

Viscoelastic Properties and Coating Performance of Acrylic Copolymers Crosslinked with Melamine Resin

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Synopsis

For 8 carboxy and hydroxy functional acrylic copolymers crosslinked with melamine resin, glass transition temperature (T_g), molecular weight of chain segments between crosslinked point (M_c), and polymer-solvent interaction parameters (χ_g) were determined by dynamic mechanical measurements and swelling measurements. T_g increases and M_c decreases with the increase of hydroxyl value and the molecular weight of acrylic copolymers. T_g decreases and M_c increases with the increase of alkyl chain length of acrylate in acrylic copolymers. The film hardness, T_g and polarity of methyl methacrylate (MMA) containing acrylic-melamine-cured films are higher than those of styrene-containing acrylic-melamine-cured films, but both films are almost the same in the degree of crosslinking (maximum loss tangent, $\tan \delta_{\max}$, and M_c). T_g increases and M_c decreases with the increase of melamine resin content for acrylic-melamine coatings. The cured film consists of the acrylic-melamine segments and the melamine-melamine segments at crosslinking points. The carboxy group enhances the crosslinking reactions at low temperatures. All films crosslinked have single glass transition temperatures and broad damping peaks, which show good compatibility. The values of χ_g of acrylic copolymer-melamine films in polar and nonpolar solvents depend on the polarity of acrylic composition and the degree of crosslinking. χ_g values of carboxy functional acrylic-melamine film in any solvents are smaller than that of carboxy and hydroxy functional acrylic-melamine film. χ_g values of MMA-containing acrylic-melamine film in polar solvents are smaller than those of styrene-containing acrylic-melamine film, but χ_g values of MMA-containing acrylic-melamine film in nonpolar solvents are larger than those of styrene-containing acrylic-melamine film. χ_g values of acrylic-melamine film in polar and nonpolar solvents increase with the increase of alkyl chain length of acrylate. The χ_g values of acrylic-melamine coatings in toluene are less than 0.3 and smaller than those of alkyl coatings.

INTRODUCTION

The thermosetting acrylic coatings are used widely in appliances, automobile, structural building panels, metal precoated prior to fabrications, and many other commercial applications.

In general, these crosslinking coatings can be characterized as polymers containing derivatives of acrylic and/or methacrylic acid and styrene. The acrylic copolymers have the carboxy group and the hydroxy group for the functional groups and the amino resins are used as the crosslinking agents. The curing mechanisms of the crosslinking acrylic coatings are similar to those of amino-alkyd coatings. The basic reactions of the functional groups have been discussed by many workers.¹⁻⁵

In this article, 8 acrylic copolymers with pendant functional groups and butylated melamine formaldehyde resin were prepared, and the effects of

carboxy group and hydroxy group on the cure chemistry and network formation of acrylic-melamine coatings have been investigated. The dynamic mechanical properties and the coatings performance of the crosslinking acrylic coatings obtained from the reaction of acrylic copolymers with butylated melamine formaldehyde resin were discussed in terms of acrylic copolymer compositions and the concentration of melamine resin.

EXPERIMENTAL

Materials

Acrylic Copolymers

Eight acrylic copolymers with pendant functional groups were prepared.

A three-neck 2-liter flask was fitted with a stirrer, inert gas (CO₂) inlet and outlet, and a thermometer. The flask was charged with butanol and xylene. It was brought to reflux using a heating mantle. The premixed monomers and catalyst (cumene hydroperoxide of 2% for monomer) were added dropwise to the refluxing solvent. The reaction was continued until complete conversion was obtained. The degree of conversion was checked by measuring the weight percent of the nonvolatile matter in copolymer solution. The degree of conversion was more than 99%. Copolymers I–VII were 50% synthesized in the monomer content, and copolymer VIII was 60% synthesized in the monomer content. The compositions and physical properties of acrylic copolymers are given in Table IA. Acrylic copolymer I has a carboxy group only and acrylic copolymers II–VIII have the carboxy and hydroxy groups as the functional groups. Hydroxy group in acrylic is from β -hydroxy ethyl acrylate,

TABLE IA
Compositions and Physical Properties of Acrylic Copolymers

Samples	I	II	III	IV	V	VI	VII	VIII
Compositions (wt %)								
Styrene	42	42	46	35	42	42		42
Methyl methacrylate							42	
Ethyl acrylate					48			
Butyl acrylate	48	48	48	48			48	48
2-Ethyl hexyl acrylate						48		
Methacrylic acid	10	2	2	2	2	2	2	2
β -Hydroxyethyl acrylate		8	4	15	8	8	8	8
Xylene	70	70	70	70	70	70	70	46.6
<i>n</i> -Butanol	30	30	30	30	30	30	30	20.0
Cumene hydroperoxide	1	1	1	1	1	1	1	1
Properties of acrylic solution copolymers								
Acrylic copolymer contents (%)	47.5	49.0	48.3	48.7	48.9	48.2	49.1	48.2
Viscosity, Gardner method	U-V	T-U	T-U	U-V	V-W	J-K	X-Y	V-W
Acid value (mg KOH/g)	21.1	4.9	5.7	5.2	4.7	4.3	5.1	7.2
Color number	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Number-average molecular weight (M_n)	4,070	4,840	5,160	4,230	4,320	3,730	5,210	5,680
Weight-average molecular weight (M_w)	50,600	45,700	50,600	54,800	65,700	55,600	74,200	75,600
M_w/M_n	12.4	9.4	9.8	13.0	15.2	14.9	14.2	13.3
Solvent	← Xylene/ <i>n</i> -Butanol 70/30 →							

TABLE IB
Physical Properties of Melamine Resin Solution

Items	Results
Properties of resin solution	
Melamine resin content (%)	50.1
Viscosity, Gardner method	C
Acid value (mg KOH/g)	less than 1
Color number, Gardner method	less than 1
Number average molecular weight (M_n)	1250
Weight average molecular weight (M_w)	3540
M_w/M_n	2.8
Characterization of melamine functional groups (Number of groups and bridges per mole of triazine)	
—CH ₂ —O—C ₄ H ₉	2.5
—CH ₂ —OH	1.3
—CH ₂ —O—CH ₂ —O—	0.3
—CH ₂ —	0.3

carboxy group in acrylic is from methacrylic acid. The molecular weights of acrylic copolymers I–VI are approximately the same. Although acrylic copolymers II and VIII are the same in monomer compositions, the molecular weight of copolymer VIII is greater than that of copolymer II. This is because, in the case of radical reaction, the higher the monomer concentration, the higher the reactivity. The molecular weight distribution of copolymer broadens with monomer concentration in the copolymerization reaction. That is, weight-average molecular weight (M_w)/number-average molecular weight (M_n) ratio of copolymer VIII is 13.3, this value is larger than the value ($M_w/M_n = 9.4$) of copolymer II.

Melamine Resin

A partially butylated, polymerized melamine resin was synthesized from commercial melamine, paraformaldehyde, and *n*-butyl alcohol in three steps: (1) reaction mixture of 6 mol *n*-butyl alcohol, 6 mol formaldehyde, 1 mol melamine, and 4 mol water was adjusted at pH 7.5 by 2 *N* NaOH, and methylolation was performed at 90°C for 2 h; (2) butyl etherealization was performed by decantation of butyl alcohol at 95°C for 10 h, after adjusted at pH 6.5 by 16% H₃PO₄, (3) condensation reaction was performed reducing the pressure by using a vacuum pump. After the viscosity of resin reached the prescribed value, the resin solid was dissolved in the required amount of mixed solvent (xylene/butyl alcohol = 2/1). The composition and the physical properties of melamine resin solution are given in Table IB.

Gel Permeation Chromatography

A gel permeation chromatograph (Japan Analytical Industry Co., Ltd. LC-08) with RI-detector was run at room temperature. Column set and solvent conditions were as follows: polystyrene gel Shodex A804, A803, A802, A801 series in this order; tetrahydrofuran, 1.0 mL/min. Molecular weights of each resin are listed in Tables IA and IB.

TABLE II
Preparation of Pigmented Acrylic Crosslinked White Enamel^a

Grind	% by weight
Rutile titanium dioxide ^b	26
Acrylic copolymer solution (50% solids)	26
Mix by three roll mill	
Acrylic copolymer solution (50% solids)	10.4
Butylated melamine formaldehyde resin (50% solids)	15.6
Xylene	10.0
<i>n</i> -Butanol	5.0
Cellosolve acetate	7.0
Nonvolatile (%)	60.0
Pigment weight concentration (%)	50.0

^a Baking schedule, 30 min at 150°C.

^b Ishiharasangyo Co., R-820.

NMR Measurement

Fourier transform ¹³C-NMR spectra of melamine resin were recorded using a FX-200 spectrometer (200 MHz, Japan Electron Optics Lab. Co. Ltd.) on solutions in 20% w/v DMSO-d₆ (Merke 99.7%).

Spectra with gated decoupling of ¹H without nuclear Overhauser effect were measured with pulse width 3 μs, pulse delay 3 s, acquisition time 0.817 μs, and data points 16384. For all spectra chemical shifts quoted with respect to tetramethylsilane as standard. The chemical shift values and their assignments were based on relevant literature.⁶⁻⁸ From integrations of various bands, the relative amounts of the functional groups were determined. The number of groups and bridges per mol of melamine are listed in Table IB.

Preparation of Pigmented Acrylic Copolymer-Melamine Resin Coatings

A typical formulation for the preparation of the pigmented acrylic crosslinked enamel is given in Table II. This formulation consists of a crosslinking acrylic solution copolymer, melamine formaldehyde crosslinking agent, and pigment. The films of acrylic crosslinked white enamels were cast on the tinned mild steel panel (150 × 50 × 0.315 mm). Crosslinking was accomplished by baking about one mil (25 μm) thickness of these coatings for 30 min at 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 sample films of white enamels are named as E-(Acrylic copolymer)-(Melamine Resin content), e.g., EI-30 represents the film of white enamels with acrylic copolymer I and 30% melamine resin.

Preparation of Clear Films

The clear films for the viscoelastic properties and the swelling measurements were cast several times on the tinned mild steel panels. The panels were baked at 60°C for 10 min each time and finally at 150°C for 3 h. The clear

films were removed from the casted panels by using amalgamatic method. The name of sample films is represented by Acrylic Copolymer-Melamine Resin Content.

Measurement of Dynamic Viscoelasticity

The dynamic mechanical measurements were performed on a Rheovibron I Type (Toyo Measurement Co., Ltd. Japan).⁹

All the measurements were made in an atmosphere at a frequency of 138 Hz over a temperature range of 20–200°C. The heating rate was approximately 1°C/min. The clear sample films were rectangular pieces of approximately 4 × 50 × 0.3 mm.

Swelling Measurement¹⁰

The clear sample films were cut into small rectangular pieces of approximately 25 × 25 × 0.3 mm, each weighing from 0.2 to 0.3 g. They were accurately weighed and immersed in about 20 mL of the solvent in closed sample bottles. The samples were taken out at intervals of 24 h. The surfaces were dried with filter paper, and the samples were placed in a previously weighed bottle and were quickly weighed by using a chemical balance. This was repeated for more than a week to determine the equilibrium swelling. All measurements were carried out at room temperature, 25°C. The equilibrium swelling was obtained by plotting the volume swelling ratio (R_v) or the weight swelling ratio (R_w) against time.¹¹

The value of R_v was calculated using sample weights before and after swelling, W and W' , and the densities of solvent and polymer, ρ_1 and ρ_p :

$$R_v = 1 + (\rho_p/\rho_1)(W'/W - 1) \quad (1)$$

$$R_w = W'/W \quad (2)$$

$$v_{2g} = 1/R_v \quad (3)$$

where v_{2g} is the volume fraction of polymer in the swollen gel.

The densities of polymer films were measured using a floating-dipping method in calcium chloride aqueous solution.¹² The reproducibility of density measurements was within $1 \times 10^{-3} \text{ g cm}^{-3}$. The average value of three measurements for each sample was taken as the experimental value.

The solvents used were reagent-grade materials.

RESULTS AND DISCUSSION

The plots of the dynamic storage modulus (E') and the plots of the loss tangent ($\tan \delta$) as a function of temperature for the clear films of 8 acrylic copolymers crosslinked with 30% melamine formaldehyde resin are shown on Figures 1–4.

There is a plateau region in the E' temperature curve at temperatures above 170°C. The films show the rubber elasticity in this temperature region.

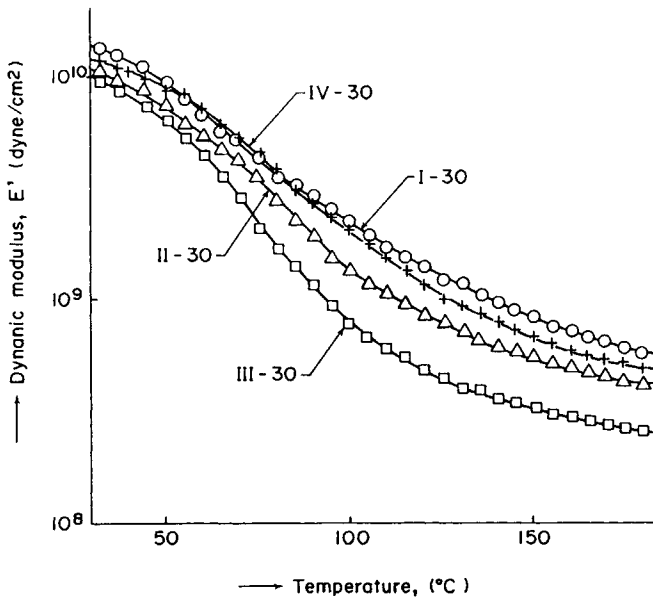


Fig. 1. Dynamic storage modulus as a function of temperature for acrylic copolymers cross-linked with 30% melamine resin. Acrylic-melamine films: (O) copolymer I, (Δ) copolymer II, (\square) copolymer III, (+) copolymer IV.

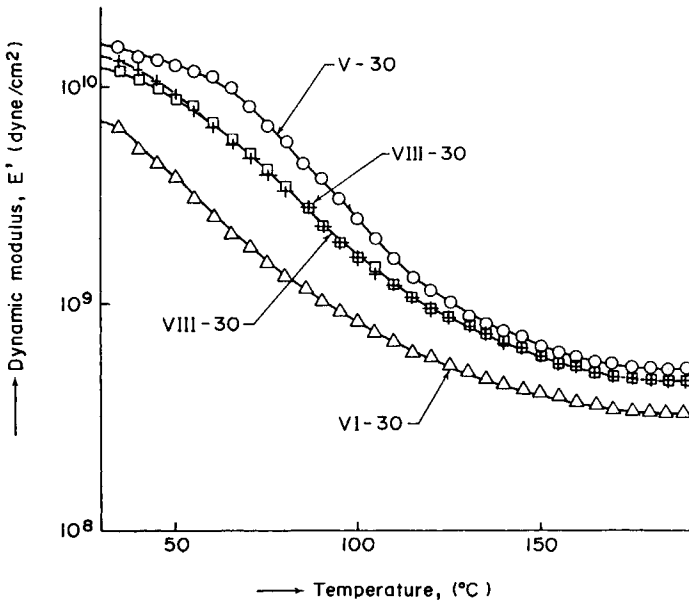


Fig. 2. Dynamic storage modulus as a function of temperature for acrylic copolymers cross-linked with 30% melamine resin. Acrylic-melamine films: (O) copolymer V, (Δ) copolymer VI, (\square) copolymer VII, (+) copolymer VIII.

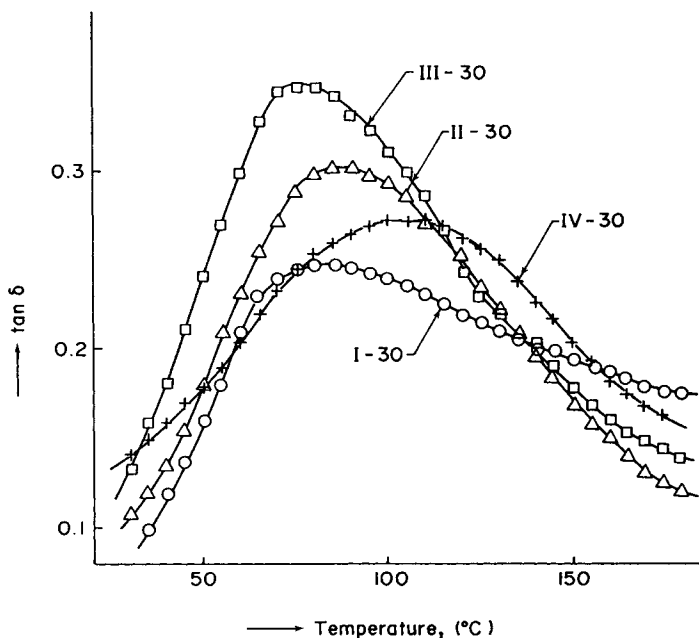


Fig. 3. Loss tangent as a function of temperature for acrylic copolymers crosslinked with 30% melamine resin. Acrylic-melamine films: (O) copolymer I, (Δ) copolymer II, (\square) copolymer III, (+) copolymer IV.

The value of molecular weight between crosslinks (M_c) is calculated by using the following equation.¹³

$$M_c = 3 \cdot \rho_p \cdot R \cdot T / E'_h \quad (4)$$

where E'_h is the storage elastic modulus at temperatures above the transition region, R is the gas constant, and T is the absolute temperature.

The glass transition temperature (T_g) can be determined from the temperature yielding the maximum value of loss tangent, $\tan \delta_{\max}$.

The values of T_g , $\tan \delta_{\max}$, dynamic storage modulus at a high temperature (180°C), E'_h , ρ_p , and M_c for crosslinked acrylic-melamine films are summarized in Table III.

The polymer solvent interaction parameter was calculated by using the following equation, derived by Flory¹⁴ and other workers.^{15,16}

$$\chi_g = \frac{-\ln(1 - v_{2g}) - v_{2g} - (\rho_p V_1 / M_c) (v_{2g}^{1/3} - v_{2g} / 2)}{v_{2g}^2} \quad (5)$$

where χ_g is the polymer solvent interaction parameter for the solvent polymer pair, v_{2g} is the volume fraction of polymer in the swollen gel, ρ_p is the density of polymer, V_1 is the molar volume of solvent, and M_c is the molecular weight between crosslinks in the polymer.

The values of R_w , R_v , and χ_g for acrylic copolymers crosslinked with 30% melamine resin swollen in some solvents are shown in Table IV. The physical

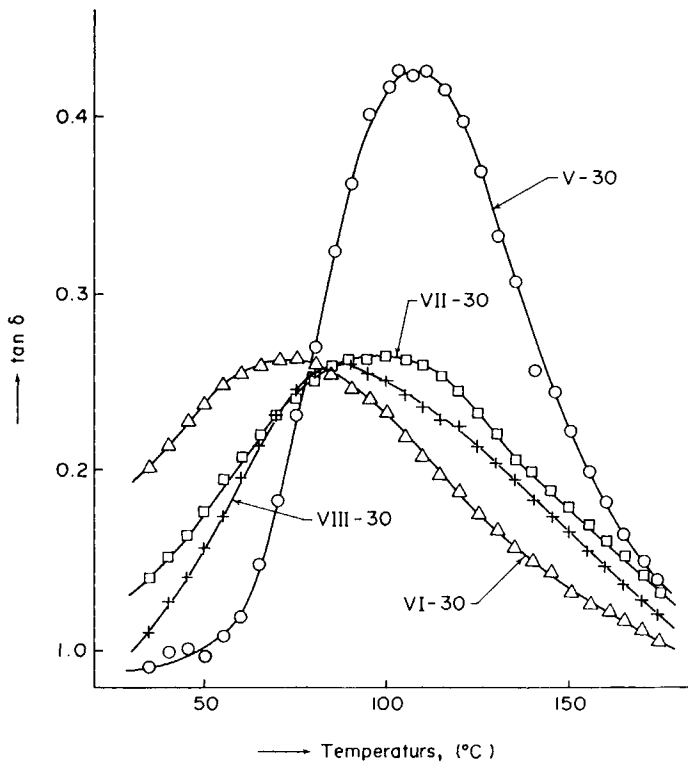


Fig. 4. Loss tangent as a function of temperature for acrylic copolymers crosslinked with 30% melamine resin. Acrylic-melamine films: (O) copolymer V, (Δ) copolymer VI, (\square) copolymer VII, (+) copolymer VIII.

properties of some solvents used in this study are shown in Table V.¹⁷ R_w and R_v values of cured films are low in methanol and high in toluene, methyl ethyl ketone, and ethyl acetate. χ_g value is apparently an inverse function of R_w and R_v , it also depends on M_c .

The film properties of acrylic white baking enamels are also shown in Table VI. The gloss of VII white enamel is lower than that of others, but the gloss of VII-30 black enamel is higher than that of others. These phenomena are caused by the difference of the pigment dispersibility of vehicle. When the functional group content of acrylic copolymer is too large, the mechanical

TABLE III

Glass Transition Temperatures (T_g), Maximum Loss Tangents ($\tan \delta_{\max}$), Dynamic Storage Moduli at High Temperature (180°C) (E'_h), Densities (ρ_p), and Molecular Weight between Crosslinks (M_c) for Acrylic Copolymers Crosslinked with 30% Melamine Formaldehyde Resin

Samples	I-30	II-30	III-30	IV-30	V-30	VI-30	VII-30	VIII-30
T_g (°C)	83	85	76	105	106	75	101	88
$\tan \delta_{\max}$	0.25	0.30	0.35	0.27	0.43	0.26	0.26	0.26
E'_h (dyne/cm ²)	5.5×10^8	4.3×10^8	2.6×10^8	4.8×10^8	5.1×10^8	3.5×10^8	4.7×10^8	4.7×10^8
ρ_p (g/cc)	1.122	1.075	1.090	1.055	1.065	1.086	1.162	1.095
M_c	230	282	474	248	236	350	276	263

TABLE IV
Equilibrium Weight Swelling Ratios (R_w), Equilibrium Volume Swelling Ratios (R_v), and Polymer Solvent Interaction Parameters (χ_g) for Acrylic Copolymers Crosslinked with 30% Melamine Resin in Various Solvents at 25°C

Solvents	I-30	II-30	III-30	IV-30	V-30	VI-30	VII-30	VIII-30
Equilibrium weight swelling ratio, R_w								
Methanol	1.182	1.153	1.163	1.151	1.186	1.117	1.200	1.195
Methyl ethyl ketone	1.447	1.442	1.525	1.344	1.456	1.429	1.437	1.449
Ethyl acetate	1.474	1.472	1.562	1.355	1.480	1.494	1.469	1.466
Toluene	1.550	1.560	1.685	1.404	1.541	1.598	1.502	1.544
White spirit	1.220	1.220	1.265	1.162	1.269	1.105	1.172	1.224
Equilibrium volume swelling ratio, R_v								
Methanol	1.258	1.207	1.224	1.201	1.250	1.160	1.293	1.269
Methyl ethyl ketone	1.623	1.590	1.711	1.451	1.603	1.579	1.631	1.611
Ethyl acetate	1.590	1.563	1.680	1.416	1.567	1.596	1.604	1.566
Toluene	1.712	1.695	1.861	1.492	1.665	1.750	1.673	1.687
Polymer solvent interaction parameter, χ_g								
Methanol	1.085	1.243	0.246	1.248	1.114	1.417	1.038	1.085
Methyl ethyl ketone	0.275	0.449	0.532	0.578	0.346	0.548	0.351	0.390
Ethyl acetate	0.262	0.439	0.528	0.592	0.341	0.495	0.333	0.387
Toluene	0.030	0.236	0.347	0.435	0.157	0.296	0.195	0.187

TABLE V
Molar Volume (V_1), Density (ρ_1), and Solubility Parameter (δ_1) for Solvents at 25°C

Solvents	V_1 (cc/mol)	ρ_1 (g/cc)	δ_1 (cal/cc) ^{1/2}
Methanol	40.41	0.7929	15.00
Methyl ethyl ketone	89.57	0.8050	9.24
Ethyl acetate	97.79	0.9009	8.85
Toluene	106.29	0.8668	8.92

properties of cured films deteriorate. When the molecular weight of acrylic copolymer is too large, the adhesion properties of cured films deteriorate. Therefore, there is an optimum acrylic composition for the coatings performance. EII-30 is good in appearance, mechanical properties, and chemical resistances.

Effects of Acrylic Carboxy Group on the Crosslinking Reaction

Acrylic copolymer I has a carboxy group only and acrylic copolymer II has the carboxy and hydroxy groups as functional groups. The film I-30 was compared with the film II-30 to discuss the effects of the functional groups (OH, COOH) of acrylic copolymer on the crosslinking reactions.

Hardness and modulus at the room temperature and 180°C of the film I-30 are larger than those of the film II-30. Although the T_g values of I-30 and II-30 are almost the same, the M_c value of the film I-30 is smaller than that of the film II-30. Concerning to the $\tan \delta - T$ curve, the width of temperature dispersion of $\tan \delta$ of film I-30 is broader than that of film II-30, and the value of $\tan \delta_{\max}$ of film I-30 is smaller than that of film II-30. That is, the

TABLE VI
 Film Properties of Thermosetting Acryl/Melamine White Baking Enamels^a

White baking enamels	EI-30	EII-30	EIII-30	EIV-30	EV-30	EVI-30	EVII-30	EVIII-30
Hardness, Sward Rocker	56	48	50	48	64	28	50	50
Impact resistance, du Pont tester, reverse g/cm	300/10	500/20	500/10	300/10	300/10	500/40	300/10	300/10
Flexibility, Mandrel tester, 1/8 inch	E	E	E	E	G	E	E	E
Ericksen tester, mm	538	550	547	496	457	560	517	485
Water resistance, 1 day	E	E	E	E	E	G	P	G
Boiling water resistance, 1 h	E	E	B	P	G	G	P	G
Soap resistance, 82°C, 1 h	G	F	F	F	E	E	G	F
Gasoline resistance, 5 h	E	G	G	G	E	P	E	E
Turpentine oil resistance, 5 h	E	G	B	E	E	B	G	P
95% Ethyl alcohol resistance, 1 day	G	G	E	E	G	G	E	F
5% NaOH soln. resistance, 24 h	B	G	F	G	G	G	P	G
5% H ₂ SO ₄ soln. resistance, 24 h	B	G	E	E	E	G	B	F
Gloss, 60° percent reflection								
White enamel 10	93	93	93	93	96	92	86	91
PVC ^b 20	86	86	91	86	81	88	64	85
30	11	50	30	38	42	64	14	46
Black enamel 3	84	81	79	86	78	75	83	75
PVC ^b 7	15	19	15	16	21	14	31	17
15	20	20	14	17	21	14	30	31

^a Evaluation; E (excellent), G (good), F (fair), P (poor), B (bad).

^b Pigment volume concentration.

crosslinking density of film I-30 is larger than that of film II-30.

Crosslinking chemistry and network formation in hydroxy and carboxy functional acrylic copolymer cured with partially butylated melamine formaldehyde crosslinking agents are dominated by two reactions. The first is the condensation of acrylic hydroxy and carboxy groups with alkoxy 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.¹⁻³ The addition of acid catalysts greatly enhances the crosslinking reactions at low temperature and favors melamine-melamine formation.⁴ Since the concentration of carboxy group of acrylic I is higher than that of acrylic II, the catalytic reaction of acrylic I is stronger than that of acrylic II. We assumed that the I-30 film contains more melamine-melamine bonds than the II-30 film at the same crosslinking density.

In the swelling measurements, the R_w and the R_v values of I-30 in polar and nonpolar solvents are larger than those of II-30, and the χ_g values of I-30 are smaller than those of II-30. These characteristics may be attributed to the acrylic-melamine segments of II-30 which are more resistant to solvent attack than are the melamine-melamine segments of I-30. The chemical resistances (alkali and acid) of EII-30 are superior to that of EI-30, and the oil resistances (gasoline and turpentine oil) of EII-30 are inferior to that of EI-30.

Effects of Acrylic Hydroxy Group on the Crosslinking Reaction

The concentration of acrylic hydroxy group increases in the order of acrylic copolymers III < II < IV.

The values of T_g , E' , and E'_h (180°C) increase and the values of $\tan \delta_{\max}$, M_c , and ρ_p decrease with the increase of the concentration of hydroxy on acrylic copolymers. That is, the crosslinking density of acrylic-melamine film increases with increasing of acrylic hydroxy content.

Regarding the adhesive properties, the EII-30 coating was the best among the three enamels. If the adhesive strength depends on the adsorption force of polar groups on the substrate, the adhesive strength would increase in the order of EIII-30 < EII-30 < EIV-30. It is assumed that the poor adhesion property of EIV-30 is due to less stress relaxation and larger residual stress. The residual stress of coatings is the sum of the curing stress and the thermal shrinkage stress. The thermal shrinkage stress is generated by the temperature difference between the glass transition temperature and the room temperature.¹⁸ Since the T_g , the E' , and the E'_h of IV-30 are the highest among the three films, the thermal shrinkage stress of EIV-30 would be large.

The R_w and the R_o values of films in polar and nonpolar solvents decrease with the increase of the crosslinking density. The oil, gasoline, and the turpentine oil resistance of baking enamels increase in the order of the films EIII-30 < EII-30 < EIV-30. These results are due to the increase of the polar group content, the decrease of styrene content and the increase of crosslinking density. However, chemical resistance such as the boiling water, alcohol, and sulfuric acid resistance do not show the simple trend as the function of chemical compositions. The complication of chemical resistances of the film indicates that the crosslinking effect competes with the polar effect.

Effects of the Alkyl Chain Length of Acrylate in Acrylic Copolymer

The alkyl chain length of acrylate increases in the order of acrylic copolymer V < II < VI. In this case, the longer the alkyl chain length, the stronger the inner molecular plasticization. The long alkyl chain lowers the temperature of maximum damping. In addition to lowering the T_g , the long alkyl chain lowers the value of $\tan \delta_{\max}$ and broadens the transition region. The broadening is related to the mutual solubility and/or crosslinking reaction of the acrylic copolymer and the melamine resin. In the case of the VI-30 film, since the melamine resin has a limited solubility in copolymer VI, a broad damping peak is found. This is probably an indication that considerable aggregation or association of like segments is taking place in the soluble mixture. The film hardness and the values of E' at room temperature and 180°C decrease in the order of V-30 > II-30 > VI-30. This is due to the action of the inner molecular plasticization. The values of M_c increase gradually in the order of V-30 < II-30 < VI-30. These phenomena are reflected in the mechanical properties such as Mandrel bending resistance, du Pont impact resistance, and Erichsen adhesion property.

Since the alkyl chain is a highly hydrophobic group, the values of R_w and R_o of the film in toluene increase, and the values of R_w and R_o of the film in methanol and methyl ethyl ketone decrease with increasing of the alkyl chain

length on acrylic compositions. The χ_g values for the cured films measured in methanol, methyl ethyl ketone, and toluene increase with the increase of the alkyl chain length. The χ_g values of the films V-30, II-30, and VI-30 swollen in toluene are less than 0.3, and the three films have a strong affinity to toluene.

Comparison of Methyl Methacrylate Monomer with Styrene Monomer

Acrylic VII is methyl methacrylate (MMA) containing copolymer and acrylic VIII is styrene (St) containing copolymer. Both copolymers resemble each other in the solution viscosity, molecular weight, and monomer composition.

The patterns of $E' - T$ curve and of $\tan \delta - T$ curve, the E' values at room temperature and 180°C , and the values of $\tan \delta_{\max}$ and M_c of VII-30 (MMA) are approximately equal to these of VIII-30. However, the film hardness, T_g value, and ρ_p value of VII-30 are higher than that of VIII-30, the Erichsen flexibility and the cross-cut adhesive property of EVII-30 are superior to EVIII-30. Concerning the swelling measurements, χ_g values of VII-30 in methanol, methyl ethyl ketone, and ethyl acetate are smaller than that of VIII-30, and χ_g value of VII-30 in toluene is larger than that of VIII-30. The EVII-30 coating film exhibits a good oil resistance, while the EVIII-30 coating film has good water resistance. χ_g value is apparently an inverse function of R_v , and the swelling measurements were in agreement with the results of the chemical resistance and the solvent resistance of the baked enamels.

Since the solubility parameters of polystyrene and polymethyl methacrylate are 8.5–9.5 and 9.0–9.5,¹⁹ respectively, the polarity of polymethyl methacrylate is higher than that of polystyrene. The superior adhesive properties and oil resistance and the poor water resistance of the EVII-30 coating film are due to a high polarity.

Effects of Molecular Weight of Acrylic Copolymer

Acrylics II and VIII are of the same monomer composition, but acrylic VIII is greater than acrylic II in molecular weight. We investigated the effects of the molecular weight of acrylic copolymer on the viscoelastic properties by comparing the II-30 film with the VIII-30 film.

The II-30 film is lower than the VIII-30 film in the T_g , the E'_h (180°C), and the ρ_p .

An important equation relating the molecular weight to the glass transition temperature is²⁰

$$T_g = T_g(\infty) - C/M_n \quad (6)$$

where $T_g(\infty)$ is the glass transition temperature of a polymer of infinite molecular weight, M_n is a number-average molecular weight, and C is a material constant. The concentration of terminal groups of polymers varies in proportion to $1/M_n$. The end groups act as imperfections which adversely affect the T_g . In crosslinking polymers, the molecular weight of chain segments between crosslinks is one of the factors which control the T_g . Crosslink-

ing raises the T_g value and broadens the transition region. The shift in T_g value is estimated from the following equation²¹⁻²³ on the analog of eq. (6).

$$T_g(M_c) = T_{g\infty} + K/M_c \quad (7)$$

where $T_g(M_c)$ is the glass transition temperature for the crosslinked polymer, $T_{g\infty}$ is the glass transition temperature of the uncrosslinked material, and K is the constant. Since the M_c decreases as the molecular weight of prepolymer increases, the $T_g(M_c)$ increases.

The film properties of EII-30 are superior to that of EVIII-30 in adhesion, mechanical properties, water resistance and turpentine oil resistance, etc., as shown in Table VI. The swelling ratios of the II-30 film are lower than those of the VIII-30 film in methanol, methyl ethyl ketone white spirit, while the swelling ratios of the II-30 film are higher than those of the VIII-30 film in ethyl acetate and toluene. The χ_g values of II-30 are 1.243 in methanol, 0.449 in methyl ethyl ketone, 0.439 in ethyl acetate, and 0.236 in toluene. These χ_g values of II-30 are greater than those of VIII-30 in corresponding solvents.

The values of χ_g of acrylic copolymer crosslinked with 30% melamine resin in toluene are less than 0.3. Alkyd resin films swell easily in methyl ethyl

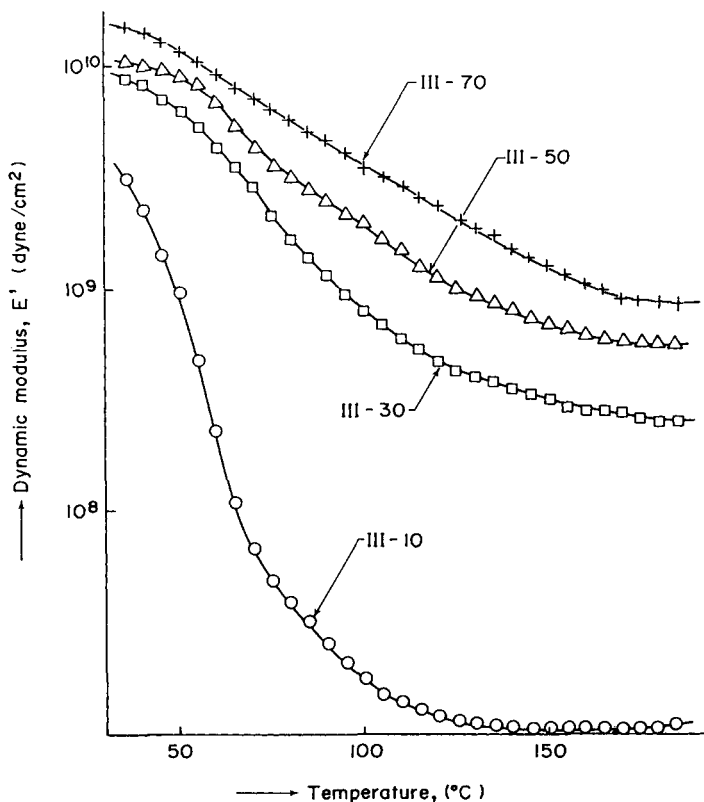


Fig. 5. Dynamic storage modulus as a function of temperature for acrylic copolymer III crosslinked with melamine resin. Copolymer III-melamine films: (O) 10% melamine, (□) 30% melamine, (Δ) 50% melamine, (+) 70% melamine.

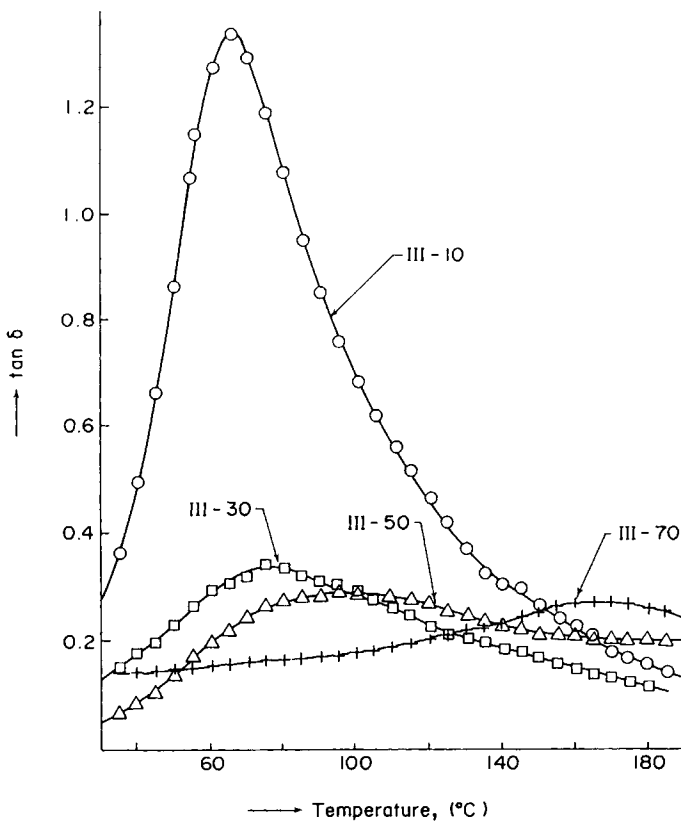


Fig. 6. Loss tangent as a function of temperature for acrylic copolymer III crosslinked with melamine resin. Copolymer III-melamine films: (○) 10% melamine, (□) 30% melamine, (Δ) 50% melamine, (+) 70% melamine.

ketone,²⁴ while acryl-melamine films swell easily in toluene. Acryl-melamine films have a strong affinity to aromatic hydrocarbon solvents such as toluene. This means that it is difficult to evaporate toluene from the acrylic coatings film. The solvent-released property of coatings film is closely related to the χ_g value.

Effects of Melamine Resin Content for Acrylic Copolymer / Melamine Resin Coatings

Figures 5 to 10 show the dynamic mechanical spectroscopy for copolymers III, II, and IV/melamine resin coating films.

E' versus T curves for each film shows a plateau region (rubbery state) at high temperatures. The E'_h (180°C) values are 10^7 – 10^9 dyne/cm². These values are equal to those of alkyd resins crosslinked with melamine resin,²⁵ special alkyd resins,²⁶ and rigid unsaturated polyester resins.²⁷ The E'_h values of acrylic-melamine films are larger than the E'_h values (10^7 dyne/cm²) of alkyd resins,²⁷ urethane resins modified with vegetable oil,^{28,29} and epoxy ester resins modified with fatty acid.³⁰ The width of damping increases with increased concentrations of melamine resin.

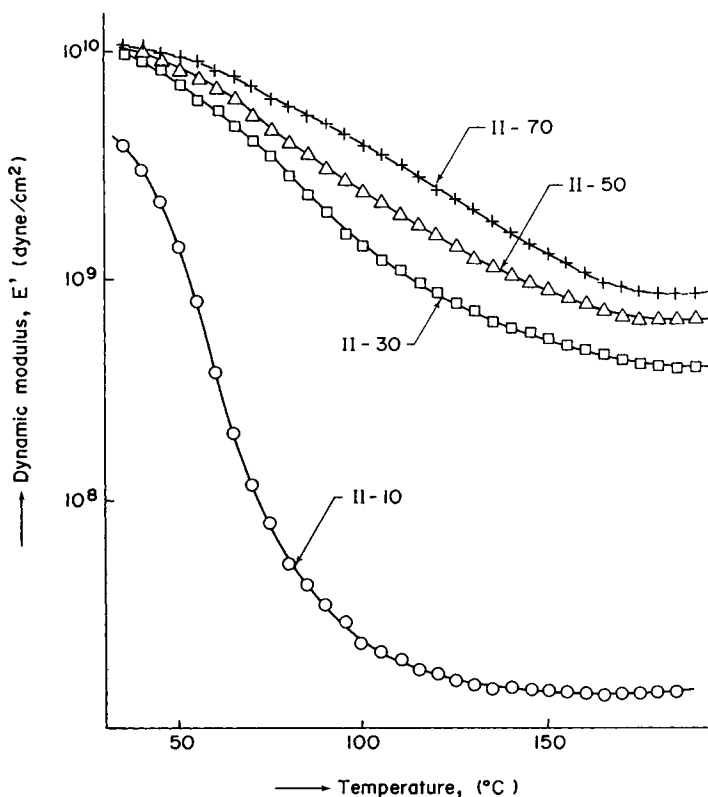


Fig. 7. Dynamic storage modulus as a function of temperature for acrylic copolymer II crosslinked with melamine resin. Copolymer II-melamine films: (○) 10% melamine, (□) 30% melamine, (△) 50% melamine, (+) 70% melamine.

Figure 11 shows the plots of the modulus at high temperature as a function of melamine resin content for acrylic copolymers III, II, and IV/melamine resin films. The hydroxyl value of acrylic is larger, the value of E'_h is larger. The E'_h values show the maximum in the composition range of 50–70% of melamine resin content. The coating compositions yielding the maximum value of E'_h shift to a poor melamine resin content with the increase of the hydroxyl value of acrylic copolymer.

Figure 12 shows the plots of the $\tan \delta_{\max}$ as a function of melamine resin content. The $\tan \delta_{\max}$ values decrease with the increase of melamine resin content as well as with the increase of hydroxyl value of acrylic copolymer.

Figure 13 shows the plots of T_g as a function of melamine resin content for acrylic copolymers III, II, and IV crosslinked with melamine resin. The value of T_g increases with the increase of melamine resin content. The T_g values of acrylic copolymers crosslinked with 10%, 30%, and 50% melamine resin increase with increased hydroxyl value of acrylic copolymer. However, the T_g values of acrylic copolymers crosslinked with 70% melamine resin decrease in the order of III-70 > II-70 > IV-70.

The extent of the reaction of acrylic copolymer crosslinked with 10%, 30%, and 50% melamine resin increases with increased hydroxyl value of acrylic

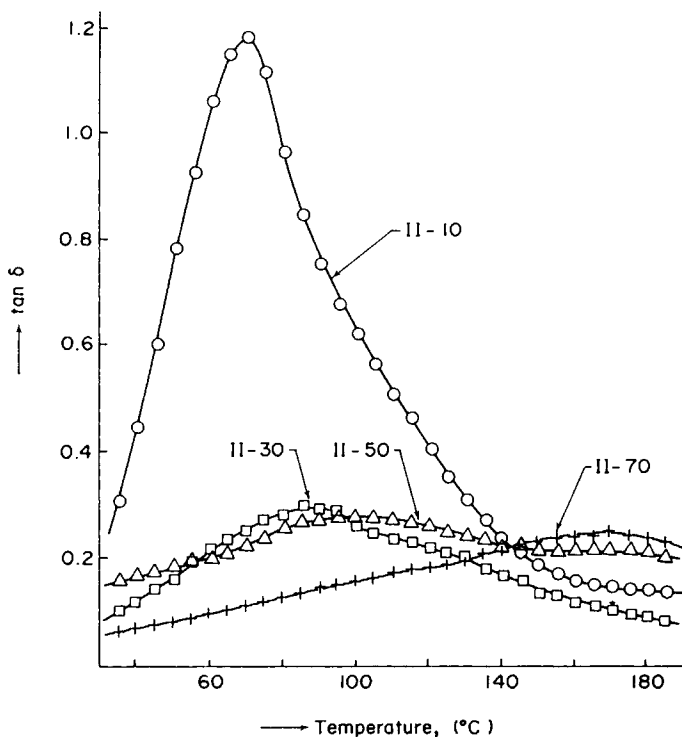


Fig. 8. Loss tangent as a function of temperature for acrylic copolymer II crosslinked with melamine resin. Copolymer II-melamine films: (○) 10% melamine, (□) 30% melamine, (△) 50% melamine, (+) 70% melamine.

copolymer, but the extent of crosslinking of acrylic copolymer with 70% melamine resin decreases with increased hydroxyl value of acrylic copolymer. This suggests that most networks are more or less heterogeneous. Network structure consists of acrylic-melamine crosslink and melamine-melamine crosslink. Network molecules have different chemical compositions and a distribution of sequence lengths.

Figures 5-10 and 12 illustrate the broadening of the transition region by increasing the heterogeneity. The kinetics of various reactions appear to be complex functions of bake time, bake temperature, catalyst strength, equivalent weight of functionality and the distribution of functionality.^{3,4} The heterogeneity of networks is regulated by the relative reactivity of melamine-melamine to acryl-melamine. In general, low bake temperatures and weak acids favor polymer-melamine crosslink formation, while high bake temperatures and strong acids favor melamine-melamine crosslink formation.⁴ Thus, at the beginning of the crosslinking reactions, the network structure will be rich in the crosslinks of the more reactive prepolymer (e.g., acryl-melamine), while the network structure formed near the end of reaction will be rich in the crosslinks of the less reactive prepolymer and/or residual prepolymer (e.g., acryl or melamine-melamine). It is assumed that these crosslinking reactions are similar to those of alkyd/melamine coatings.²⁵ Although acrylic-melamine crosslink and melamine-melamine crosslink are heterogeneous in the prepoly-

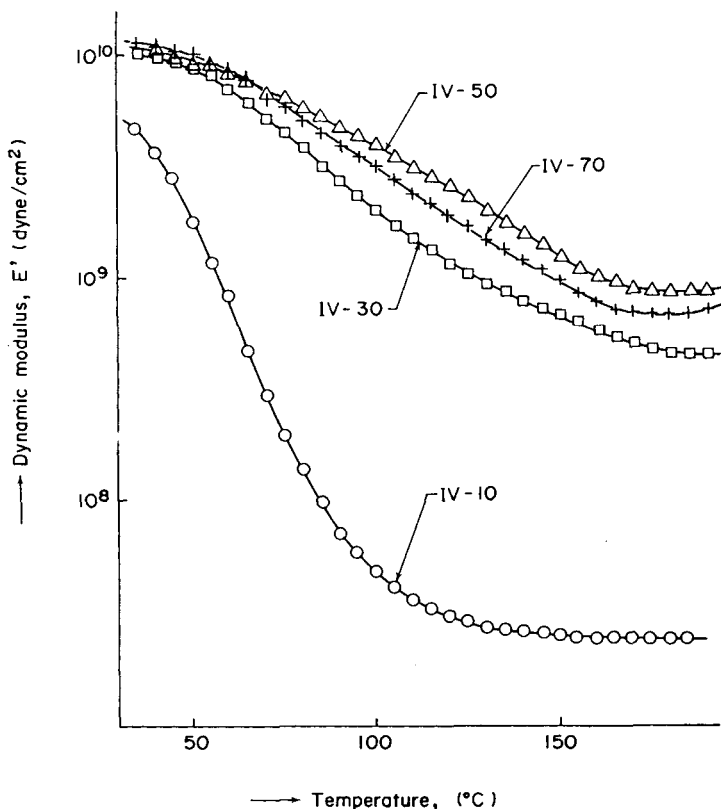


Fig. 9. Dynamic storage modulus as a function of temperature for acrylic copolymer IV crosslinked with melamine resin. Copolymer IV-melamine films: (O) 10% melamine, (□) 30% melamine, (Δ) 50% melamine, (+) 70% melamine.

mer sequence (i.e., in the microstructure of network chains), two component networks are homogeneously mixed in the scale of segmental size (molecular motion unit) in one another. They have single glass transition temperatures, which shows good compatibility, and a broad damping peak due to the microheterogeneity in the prepolymer sequence. However, the real structure and morphology of the polymer networks formed must be observed experimentally in more detail.

CONCLUSION

1. Hardness and modulus of carboxy functional acrylic copolymer I crosslinked with 30% melamine resin (I-30) is larger than those of carboxy and hydroxy functional acrylic copolymer II crosslinked with 30% melamine resin (II-30). Although the T_g values of I-30 and II-30 are almost the same, the M_c value of I-30 is smaller than that of II-30. The width of temperature dispersion of $\tan \delta$ of I-30 is broader than that of II-30. The R_w and R_p values of I-30 in polar and nonpolar solvents are larger than those of II-30, and the χ_g values of I-30 are smaller than those of II-30. These phenomena were in agreement with the chemical resistance (alkali and acid) of baked films. But

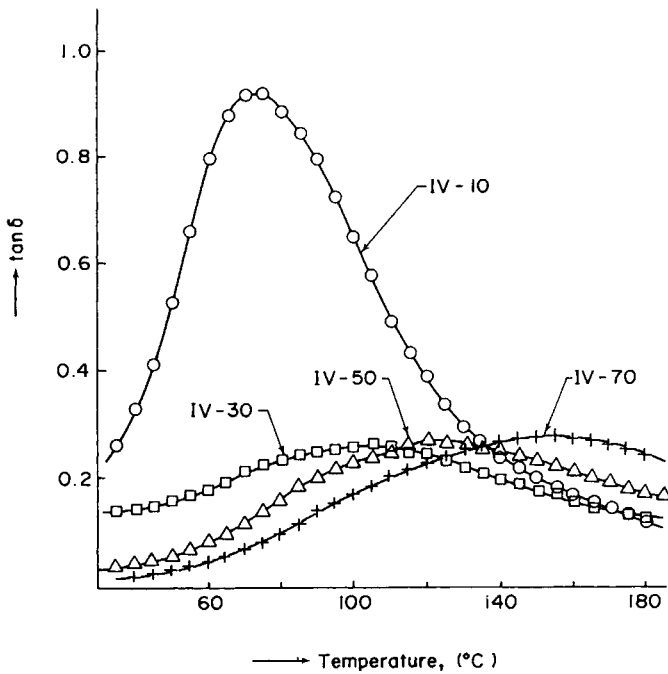


Fig. 10. Loss tangent as a function of temperature for acrylic copolymer IV crosslinked with melamine resin. Copolymer IV-melamine films: (O) 10% melamine, (□) 30% melamine, (Δ) 50% melamine, (+) 70% melamine.

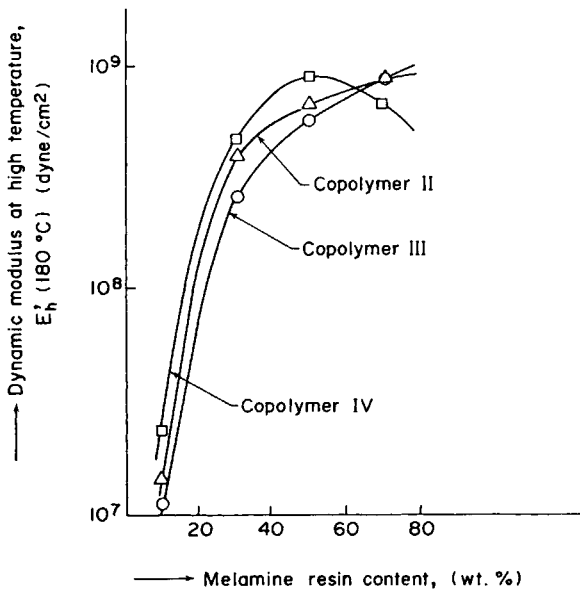


Fig. 11. Dynamic storage modulus at high temperature as a function of melamine resin content for acrylic copolymers crosslinked with melamine resin. Acrylic-melamine films: (O) copolymer III, (Δ) copolymer II, (□) copolymer IV.

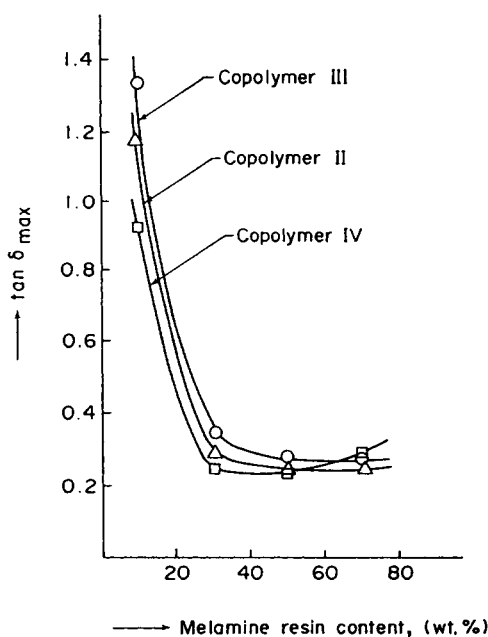


Fig. 12. Maximum loss tangent as a function of melamine resin content for acrylic copolymers crosslinked with melamine resin. Acrylic-melamine films: (O) copolymer III, (Δ) copolymer II, (\square) copolymer IV.

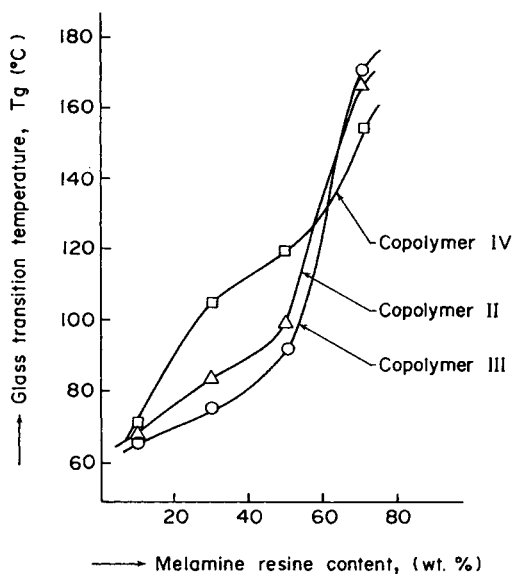


Fig. 13. Glass transition temperature as a function of melamine resin content for acrylic copolymers crosslinked with melamine resin. Acrylic-melamine films: (O) copolymer III, (Δ) copolymer II, (\square) copolymer IV.

the gasoline and turpentine oil resistances of EI-30 were better than those of EII-30.

2. The values of T_g , E' , and E'_h increase, while the values of $\tan \delta_{\max}$, M_c , and ρ_p decrease with the increase of the hydroxyl value of acrylic copolymer for acrylic-melamine films. When the hydroxyl value becomes large, the turpentine oil resistance and alkali resistance of baked enamels improve, while the boiling water and alcohol resistances do not show the simple trend as a function of the chemical composition. Likewise, when the hydroxyl value is too large, the residual stress of baked film becomes large, the adhesive strength of coatings on steel weakens.

3. The T_g , E' , E'_h , $\tan \delta_{\max}$, and film hardness decrease and the M_c increases with the increase of alkyl chain length of acrylate for acrylic-melamine coatings. The phenomena of inner molecular plasticization is reflected in the mechanical properties such as Mandrel bending resistance, du Pont impact resistance, and Erichsen adhesive property. The χ_g values for cured film in methanol, methyl ethyl ketone, ethyl acetate, and toluene increase with the increase of the alkyl chain length of acrylate.

4. MMA-containing acrylic-melamine film (VII-30) is similar to styrene-containing acrylic-melamine film (VIII-30) in the values of E' , E'_h , $\tan \delta_{\max}$, and M_c . The film hardness, T_g , and polarity of VII-30 are higher than those of VIII-30, respectively. EVII-30 has good oil resistance, and EVIII-30 has good water resistance.

5. The values of T_g , E' , E'_h , and ρ_p increase with increased molecular weight of acrylic copolymer. However, when the molecular weight of acrylic copolymer is too large, the adhesive property deteriorates and the χ_g values decrease.

6. The T_g and the E'_h increase and the $\tan \delta_{\max}$ decreases with the increase of melamine resin content for acrylic-melamine film.

7. The T_g of acrylic copolymer crosslinked with 10%, 30%, and 50% melamine resin increases with the increase of hydroxyl value of acrylic copolymer. However, the T_g of acrylic copolymer crosslinked with 70% melamine resin decreases with the increase of hydroxyl value of acrylic copolymer.

8. Concerning to the MMA-containing acrylic-melamine coatings, the gloss of white enamel is lower than that of other vehicles, but the gloss of black enamel is higher than that of others. The gloss of enamel depends on the pigment dispersibility (polarity) of vehicles.

9. The viscoelastic properties and swelling behaviors of high polymers are of great practical value, and these measurements enable one to readily evaluate many of the film properties of coatings.

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