New Coating Materials Prepared by Radiation-Induced Polymerization. II. Study on The Polymerization Mechanism of Mar-Resistant Coating Composition

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Synopsis

It was previously reported that excellent mar resistance coating systems could be obtained by the combination of silicone compounds and vinyl compounds, such as KBM 403–GMA systems. Radiation-induced polymerization was the most efficient means of prepolymerization to give the viscosity suitable for coating. In this report, change in conversion and the predominant mechanism of prepolymerization were investigated by measuring the change in refractive index. It was shown that the conversion change and the predominant prepolymerization mechanism could be identified by the refractive index. The relationship between the refractive index and coating properties such as film thickness and haze value was also studied. Dripping of GMA prepolymer occurred, and coating thickness was small in GMA including prepolymer systems obtained predominantly by radical mechanism; the thickness was relatively large in the prepolymer systems obtained by epoxy ring opening-type polymerization mechanism. However, the mar resistance in the former was excellent in spite of reduced thickness.

INTRODUCTION

In the previous report,[1] it was found that an excellent mar-resistant coating was obtained by the combination of silicone and vinyl compounds such as KBM 403 (γ-glycidoxypropyltrimethoxysilane and GMA (glycidyl methacrylate). It was necessary for the coating to have a suitable viscosity for processing, which was achieved by radiation-induced prepolymerization. The prepolymer thus obtained was coated and cured by heating with a catalyst.

The monomeric system for mar-resistant coating includes binary components which are completely different in chemical structure and polymerization mechanism. That is, both types of polymerization are possible in the prepolymerization of the KBM 403–GMA system, the vinyl polymerization and epoxy ring-opening polymerization. It was assumed that the mechanism of prepolymerization affected the various properties such as the viscosity of prepolymer, thickness of coating, and the mar-resistance.

In this report, the relationship between the polymerization conditions and the predominant mechanism of prepolymerization was studied as well as its effect on the resulting properties of the coating.

0021-8995/78/0022-0823$01.00

Experimental

The preparation of the prepolymer, the coating on the polymer substrate, and the curing were carried out by the same method as described in part I.[1] Conversion was determined by the weighing method using ethyl ether as a precipitating agent. Mar-resistance and heat durability were also tested in the same way as previously described. Refractive index was followed with an Abbe-type refractive index meter (Atago Optical Works Co.).

RESULTS AND DISCUSSION

Relationship Between Conversion and Viscosity

The relationship between conversion based on the vinyl monomer content and the viscosity of the KBM 403–GMA system after irradiation is shown in Figure 1. It was found previously that 100% conversion was reached after irradiation by 1.0×10^6 röntgens. The suitable viscosity range for coating was 50–200 cp, and this viscosity was obtained easily by 100% conversion of GMA in the prepolymer (Fig. 1). However, the viscosity continued to increase with time after 100% conversion was reached, as shown in Figure 1. This fact suggests that nonvinyl-type polymerization continued after irradiation. This postpolymerization was probably the epoxy ring-opening reaction of KBM 403 and GMA. The open-ring catalyst such as perchloric acid coexists in the monomeric system. It is difficult to homogeneously mix the catalyst with the viscous prepolymer, and the epoxy ring-opening reaction was already partly initiated by direct ring scission during irradiation or by hydrochloric acid formation as a radiolysis product; the main reaction by irradiation was the vinyl polymerization.
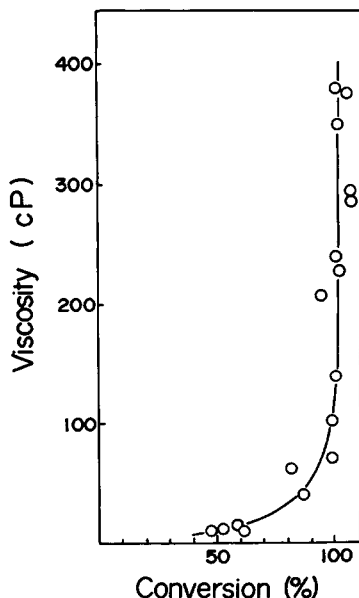

Fig. 1. Relationship between conversion and viscosity of prepolymer in γ-glycidoxypropyltrimethoxysilane (KBM 403)–glycidyl methacrylate (GMA) system: KBM 403 75 vol-%–GMA 25 vol-%; dose rate 5×10^5 R/hr, at 25°C, in air.

Relationship Between Conversion and Refractive Index

The change in refractive index was investigated to follow the conversion in prepolymerization under various initiation means; it was difficult to determine the conversion of prepolymerization by methods such as weighing or viscosity measurement. Three kinds of initiation means were tested for prepolymerization: benzoyl peroxide as a radical catalyst and irradiation in the presence or absence of ring-opening catalyst for the vinyl-type polymerization, respectively, and perchloric acid as an initiator for the epoxy ring opening-type polymerization. The results of the investigation are listed in Table I. The relationship between the conversion and the refractive index in the polymerization of the GMA single system is plotted in Figure 2.

According to Figure 2, it is possible to distinguish the predominant prepolymerization mechanisms. The dotted line in Figure 2 indicates the theoretical curve in the case in which only vinyl-type polymerization of GMA occurred and no silicone reacted. This theoretical curve was obtained by measuring the refractive index of the GMA monomer and polymer obtained by vinyl polymerization and calculating the refractive index of the polymer–monomer binary mixture at various compositions on the basis of additivity. The observed relationship in the case of predominant radical initiation agreed with the theoretical curve. On the other hand, the relationship in ring-opening initiation considerably deviated from the theoretical curve. This means that in the presence of a radical initiator or in irradiation, vinyl polymerization predominantly occurred, and in the presence of ring-opening initiator, epoxy ring opening-type polymerization predominantly occurred. Thus, the relationship between the conversion and refractive index can be divided into two regions (Fig. 2). We can identify the predominant mechanism of prepolymerization by these regions.

A similar result was observed in the prepolymerization of KBM 403-GMA (50:50) system as shown in Table I and Figure 3.

In this case, the theoretical curve was also drawn by measuring the refractive index of KBM 403 monomer, GMA monomer, and poly-GMA and calculating the refractive index of their mixture at various conversion of GMA by radical mechanism assuming additivity of the components' refractive index. According to these results, the relationship between conversion and refractive index in prepolymerization induced by a radical initiator and radiation almost agrees with the theoretical curve for vinyl polymerization, while the relationship in prepolymerization initiated by the ring-opening catalyst differs greatly from that of the theoretical curve. Thus, we can identify the predominant mechanism of prepolymerization by measuring the refractive index of the reaction system. The same relationship was also obtained in the cases of various compositions of KBM 403–GMA systems, as shown in Figure 4. The dotted curve indicates the theoretical relationship in KBM 403 single system polymerizing by a ring-opening initiator. That is, the refractive index of the KBM 403 monomer–polymer mixture system was calculated from the refractive index of KBM 403 monomer and polymer assuming the additivity. The relationship in Figure 4 shifts with increase GMA content from that of theoretical KBM 403 single system to the region of higher refractive index values and comes closer to the relationship in the GMA single system by the vinyl polymerization.

It was concluded from these results that the change in the refractive index

TABLE I
Effect of Prepolymerization Conditions on Properties of Prepolymer and Coating

Run no.	Composition vol-%		Prepolymerization			Prepolymer		Coating	
	KBM 403	GMA	Method	Temp., °C	Time or dose	N_D^{20}	Conver- sion, %	Thick- ness, μ	Haze value, %
1	100	0	0.5% HClO$_4$	55	0 hr	1.4255	—[c]	~1	—
2	100	0	0.5% HClO$_4$	55	3 hr	1.4325	—	2	15.5
3	100	0	0.5% HClO$_4$	55	16 hr	1.4413	—	27	10.1
4	100	0	0.5% HClO$_4$	55	40 hr	1.4580	—	58	8.3
5	50	50	0.5% HClO$_4$ irradiation	25	5×10^4 R	1.4387	trace	~1	16.6
6	50	50	0.5% HClO$_4$ irradiation	25	7×10^4 R	1.4391	19.8	~1	15.4
7	50	50	0.5% HClO$_4$ irradiation	25	9×10^4 R	1.4392	30.4	~1	13.7
8	50	50	0.5% HClO$_4$ irradiation	25	1×10^5 R	1.4401	36.1	1	12.2
9	50	50	0.5% HClO$_4$ irradiation	25	2×10^5 R	—	gelation	—	—
10	50	50	0.5% HClO$_4$[a] 4% t-BPO[c]	75[a]	1 hr	1.4389	8.1	~1	20.1
11	50	50	0.5% HClO$_4$[a] 4% t-BPO[c]	75[a]	2 hr	1.4396	14.9	~1	19.3
12	50	50	0.5% HClO$_4$[a] 4% t-BPO[c]	75[a]	3 hr	1.4408	19.6	~1	15.4
13	50	50	0.5% HClO$_4$[a] 4% t-BPO[c]	75[a]	3.3 hr	1.4418	36.8	~1	16.9
14	50	50	0.5% HClO$_4$[a] 4% t-BPO[c]	75[a]	3.7 hr	1.4439	43.0	1	13.8
15	50	50	0.5% HClO$_4$[a] 4% t-BPO[c]	75[a]	4 hr	—	gelation	—	—
16	50	50	0.5% HClO$_4$[b] 0.5% t-BPO	55[b]	6 hr	1.4455	1.0	2	15.3
17	50	50	0.5% HClO$_4$[b] 0.5% t-BPO	55[b]	16 hr	1.4480	6.3	4	12.9
18	50	50	0.5% HClO$_4$[b] 0.5% t-BPO	55[b]	30 hr	1.4491	11.4	7	12.0
19	50	50	0.5% HClO$_4$[b] 0.5% t-BPO	55[b]	48 hr	1.4529	17.3	18	10.2
20	40	60	0.5% HClO$_4$ irradiation	25	3×10^4 R	1.4392	trace	~1	17.7
21	40	60	0.5% HClO$_4$ irradiation	25	5×10^4 R	1.4400	1.0	~1	16.1
22	40	60	0.5% HClO$_4$ irradiation	25	7×10^4 R	1.4403	6.9	~1	15.4
23	40	60	0.5 HClO$_4$ irradiation	25	9×10^4 R	1.4416	38.6	~1	12.5
24	40	60	0.5 HClO$_4$ irradiation	25	1×10^5 R	1.4428	46.2	1	9.8
25	40	60	0.5% HClO$_4$ irradiation	25	2×10^5 R	—	gelation	—	—
26	20	80	0.5% HClO$_4$ irradiation	25	3×10^4 R	1.4445	trace	~1	11.9
27	20	80	0.5% HClO$_4$ irradiation	25	5×10^4 R	1.4450	9.8	~1	11.5

TABLE I (continued)

Run no.	Composition vol-% KBM 403	GMA	Prepolymerization Method	Temp., °C	Time or dose	Prepolymer N_D^{20}	Conversion, %	Coating Thickness, μ	Haze value, %
28	20	80	0.5% $HClO_4$ irradiation	25	7×10^4 R	1.4456	20.4	~1	10.7
29	20	80	0.5% $HClO_4$ irradiation	25	9×10^4 R	1.4459	43.2	~1	12.0
30	20	80	0.5 $HClO_4$ irradiation	25	1×10^5 R	1.4465	55.1	1	10.8
31	20	80	0.5% $HClO_4$ irradiation	25	2×10^5 R	—	gelation	—	—
32	0	100	0.5% t-BPO	55	1 hr	1.4554	12.5	1	61.4
33	0	100	0.5% t-BPO	55	2 hr	1.4570	24.0	1	64.8
34	0	100	0.5% t-BPO	55	2.5 hr	1.4590	32.6	2	59.9
35	0	100	0.5% $HClO_4$ irradiation	25	8×10^4 R	1.4448	trace	~1	—
36	0	100	0.5% $HClO_4$ irradiation	25	1×10^5 R	1.4448	trace	~1	—
37	0	100	0.5% $HClO_4$ irradiation	25	3×10^4 R	1.4464	10.4	~1	70.4
38	0	100	0.5% $HClO_4$ irradiation	25	4×10^4 R	1.4557	15.9	1	67.2
39	0	100	0.5% $HClO_4$ irradiation	25	5×10^4 R	—	gelation	—	—
40	0	100	0.5% $HClO_4$	55	1 hr	1.4593	14.9	6	33.1
41	0	100	0.5% $HClO_4$	55	2 hr	1.4672	19.8	14	32.4
42	0	100	0.5% $HClO_4$	55	3 hr	1.4720	24.5	39	29.1
43	0	100	0.5% $HClO_4$[b] 0.5% t-BPO	55[b]	0 hr	1.4448	0	~1	—
44	0	100	0.5% $HClO_4$[b] 0.5% t-BPO	55[b]	1 hr	1.4614	11.0	6	38.2
45	0	100	0.5% $HClO_4$[b] 0.5% t-BPO	55[b]	2 hr	1.4715	20.3	11	33.8
46	0	100	0.5% $HClO_4$[b] 0.5% t-BPO	55[b]	4 hr	1.4732	30.5	32	37.2

[a] Vinyl-type prepolymerization occurred predominantly.
[b] Ring opening-type prepolymerization occurred predominantly.
[c] — = Impossible to measure or impossible to coat; t-BPO = t-butyl peroxide.

corresponded to the increase in conversion and that the relationship between conversion and refractive index differed by the prepolymerization mechanism. Then, the propagation and the predominant mechanism of prepolymerization could be followed by measuring of the refractive index.

Relationship Between Refractive Index, Coating Thickness, and Haze Value

It was discovered previously[1] that the thickness and the mar resistance were affected by the viscosity of the prepolymer. Therefore, it was expected that the refractive index could be related to the thickness and the mar resistance of the coating, and the change in viscosity. Moreover, it is interesting to know the relationship between the predominant prepolymerization mechanism and the
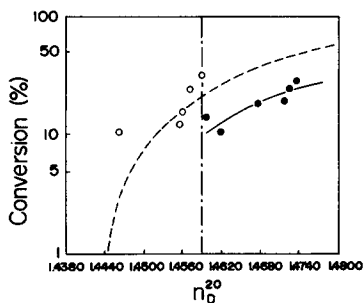
Fig. 2. Relationship between conversion and refractive index of prepolymer in GMA single system: (O) prepolymerization by irradiation (in presence or absence of HClO$_4$) or by heating with 0.5% t-BPO (*tert*-butyl peroxide); (●) prepolymerization by heating with HClO$_4$; (- - -) theoretical curve of refractive index change with conversion in vinyl polymerization of GMA . by radical mechanism, determined by the refractive index of monomer (1.4448) and polymer (1.5090) assuming additivity.
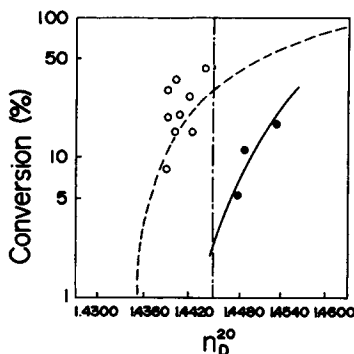

Fig. 3. Relationship between conversion and refractive index of prepolymer in KBM 403 50 vol-%–GMA 50 vol-% system: (O) prepolymerization by irradiation (presence or absence or HClO$_4$) or by heating with 0.5 % t-BPO; (●) prepolymerization by heating with HClO$_4$; (- - -) theoretical curve of refractive index change with the conversion in vinyl polymerization of this system.

coating properties. The thickness of the coating and the H value after the sand-falling test were measured and examined in relation to the refractive index. The result in the KBM 403 single system is shown in Figure 5. It was found that the coating thickness increased with increase in the refractive index and the mar resistance increased with increasing thickness, as shown in Figure 5.

The values in the GMA single system are plotted in Figure 6 over the region of the two types of prepolymerization mechanism. It was observed that the thickness was very small in the region of lower refractive index, that is, in the region of vinyl polymerization, while the thickness increased rapidly with increasing refractive index in the region of predominant ring-opening polymerization (Fig. 6). A similar phenomenon was observed in the KBM 403–GMA (50:50) system (Fig. 7). The relationship between the H value and refractive index in the KBM 403–GMA system at various GMA compositions is also shown in Figure 4. In general, the H values decreased with increase in refractive index.

The reason why a relatively large thickness, more than about 1 μ, could not be obtained in the case of predominant vinyl-type polymerization might be due
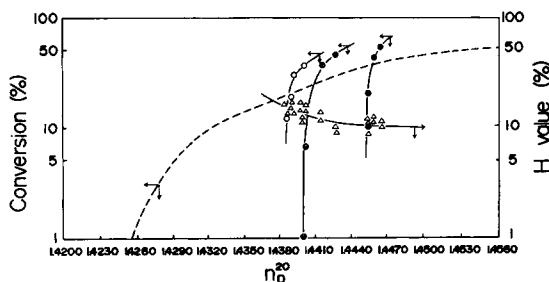
Fig. 4. Relationship between conversion of prepolymer, haze value of coating, and refractive index of prepolymer in KBM 403–GMA systems of various compositions: (O) KBM 403 50 vol-%–GMA 50 vol-%; (⊕) KBM 403 40 vol-%–GMA 60 vol-%; (●) KBM 403 20 vol-%–GMA 80 vol-%; (△) relation between refractive index and haze value in KBM 403–GMA systems of various compositions above prepolymerization; irradiation at 25°C; curing, 100°C, 1 hr, then 60°C for 24 hr; (- - -) theoretical curve of refractive index change with the conversion in catalytic polymerization of KBM 403 single system by heating with $HClO_4$, determined by the refractive index of KBM 403 monomer (1.4255) and polymer (1.4890), assuming additivity.
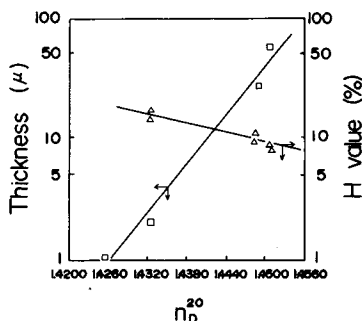
Fig. 5. Relationship between thickness, haze value of coating, and refractive index of prepolymer in KBM 403 single system: prepolymerization, heating with 0.5% $HClO_4$; curing, 100°C 1 hr, then 60°C for 24 hr; (△) relationship between refractive index and haze value; (□) relationship between refractive index and coating thickness.
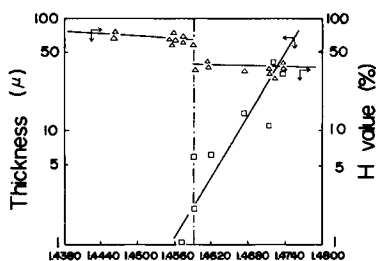

Fig. 6. Relationship between thickness, haze value of coating, and refractive index of prepolymer in GMA single system: prepolymerization, irradiation or heating with $HClO_4$; curing, 100°C 1 hr, then 60°C for 24 hr; (△) relationship between refractive index and haze value; (□) relationship between refractive index and coating thickness.

to dripping of the coated prepolymer during the curing stage. The dripping of prepolymer could be explained as follows: The prepolymer obtained by ring-opening polymerization was probably the more complete copolymer of KBM 403 and GMA by the epoxy ring-opening reaction. The viscosity of the prepolymer was relatively large owing to the more complete homogeneity of the pre-polymerized system and the partly formed network structure in the copolymer.
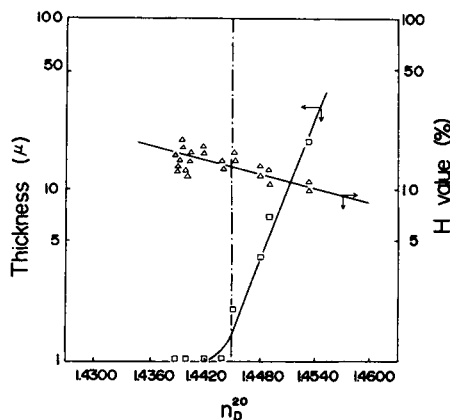
Fig. 7. Relationship between thickness, haze value of coating, and refractive index of prepolymer in KBM 403 50 vol-%–GMA 50 vol-% system: prepolymerization, irradiation or heating with HClO₄; curing, 100°C 1 hr, then 60°C for 24 hr; (△) relationship between refractive index and haze value; (□) relationship between refractive index and coating thickness.

On the other hand, the linear prepolymer of GMA obtained by vinyl polymerization had a lower viscosity and less affinity with the silicone component, though the viscosity control and the coating operation could be carried out more easily. As a result, dripping occurred in the curing stage in this case. The dripped composition was collected before curing and the change in refractive index due to heating was examined (Fig. 8). According to Figure 8, the dripped composition of the GMA single system showed almost the same slope of refractive index increase with curing time. This fact suggested that the dripped liquid was almost
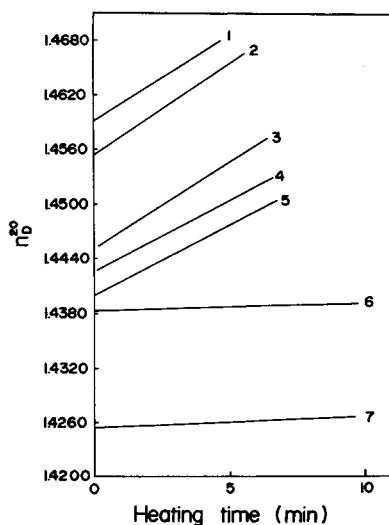

Fig. 8. Change in refractive index of dripped prepolymer with heating time: (1) GMA prepolymer polymerized with 4% t-BPO in the presence of 0.5% HClO₄; (2) GMA prepolymer polymerized by irradiation of 4×10^5 R at 25°C in the presence of 0.5% HClO₄; (3) GMA monomer (without prepolymerization) containing 0.5% HClO₄; (4) KBM 403 40 vol-%–GMA 60 vol-% system prepolymer polymerized by irradiation of 1×10^5 R at 25°C in the presence of 0.5% HClO₄; (5) KBM 403 50 vol-%–GMA 50 vol-% system prepolymer polymerized by irradiation of 1×10^5 R at 25°C in the presence of 0.5% HClO₄; (6) KBM 403 prepolymer polymerized with 0.5% HClO₄; (7) KBM 403 monomer (without prepolymerization) containing 0.5% HClO₄.

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the same composition and the second reaction of dripped composition by heating was similar. This second reaction was probably the ring-opening polymerization of dripped GMA prepolymer, because the dripped prepolymer of KBM 403–GMA binary system in which GMA was polymerized by vinyl polymerization showed the same slope of refractive index as in the GMA single system. This fact revealed that the dripped composition in the KBM 403–GMA system was the GMA-rich prepolymer mixture. The linear vinyl polymer of GMA was easily isolated from the silicone-rich part and dripped. On the other hand, in the KBM 403 single system and the KBM 403–GMA binary system, prepolymerized by ring opening-type prepolymerization, the slope of the refractive index increase was very small and, by heating, differed from that of prepolymer systems obtained by predominant vinyl mechanism. The quantity of dripped coating was very small in these systems prepolymerized by predominant ring-opening polymerization, because the GMA component copolymerized with the silicone component by epoxy ring-opening reaction; the copolymer formed a homogeneous mixture. This was probably the reason why the thickness of the coating was larger in the ring opening-type-initiated prepolymer systems than the thickness in vinyl-type-prepolymerized systems. According to Figure 7, in the KBM 403–GMA (50:50) system good mar resistance was obtained even in the vinyl-type prepolymerized system, though the thickness was very small. This fact also supports the position that the dripped composition was GMA prepolymer rich and the remaining coating was KBM 403 rich which was good in mar resistance.

Relationship Between Thickness and Thermal Durability of the Coating

The effect of coating thickness and prepolymerization conditions on heat durability of the coating on CR-39 resin was investigated by measuring the time of forming a crack in the coating by heating at 200°C (Fig. 9). According to Figure 9, it was found that the heat durability decreased with increasing thick-
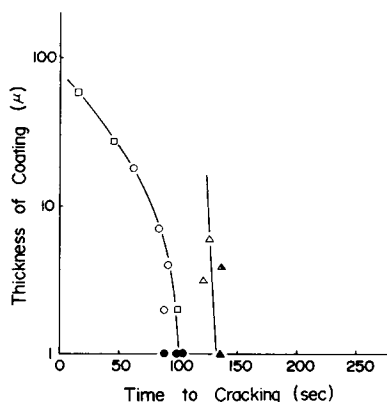

Fig. 9. Relationship between coating thickness and crack formation under heating at 200°C: (□) KBM 403 prepolymerized with 0.5% HClO₄; (○) KBM 403 50 vol-%–GMA 50 vol-% system prepolymerized with 0.5% HClO₄; (●) KBM 403 50 vol-%–GMA 50 vol-% system prepolymerized by irradiation; (△) GMA prepolymerized by irradiation in the presence of 0.5% HClO₄; (▲) GMA prepolymerized with 5% t-BPO; (▲) GMA prepolymerized with 0.5% HClO₄; curing, 100°C 1 hr, then 60°C for 24 hr.

ness, but independent of the prepolymerization mechanism, vinyl or ring-opening, in KBM 403 single and KBM 403–GMA binary systems. However, the relationship in the GMA single system differed from the relationship in the above two systems, and the heat durability of the GMA single system was better than those in KBM 403 systems. This fact can perhaps be attributed to the better adhesion of the GMA single system to CR-39 base resin. The difference in heat durability by prepolymerization mechanism, vinyl or ring-opening, was not observed in the GMA single system (Fig. 9).

References

1. H. Okubo, M. Kato, M. Yoshida, and I. Kaetsu, *J. Appl. Polym. Sci.*, **22**, 833 (1978).