

# Crosslinked Polyesters from "Bisacid A2." The Mechanical Properties of Glass Fiber-Reinforced Laminates

R. S. LENK, *Department of Chemistry and Polymer Technology,  
Polytechnic of the South Bank Borough Road,  
London, SE1, OAA, England*

## Synopsis

This paper reports the flexural and tensile test results on glass fiber laminates prepared from solutions in styrene of polyesters containing bisacid A2 and from standard commercial liquid polyester resins. The results are compared with each other. Suggestions are made for differences in strength, modulus, and strain. The results are presented in tables which give a statistical evaluation of numerous tests in terms of mean, range, and standard deviation.

## INTRODUCTION

The object of this work was the evaluation of the classical mechanical properties of polyester laminates at room temperature (23°C) based on sufficiently large numbers of test specimens so that a statistical analysis could be made. The comparison of results with those obtained from specimens of cast (unreinforced) sheet and the correlation, if possible, of results with the structure and composition of the resins was a further objective.

## EXPERIMENTAL

**Laminates.** The laminates were prepared in accordance with the appropriate specification<sup>4</sup> except that, in order to obtain adequate thickness, it was necessary to use three layers of FGE 2000 (1½ oz/ft<sup>2</sup>) chopped strand mat instead of two layers as laid down in ASTM C581. The resin/glass ratio was 2.5, the catalyst-accelerator system was based on MEK peroxide and cobalt naphthenate, and the styrene content of the liquid resin was 48% (unless otherwise indicated) in order to give convenient viscosities. The laminates were made between Melinex sheets, using one layer of glass surface tissue either side. After initial cure, the laminates were postcured at 80°C for 3 hr.

**Test Specimens.** Parallel-sided rectangular bars were used for both tensile and flexural tests. The thickness of the bars was the laminate thickness, i.e., about 3 mm, the width generally around 12 mm. The

specimens were prepared by milling. The actual widths of the specimens were determined to the nearest 0.01 mm before test, and the thickness (which was slightly variable along the specimen length) was similarly measured in the region of break after the test. In the tensile tests, the free specimen length between the grips was generally between 40 and 70 mm; and in the flexural tests, the distance between supports was 50.8 mm. The rate of separation of grips was 6.4 mm/min.

**Flexural Tests.** In the flexural tests, the resulting stress-strain curves showed an initial linear (Hookean) region, whereupon they began to curve toward the deformation axis, reaching a maximum and falling off rapidly thereafter. It is thought that the point of deviation from Hookean linearity roughly coincided with the first audible manifestations of cracks in the resin-rich surface which was under tension. From each individual graph, the Hookean limit load  $W_H$ , the Hookean limit deformation in the direction of flexure  $y_{\max}$ , and the ultimate failure load  $W_{\max}$  were read off. The Hookean limit stress  $\sigma_H$ , the Hookean modulus  $E_H$ , and the ultimate failure stress  $\sigma_{\max}$  were calculated according to the following equations:

$$\sigma_H = \frac{3}{2} \frac{gW_H l}{ab^2}$$

$$E_H = \frac{gW_H l^3}{4ab^3 y_{\max}}$$

$$\sigma_{\max} = \frac{3}{2} \frac{gW_{\max} l}{ab^2}$$

where  $g$  = the gravitational constant = 9.81;  $l$  =  $5.08 \times 10^{-2}$  meter;  $a$  = specimen width, in meters; and  $b$  = specimen thickness, in meters.

**Tensile Tests.** The stress-strain curves in uniaxial tension were invariably linear right up to rupture. After reading off the maximum load ( $W_{\max}$ ) and the extension ( $dl$ ) and having noted the initial free length of specimen between grips ( $l_0$ ), the strain  $\gamma$ , the maximum stress  $\sigma_{\max}$ , and the modulus  $E$  were calculated according to the following equations:

$$\gamma = \frac{dl}{l_0}$$

$$\sigma_{\max} = \frac{gW_{\max}}{ab}$$

$$E = \frac{gW_{\max}}{ab\gamma}$$

where  $g$ ,  $a$ , and  $b$  have the same significance as before.

## RESULTS

The results are given in Tables I through IV. Table I presents flexural data of the laminates; Table II, tensile data of the laminates. Tables III

TABLE I  
Flexural Data

Acid value and styrene content of resin	Molar ratio of maleic bisacid A2	Molar ratio of maleic phthalic	Number of specimens tested	$\sigma_B$ , psi $\times 10^4$			$\sigma_{max}$ , psi $\times 10^4$			$E_B$ , psi $\times 10^6$		
				Mean	Range	S.D.	Mean	Range	S.D.	Mean	Range	S.D.
				9.5; 48%	—	1	5	1.57	1.45 to 1.74	0.11	1.77	1.68 to 1.89
34; 31% (commercial)	—	1	10	1.10	0.92 to 1.36	0.14	2.10	1.75 to 2.53	0.24	0.63	0.56 to 0.78	0.06
8.4; 48% <sup>a</sup>	1	—	5	1.51	1.27 to 1.95	0.26	1.77	1.48 to 2.00	0.19	0.62	0.60 to 0.63	0.01
8.7; 48%	1	—	10	1.61	1.13 to 1.90	0.23	1.91	1.43 to 2.25	0.24	0.61	0.47 to 0.71	0.07
9.7/s; 48%	2	—	10	1.45	1.19 to 2.00	0.25	1.73	1.44 to 2.11	0.20	0.63	0.47 to 0.72	0.07
10.0; 48% <sup>b</sup>	3	—	10	1.29	0.66 to 0.68	0.30	1.89	1.27 to 2.49	0.38	0.72	0.38 to 0.96	0.14
23.5; 48% <sup>b</sup>	3	—	10	1.39	0.78 to 2.06	0.36	2.32	1.85 to 2.75	0.24	0.79	0.68 to 0.93	0.07
12.6/s; 48%	4	—	10	1.27	1.02 to 1.80	0.29	2.03	1.52 to 2.72	0.41	0.70	0.61 to 0.81	0.06
11.5; 48% (commercial) <sup>c</sup>	—	—	11	1.17	0.94 to 1.49	0.14	1.88	1.56 to 2.19	0.17	0.55	0.45 to 0.62	0.06

<sup>a</sup> Resin slightly overheated during esterification.<sup>b</sup> Note differences in acid value.<sup>c</sup> Bisphenolglycol/maleic polyester.

TABLE II  
Tensile Data

Acid value and styrene content of resin	Molar ratio of maleic/ bisacid A2	Molar ratio of maleic/ phthalic	Number of speci- mens tested	$\sigma_{max}$ , psi $\times 10^4$		$E$ , psi $\times 10^6$		$dl/l_0$ , %					
				Mean	S.D.	Mean	S.D.	Mean	S.D.				
				Range	S.D.	Range	S.D.	Range	S.D.				
9.5; 48%	—	1	10	1.00	0.83 to 1.18	0.10	0.92	0.77 to 0.25	0.15	11.1	0.15	8.00 to 13.3	1.6
34; 31% (commercial)	1	1	24	0.91	0.79 to 1.01	0.07	0.82	0.50 to 1.07	0.07	11.8	0.07	8.5 to 16.3	2.6
8.4; 48% <sup>a</sup>	1	—	24	1.15	0.98 to 1.34	0.09	1.22	0.80 to 1.60	0.22	9.6	0.22	7.2 to 14.3	2.1
8.7; 48%	1	—	30	1.06	0.85 to 1.32	0.09	1.08	0.84 to 1.43	0.14	9.9	0.14	7.0 to 12.0	1.1
9.7; 48%	2	—	30	1.05	0.77 to 1.29	0.13	1.05	0.83 to 1.46	0.13	10.1	0.13	7.5 to 12.7	1.4
10.0; 48% <sup>b</sup>	3	—	35	0.86	0.46 to 1.76	0.26	0.86	0.50 to 1.25	0.15	9.9	0.15	7.3 to 13.3	1.6
23.5; 48% <sup>b</sup>	3	—	32	1.22	0.84 to 1.49	0.15	1.16	0.88 to 1.75	0.25	10.8	0.25	6.3 to 13.5	1.8
12.6; 48%	4	—	46	0.96	0.64 to 1.30	0.19	0.90	0.70 to 1.27	0.13	10.8	0.13	7.0 to 15.1	2.0
11.5; 48% (commercial) <sup>c</sup>	—	—	24	1.11	0.95 to 1.44	0.15	0.85	0.68 to 0.99	0.07	13.2	0.07	9.4 to 17.4	2.1

<sup>a</sup> and <sup>b</sup> See Discussion.

<sup>c</sup> Bisphenolglycol/maleic polyester.

TABLE III  
Flexural Moduli of Laminates and Unreinforced Cast Sheet (All Moduli in  $\text{psi} \times 10^4$ )

Acid value of resin	Molar ratio of maleic/bisacid A2	Molar ratio of maleic/phthalic	Mean flexural modulus of laminate (liquid resin at 48% styrene)	Mean flexural modulus of unreinforced cast sheet at various styrene contents of liquid resin				
				30%	35%	45%	50%	55%
9.5	—	1	0.64	0.55	0.52	0.48	—	—
34	—	1	0.63 <sup>a</sup>	0.52 <sup>a</sup>	—	—	—	—
8.4 <sup>b</sup>	1	—	0.62	—	—	0.50	0.51	0.49
8.7	1	—	0.61	0.53	0.48	0.49	0.52	0.50
9.7	2	—	0.63	0.54	0.52	0.48	0.51	0.49
10.0	3	—	0.72	—	—	0.42	0.46	0.44
23.5	3	—	0.79	—	—	0.46	0.46	0.45
12.6	4	—	0.70	—	—	0.46	0.47	0.45
11.5	—	—	—	—	—	—	—	—
(commercial) <sup>d</sup>	—	—	0.55	—	—	—	0.41 <sup>c</sup>	—

<sup>a</sup> Styrene content 31%.

<sup>b</sup> Resin slightly overheated during esterification.

<sup>c</sup> Styrene content 48%.

<sup>d</sup> Bisphenolglycol/maleic polyester.

TABLE IV  
Tensile Moduli of Laminates and Reinforced Cast Sheet (All Moduli in psi  $\times 10^3$ )

Acid value of resin	Molar ratio of maleic/bisacid A2	Molar ratio of maleic/phthalic	Mean tensile modulus of laminate liquid resin at 48%	Mean tensile modulus of unreinforced cast sheet at various styrene contents of liquid resin			
				30%	35%	45%	55%
9.5	—	1	0.92	0.86	0.67	0.98	—
34	(commercial)	1	0.80 <sup>a</sup>	0.72	—	—	—
8.4 <sup>b</sup>	1	—	1.22	—	—	0.82	1.20
8.7	1	—	1.08	1.08	0.81	1.11	1.09
9.7	2	—	1.05	0.66	0.84	1.04	0.91
10.0	3	—	0.86	—	—	0.81	0.74
23.5	3	—	1.16	—	—	0.78	0.85
12.6	4	—	0.90	—	—	0.68	0.52
11.5	(commercial) <sup>d</sup>	—	0.85	—	—	—	1.15 <sup>c</sup>

<sup>a</sup> Styrene content 31%.

<sup>b</sup> Resin slightly overheated during esterification.

<sup>c</sup> Styrene content 48%.

<sup>d</sup> Bisphenolglycol/maleic polyester.

and IV give a comparison of mean flexural and tensile moduli respectively of laminates made from a liquid resin containing 48% styrene, unless otherwise stated, with the mean flexural moduli of cast sheet based on the same resins but at different styrene contents.

## DISCUSSION

### Flexural Data

Table I shows that the means, ranges, and standard deviations of the Hookean limit stress  $\sigma_H$ , of the ultimate flexural strength  $\sigma_{max}$ , and of the Hookean modulus in flexure are very similar for all laminates, irrespective of whether the laminate was made from a liquid resin containing 48% or 31% styrene, whether the resin was somewhat overheated during esterification or not, or whether the resin was reacted to an acid value of about 10 or to an acid value of about 30.

Marginal differences appeared in the high-acid value (34), low-styrene (31%) commercial resin where the Hookean limit stress was rather lower than in the other laminates; and in the commercial bisphenolglycol/maleic polyester where the modulus was lower than in the other laminates. A comparatively low modulus of the bisphenolglycol/maleic polyester laminate would not be unexpected in view of the relative abundance of ether links in the polyester main chains.

Slightly high modulus and stress figures were found in the tests on the laminate of high acid value (23.5) and of high molar ratio of maleic/bisacid A2. This difference could be explained by the probability that in a low molecular weight chain with high crosslink potential, this potential is more readily attained during cure without the buildup of internal stresses. The polystyrene sequences in the crosslinks after curing would also be shorter for such a resin. This is a fact which stands out when the laminate is compared with another which differs in composition only in that the resin had a lower acid value (10.0) and hence a greater main-chain length (see Table II, results marked<sup>b</sup>).

The reproducibility of results was excellent with respect to the modulus. Although the range of strength appears to be wide in some cases, this is due to the odd stray high and low results, and these also affect the standard deviation. It would not have been unreasonable to dismiss those odd results, especially since the number of multiplicates was more than adequate, and no doubt this would have produced a closer range and a much lower standard deviation. However, the temptation to do this was resisted.

### Tensile Data

The stresses, modulus, and strain data of the laminates are shown in Table II. The uniformity of results here is remarkable, and the only outstanding features again concern the following:

(a) Two laminates marked<sup>b</sup> which were made from polyesters reacted to different acid values, but otherwise identical in composition. The more

fully reacted (lower acid value) resin was significantly weaker and had a lower modulus than the comparable higher acid value resin, probably for similar reasons to those put forward in the discussion of flexural data above.

(b) The commercial bisphenolglycol/maleic polyester laminate had a substantially higher extension than the other laminates. The comparatively low modulus here is not due to lower strength but only to this high extension, which may again be attributed to the abundance of flexible ether links in the polyester chain.

The reproducibility of tensile data (except for the modulus) was not as good as that for the flexural data. For this reason, the number of specimens tested was high, and a substantial amount of scatter occurred, but typical results still crowded fairly closely around the mean figures for each laminate. Again, the author desisted from excluding apparently unduly high and unduly low results, so that the range and standard deviation gave figures which suggest rather less concordance than might reasonably be said to exist.

#### **Comparison of Moduli of Laminates with Those of Specimens Taken from Unreinforced Cast Sheet**

**Flexural Moduli.** This comparison is embodied in Table III, which includes results on cast sheet having styrene contents ranging from 30% to 55%. The laminates had styrene contents of 48%, except in the sample marked.<sup>a</sup>

The moduli of the cast sheet were remarkably constant between 0.4 and  $0.5 \times 10^6$  psi, irrespective of styrene content or thermal history during the esterification reaction. The only significantly lower modulus was found in the bisphenolglycol/maleic cast resin marked<sup>b</sup> in Table IV. The low modulus of the cast sheet corresponds to a low modulus in the laminate of the same polyester. The probable reasons for this are the same as those given before.

In general, it is to be noted that the laminates made according to the specification given have flexural moduli which are about one third as much again as those of the corresponding cast reinforced sheet, which is a smaller increase on glass reinforcement than is observed in commercial testing laboratories.

**Tensile Moduli.** Table IV shows the tensile moduli of cast, unreinforced sheet at styrene contents from 30% to 55% side by side with the moduli of the laminate made from the polyester at a constant styrene content at 48% on the liquid resin.

Unfortunately, tensile strength data on cast, unreinforced sheet are poorly reproducible. But one may say is that there does not seem to be any observable trend of modulus changes as a result of changes in styrene content of cast, unreinforced sheet, nor does there seem to be any significant difference between the moduli of the laminates and their corresponding unreinforced cast sheets, although one would have expected the moduli for the laminates to be substantially higher than those of the cast sheet. The moduli were all around  $10^5$  psi.



### SUMMARY

The preparation and purification of bisacid A2 and of crosslinkable polyesters therefrom as well as the thermal properties of cast, cured unfilled polyester sheet were subjects of earlier communications.<sup>1-3</sup> The present paper reports the results of tensile and flexural tests on glass fiber laminates prepared from liquid resins containing bisacid A2 as well as from liquid resins at present in commercial production.

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### References

1. R. S. Lenk, *J. Appl. Polym. Sci.*, **15**, 311 (1971).
2. R. S. Lenk, *J. Appl. Polym. Sci.*, **15**, 1753 (1971).
3. R. S. Lenk, *J. Appl. Polym. Sci.*, **15**, 2211 (1971).
4. ASTM C581.

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