

## Crosslinked Polyesters from Allyl Glycidyl Ether and Maleic Anhydride\*

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### INTRODUCTION

It has been shown<sup>1</sup> that bases, such as tertiary amines, improve both the rate and course of the reaction between epoxides and anhydrides. An exception was maleic anhydride, which reacted very slowly and gave black, gelled, and poorly cured products.

We have now found that if maleic anhydride is copolymerized with allyl glycidyl ether under acidic or neutral conditions, the products are cross-linked polyesters possessing a number of highly desirable properties (an observation that has been made earlier<sup>2</sup>). Of these, the hardness is most remarkable, ranging from 50 to 60 at room temperature to 30 at 150°C. This is harder at 150°C. than most resins are at room temperature. Other outstanding properties of the cured system are high heat distortion temperature (165–168°C.) and brilliant clarity. The color ranges from yellow to amber, and good strength properties are also obtained. The cured properties, taken with the ease of preparation and low initial viscosity of the mix, make the system a potentially attractive candidate for commercial development.

The major disadvantages are (1) the exothermic nature of the reaction, which makes it difficult to control in large castings, (2) the sensitivity of the radicals to inhibition, and (3) the poor long-term water soak resistance of the cured system. Castings are stable to water for as long as a week, however. The excellent appearance of castings and laminates is shown in Figure 1.

### CHEMISTRY

Theoretically, allyl glycidyl ether (AGE) and maleic anhydride (MA) can be at least tetrafunctional with respect to each other. For example, they can give a radical-initiated copolymer on next page:

\* Presented in part at the Gordon Research Conference, Meriden, New Hampshire, July 1961.



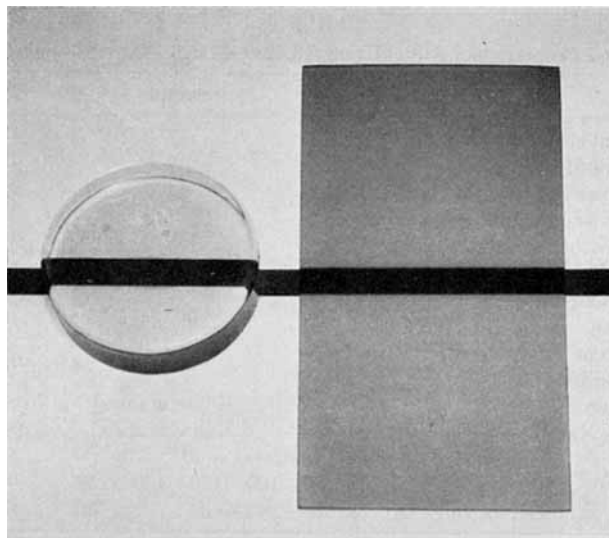


Fig. 1. Products of allyl glycidyl ether and maleic anhydride: (left) clear casting about 1 in. thick; (right) 14-ply glass cloth laminate.

*Phase 2.* The mixture is cooled and a peroxide is added. At this point it is ready to be poured directly into molds or diluted with styrene and used for laminates or surface coatings. Since the reaction is still exothermic, large volumes must be cured very carefully. Final curing is done at 150–180°C., at which point all double bonds and all anhydrides have been converted.

The following variations gave poorer results. (1) Inclusion of peroxide without prior thickening. Several attempts gave castings with excessive shrinkage after gelation. This in turn caused myriads of internal stress cracks in the cured resin. (2) Inclusion of styrene in the original mixture. The great activity of styrene gave styrene–maleic anhydride copolymer, leaving most of the allyl glycidyl ether unreacted.

### THE CURED SYSTEM

Typical physical properties of two early castings are listed in Table I.

### PREPARATION OF LAMINATES

Of many attempts to make glass cloth laminates with the pure AGE-MA prepolymer, only one gave an acceptable product. This was accomplished by allowing the laminate to stand at room temperature for several weeks prior to curing. Attempts to find practical conditions led to dark, gummy, uncured systems.

After it was shown that insertion of any high-surface glass into the mixture inhibited the cure, it seemed likely that the relatively inactive allyl and maleic radicals involved in the crosslinking were being terminated by

TABLE I  
Physical Properties of Allyl Glycidyl Ether-Maleic Anhydride Castings

	Sample 1	Sample 2					
Flexural strength, psi $\times 10^{-3}$	17.8	19.4					
Flexural modulus, psi $\times 10^{-5}$	7.8	7.6					
Compressive strength, psi $\times 10^{-3}$	41.6	32.3					
Compressive modulus, psi $\times 10^{-5}$	7.8	6.5					
Heat distortion temp., °C.	168.5	165					
Izod impact, ft.-lb./in. no.	0.38	0.48					
Tensile strength, psi $\times 10^{-3}$	8.8	5.1					
Increase, one month, wt.-%							
Acetone	-0.10	-0.11					
Benzene	+0.43	+0.60					
Water	Edges cracked	+4.6					
10% NaOH	Edges cracked	+3.2					
	Barcol hardness						
Temp., °C.	25	60	80	100	120	140	150
Barcol val.	61	52	50	42	37	32	30

the glass surface. (We are indebted to Dr. H. E. de la Mare for this explanation.) Addition of styrene to the thickened mix gave more active terminal radicals and completely solved the problem. The use of 10-20 pphr of styrene gave mixes with unusually smooth laminating properties, easy cure cycles, and cured laminates of unusual beauty and high-temperature strength.

A typical laminating recipe follows:

Charge: AGE-maleic anhydride, 1:1 molar.

Treatment: Body 1 hr. at 110°C. to viscosity 50 cpoises. Add 10 pphr of styrene and 0.5% of benzoyl peroxide.

Cure:  $\frac{1}{2}$  hr. at 80°C.;  $\frac{1}{2}$  hr. at 100°C.; 1 hr. at 150°C.

Laminate properties: Flexural strength, ultimate, psi.

Temperature: Room 300°F. 500°F.

Flexural strength, psi: 73,000 40,000 13,500

Concentrations of styrene lower than 10% gave better high-temperature strength, but were difficult to cure. At 30% or higher in styrene, the system became incompatible. Although good laminates showed good initial 500°F. strength, after 200 hrs. at 500°F. they had lost all their strength.

### EFFECT OF STYRENE ON BULK PROPERTIES

Despite the beneficial effect of styrene in laminates, it gave inferior thermal properties, solvent resistance, and strength to castings, while contributing only slightly to water and alkali resistance. Table II summarizes the pertinent data.

TABLE II  
Effect of Styrene on AGE-Maleic Anhydride Castings

Styrene present, pphr	Flexural strength, psi	Heat dist. temp., °C.	Izod impact, ft.-lb./in. no.	Water uptake 1 mo. soak, %
0	18,000	150	0.59	+11.4
10	14,900	109	0.40	+8.1
20	9,900	97	0.28	+9.5

## OTHER MODIFICATIONS

Use of excess AGE (to compensate for epoxide homopolymerization) gave inferior castings: flexural strength, 8800 psi; heat distortion, 70°C.; Izod impact, 0.30 ft.-lb./in. no.

Inclusion of small amounts of allyl alcohol improved the color but decreased the quality of the castings. Equimolar quantities (allyl maleate) gave completely colorless but cheesy castings. Butenediol was also an inhibitor. Mixtures with Epon 828 gelled slowly and required long cure cycles. For example, an equal weight mix, catalyzed with  $\text{BF}_3$ -phenol and cured 4.5 hrs. at 190°C. had a Barcol hardness of 40.

An equimolar mixture of vinylcyclohexene monoepoxide with maleic anhydride reacted spontaneously and exothermically, forming a crystalline product as well as an oil. Further heating to 120°C. gave a gel.

## EXPERIMENTAL

### Preparation of Prepolymer

#### *Acid-Catalyzed*

A solution of 196 g. (2.0 moles) of maleic anhydride in 228 g. (2.0 moles) of allyl glycidyl ether was treated with 8 drops (0.24 g.) of a 33% solution of  $\text{BF}_3$ -phenol in ethylene glycol. The resultant exotherm was controlled at 40–45°C. by water-cooling for 1 hr. after which the mixture was cooled to room temperature and poured into molds for curing.

#### *Thermal*

The mixture of 2 moles of each monomer (viscosity 0.04 poise) in a 1-l. Erlenmeyer flask was immersed in a 106°C. oil bath. In 34 min. the temperature of the reaction mixture had risen to 108°C. It was held at 108–112°C. with intermittent outside cooling for 35 min. and then cooled to 30°C. in an ice bath. At this point the viscosity was 44 cpoises.

Analytical data on an aliquot portion showed the following:

	Mol. wt.	Epoxide val., equiv./100 g.	Acidity, equiv./100 g.	I <sub>2</sub> No., g./100 g.
Original sample	106	0.472	0.472	120
Prepolymerized sample	150	0.362	0.488	102
% reaction (calcd.)	(41)	23.4	0	15

Addition of 10 pphr of styrene to the mix lowered the viscosity to 28 centipoises.

### Curing

The following test reactions were run with the acid-catalyzed prepolymer described above:

Total cure time, hr.	Temp., °C.	Barcol hardness at room temp.
24	100	31
48	110	51
72	110	56
144	110	58

Later testing on this sample gave the following temperature profile:

Temp., °C.	Rm. temp.	60	80	100	120	140	150
Barcol hardness	61	52	50	42	37	32	30

A final cure of 6 hrs. at 150°C. was adopted as dependable, but not necessarily optimum.

### Testing

Sheets  $\frac{1}{8}$  in. thick were prepared between Herculite glass plates, with Teflon sheets as mold releases. None of the release agents tried was completely satisfactory, but Teflon reduced the number of problems to one, i.e., wrinkling during the heating cycle. In general, however, it was possible to find wrinkle-free areas in most castings. Standard ASTM samples were cut, and all tests were conducted in the ASTM approved manner. The results obtained in such tests are given in Table III.

### Solvent Resistance

Because of limitations of material the samples tested were 1 in. x 1 in., but otherwise the tests were run in accordance with ASTM procedures. The results given in Table IV show that optimum solvent resistance is obtained with the 1:1 reaction mixture and acid catalysis. With this system even the alkali resistance was fair, despite the fact that the system is a polyester. Actually, for any but the most severe service the water and

TABLE III  
Bulk Properties, Cured AGE-MA-Styrene System

Sample no.	Mole ratio AGE/MA	Styrene, pphr	Cure cycle	Flexural strength		Strength properties		
				Flex., psi	Mod., psi $\times 10^6$	Tensile strength, psi	Heat dist., $^{\circ}\text{C}$ .	Izod impact, ft.-lb./in. no.
3628-145	1:1	0	16 hr./80 $^{\circ}\text{C}$ . 6 hr./110 $^{\circ}\text{C}$ .	19,400	7.6	32,300 <sup>a</sup>	165	0.48
4939-154	1:1	0	1 hr./100 $^{\circ}\text{C}$ . 6 hr./150 $^{\circ}\text{C}$ .	18,800	6.5	<sup>b</sup>	149.5	0.59
4939-155	1:1	10	1 hr./100 $^{\circ}\text{C}$ . 6 hr./150 $^{\circ}\text{C}$ .	14,900	5.0	<sup>b</sup>	108.5	0.40
4939-150	1:1	20	3 hr./100 $^{\circ}\text{C}$ . 4 hr./150 $^{\circ}\text{C}$ .	9,900	3.2	7,300	96.5	0.28
4939-151	1.33:1	0	6 hr./150 $^{\circ}\text{C}$ .	8,800	3.2	—	70.0	0.30

<sup>a</sup> Compressive strength.

<sup>b</sup> Specimens break inside grips.

TABLE IV  
 Per Cent Weight Change AGE-MA-Styrene System

Sample no.	Styrene, pphr	Cycle	Acetone	Benzene	Ethanol	<i>n</i> -Heptane	10% NaOH	Water	Original catalyst	Curing catalyst
3628-145	0	24 hr.	-0.08	-0.01	-0.08	+0.01	+0.24	+0.20	BF <sub>3</sub>	None
		1 wk.	-0.15	+0.14	-0.16	+0.11	+0.94	+1.0		
		1 mo.	-0.11	+0.60	-0.20	+0.46	+3.2	+4.6		
4939-154	0	24 hr.	-0.07	+0.01	-0.10	—	+0.61	+0.25	None	Benzoyl Peroxide
		1 wk.	-0.14	+0.08	—	—	*	+1.9		
		1 mo.	-0.15	+0.31	-0.30	—	—	+11.4		
4939-155	10	24 hr.	-0.07	-0.0	-0.16	+0.01	+0.76	+0.32	None	Benzoyl Peroxide
		1 wk.	+0.27	+0.02	-0.04	+0.05	+2.7	+1.3		
		1 mo.	+6.3	+0.14	-0.65	+0.21	+7.6	+8.1		
4939-150	20	24 hr.	+1.6	-0.0	+0.18	+0.01	2.4	0.38	None	Benzoyl Peroxide
		1 wk.	*	+0.03	-0.41	+0.05	*	+1.6		
		1 mo.	—	+0.22	-0.40	+0.27	—	+9.5		
4939-151	0	24 hr.	0.67	0.0	-0.21	+0.02	+1.4	+0.54	SnCl <sub>4</sub>	None
		1 wk.	*	+0.04	-0.49	+0.06	*	+2.6		
		1 mo.	—	+0.28	-0.45	+0.33	—	+16.1		

\* Disintegrated.



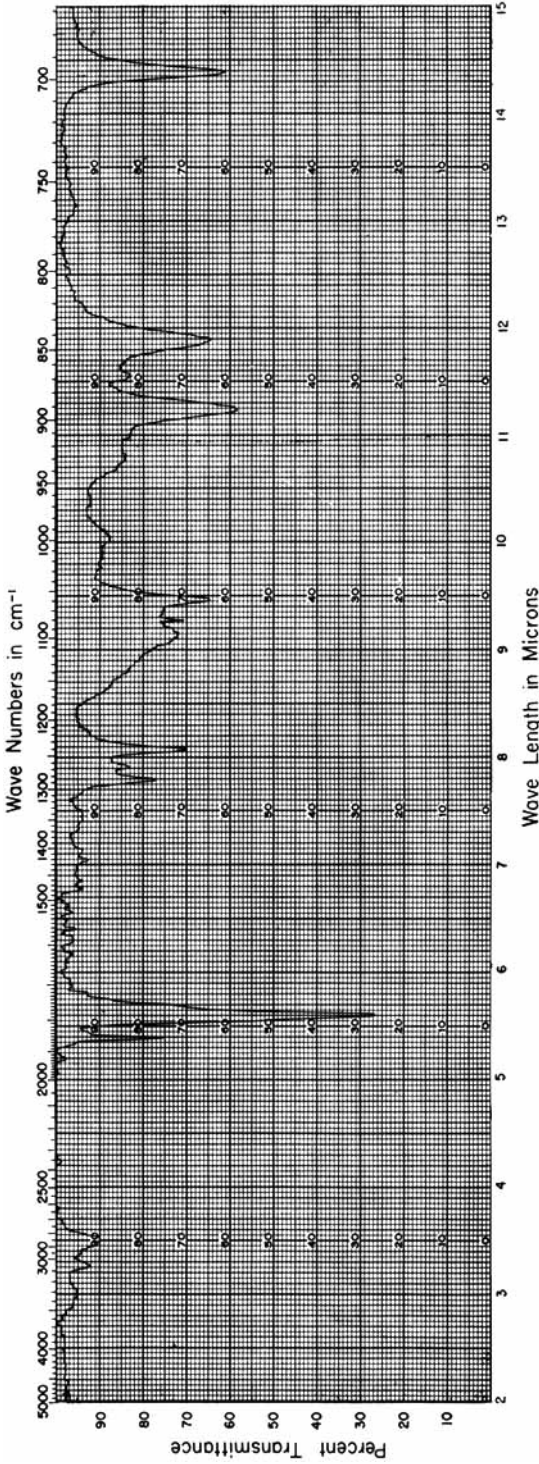


Fig. 2. AGE-MA reaction mixture.

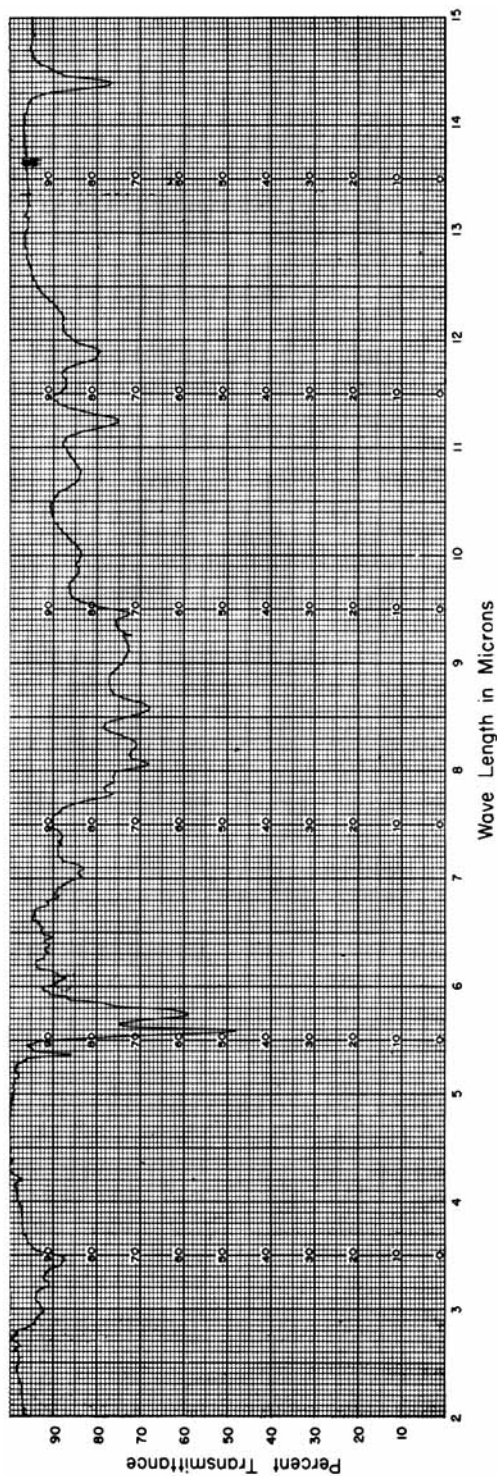


Fig. 3. AGE-MA system at first gel formation, 3 days at 25°C.

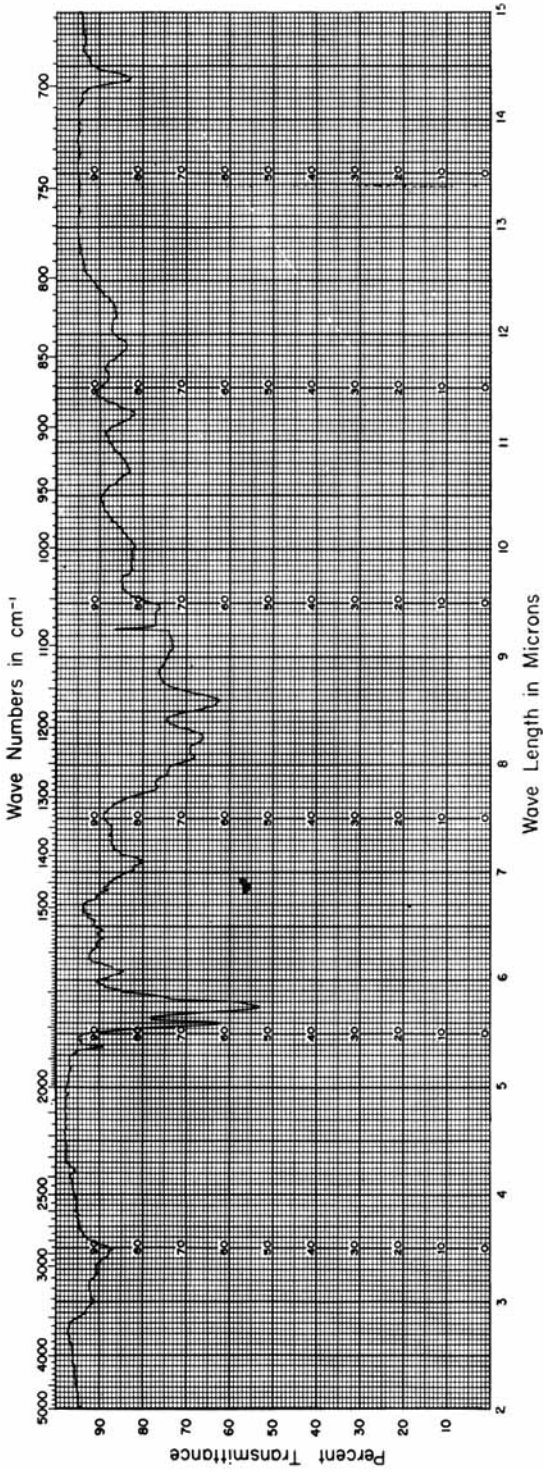


Fig. 4. AGE-MA system, 5 days at 25°C.

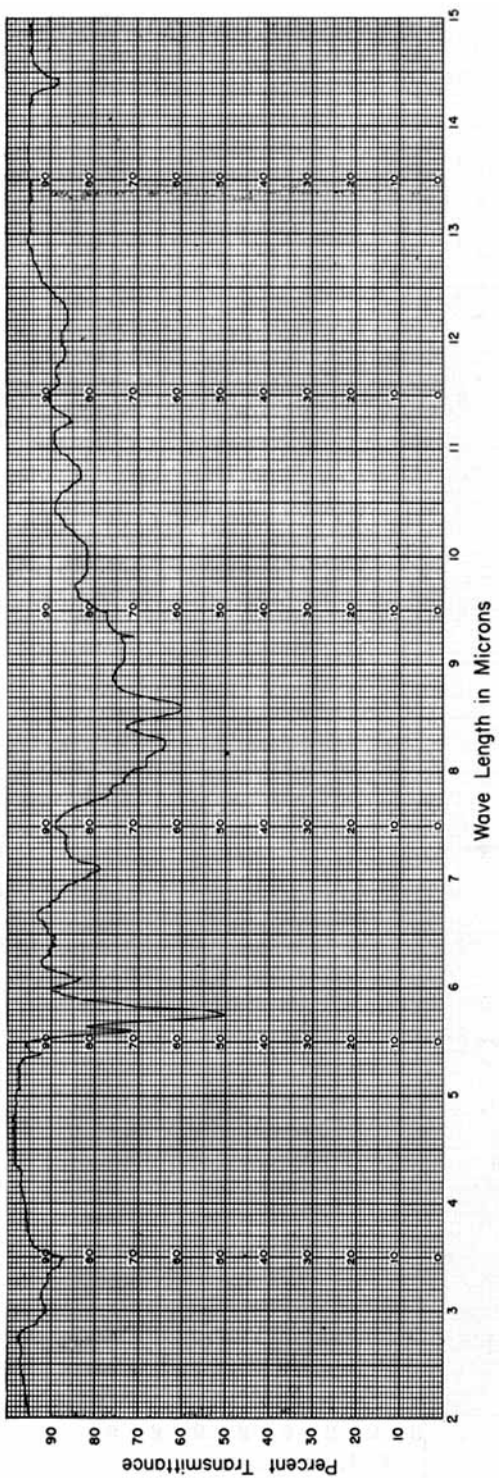


Fig. 5. AGE-MA system at full gel period, 11 days at 25°C.

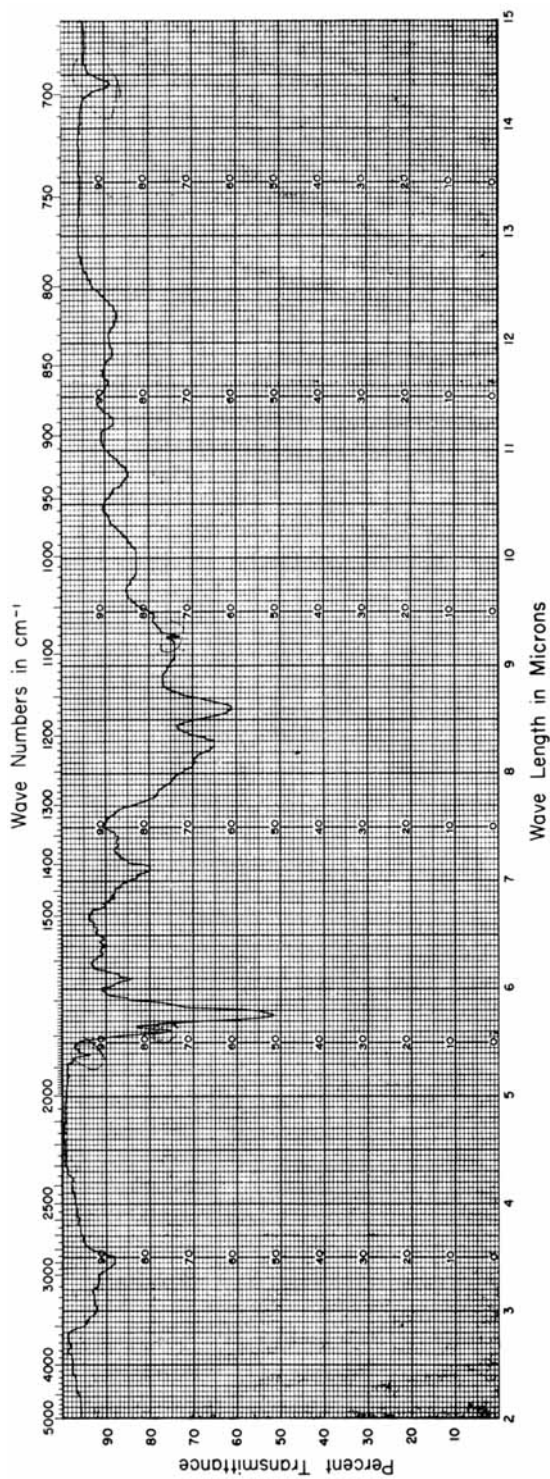


Fig. 6. AGE-MA system, 3 additional days at 50°C.

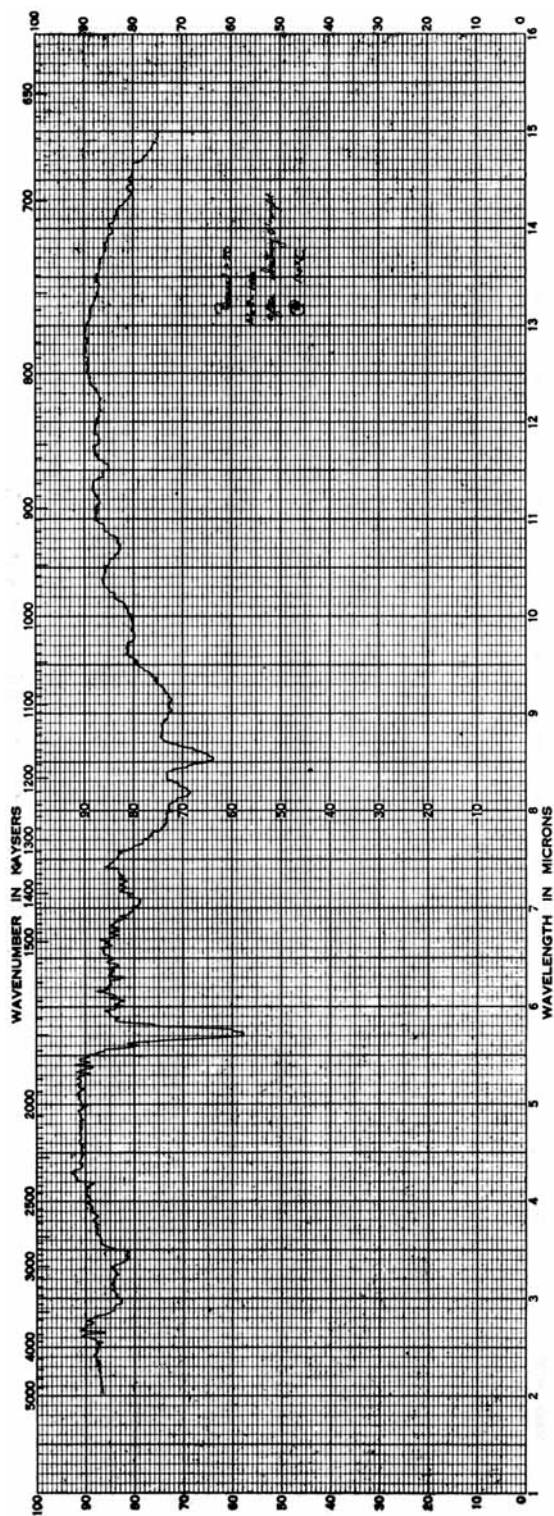


Fig. 7. AGE-MA system: 11 days at 25°C.; 3 days at 50°C.; 16 hrs. at 100°C.

alkali resistances of a properly cured system are good, and organic solvent resistance is excellent.

### Infrared Analysis of the Curing Mechanism (a)

In order to follow the cure of the crosslinked system, the free space between two salt plates was filled with the fresh 1:1 molar mixture of AGE-MA. The infrared absorption spectrum of the mixture is reproduced in Figure 2. Note especially the double peak at 5.4 and 5.6  $\mu$  and the single at 14.4  $\mu$ , both characteristic of maleic anhydride.

Simultaneously, a portion of this reaction mixture was placed in a container for curing studies. At the first gel formation (3 days, room temperature) the spectrum shown in Figure 3 was obtained. Diminution of the double peak at 5.4 and 5.6  $\mu$  is matched by appearance of a new peak at 5.75  $\mu$ , probably due to ester.

After 2 more days (total 5 days at 25°C.) the 5.75  $\mu$  band has increased further at the expense of the 5.4-5.6  $\mu$  couple; see Figure 4.

After 11 days (Fig. 5) the 5.75  $\mu$  band is the major one, with only minor amounts of the 5.4-5.6  $\mu$  couple. At this point the casting was entirely gelled, but cheesy. Further standing at room temperature did not affect either the IR absorption spectrum or the cure.

Three additional days at 50°C. gave a noncured but handleable casting, which still, however, had free maleic anhydride groups (see Fig. 6).

Only on heating (for instance, at 100°C. for 16 hrs.) is the last of the maleic anhydride converted entirely to ester (see Fig. 7). At this stage the sample was fully-cured (Barcol hardness 50).

### Preparation of Laminates (b)

Standard 14-ply 5 in. x 9 in. glass cloth (Type 181 Volan A) laminates (warp direction parallel, fill threads nested) were prepared from prepolymerized AGE-MA of 50 epoise viscosity after addition of varying proportions of alkali-washed styrene and benzoyl peroxide. The laminates were prepared by the Mylar bag technique and cured in a press at 50 psig. After some experimentation the following cure cycle was found to be satisfactory:

1/2 hr. at 80°C. followed by  
1/2 hr. at 100°C. followed by  
1 hr. at 150°C.

The data (obtained parallel to the warp direction) are summarized in Table V.

### Surface Coatings

The simple AGE-MA copolymer did not cure on wood, cork, or other nonmetallic substrates, possibly because of inhibition by natural antioxidants. However, inclusion of styrene in the mix gave surface coatings of

TABLE V  
Data on 5 in. X 9 in. Laminates Made with Allyl Glycidyl Ether-Maleic Anhydride-Styrene

Sample no.	Styrene, %	Active catalyst, %	Cure cycle		Postcure at 150°C., hr.	Flexural strength						Remarks				
			Hr.	°C.		Rm. temp., psi X 10 <sup>-3</sup>	Mod., psi X 10 <sup>-3</sup>	300°F.		500°F.			Aged 200 hr. at 500°C.			
								Hr.	°C.	psi X 10 <sup>-3</sup>	psi X 10 <sup>-3</sup>			psi X 10 <sup>-3</sup>	psi X 10 <sup>-3</sup>	Flex. Wt. loss, %
4550-45	0	0.5	22	125	4	150	—	66.5	2.7	24.3	2.4	23.0	3.0	—	Dark colored	
4550-48A	5	0.5	1/2	100	1	150	1	57.6	2.7	33.4	2.6	23.8	2.8	1.6	22.4	Dark brown
B	10	0.5	1	100	1	150	1	55.1	2.9	15.6*	2.3	18.1	2.9	1.4	22.2	Pale green
C	15	0.5	1	100	1	150	1	47.5	2.2	12.2*	1.2	15.1	2.2	Delaminated	Pale green	
D	20	0.5	1/2	100	16	150	1	71.4	3.1	30.1	2.5	14.8	2.7	1.5	22.2	Pale green
E	25	0.5	1/6	100	1/2	150	1	76.3	3.1	13.9*	1.4	16.1	2.7	1.4	21.0	Pale green
4248-126A	10	1	1	100	1	150	None	77.1	3.3	18.3	1.8	17.8	2.5	1.4	21.2	Brown-green
127D	20	1	1/2 ea.	80	100	150	None	71.6	3.1	14.1	1.6	10.2	2.2	1.5	20.5	Clear, pale green
126B	30	1	1/2 ea.	75	100	150	None	52.0	2.6	9.3	1.0	9.2	1.8	1.3	19.9	Incompatible, pale green
126C	40	1	1/2 ea.	80	100	150	None	43.8	2.8	7.4	0.9	5.2	1.2	0.9	18.2	Incompatible, pale green



4248-129A	10	0.25	1/2 ea.	80	1	150	3	69.2	2.8	33.3	2.4	15.1	2.5	1.8	24.0	Greenish brown
				100												
B	20	0.25	1/2 ea.	80	1	150	3	71.6	3.2	33.3	2.9	13.8	2.7	1.4	20.1	Pale, clear green
				100												
C	30	0.25	1/2 ea.	80	1	150	3	77.1	3.1	28.0	2.5	12.7	2.3	1.4	19.3	Incompatible, pale green
				100												
D	40	0.25	1/2 ea.	80	1	150	3	69.5	3.3	19.1	2.0	8.3	2.0	1.1	17.9	Incompatible, pale green
				100												
4248-131A	10	0.5	1/2 ea.	80	1	150	3	72.6	3.0	40.1	2.6	13.5	2.5	1.4	22.6	Brown-green
				100												
B	20	0.5	1/2 ea.	80	1	150	3	71.3	3.0	36.2	2.7	13.1	2.5	1.4	20.5	Green-clear
				100												
132C	30	0.5	1/2 ea.	80	1	150	3	79.3	3.4	32.6	2.7	11.4	2.3	1.4	18.7	Incompatible
				100												
D	40	0.5	1/2 ea.	80	1	150	3	78.8	3.2	23.6	2.4	9.4	2.0	1.5	17.5	Incompatible
				100												
4248-135A	10	0.75	1/2 ea.	80	1	150	3	86.1	2.9	38.5	2.5	19.2	2.1	1.3	23.2	Brownish green
				100												
B	20	0.75	1/2 ea.	80	1	150	3	80.5	3.0	32.9	2.4	14.5	2.2	1.6	21.7	Green-clear
				100												
4248-136	10 <sup>b</sup>	0.75	1/2 ea.	80	1	150	3	85.5	3.3	30.1	2.6	20.3	2.4	Delaminated	23.3	Brownish green
				100												

<sup>a</sup> Undercured.<sup>b</sup> Methyl methacrylate.

some merit. The prepolymer with styrene could be applied in thick coats and baked hard in 5 min. at 100°C. This through-cure property is superior to ordinary polyesters which retain surface tackiness. The short pot-life of the AGE-MA system requires a special technique in applying surface coatings, however.

(a) We are indebted to Mr. J. L. Gordon for his generous and stimulating assistance in setting up the apparatus. (b) We are especially indebted to Mr. F. C. Hopper, Shell Chemical Corporation, for his guidance in preparation of laminates

### References

1. Fischer, R. F., *J. Polymer Sci.*, **44**, 155 (1960).
2. Devlin, P. A., and E. C. Shokal, Shell Development Co., Emeryville, California, private communication.

### Synopsis

Allyl glycidyl ether and maleic anhydride, mixed in equimolar quantities, cure together readily in the presence of air, peroxide, and/or Lewis acids. Outstanding properties of the castings formed are hardness (Barcol 50-60 at 25°C., 30 at 150°C.), clarity and heat distortion temperature (165-168°C.). Color is yellow to amber, and strength properties are adequate. Water resistance is fair. The mixture is too thin for convenient use in laminating, but it can be bodied by heating (1 hr., 110°C.), giving a syrup of 50 cpoise. In glass cloth laminates, through-cure appears to be inhibited by the glass. The addition of styrene overcomes this effect. Small amounts are best (5-20%), since large quantities impair elevated temperature strength. Unusually good strength is attained even at 500°F., but resistance to aging at 500°F. is poor.

### Résumé

L'éther alkylglycidique et l'anhydride maléique mélangés en quantités équimoléculaires, vulcanisent ensemble rapidement en présence d'air, de peroxydes et d'acide de Lewis. Les propriétés marquantes des moulages formés sont: la dureté (Barcol 50-60 à 25°C, 30 à 150°C), la transparence et la chaleur de distortion (165-168°C). La couleur est jaune à ambre et les propriétés de solidité sont adaptées. La résistance à l'humidité est moyenne. Le mélange est trop mince pour un usage possible en laminage; mais il peut être solidifié par chauffage (1 H. à 110°C), donnant un sirop de 50 centipoises. Dans la laine de verre, les lamelles, après vulcanisation, semblent être inhibées par le verre. L'addition de styrène élimine cet effet. De petites quantités sont préférables (de 5 à 20%) puisque de grandes quantités affaiblissent la résistance à des températures plus élevées. De bonnes résistances inhabituelles sont obtenues même à 500°F, mais la résistance au vieillissement à 500°F est faible.

### Zusammenfassung

Äquimolare Gemische von Allylglycidyläther und Maleinsäureanhydrid liefern in Gegenwart von Luft, Peroxyden und Lewis-Säuren leicht Polymere. Die gebildeten Produkte zeichnen sich durch Härte (Barcol 50-60 bei 25°C, 30 bei 150°C), Klarheit und Hitzeverformungsbeständigkeit (165-168°C) aus. Sie sind gelb bis bernsteinfarbig und besitzen eine befriedigende Festigkeit. Die Wasserbeständigkeit ist gut. Die Mischung ist für eine bequeme Anwendung zur Schichtpressstoffbildung zu dünn kann aber durch Erhitzen (1 Stunde, 110°C) auf die Konsistenz eines Syrups von 50 Centipoise gebracht werden. In Schichtpressstoffen mit Glasgeweben scheint die vollständige

Aushärtung durch das Glas verhindert zu werden. Durch Zusatz von Styrol kann dieser Effekt beseitigt werden. Am günstigsten sind kleine Mengen (5-20%), da durch gross Zusätze die Festigkeit bei erhöhter Temperatur verschlechtert wird. Die Produkte besitzen eine ungewöhnlich gute Festigkeit, sogar bei 500°F, ihre Alterungsbeständigkeit bei 500°F ist dagegen schlecht.

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