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Kahei Sakaguchi^a

^a Kao-Atlas Laboratories, Wakayama, Japan

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Effect of Peak Exotherm Temperature on the Degree of Cure of Unsaturated Polyester Resins in Copolymerization with Styrene

KAHEI SAKAGUCHI*

Kao-Atlas Laboratories
1334 Minato Yakushubata
Wakayama, Japan

ABSTRACT

In order to prepare full-cured resin by room temperature curing, the effect of the peak exotherm temperature on the degree of cure was investigated by using three types of unsaturated polyester resins including bisphenol-type, iso-type, and G-type resins. The degree of cure was examined by Barcol hardness, the conversion of styrene, and the conversion of fumarate double bond.

In the resin cured with the methyl ethyl ketone peroxide (MEKP)/cobalt naphthenate (Co-naph)/dimethyl aniline (DMA) system or the MEKP/Co-naph system at 25°C, the degree of cure was influenced by the peak exotherm temperature, and there was an optimum region that ranged from 90 to 160°C. The resins cured at the lower peak exotherm temperature have decreased degrees of cure, but they could be cured completely by postcure at 100°C for 2 hr, because a sufficient amount of peroxide had remained unreacted in the resin after the room temperature cure. The degree of cure of the resin cured at the

*Present address: 1-1 Kayabacho, Nihonbashi, Chuo-ku, Tokyo 103, Japan.

higher peak exotherm temperature decreases with an increase in the peak exotherm temperature, and the degree of the cure was not greatly increased by postcure because the amount of residual peroxide was limited.

INTRODUCTION

Polyester resins have been widely used as fiber reinforced plastics (FRP). The physical and chemical properties of the products are well known to be related to the degree of cure of the resin. Practically, a full-cured resin gives the optimum corrosion resistance for a corrosion resistant FRP. Large FRP chemical equipment is usually fabricated by contact molding techniques at room temperature, and postcure is not applied because of the difficulty in handling and the extra cost. Unsaturated polyester resins can be easily cured by a redox-catalyst system, and the exotherm on curing is utilized to complete curing. Experience in the room temperature cure of unsaturated polyester resins in contact molding has suggested that sufficient exotherm is necessary to obtain a full-cured laminate.

The purpose of the present study was to investigate the effect of peak exotherm temperature on the degree of cure of the resin and establish an optimum condition to give a full-cured resin. The degree of cure of unsaturated polyester resins has been examined by many investigators [1-13] using various physical and chemical methods. Practically, FRP fabricators have used a simple method, the so-called "acetone test," in which a few drops of acetone are put on the cured resin and the surface is rubbed with the fingers. The Barcol hardness meter has been widely used for its ease of handling. Robinson [1] has recommended the application of the Barcol hardness meter for both inspection and quality control of FRP. The acetone-extraction method has been examined by Subcommittee 2 of the Joint Services Research and Develop Committee on Plastics [10]. Smith [14] has studied the effect of curing condition on the degree of cure of polyester resin by using the acetone extraction method.

In the previous report [15] a method based on chloroform extraction followed by analysis of the unreacted styrene was presented. The conversion of fumarate double bond was determined with the extracted resin on the basis of the theoretical equations which were derived from the basic theory of Flory [16]. The present experiment is based on Barcol hardness measurement, chloroform extraction followed by analysis of the residual styrene and peroxide, and the calculation of fumarate double bond from the amount of soluble resin.

EXPERIMENTAL

The unsaturated polyester resins used were typical commercial polyester resins including bisphenol-type, iso-type and G-type resins. The chemical characteristics are shown in Table 1.

Castings

Polyester resin catalyzed with the proper catalyst systems was cured in a 100-ml paper cup at 25°C. The exotherm temperature was measured by means of a thermocouple embedded in the resin. The peak exotherm temperatures were varied by the thickness of the resin. The castings were cut with a saw with a diamond edge wheel. The hardness on the cut surface was measured by a Barcol hardness meter, GYZJ-934-1, at 25°C. The cured resins were then rasped and extracted with chloroform by using the procedures described in the previous paper [15]. The extract solution was subjected to gas chromatography for analysis of unreacted styrene. The content of residual peroxide was determined by the potassium iodide method. The solution was then evaporated on a steam bath and dried in vacuo at 100°C for 10 hr. The conversion of fumarate double bond was determined from the relationship between the soluble part, W , of the polyester resins and the conversion of fumarate double bond, g [15]:

$$W = \sum_{x=1}^{\infty} W_x (1 - q)^x$$

where x is the number of units in the polyester chain, and W_x is the weight fraction of molecules containing x units.

Laminates

A wooden flat board was used as the mold on which a polyester film of a 0.05 mm thickness was laid. The polyester resin containing peroxide catalyst was placed on the film, and then one ply of the surfacing mat (SMB 3600C supplied by Asahi Fiber Glass Co., Ltd., C glass type and 30 g/m²) and two plies of the chopped strand mat (CM 455FA supplied by Asahi Fiber Glass Co., Ltd., E glass type and 450 g/m²) were laminated by a hand lay-up method. The alternate lay-ups of the woven roving (EWR 80 supplied by Nippon Glass Fiber Co., Ltd., E glass type and 810 g/m²) and the chopped strand

TABLE 1. Characteristics of Polyester Resin Used

Resin no.	Resin solution		Unsaturated polyester resin ^a							
	Type	Styrene wt% Mole fraction	Composition	Equivalent of double bond/100 g ^b	\bar{M}_0^c	Acid no.	Hydroxyl no.	\bar{M}_n^d	\bar{X}^e	
B-1	Bisphenol	50.0	0.814	FA/PO(2)BPA	0.219	456	11.9	28.3	2791	6.1
B-2	Bisphenol	50.8	0.819	FA/PO(2)BPA	0.219	456	14.6	24.4	2875	6.3
I-1	Iso	38.9	0.788	IPA/MA/PG	0.164	610	19.6	15.7	3180	5.2
G-1	G	28.9	0.674	PA/MA/PG	0.189	529	47.4	33.2	1392	2.6

^aComposition: FA, fumaric acid; PO(2)BPA, 2,2-propoxylated bisphenol A; BPA, bisphenol A; IPA, isophthalic acid; MA, maleic anhydride; PG, propylene glycol; PA, phthalic anhydride.

^bEquivalent of double bond/100 g was determined by a hydrogenation method.

^c \bar{M}_0 = The number-average molecular weight between fumarate double bonds.

^d \bar{M}_n = The number-average molecular weight for polyester resin determined by end-group analysis.

^e $\bar{X} = \bar{M}_n / \bar{M}_0$.

mat were layered for laminates thicker than three plies. The laminates were then allowed to cure at 25°C. The exotherm temperature was measured by a thermocouple embedded in the center of the laminate. Barcol hardness was measured on the surface which was contacted by the mold. The laminates were rasped, and the powder was analyzed for glass content by the ignition loss method and extracted by chloroform. The conversion of styrene, C_s , the residual peroxide, R_{po} , and the conversion of fumarate double bond, q , were obtained by the same techniques as those for castings.

Catalyst Systems

The MEKP/Co-naph/DMA system and the MEKP/Co-naph system were used.

The abbreviations used are:

MEKP: 55% methyl ethyl ketone peroxide

Co-naph: 6% cobalt naphthenate

DMA: 100% dimethyl aniline

RESULTS AND DISCUSSION

The results of the exotherm properties and the development of Barcol hardness with time for all the polyester resins are shown in Table 2 to 8. Figure 1 shows the variations of the gel time, the gel to peak time, and the peak exotherm temperature by the change of thickness of castings (or the laminates). As the thickness of the castings or the laminates increases, the gel time and the gel to peak time decrease and the peak exotherm temperature increases. The highest peak exotherm temperature for the castings is higher than that for the laminates. The exotherm temperature in the castings or the laminates has a close relation with the development of the Barcol hardness.

In the cure systems of MEKP/Co-naph/DMA and MEKP/Co-naph for all the polyester resins, the peak exotherm temperatures lower than 90°C give lower Barcol hardness. Barcol hardness increases with an increase of the peak exotherm temperature up to 160°C, and then it begins to decrease. Barcol hardness did not develop much in standing at room temperature for 1 day to 4 weeks. The optimum peak exotherm temperature giving the highest Barcol hardness changes in a range of 90 to 160°C according to the cure conditions shown in Table 9. The resin cured at the optimum region of the peak exotherm temperature shows Barcol hardness values which are very close to those of the completely cured resin in 1 day.

TABLE 2. Cure Properties and Development of Barcol Hardness of the Castings of Bisphenol-Type Resin (B-1)^a

Exp. no.	Thickness of casting (mm)	Cure properties				Development of Barcol hardness					
		Gel time (min)	gel to peak time (min)	Peak time (min)	Peak temperature (°C)	1 day	1 week	2 weeks	3 weeks	4 weeks	Post-cured
1	4.0	9	23	32	39	15	15	15	16	16	38
2	4.0	9	21	30	41	13	13	14	15	16	38
3	6.0	8	20	28	97	29	30	30	30	31	39
4	7.0	8	17	25	125	33	33	34	34	34	40
5	10	8	15	23	160	37	37	37	37	37	37
6	46	8	13	21	185	31	31	31	31	31	31
7	50	8	11	19	208	29	29	29	29	29	29

^aCure conditions: MEKP, 1.0 wt%; Co-naph, 0.5 wt%; DMA, 0.1 wt%; temperature, 25°C.

TABLE 3. Cure Properties and Development of Barcol Hardness of the Castings of Bisphenol-Type Resin (B-2)^a

Exp. no.	Cure properties				Development of Barcol hardness					
	Thickness of castings (mm)	Gel time (min)	Gel to peak time (min)	Peak temperature (°C)	1 day	2 weeks	3 weeks	4 weeks	Post-cured	
30	3.0	60	23	83	35	9	22	25	25	38
31	3.5	50	23	73	40	12	25	28	28	28
32	3.8	48	21	69	54	20	22	25	25	40
33	6.5	35	13	48	90	37	37	37	38	40
34	7.5	34	12	46	110	38	38	38	38	39
35	7.7	34	12	46	130	33	33	33	34	36
36	13	33	13	46	160	25	26	26	26	31
37	46	33	12	45	194	22	22	25	26	27

^aB-2 is preaccelerated by incorporating DMA. Cure conditions: MEKP, 1.0 wt%; Co-naph 1.0 wt%; temperature, 25°C.

TABLE 4. Cure Properties and Development of Barcol Hardness of the Castings of Iso-Type Resin (I-1)^a

Exp. no.	Thickness of castings (mm)	Cure properties			Development of Barcol hardness						
		Gel time (min)	Gel to peak time (min)	Peak temperature (°C)	1 day	1 week	2 weeks	3 weeks	4 weeks	Post-cured	
40	3.8	11	39	50	31	19	31	32	33	37	46
41	4.0	11	38	49	36	22	36	36	38	38	46
42	8.0	11	34	45	74	25	38	40	41	42	46
43	9.0	11	24	35	80	41	41	41	42	42	46
44	10.0	11	23	34	129	45	45	45	45	45	45
45	17	11	22	33	143	42	42	42	42	42	44
46	20	11	19	30	163	40	42	42	42	42	44
47	37	11	17	28	176	40	41	41	41	41	44
48	43	11	14	25	185	38	39	39	39	39	41
49	43	11	12	23	202	37	37	37	37	37	37

^aCure conditions: MEKP, 1.0 wt%; Co-naph 1.0 wt%; temperature 25°C.

TABLE 5. Cure Properties and Development of Barcol Hardness of the Castings of G-Type Resin (G-1)^a

Exp. no.	Thickness of castings (mm)	Cure properties			Development of Barcol hardness						
		Gel time (min)	Gel to peak time (min)	Peak temperature (°C)	1 day	2 weeks	3 weeks	4 weeks	Post-cured		
50	7.0	12	29	41	44	32	38	40	41	43	50
51	8.0	12	28	40	60	35	40	42	43	44	50
52	14	12	27	39	91	43	45	46	46	46	50
53	17	12	24	36	103	46	46	46	47	47	50
54	18	12	23	35	110	46	46	46	47	47	50
55	24	12	21	33	132	46	47	47	48	48	50
56	25	12	21	33	136	49	49	49	49	49	50
57	30	12	20	32	152	48	48	48	48	48	49
58	36	12	19	31	164	45	45	45	45	46	47
59 ^b	48	50	7	57	169	45	45	45	45	45	46
60 ^c	48	22	34	56	182	44	44	44	44	44	44

^aCure conditions: MEKP, 0.5 wt%; Co-naph 0.5 wt%; temperature, 25°C.

^bMEKP, 1.0 wt%; Co-Naph, 0.5 wt%; tertiary butyl catechol, 0.01 wt%.

^cMEKP, 1.0 wt%; Co-Naph, 0.5 wt%; tertiary butyl catechol, 0.05 wt%.

TABLE 6. Cure Properties and Development of Barcol Hardness of the Laminates^a of Bisphenol-Type Resin (B-1)^a

Exp. no.	Laminates		Cure properties							Development of Barcol hardness			
	Plies	Thickness (mm)	Thickness as resin (mm)	Gel time (min)	Gel to peak time (min)	Peak time (min)	Peak temperature (°C)	1 day	1 week	2 weeks	3 weeks	4 weeks	Post-cured
70	3	2.8	2.2	20	28	48	40	22	28	30	30	30	44
71	5	4.5	3.8	20	26	46	46	23	28	30	31	31	44
72	5	4.6	3.9	20	26	46	49	26	30	31	32	32	44
73	7	6.6	6.0	16	29	45	53	27	33	33	34	34	44
74	7	6.7	5.7	15	28	43	72	28	32	33	33	34	44
75	9	8.0	7.4	15	27	42	104	28	35	36	36	36	44
76	11	10.2	8.5	14	22	36	116	35	40	40	40	40	44
77	13	12.0	10.4	14	21	35	121	36	38	39	39	40	44
78	15	13.6	10.6	14	19	33	138	42	42	42	42	42	44
79	19	17.0	15.2	14	18	32	155	42	42	42	42	42	44
80	25	22.5	20.9	14	18	32	160	41	41	42	42	42	43
81	49	42.0	29.5	14	18	32	166	40	40	40	40	40	41

^aCure conditions: MEKP, 1.0 wt%; Co-naph 0.5 wt%; DMA, 0.1 wt%; temperature, 25°C.

TABLE 7. Cure Properties and Development of Barcol Hardness of the Laminates of Bisphenol-Type Resin (B-2)^a

Exp. no.	Laminates		Cure properties					Development of Barcol hardness				
	Plies	Thickness (mm)	Thickness as resin (mm)	Gel time (min)	Peak time (min)	Peak temperature (°C)	1 day	1 week	2 weeks	3 weeks	4 weeks	Post-cured
85	3	3.0	2.4	38	27	65	35	22	27	30	30	44
86	5	4.5	3.9	37	28	65	48	26	28	30	31	44
87	5	4.5	3.7	38	28	66	63	26	30	31	31	44
88	7	7.0	5.5	36	24	60	108	32	34	34	35	44
89	9	9.0	6.9	36	18	54	133	40	40	41	41	43
90	11	11	8.8	35	18	53	137	40	40	41	41	43
91	13	12.5	9.0	35	17	52	150	40	40	40	40	42
92	15	14	11.0	35	18	53	156	41	41	41	41	41
93	19	17.5	15.1	35	17	52	155	41	41	41	41	41
94	25	24	17.7	35	15	50	157	41	41	41	41	41
95	49	42	32.0	35	15	50	165	41	41	41	41	41

^aB-2 is preaccelerated by incorporating DMA. Cure conditions: MEKP, 1.0 wt%; Co-naph 1.0 wt%; temperature, 25°C.

TABLE 8. Comparison of Cure Properties and Development of Resins

Exp. no.	Resin ^a	Laminates, plies (mm)		Castings (mm)	MEKP (wt%)	Co-naph (wt%)	DMA (wt%)
101	B-1	7	5.8	-	1.0	0.5	0.1
102	B-1	-	-	5.0	1.0	0.5	1.0
103	B-2	7	5.5	-	1.0	1.0	-
104	B-2	-	-	5.0	1.0	1.0	-
105	I-1	7	5.5	-	1.0	0.5	-
106	I-1	-	-	4.7	1.0	0.5	-
107	G-1	7	6.3	-	0.5	0.5	-
108	G-1	-	-	4.5	0.5	0.5	-

^aB-2 is preaccelerated by incorporating DMA.

The castings and the laminates were postcured in an oven at 100°C for 2 hr. Barcol hardness was raised by postcure up to the hardness for a completely cured resin when the peak exotherm temperature was lower than 90°C. On the other hand, Barcol hardness is raised only a few points by postcure when the peak exotherm temperature was higher than 160°C. These results suggest that the resin cured at the lower peak exotherm temperatures has a potential to be cured completely by postcure, whereas the resin cured at the higher peak exotherm temperatures cannot attain complete cure. The potential of postcure may be related to the residual peroxide existing in the resin after the exotherm returns to room temperature.

The degree of cure was further investigated by the chloroform extraction method. The results for the resins which were cured at 25°C for 24 hr or postcured at 100°C for 2 hr after a room temperature cure of 24 hr are shown in Figs. 2 to 7.

Barcol Hardness of the Castings and the Laminates for Various Polyester

Cure properties at 25°C									
Gel time (min)	Gel to peak time (min)	Peak time (min)	Peak temperature (°C)	Development of Barcol hardness					
				1 day	1 week	2 weeks	3 weeks	4 weeks	Post-cured
27	27	54	42	18	33	35	35	36	44
19	24	43	42	3	13	15	18	20	40
43	33	76	57	24	31	32	33	34	44
43	22	65	93	31	31	31	31	31	40
55	48	103	34	25	38	39	42	43	50
55	31	86	32	12	27	29	32	33	46
16	35	51	37	30	41	42	44	45	53
16	25	41	35	21	38	35	38	42	50

TABLE 9. Range of the Optimum Peak Exotherm Temperature

Castings or laminates	Resin	Cure system			Range of optimum peak exotherm temperature (°C)
		MEKP (wt%)	Co-naph (wt%)	DMA (wt%)	
Castings	B-1	1.0	0.5	0.1	130-150
Castings	B-2 ^a	1.0	1.0	-	90-110
Castings	I-1	1.0	1.0	-	120-150
Castings	G-1	0.5	0.5	-	110-150
Laminates	B-1	1.0	0.5	0.1	130-160
Laminates	B-2 ^a	1.0	1.0	-	130-160

^aB-2 is a preaccelerated version of bisphenol-type resin.

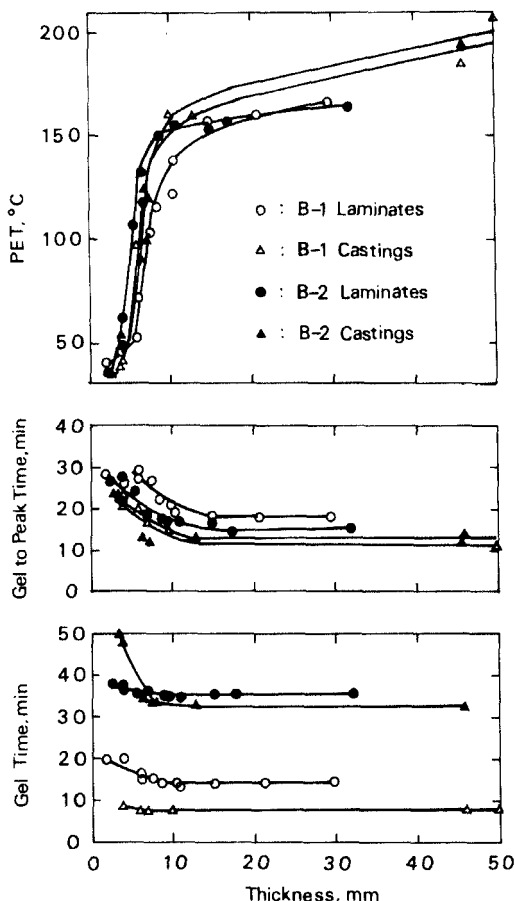


FIG. 1. The relationships between the thickness of the castings (or the laminates) and the gel time, the gel to peak time, and the peak exotherm temperature. Abbreviations in Figs. 1 to 8: PET, the peak exotherm temperature; BH, the Barcol hardness; C_s , the conversion of styrene; q , the conversion of fumarate double bond; and R_{po} , the residual peroxide.

Barcol hardness, the conversion of styrene, and the conversion of fumarate double bond are shown as a function of the peak exotherm temperature. The previous conclusion [15] that Barcol hardness is proportional to the conversion of styrene but is not related to the

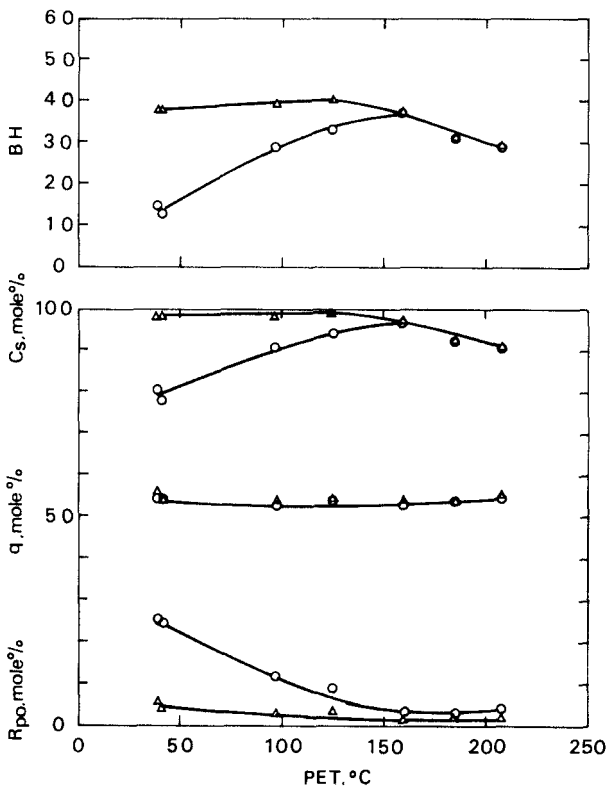


FIG. 2. Effect of the peak exotherm temperature on Barcol hardness, the conversion of styrene, the conversion of fumarate double bond, and the residual peroxide for the castings of bisphenol-type resin (B-1). Cured with 1.0 wt% of MEKP, 0.5 wt% of Co-naph, and 0.1 wt% of DMA at 25°C for 24 hr (○) and postcured at 100°C for 2 hr (△).

conversion of fumarate double bond has been reconfirmed in the present study.

In the polyester resins which are cured by the MEKP/Co-naph/DMA and the MEKP/Co-naph systems, Barcol hardness and the conversion of styrene increase with the peak exotherm temperature up to an optimum peak exotherm temperature between 90 and 160°C, but they decrease beyond the optimum region.

On the other hand, the conversion of fumarate double bond is not affected as much as the conversion of styrene, but it is slightly

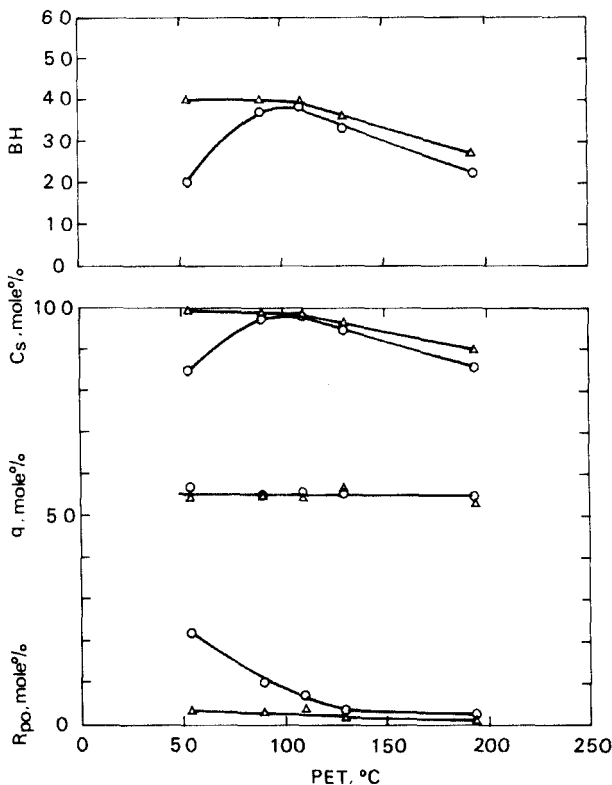


FIG. 3. Effect of the peak exotherm temperature on Barcol hardness, the conversion of styrene, the conversion of fumarate double bond, and the residual peroxide for the castings of bisphenol-type resin (B-2). Cured with 1.0 wt% of MEKP and 1.0 wt% of Co-naph at 25°C for 24 hr (○) and postcured at 100°C for 2 hr (Δ).

increased at the peak exotherm temperature. The effect of the peak exotherm temperature on the degree of cure can be satisfactorily explained by the relationship between the peak exotherm temperature and the residual peroxide. The fact that a large amount of unreacted peroxide is found in the resin cured at the low peak exotherm temperatures is quite compatible with the low values of Barcol hardness and the conversion of styrene. By postcure, Barcol hardness and the conversion of styrene are raised to the values for the complete cured resin. On the other hand, resins cured at peak exotherm temperatures higher than the optimum

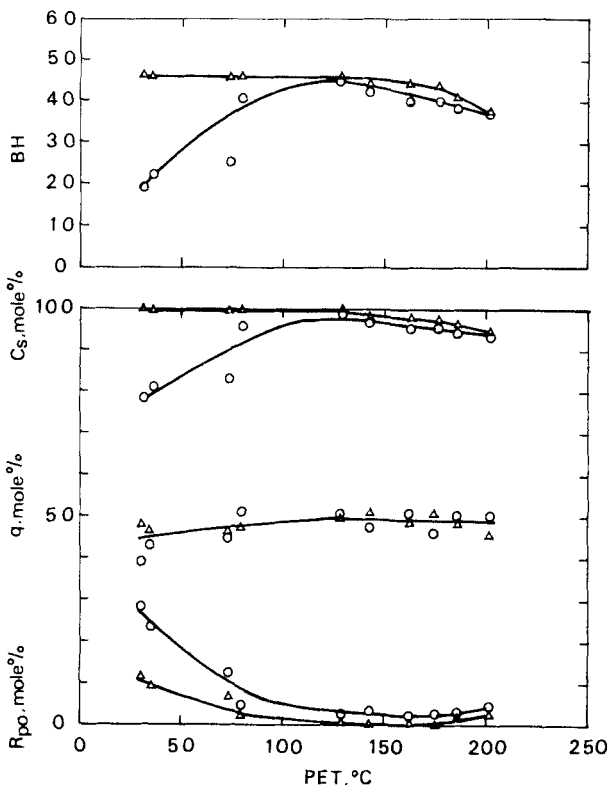


FIG. 4. Effect of the peak exotherm temperature on Barcol hardness, the conversion of styrene, the conversion of fumarate double bond, and the residual peroxide for the castings of iso-type resin (I-1). Cured with 1.0 wt% of MEKP and 1.0 wt% Co-naph at 25°C for 24 hr (O) and postcured at 100°C for 2 hr (Δ).

temperatures increase only to a small extent in Barcol hardness and the conversion of styrene. The conversion of fumarate double bond is not changed significantly by postcure. These results were observed with all three types of unsaturated polyester resins. The laminates show the same behavior as the castings in the same catalyst system.

The copolymerization of unsaturated polyester resins with styrene proceeds by a free radical process. The initiator, MEKP, decomposes with the help of a cocatalyst such as Co-naph or DMA at room temperature, and the resulting peroxide radical adds to

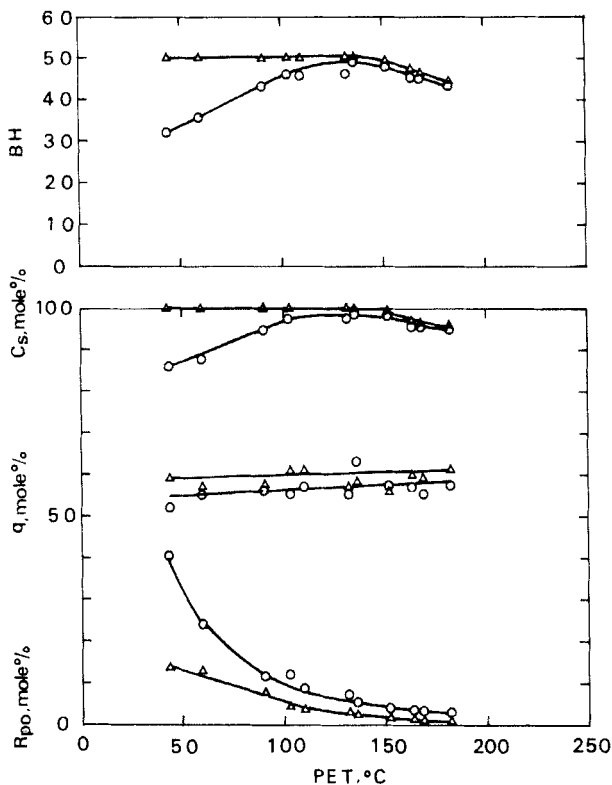


FIG. 5. Effect of the peak exotherm temperature on Barcol hardness, the conversion of styrene, the conversion of fumarate double bond, and the residual peroxide for the castings of G-type resin (G-1). Cured with 0.5 wt% MEKP and 0.5 wt% of Co-naph at 25°C for 24 hr (○) and postcured at 100°C for 2 hr (△).

the styrene monomer and initiates polymerization. The styrene radical produced reacts with a fumarate double bond in the unsaturated polyester resin to give copolymer chains which form three-dimensional networks. As the reaction proceeds, the exotherm is accumulated after the gelation of the resin because the heat conductivity of a cured resin is remarkably decreased. The thicker the resin sample is, the higher the peak exotherm temperature becomes. After gelation, the mobilities of the radicals and the styrene monomer are restricted by the

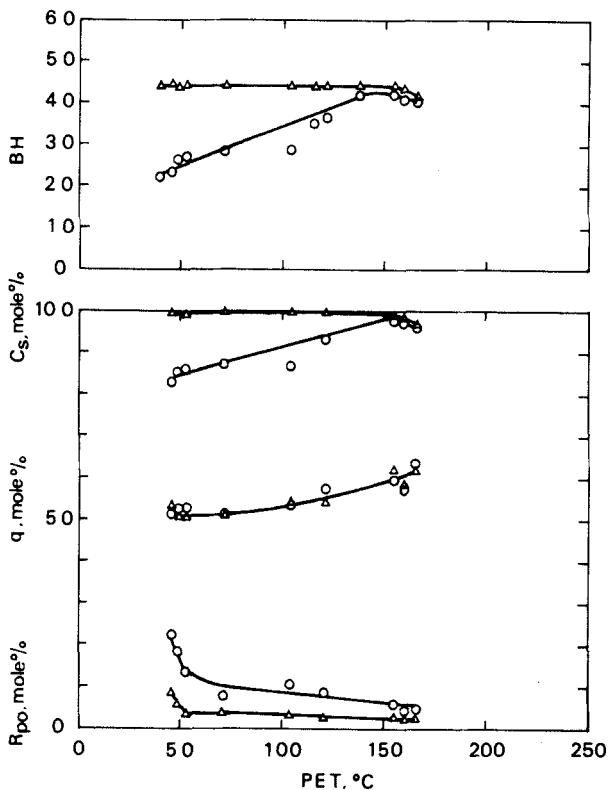


FIG. 6. Effect of the peak exotherm temperature on Barcol hardness, the conversion of styrene, the conversion of fumarate double bond, and the residual peroxide for the laminates of bisphenol-type resin (B-1). Cured with 1.0 wt% of MEKP, 0.5 wt% of Co-naph and 0.1 wt% of DMA at 25°C for 24 hr (○) and postcured at 100°C for 2 hr (△).

frozen state of the network and the decomposition of peroxide is accelerated by the exotherm, and consequently the initiator radical produced all at once would be wasted. The initiator efficiency after gelation would be lower for the resin cured at the elevated peak exotherm temperatures than for the resin cured at lower temperatures because the exotherm curve rises more sharply and the peroxide decomposes more rapidly.

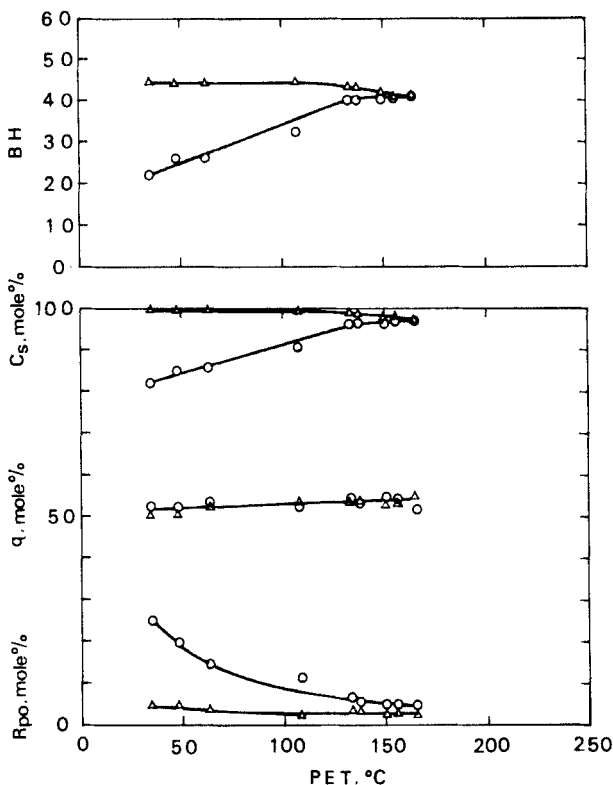


FIG. 7. Effect of the peak exotherm temperature on Barcol hardness, the conversion of styrene, the conversion of fumarate double bond, and the residual peroxide for the laminates of bisphenol-type resin (B-2). Cured with 1.0 wt% of MEKP and 1.0 wt% Co-naph at 25°C for 24 hr (○) and postcured at 100°C for 2 hr (△).

CONCLUSION

In order to obtain a full-cured resin by room temperature cure, the exotherm occurring in the polymerization is useful. There is an optimum region in the peak exotherm temperature which can be controlled by changing the thickness of the resin. In the MEKP/Co-naph/DMA system and the MEKP/Co-naph system, there is an optimum peak exotherm temperature ranging from 90 to 160°C. The resins cured at the lower peak exotherm

temperatures below the optimum region were undercured after room temperature cure, but they were cured completely by postcure at 100°C for 2 hr because sufficient peroxide had remained unreacted in the resin. The degree of cure of the resin cured at the higher peak exotherm temperatures above the optimum region decreases with the peak exotherm temperature, and the degree of cure was raised only to a small extent by postcure.

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