

Bromostyrene-Crosslinked Polyesters. III. Electrical Properties

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Synopsis

Volume resistivity, dielectric strength, dielectric constant, and loss tangent of unsaturated polyester resins and their GRP were studied as a function of the bromine content of the resin. The bromine was introduced by using bromostyrene as the crosslinking monomer. Bromine content was established by partial or total replacement of the styrene. Also, the effects of short and long water-boil treatments on these properties were investigated. The electrical and dielectrical properties were shown to be independent of the bromine content of the resin.

INTRODUCTION

Bromostyrene-crosslinked polyesters and their glass fiber composites (GRP) were investigated elsewhere with respect to thermal stability and flame retardancy¹ and mechanical properties and weathering stability.² It was shown that the presence of the aromatic bromine reduced the extent of oxidative degradation of the resin, and that the rate of burning decreased linearly with the bromine content leading to self-extinguishing compositions. Also, the introduction of the bromine into the resin did not alter its original mechanical properties, while retarding markedly its humidity induced crazing.

The use of polyester resins in various electrical devices functioning at elevated temperatures creates a need for such materials which exhibit good mechanical performance together with flame retardancy. Thus, in view of the properties of the bromostyrene-crosslinked polyesters, it was desirable to examine their potential for electrical applications. This was carried out in the present work by studying the effect of the bromine content on the electrical properties, i.e., volume resistivity, dielectric strength, dielectric constant, and loss tangent of the bromostyrene-crosslinked polyesters and of their GRP. Also, the improved stability of the bromine containing resin under high-temperature humidity conditions initiated research on the effect of these conditions on the electrical properties of the polyesters.

EXPERIMENTAL

Preparation of the Polyesters

The raw materials for the polyester resins consisted of the alkyd component of "Crystic" 196, styrene, and bromostyrene. The catalyst used was methyl ethyl

TABLE I
Compositions of the Polyester Resins

Bromostyrene of total monomer, mole fraction	Total monomer in resin, wt %	Total Br in resin, wt %
0	33.0	0
0.2	36.5	4.9
0.4	39.3	9.3
0.6	42.0	13.4
0.8	44.0	17.1
1.0	46.8	20.4

ketone peroxide. The alkyd was heated until liquefied and the monomers containing 1 ppm copper naphthenate (in benzene solution) were then added to the alkyd and thoroughly mixed. The proportions of alkyd to monomer were such that various compositions of mole fraction of bromostyrene (from 0 to 1) were obtained, retaining a constant total monomer concentration of 48 mmoles per 1 g alkyd. This concentration is equivalent to a ratio of 0.5 g styrene to 1 g alkyd, typical of "crystic" 196.^{1,2} Table I gives the compositions of the polyesters used, and it presents the total monomer weight % and the Br weight % in the resin (alkyd + monomers) as functions of the bromostyrene mole % of the total 48 mmoles. Curing was carried out by adding 2% of the catalyst and heating the mixture for 2 hr at 80 °C. Postcure was done at 70°C for 48 hr.

Preparation of the Test Specimens

Two types of specimens were made for the electrical tests: Flat panels of 100 × 100 × 2.0 mm³ for the resistivity and dielectric strength measurements and thicker panels, 8 mm thick, for the dielectric constant and loss tangent measurements.

The thin panels were made by casting a readily mixed bubble-free resin between two glass plates previously coated with poly(vinyl alcohol) and spaced apart by a rubber flange. The resin was cured between the plates, released, cleaned, and trimmed.

The thick panels were obtained by casting the resin into an open-top metal mold. The cured panels were cut and filed to match the size of the waveguide.

GRP specimens with an E-glass reinforcement were also prepared. The glass used was a 181 sateen weave finish for polyester. The composite specimens were prepared by laminating the glass cloth impregnated with an excess of resin in a press between spacers. The cure was otherwise identical to that of the pure resin.

The resin content in the cured GRP specimens was about 60% of the total volume. Specimens for the dielectric constant and dielectric strength were prepared from the composite panels.

Treatment of Test Specimens

Polyester specimens were boiled for various periods of time in distilled water and then dried at 105°C for 4 hr. The composite specimens were boiled for 66

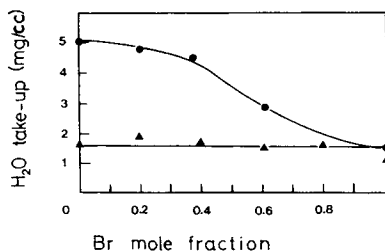


Fig. 1. Water take-up by cracks in resins after 12 hr (▲) and 107 hr (●) of water-boil treatment (mg water per cc resin).

hr in distilled water and then dried as above. All the specimens were conditioned for at least 24 hr at 22°C and 80% relative humidity before testing.

Electrical Measurements

Volume Resistivity. The volume resistivity measurements were conducted in accordance with reference 3. The measuring system included a power generator, electrodes, and a sensitive ammeter. The specimens were inserted between the electrodes, and readings were taken 3 min after the application of a potential difference of 500 V. Less than 3 min was required for the electric current to stabilize.

Dielectric Strength. The dielectric strength measurements were conducted by immersing the electrodes in oil with the specimen held between them. The voltage applied to the electrodes was increased at a rate of 2 kV/sec.

Dielectric Constant and Loss Tangent. Measurements were conducted in the frequency range of 8–12 GHz. The measuring setup consisted of a microwave generator, a VSWR (Voltage Standing Wave Ratio) meter, and a slotted line terminated by a waveguide. (A detailed description of the test method is given elsewhere.⁴) The specimen was plugged tightly to the end of the waveguide and a metal plate was then bolted to the waveguide terminal. Measurements of the reflected waves were carried out with and without the specimen in the waveguide. The dielectric constant and the loss tangent were calculated from the relative position of the minima and the VSWR.

RESULTS

Water-Boil Treatment

A variety of water take-up measurements have been often used for assessing resin morphology and cracking (see, for example, ref. 13). The extent of resin cracking due to the water-boil treatment was determined by measuring the water take-up of the preformed cracks as follows. Treated and untreated specimens were immersed in cold water for 24 hr. The water take-up of the cracks was determined by deducing the figure obtained for an untreated specimen from the corresponding one obtained for a water-boil-treated specimen. The results are presented in Figure 1, where it is shown that after a short water-boil treatment (12 hr), the extent of resin cracking is small and is unaffected by the bromine content. However, after 107 hr, the styrene-crosslinked resin takes up as much as three times more water than the bromostyrene-crosslinked resin. The water

TABLE II
Resistivities and Dielectric Strengths of the Polyesters and GRP

Bromostyrene of total monomer, mole fraction	Resistivity, $10^{15} \Omega\text{-cm}$			Dielectric strength, kV/mm		
	Resin	Resin boiled 12 hr	Composite 66 hr	Resin	Resin boiled 24 hr	Composite boiled 66 hr
0	4.42	3.37	3.53	20.9	14.1	16.9
0.2	4.33	2.97	4.30	15.0	16.6	15.3
0.4	4.19	3.72	4.18	17.9	15.3	17.9
0.6	4.56	3.71	3.44	17.3	15.9	15.5
0.8	4.42	3.65	4.05	17.0	14.8	13.0
1.0	4.04	3.84	3.49	14.0	12.9	16.6

take-up of the latter practically does not change with the water-boil treatment, indicating that the presence of bromine enhances the water-attack resistance of the resin. This result agrees with visual observations, which reveal drastic cracking of the styrene-crosslinked polyester in contrast to the bromostyrene-crosslinked one; and furthermore, the extent of cracking reduces gradually with the bromine content.

Infrared absorption spectra of treated and untreated resins did not reveal any significant differences. However, the waters in which the specimens were boiled were acidic irrespective of the bromine content of the resin; and with bromine present in the resin, the boiled waters contained Br^- .

Resistivity and Dielectric Strength

The results of the volume resistivity and of the dielectric strength of some of the polyester and GRP sets are listed in Table II. The experimental errors were $\pm 0.03 \times 10^{15} \Omega\text{-cm}$ and $\pm 0.2 \text{ kV/mm}$ for the volume resistivity and the dielectric strength, respectively.

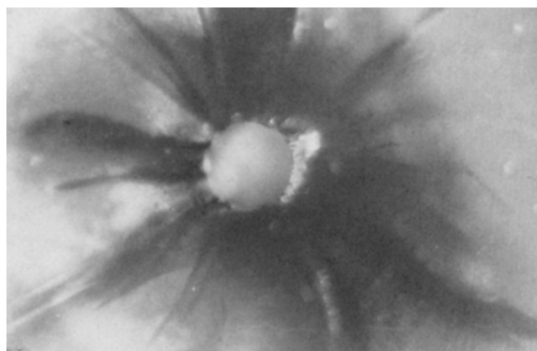
From Table II it is possible to derive the following observations: The volume resistivity and the dielectric strength do not depend on the bromine content. The respective average values for the polyesters are $4.3 \times 10^{15} \Omega\text{-cm}$ and 17.0 kV/mm , and for the GRP, $3.82 \times 10^{15} \Omega\text{-cm}$ and 21.1 kV/mm . The effect of the water-boil treatment on these electrical properties is to reduce their values; yet even after this treatment, neither the polyesters nor the GRP show any consistent dependence on the bromine content. The original resistivities of the GRP are slightly lower, and their original dielectric strength is higher than the corresponding values of the pure resin.

Although the values of the dielectric strength were not influenced by the bromine concentration, the shape of the hole formed during the dielectric breakdown was highly dependent on this factor, since it determined the extent of water boil-induced cracking (Fig. 2). The original circular cross section of the hole was retained in the bromostyrene-crosslinked polyester; while in the styrene-crosslinked polyester, it was elongated since the breakdown occurred through an existing crack formed during the water-boil treatment.

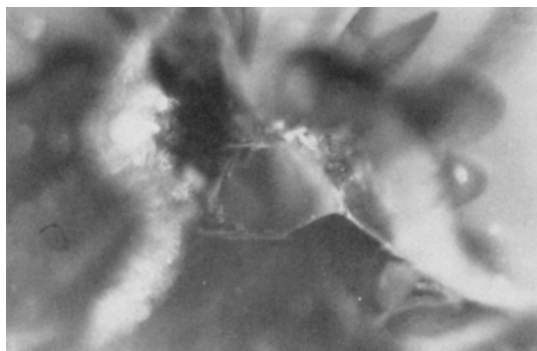
Dielectric Constant and Loss Tangent

Figure 3 gives the values of the dielectric constants (ϵ') and of the loss tangents ($\tan \delta$) of the pure resins measured in the frequency range of 8–12 GHz. These values are given for each of the resin compositions before and after the water-boil treatment. From Figure 3, it can be seen that the bromine content affects the trends of ϵ' and $\tan \delta$ similarly in any of the measured frequencies. These trends are demonstrated in Figure 4, which presents the typical behavior of ϵ' and $\tan \delta$ as functions of the bromine content at a frequency of 9 GHz. The results of ϵ' and $\tan \delta$ for the GRP are listed in Table III.

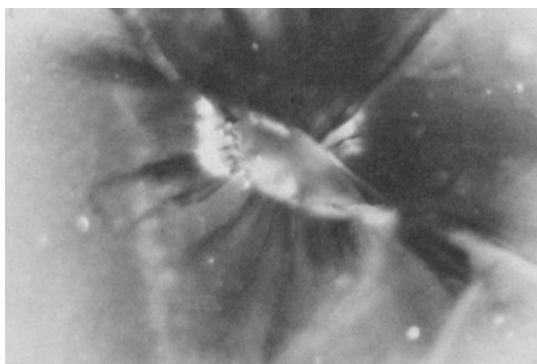
The following observations may be derived with respect to the results in Figures 3 and 4 and in Table III: The pretreatment ϵ' values are reasonably unaffected by either the resin composition or the measurement frequency, while $\tan \delta$, which also seems to be independent of the bromine concentration, increases sharply at high frequencies for every resin composition. A short water-boil



(a)



(b)



(c)

Fig. 2. Holes resulting from dielectric breakdown through untreated styrene-crosslinked resin (a) and through water-boil-treated (12 hr) bromostyrene- (b) and styrene-crosslinked (c) resins.

treatment results in small increases in the values of ϵ' and $\tan \delta$, which remain independent of the bromine content. After such a short treatment, ϵ' still remains independent of the frequency, but $\tan \delta$ exhibits a new trend with a maximum in the frequency range of 9–11 GHz, where $\tan \delta$ is higher than the original values. At frequency ranges of 8–9 and 11–12 GHz, $\tan \delta$ exhibits values which are generally below those of the unboiled resin. After a long water-boil

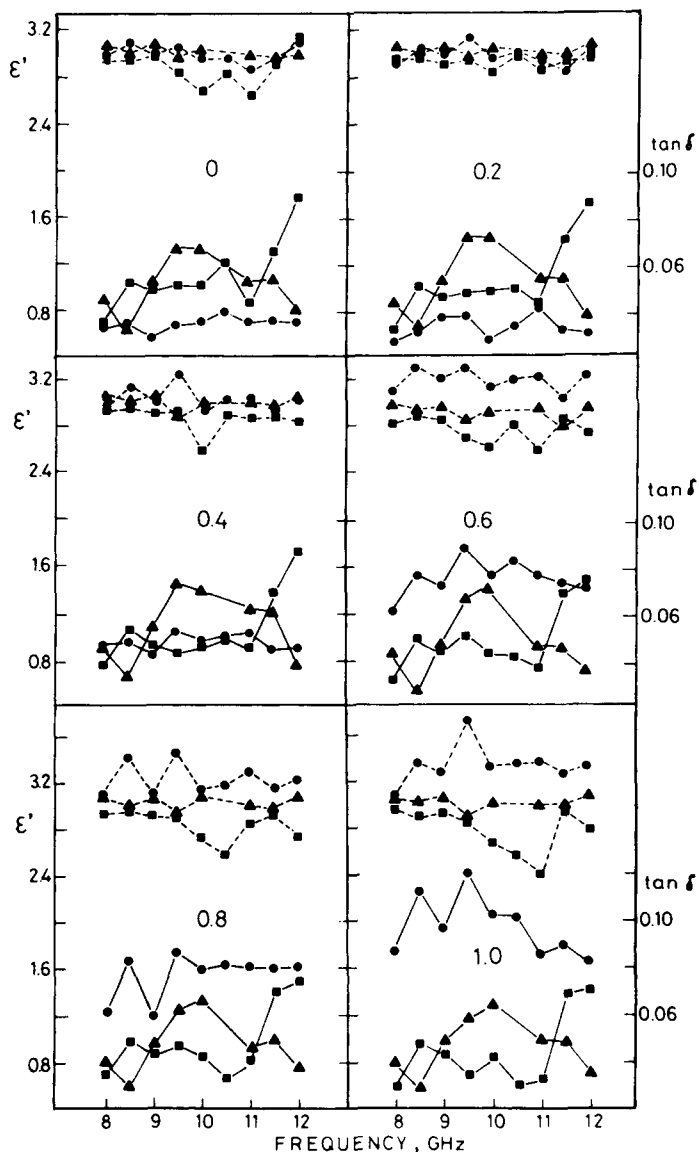


Fig. 3. Results of ϵ' (---) and $\tan \delta$ (—) as a function of frequency for untreated (■), 12 hr-treated (▲), and 107 hr-treated (●) specimens. The numbers 0, 0.2, ..., 1.0 describe the bromostyrene mole fraction.

treatment, values of ϵ' become higher than the pretreatment values, and they exhibit an increase directly proportional to the bromine content. $\tan \delta$ also exhibits such a trend as a function of the bromine concentration; however, the posttreatment values are smaller than the pretreatment values at the small bromine concentrations and become higher at larger concentrations. In GRP, ϵ' is about 25% higher than the corresponding value of the pure resin, while $\tan \delta$ seems to be unaffected by the presence of the glass cloth.

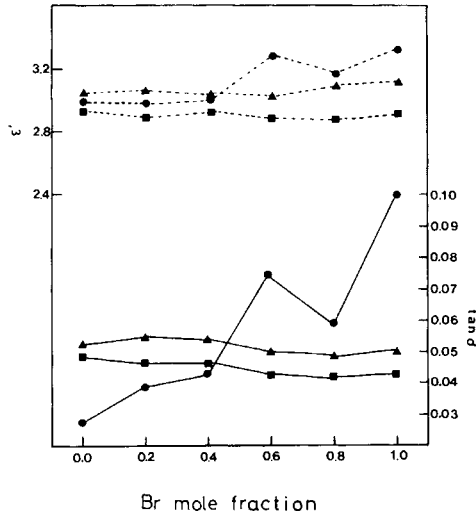


Fig. 4. Trends of ϵ' and $\tan \delta$ as a function of Br content at 9 GHz, for untreated (■), 12 hr-treated (▲), and 107 hr-treated (●) specimens.

DISCUSSION

Resistivity and Dielectric Strength

The mechanism of the electrical conductivity in thermoset polymers is probably based on ion diffusion.^{5,6} Electrical conductivity by this mechanism depends more on the structure of the material and on the presence of impurities, and less on its composition (viz., bromine concentration). The resistivities found in the present study are one to two orders of magnitude higher than those given by Learmonth^{7,8} for similar polyesters without bromine. This difference probably results from the fact that their polyesters were cured by a catalyst-accelerator system which introduces ionic impurities into the cured resin.

The resistivity of the GRP depends on the resistivity of the components which are of the same order. The lower values measured here of the GRP compared with the pure polyesters may result from additional impurities—the source of which may be the coupling agent.

The observations that the dielectric strengths of the polyesters are similar irrespective of bromine concentration and that the values of the GRP are higher suggest that these values do not depend on the resin composition and that they improve with increasing mechanical strength. Thus, it is reasonable to assume that from the possible mechanisms of dielectric breakdown,⁹ the thermal breakdown, which does not depend on the composition, and the mechanical breakdown, which depends on the mechanical strength, are active in these materials.

The water-boil treatment results in shortening the polymeric chains through hydrolysis¹⁰ and in the formation of H^+ and Br^- ions. The presence in the resin of these ions is thought to be responsible for the observed reduction in the resistivity and dielectric strength. The resistivities and the dielectric strengths of the posttreatment resins seem to be independent of the bromine concentration, although this factor determines the extent of cracking. However, since the

TABLE III
Dielectric Constants and Loss Tangents of the GRP

Bromostyrene of total monomer, mole fraction	8 GHz ^a		9 GHz		10 GHz		11 GHz		12 GHz	
	ϵ'	$\tan \delta$	ϵ'	$\tan \delta$	ϵ'	$\tan \delta$	ϵ'	$\tan \delta$	ϵ'	$\tan \delta$
0	3.892	0.036	4.136	0.032	4.096	0.049	4.132	0.040	4.092	0.030
0.2	3.924	0.034	4.125	0.030	4.109	0.053	4.153	0.042	4.020	0.030
0.6	3.979	0.033	4.231	0.027	4.220	0.052	4.201	0.043	4.183	0.031
0.8	4.170	0.037	4.287	0.030	4.288	0.054	4.275	0.039	4.199	0.032

^aMeasurement frequency.

breakdown occurs through a crack (Fig. 2), it is plausible that after a longer boiling period the values of the styrene-crosslinked polyester will drop below those of the bromostyrene-crosslinked resin owing to the more extensive cracking of the former.

Dielectric Constant and Loss Tangent

Although the addition of bromine to the polyester resin increases its polarity, the dielectric constant remains unaffected, probably because of the rigid cross-linked structure. The differences in the values of ϵ' and $\tan \delta$ between resins with various bromine concentrations become apparent after the water-boil treatment due to multiple factors: such a treatment, on the one hand, results in hydrolysis of some of the ester bonds of the resin, thus increasing the polarity through the formation of new hydroxylic and carboxylic groups;¹⁰ also, the shortening of the polymeric chains probably enables a more free movement of polar groups, and since more of these groups are present in the bromine containing resins, they will tend to exhibit a higher increase in ϵ' and $\tan \delta$. On the other hand, the water-boil treatment yields cracking of the resin, and this cracking is expected to induce an intense decrease in ϵ' and $\tan \delta$ owing to a drop in the resin density, formation of voids, and the introduction of air into the cracks. Since the presence of bromine retards cracking, the decrease in ϵ' and $\tan \delta$ is more moderate in bromine-containing polyesters. This is also shown by the fact that in resins with no bromine or with low bromine contents, where relatively fewer polar groups might become mobile due to hydrolysis, the posttreatment value of $\tan \delta$ is even lower than the original one.

The dielectric constant of the GRP is expected to be assessed by a rule of mixtures for a case where the electric field is parallel to the plane of the glass cloth layers. The appropriate rule of mixtures in this case is

$$\epsilon'_c = \epsilon'_m V_m + \epsilon'_f V_f$$

where V denotes volume fraction and the subscripts m and f denote fiber and matrix, respectively.¹¹ Taking $\epsilon'_f = 6.13$ (as measured in 9.375 GHz)¹², then ϵ'_c for the styrene and for the 0.8 mole fraction bromostyrene-crosslinked GRP are 4.23 and 4.30, respectively, which is in very good agreement with the experimental values. It is important to note that the more general rule of mixtures,¹² i.e.,

$$\epsilon'_c = \epsilon'_f V_f \times \epsilon'_m V_m$$

gives less satisfactory results, possibly because it is applicable to particulate or to three-dimensional composites.

CONCLUSIONS

The addition of aromatic bromine to polyester resin does not bear any significant effect on the electrical and dielectrical properties of the resin. The fact that the presence of bromine improves high-temperature humidity resistance suggests that bromostyrene-crosslinked polyester would electrically perform better after prolonged exposure to similar conditions.

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