

## Bromostyrene-Crosslinked Polyesters. II. Mechanical Properties and Weathering Stability

M. MUSHKATEL and G. MAROM, *Casali Institute of Applied Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel*

### Synopsis

The partial replacement of styrene by bromostyrene in polyesters, in order to achieve fire-retardant resins, raised the need to explore the effect of the bromine on the mechanical performance of these resins and of their glass fiber composites. The present study reveals that under combined humidity and uv radiation conditions, the mechanical performance of the bromine-containing resin surpasses that of the original resin.

### INTRODUCTION

Polyester resins and their composites are widely used as structural materials, thus being subjected to various environmental conditions. Moisture, temperature changes, radiation, and presence of oxygen are the main factors which enhance the deterioration of the resins or the composites and which cause their environmental breakdown. In the presence of water, hydrolysis of the esteric bonds in the resin<sup>1</sup> and of the siloxane bonds in the glass-resin coupling agent<sup>2</sup> may occur. Also the diffusion of the water into the resin results in its swelling, thereby inducing internal stresses and crazing. The UV radiation may initiate further crosslinking of the resin via some remaining unsaturated bonds, and, also, this radiation may result in photooxidation. The effects of the excessive crosslinking and of the photooxidation on the properties of the resin are to increase its brittleness, to deteriorate its mechanical properties and its appearance, and to promote crazing. Temperature changes induce dilatation strain, which has a destructive influence on the resin and more so on the composite, owing to the large difference between the thermal expansivity of the resin to that of the glass fiber. Detailed information on the effect of weathering on the properties of structural resins and composites can be found, for example, in references 3 to 6.

Part I of this study<sup>7</sup> investigated the thermal stability and flammability of unsaturated alkyd resins crosslinked by bromostyrene and of their unidirectionally reinforced composites. The present work was undertaken to examine the mechanical properties of these materials and their stability under weathering and accelerated conditions. This work utilized the wide information already in the literature in an attempt to determine the effect of the presence of bromine on the above properties. The research was carried out with polyester resins and

TABLE I  
Compositions of the Polyester Resins

System no.	Bromostyrene of total monomer, mole fraction	Total monomer in resin, wt-%	Total amount of bromine, wt-%	Density of resin, g/cm <sup>3</sup>
1	0	33.0	0	1.221
2	0.2	36.5	4.9	1.280
3	0.4	39.3	9.3	1.316
4	0.6	42.0	13.4	1.346
5	0.8	44.4	17.1	1.384

TABLE II  
Types of Weathering Treatments of Polyester and GRP Sheets

Treatment symbol	Description of treatment conditions	Duration of treatment
B	boiling in distilled water	12,107,260 hr
R	alternate variation of humidity and UV radiation	480 hr
W	outdoor weathering	4.5, 7 months
T	cyclic variation of temperature	21 days

with composites which were identical to those investigated in part I<sup>7</sup> (see experimental section).

## EXPERIMENTAL

### Materials

The polyester systems were based on the alkyd Crystic 196 (Makhteshim Chemical Works Ltd.), which is a polymer of fumaric acid, phthalic acid, and propylene glycol. This alkyd resin was crosslinked by styrene/bromostyrene monomer mixtures in which the mole fraction of bromostyrene varied from 0 to 0.8, keeping a constant total amount of crosslinking monomer of 0.0048 mole per 1 g alkyd. This amount is equivalent to the optimal ratio of 0.5 g styrene monomer per 1 g alkyd for the original resin recommended by the manufacturer. The bromostyrene used was a mixture of the ortho and the para isomers in a ratio of 1:2.5. The preparation techniques of the polyester resins and of their glass fiber-reinforced composites (GRP) were as described before.<sup>7</sup> Table I specifies the compositions of the polyester resins. The volume fraction of the fibers in the GRP as manufactured was 0.39, typical of the range 0.30–0.50 common for such materials.

### Weathering Treatment

Polyester and GRP samples were exposed to various weathering treatments as described in Table II. In B-type treatment, test specimens destined for the determination of mechanical properties (see section below) were continuously boiled in water. The weight of the specimens was recorded a few times during

the boiling period to discover any weight change caused by the combined action of water absorption and hydrolysis of the resin. Specimens for R-type treatment were  $10 \times 10 \text{ cm}^2$  sheets 0.5 cm or 0.3 cm thick. The specimens were subjected to alternate variations of 24 hr of 100% humidity at 49°C, and 24 hr at  $60^\circ \pm 5^\circ\text{C}$  under UV radiation generated by a 400-W S-1 Hg arc lamp placed 15 cm from the specimen center (ASTM D-795-65T). This treatment included ten humidity and ten radiation cycles. The O-type treatment was applied to 0.5 cm-thick sheets which were exposed in Jerusalem at an angle of  $45^\circ$  facing south. Such exposures were carried out from July to December (4.5 months) and from May to December (7 months) (mostly dry, with average temperatures 25°C). The T-type treatment consisted of cyclic variations of temperature from  $-10^\circ$  to 120°C for 22 days, with an average of 12.6 hr at each extreme temperature.

### Mechanical Testing

Test specimens for the determination of the mechanical properties were of the form of 0.5 cm square-section bars 5.0 cm long. Cuts to the depth of  $\sim 0.2$  cm were introduced at the center of each bar destined for fracture energy measurement. Testing was carried out by three-point bending with a load span of 4.0 cm on a floor model Instron machine at a cross-head speed of 0.05 cm/min. Each property was determined using at least seven specimens. The mechanical properties measured were Young's modulus, ultimate strength, and fracture surface energy for the polyesters, and Young's modulus, interlaminar shear strength, fracture surface energy, and work of fracture for the GRP specimens. The work of fracture was not calculated for the polyester specimens since under the above testing conditions they fractured in a catastrophic fashion. Shear strength was calculated instead of ultimate strength for the GRP specimens since under the above testing conditions they failed by interlaminar shear (see, for example, ref. 8).

The various mechanical properties were calculated using the following relationships: Young's modulus,  $E = kl^3/4bd^3$ ; ultimate strength,  $\sigma = P_F l/2bd^2$ ; shear strength,  $\tau = 3P_F/4bd$ ; fracture surface energy,  $\gamma_I = Y^2\sigma^2c/2E$ ; and work of fracture,  $\gamma_F = u/2b(d - c)$ , where  $P_F$  is the load at fracture,  $b$  is the width and  $d$  the depth of the specimen,  $l$  is the beam span,  $c$  is the depth of the cut,  $k$  is the slope of the load-deflection curve,  $u$  represents the total energy to fracture obtained by integration of the load-deflection curve, and  $Y$  is a geometric factor.<sup>9</sup>

### RESULTS

Tables III and IV present the effect of the various weathering treatments on the mechanical properties of the resins and the GRP, respectively. The results in the tables show that when a constant degree of crosslinking of the polyester is retained, the original mechanical properties are independent of the relative amount of bromostyrene in the resin. The water-boil treatment results in similar relative decreases in the value of  $E$  of the polyesters and in the values of  $E$ ,  $\tau$ ,  $\gamma_I$ , and  $\gamma_F$  of the GRP. However, such treatment induces a lower relative reduction in the values of  $\sigma$  and  $\gamma_I$  of polyesters containing bromostyrene compared with that containing styrene only. It is obvious that the relative reduction in  $\sigma$  and

TABLE III  
Effect of the Various Weathering Treatments on the Mechanical Properties of the Polyesters<sup>a</sup>

Bromine in resin, wt-%	Original resin									
	Treatment B					Treatment W				
	12 hr		107 hr			4.5 months		7 months		
$E$ , GN/m <sup>2</sup>	$\sigma$ , MN/m <sup>2</sup>	$\gamma_L$ , J/m <sup>2</sup>	$E$ , GN/m <sup>2</sup>	$\sigma$ , MN/m <sup>2</sup>	$\gamma_L$ , J/m <sup>2</sup>	$E$ , GN/m <sup>2</sup>	$\sigma$ , MN/m <sup>2</sup>	$\gamma_L$ , J/m <sup>2</sup>	$E$ , GN/m <sup>2</sup>	$\sigma$ , MN/m <sup>2</sup>
0	3.39	95.4	134.2	2.89 (85)	55.5 (58)	2.50 (74)	26.0 (27)	64.0 (48)	3.29 (97)	72.8 (76)
4.9	3.43	89.9	135.1	2.99 (87)	52.5 (53)	2.46 (72)	26.5 (27)	72.5 (54)	3.29 (96)	82.0 (91)
9.3	3.42	88.0	142.7	2.96 (87)	51.9 (59)	2.45 (72)	25.8 (29)	74.3 (52)	3.12 (91)	82.1 (93)
13.4	3.39	89.9	133.5	2.69 (87)	58.5 (65)	2.51 (74)	32.8 (37)	99.1 (74)	3.30 (97)	80.8 (89)
17.1	3.39	88.9	136.7	2.82 (83)	53.1 (60)	2.50 (74)	36.3 (41)	114.6 (84)	3.40 (100)	80.4 (90)

<sup>a</sup> A number in parentheses indicates the percentage of the original value.

TABLE IV  
Effect of the Various Weathering Treatments on the Mechanical Properties of the GRPs<sup>a</sup>

Bromine in resin, wt-%	Original GRP									
	Treatment B, 260 hr					Treatment W (4.5 months)				
	$E$ , GN/m <sup>2</sup>	$\tau$ , MN/m <sup>2</sup>	$\gamma_L$ , kJ/m <sup>2</sup>	$\gamma_F$ , kJ/m <sup>2</sup>	$\gamma_L$ , kJ/m <sup>2</sup>	$\tau$ , MN/m <sup>2</sup>	$E$ , GN/m <sup>2</sup>	$\tau$ , MN/m <sup>2</sup>	$\gamma_L$ , kJ/m <sup>2</sup>	$\gamma_F$ , kJ/m <sup>2</sup>
0	21.0	30.8	15.9	43.5	9.5 (59)	39.1 (90)	21.0 (100)	33.1 (108)	21.3	33.9 (110)
4.9	21.2	31.6	15.9	44.1	8.1 (51)	38.2 (87)	21.1 (100)	33.5 (106)	21.5	33.3 (105)
9.3	21.6	33.2	16.2	44.0	9.3 (57)	38.7 (90)	21.4 (100)	32.1 (97)	21.1	33.3 (100)
13.4	21.6	33.3	16.2	42.2	8.5 (52)	38.5 (91)	21.2 (100)	32.6 (96)	21.4	34.3 (104)
17.1	21.3	33.4	15.6	42.4	8.8 (56)	39.5 (93)	21.4 (100)	33.7 (101)	21.4	33.3 (100)

<sup>a</sup> A number in parentheses indicates the percentage of the original value.

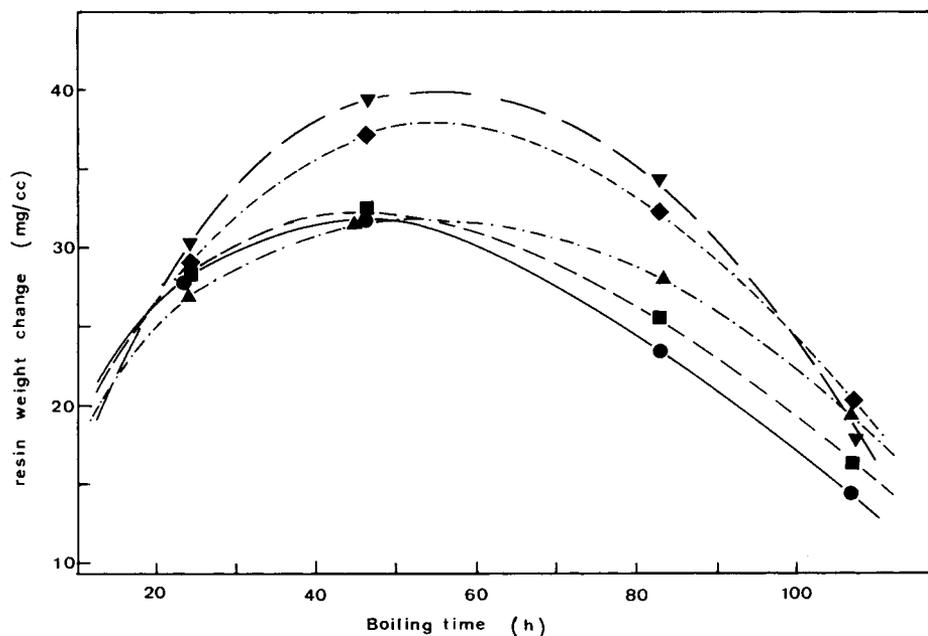


Fig. 1. Effect of boiling period on weight change of polyesters containing 0(●), 0.2(■), 0.4(▲), 0.6(◆), and 0.8(▼) mole fraction bromostyrene.

$\gamma_I$  decreases as the bromine content is increased. Whereas treatments R and W do not affect significantly the  $E$  values of the polyesters, treatment R generates a higher relative decrease in  $\sigma$  of the styrene-crosslinked polyester compared with the bromostyrene-crosslinked resins, and vice versa, for treatment W. It can be seen that under treatment W, values of  $\sigma$  of the styrene-crosslinked polyester surpass the original values. The values of  $E$  and  $\tau$  of the GRP are not affected by treatments R, W, and T, except in the latter, which induces a reduction in  $\tau$ .

Figure 1 presents the results of the weight changes of the resins as a function of the water-boil period. Each point on the graphs is a result of two inverse effects, namely, water absorption and weight loss due to hydrolysis and erosion. Since the total weight loss measured after drying the resins was equal for the different resin systems (23–25 mg/cc resin), Figure 1 indicates the trend of the water absorption. It is seen that the presence of bromine facilitates water absorption.

## DISCUSSION

Examining the results in Table III and the effects of the water-boil treatment and of the combination of humidity and UV radiation on the values of  $\sigma$  and  $\gamma_I$ , it seems that the bromine-containing polyesters are less sensitive to such treatments than the styrene-crosslinked polyester. Also, the results of  $\sigma$ , and more so those of  $\gamma_I$ , measured after the water-boil treatment show a better retention of the original values as the bromine content is increased. This observation is strengthened noticing that the moduli of the resins after the treatments are alike. Thus the values of  $\gamma_I$ , which are very sensitive to any deterioration of the resin,

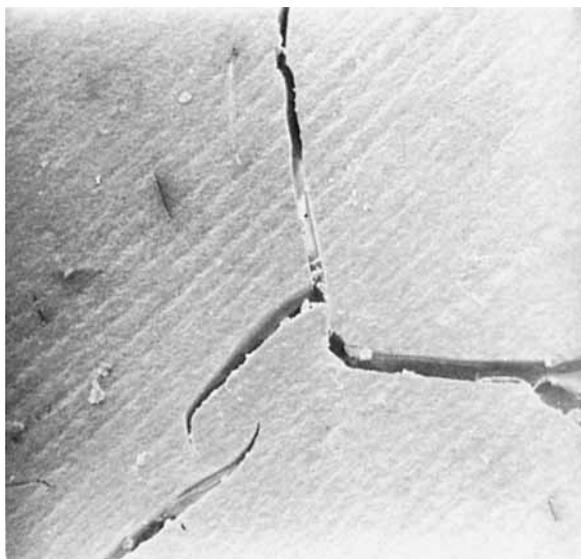


Fig. 2. Crazes developed in styrene-crosslinked specimen after 107 hr of water-boil treatment ( $\times 100$ ).

may really indicate that the presence of bromine in the resin retards crazing. This happens despite a higher water absorption capacity by the bromostyrene-crosslinked resin (Fig. 1) due to the polarity of the bromine atom.

The above observations are strongly supported by a scanning electron microscope investigation of the specimen envelopes and of the fracture face morphology. Figure 2 shows the type of crazes developed in styrene-crosslinked polyester specimens after 107 hr of water-boil treatment. Some crazing developed in polyesters having a low bromine content, but no crazing whatsoever was detected in specimens of 0.8 mole fraction bromostyrene of total monomer (17.1 wt-% bromine). Figure 3 presents the morphology of the fracture face of an untreated styrene-crosslinked polyesters. Figures 4 and 5 present the morphology of the fracture faces of water-boil treated styrene-crosslinked and bromostyrene-crosslinked polyesters, respectively. It is seen that such a treatment results in a mirror-like fracture face in the first type of materials, while in the second type the original morphology (Fig. 3) is mostly preserved. It has already been shown<sup>10,11</sup> that crack nucleation occurs within the craze along which the crack propagates producing the mirror-like fracture face. Thus, the mirror-like face in the first type of resin is an indication of the presence of crazes, while the rougher fracture surface of the second type of resin indicates an absence of such crazes.

The higher sensitivity to crazing of the styrene-crosslinked polyester was also exhibited by the appearance of the sheets, which underwent the humidity and UV radiation treatment. Figure 6 shows the face of this sheet after such treatment indicating the craze pattern formed (the grey stains are yellowing stains). Again, no crazes whatsoever were traced on bromostyrene-crosslinked polyester sheets.

It is maintained that the crazing resistance exhibited by the bromine-containing resins derives from the relative open structure of those resins, which al-

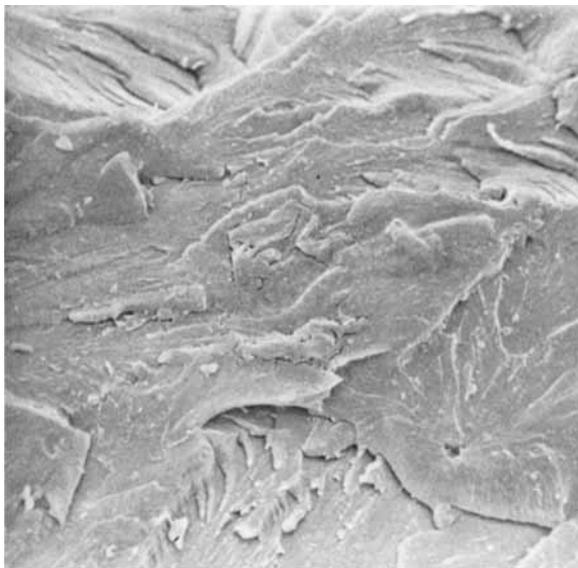


Fig. 3. Fracture face of untreated styrene-crosslinked polyester ( $\times 480$ ).



Fig. 4. Fracture face of a 107-hr water-boil-treated styrene-crosslinked polyester ( $\times 480$ ).

lows the water molecules to penetrate into the resin without creating excessive internal stresses. This is proved by the fact that the densities of the resins (Table I) are lower than expected, assuming a constant volume and allowing for the extra weight of the bromine. It is known, for example, that during polymerization styrene shrinks by 17%, while chlorostyrene shrinks by 13%,<sup>12</sup> and also, the density of polybromostyrene is only 5% higher than its monomer, while the density of polystyrene is 12% higher than its monomer. A similar effect of craze resistance has also been reported for chlorostyrene<sup>12</sup> and for vinyltoluene,<sup>1</sup> and

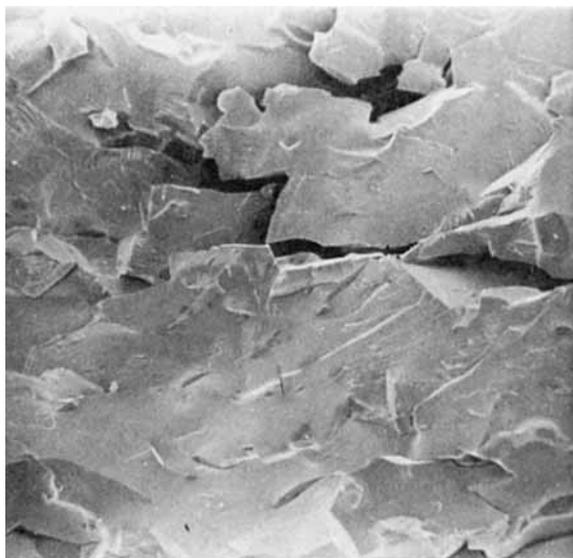


Fig. 5. Fracture face of a 107-hr water-boil-treated bromostyrene-crosslinked polyester ( $\times 480$ ).

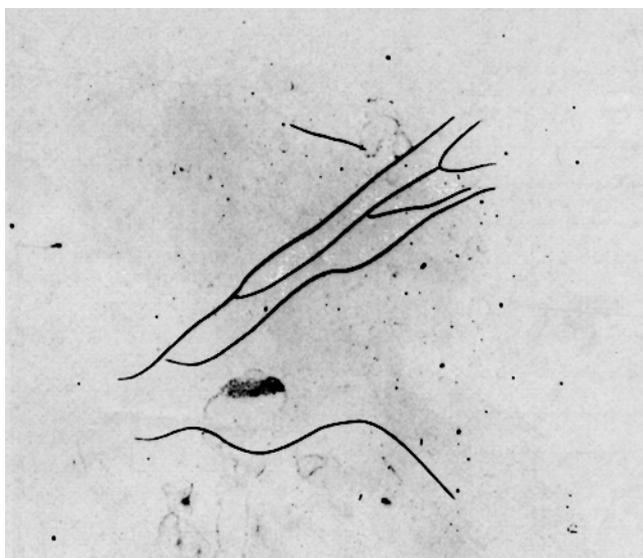


Fig. 6. Styrene-crosslinked polyester sheet after humidity and UV radiation treatment, showing the craze pattern formed ( $\times 1$ ).

it is generally thought that craze resistance capacity is inversely proportional to the density.<sup>13</sup>

Table III indicates that outdoor weathering under generally dry conditions deteriorates more strongly the strength of the bromine-containing resin, while  $\sigma$  of the styrene-crosslinked resin first increases and surpasses the original value. This difference between the two types of resin derives from two simultaneous processes, namely, (i) a further crosslinking of the resins initiated by the radiation,<sup>14</sup> and (ii) photooxidative degradation.<sup>15</sup> Whereas the first process occurs

in both types of resins, the second is accelerated in the second due to presence of bromine which enhances UV absorption.

Table IV shows that the mechanical properties of the GRP, especially  $\tau$  and  $\gamma_I$ , are affected by the various treatments. However, the bromine content of the resin does not affect these properties. This results from the fact that in the GRP the contribution of the fibers dominates the mechanical properties and shields the effects of the bromine.

## CONCLUSIONS

There is strong experimental evidence indicating that the presence of bromine in the resin retards humidity-induced crazing on the one hand and enhances photooxidative degradation which deteriorates the mechanical properties on the other hand. However, since the first effect is stronger, it is maintained that the bromine-containing resin exhibits a better mechanical performance, especially under combined humidity and UV radiation.

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