $\blacklozenge$ ) G, ( $\blacksquare$ ) I, and ( $\bullet$ ) J crosslinked with melamine resin at 120, 135, and 150°C for 30 min.



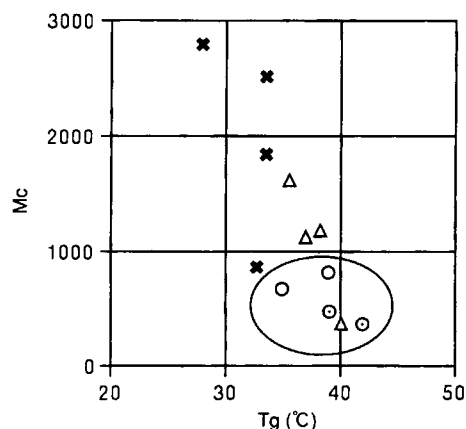
**Figure 10** Influence of  $M_c$  and  $T_g$  on solvent resistance of acrylic coating films EF, EG, EH, EI, and EJ, cross-linked with melamine resin.

dustry. The solvent resistance to MEK is shown in Figure 10, acid resistance in Figure 11, and alkali resistance in Figure 12, as a function of  $T_g$  and  $M_c$ . The coating films with lower values of  $M_c$  have good resistance to solvent, acid, and alkali. There is an optimum range shown in the circles in Figures 10–12. But this range suitable to solvent resistance is slightly different from the range to acid and alkali resistance. The coating films having  $M_c$  below about 1000 exhibit good properties for these resistances under the practical lower baking schedule at 135°C for 30 min.

Figures 13 and 14 show the influence of functional groups present in the copolymer for the above resistances. It is evident that the water-soluble coating films prepared from the acrylic copolymer with about



**Figure 11** Influence of  $M_c$  and  $T_g$  on acid resistance for acrylic coating films EF, EG, EH, EI, and EJ, crosslinked with melamine resin.

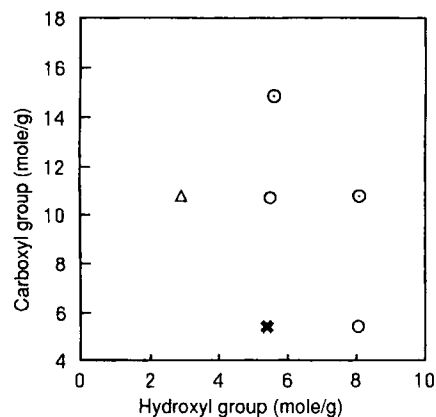


**Figure 12** Influence of  $M_c$  and  $T_g$  on alkali resistance for acrylic coating films EF, EG, EH, EI, and EJ, cross-linked with melamine resin.

8 mol/g of hydroxyl and about 11 mol/g of carboxyl groups have excellent properties for resistance to solvent, acid, and alkali. These results show that there is an optimum range in a carboxyl and hydroxyl group, and that it relates highly to the cross-linking density of acrylic-melamine crosslinked copolymer.

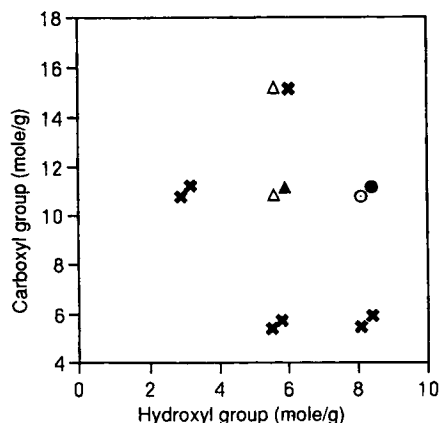
## CONCLUSION

1. The water-soluble acrylic copolymers using both  $\beta$ -hydroxyethyl methacrylate and itaconic acid as curable functional monomers afford higher crosslinks by curing with meth-



**Figure 13** Influence of functional groups in acrylic copolymers (F, G, H, I, and J) using 2-hydroxyethyl methacrylate and itaconic acid on solvent resistance, cross-linked with melamine resin at 135°C for 30 min. Evaluation: (⊙) excellent, (○) good, (Δ) fair, and (×) poor.





**Figure 14** Influence of functional groups in acrylic copolymers (F, G, H, I, and J) using 2-hydroxyethyl methacrylate and itaconic acid on chemical (alkali and acid) resistance, crosslinked with melamine resin at 135°C for 30 min. Evaluation, acid resistance: (⊙) excellent, (○) good, (Δ) fair, and (×) poor; alkali resistance: (●) excellent, (■) good, (▲) fair, and (×) poor.

oxymethyl melamine formaldehyde resin at relatively lower baking temperature.

2. Itaconic acid as a carboxyl monomer is more effective in inducing lower baking temperature, compared with acrylic acid.
3. The water-soluble acrylic copolymer of 20 wt % methyl methacrylate, 55 wt % butylacrylate, 15 wt % (about 8 mol/g)  $\beta$ -hydroxyethylmethacrylate, and 10 wt % (about 11 mol/g) itaconic acid, when neutralized with triethylamine is useful for the thermosetting water-soluble coatings.
4. This copolymer crosslinked with methoxymethyl melamine formaldehyde resin at 135°C for 30 min has lower  $M_c$  value of 464,  $T_g$  value of 39°C, modulus of  $5 \times 10^9$  dyne/cm<sup>2</sup> at 20°C, and  $2 \times 10^8$  dyne/cm<sup>2</sup> in the

rubbery state. It also has excellent resistance toward solvents and chemicals.

5. The acrylic copolymers with  $M_c < 900$  have good properties for solvent, acid, and alkali resistance.

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## REFERENCES

1. W. J. Blank and W. L. Hensley, *J. Paint Technol.*, **46**, 593 (1974).
2. S. Takahashi, N. Okoshi, T. Matsumoto, and T. Ikeda, *J. Appl. Polym. Sci.*, **36**, 613 (1988).
3. D. R. Bauer and R. A. Dickie, *J. Polym. Sci., Polym. Phys. Ed.*, **18**, 1997 (1980).
4. D. R. Bauer and R. A. Dickie, *J. Polym. Sci., Polym. Phys. Ed.*, **18**, 2015 (1980).
5. L. W. Hill and B. M. Richards, *J. Coat. Technol.*, **51**, 59 (1979).
6. W. J. Blank, *J. Coat. Technol.*, **51**, 61 (1979).
7. E. Levine and E. J. Kuzma, *J. Coat. Technol.*, **51**, 35 (1979).
8. S. Takahashi, H. Katshuragi, and H. Higashi, *Shikizai, Jpn.*, **40**, 61 (1967).
9. S. Takahashi, *Shikizai, Jpn.*, **39**, 119 (1965).
10. A. Ciferri and P. J. Flory, *J. Appl. Phys.*, **30**, 10 (1959).
11. M. Nakajima, *Kobunshi Kagaku*, **22**, 246 (1965).
12. K. Ueki, *J. Chem. Soc. Jpn.*, **65**, 137 (1962).
13. S. Takahashi, H. Katsuragi, and A. Higashi, *Shikizai, Jpn.*, **40**, 62 (1967).
14. S. Takahashi, *Shikizai, Jpn.*, **37**, 155 (1964).
15. S. Takahashi, *Shikizai, Jpn.*, **39**, 119 (1966).
16. S. T. Fukuda and M. Takahashi, *Shikizai, Jpn.*, **50**, 2 (1977).

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