

Tetrabromophthalic Anhydride in Self-Extinguishing Polyesters

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Synopsis

Polyesters based on tetrabromophthalic anhydride are self-extinguishing in the range of 8–12% bromine content and nonburning at higher levels of the latter. An increase in bromine content results in higher flexural and tensile strength and flexural modulus, while impact resistance is slightly reduced. Mechanical properties vary with bromine content in the 0–12% range and remain practically unaffected at higher levels up to 23%.

Introduction

Self-extinguishing polyester resins were recently reviewed by Nametz,¹ who summarized the various possibilities for imparting fire-retardant properties to polyesters by means of halogen-based admixtures and at the same time criticized the conventional testing methods used for characterizing the burning properties of plastics. The considerable potentialities of tetrabromophthalic anhydride, in view of its high bromine content (69%), were also mentioned. According to Nametz, difficulties in the esterification stage in systems containing tetrabromophthalic anhydride were due to the sulfuric acid residue in the commercial material and could be overcome by addition of salts such as sodium acetate in appropriate amounts. Use of tetrabromophthalic anhydride resulted in higher rates of esterification, and laminates based on these polymers were superior to those containing chlorine at the same halogen weight content.

It is known that the minimum amount of the admixture required for ensuring sufficient fire retardancy often results in poorer mechanical properties.¹ In the case of halogenated saturated dicarboxylic acids, this may be due to the large amount required, as a result of which part of the unsaturated acid may have to be replaced and leave too few double bonds available for crosslinking. Fire retardancy imparted by adding chlorinated paraffins is also often associated with poorer mechanical properties.

The present work was undertaken with a view to studying the dependence of mechanical properties on the concentration of tetrabromophthalic anhydride and the burning properties of polyesters based on it.

Experimental

Polyesters with varying tetrabromophthalic anhydride content were prepared (by use of a product of Michigan Chemical Corporation) and

analyzed by well known techniques.²⁻⁴ Esterification time was about 6 hr, with the reaction temperature maintained at 200–220°C over most of the reaction. Water was removed with the aid of a Dean and Stark trap. An inert environment was provided by bubbling nitrogen through the reaction medium. Sodium acetate was added in an equivalent amount to the content of residual sulfuric acid. Most of the reaction media became slightly yellow, and in a few cases (involving heavy discoloration) the end products after casting had poor mechanical properties.

After adding 30% styrene (in the styrenated resin) the polyester was cured by using the system cobalt naphthenate–methyl ethyl ketone peroxide.³ Curing conditions were 35°C for 24 hr, followed by 65°C for 4 hr. Aluminum molds enclosed between glass plates were used for casting.

TABLE I
Formulations for Esterification

Br in styrenated resin, %	Phthalic anhydride, mole	Tetra-bromo-phthalic anhydride, mole	Maleic anhydride, mole	Diethyl-ene glycol, mole	Propyl-ene glycol, mole	Acid number	Burning properties (D635) ^a
0.0	0.78	0.0	1.05	1.0	1.0	38	B
2.1	0.74	0.035	1.05	1.0	1.0	49	B
4.1	0.71	0.07	1.05	1.0	1.0	41	B
7.9	0.63	0.15	1.05	1.0	1.0	38	B
11.2	0.57	0.21	1.05	1.0	1.0	45	—
12.0	0.55	0.24	1.05	1.0	1.0	43	SE
15.0	0.47	0.31	1.05	1.0	1.0	49	NB
18.7	0.38	0.40	1.05	1.0	1.0	51	NB
22.9	0.24	0.54	1.05	1.0	1.0	46	NB

^a B = burns; SE = self-extinguishing; NB = nonburning.

Flexural and tensile properties were determined according to ASTM D790–63 and D638–49, respectively. (Flexural strength and modulus were also measured on glass–polyester laminates.) Unnotched cylindrical specimens (7.25 mm in diameter and 50 mm in length) were cast in glass tubes, and their impact resistance was measured by the Charpy method.

Viscosity measurements were taken in a cone-and-plate viscometer at 30°C and shear rates of 305 and 1525 sec⁻¹.

Resistance to burning was measured according to ASTM D635.*

Glass–polyester laminates were prepared by using ten plies of glass fabric. The above mentioned curing system and curing conditions were used for the preparation of laminates.

* This method is normally prescribed for preliminary screening only, but was used in this case also for preliminary determination of the burning rates, instead of D757.

Results

Table I summarizes the formulations for esterification and the resin acid number obtained.

As is seen, a constant level of double bonds was maintained by using a constant molar concentration of maleic anhydride. Glycols were added in

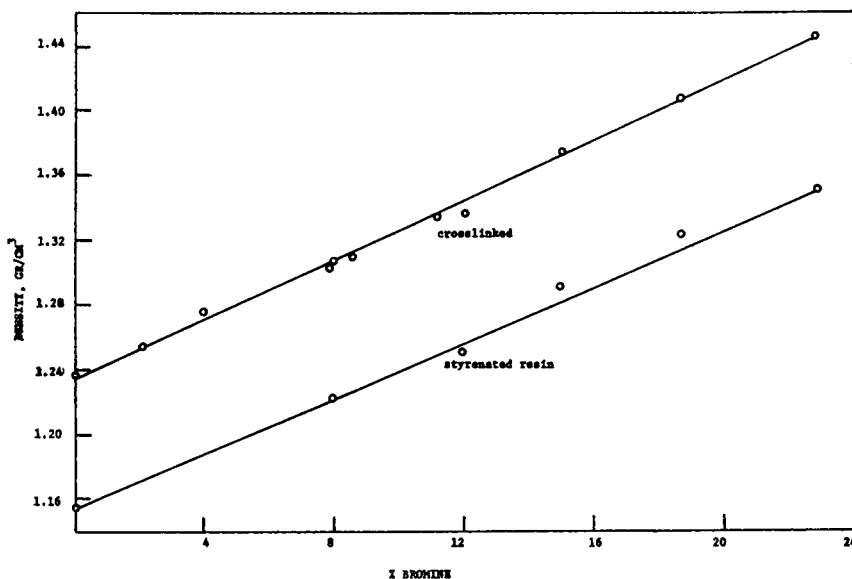


Fig. 1. Dependence of density of styrenated resins and crosslinked polyesters on bromine content.

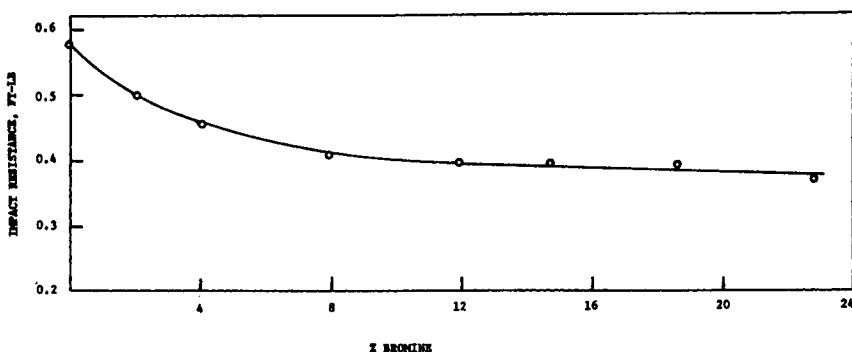


Fig. 2. Dependence of impact resistance on bromine content.

10% mole excess over the acids. The total molar concentration of saturated acids was kept constant, with the ratio of tetrabromophthalic to phthalic anhydride varying within it.

The various parameters studied are plotted against bromine content in Figures 1-5.

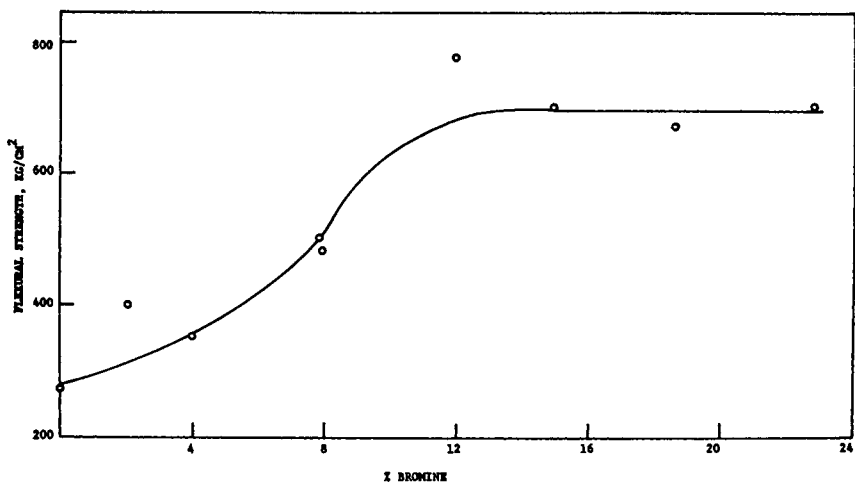


Fig. 3. Dependence of flexural strength on bromine content.

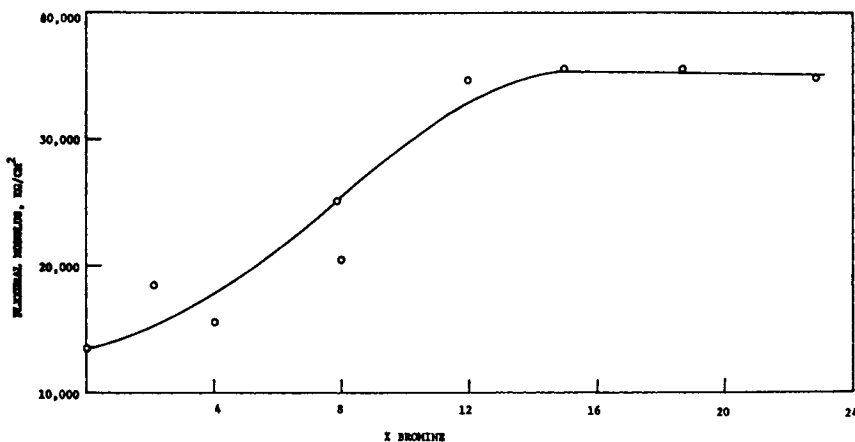


Fig. 4. Dependence of flexural modulus on bromine content.

The density of the styrenated resin before and after curing is shown in Figure 1. Both curves have an upward slope due to the heavy bromine atoms, and the volumetric shrinkage due to crosslinking is about 7%.

Impact resistance is shown in Figure 2. A decrease of about 30% is found up to 10% bromine, with practically no further change at higher levels.

Flexural strength and modulus are shown in Figures 3 and 4, respectively. After an initial increase in both parameters (276 to about 705 kg/cm², 13,000 to 35,000 kg/cm², respectively) for 0 to 12% bromine content, both similarly remain unchanged at higher levels. Results for glass-polyester laminates are summarized in Table II, showing an increase in flexural parameters with increasing bromine content.

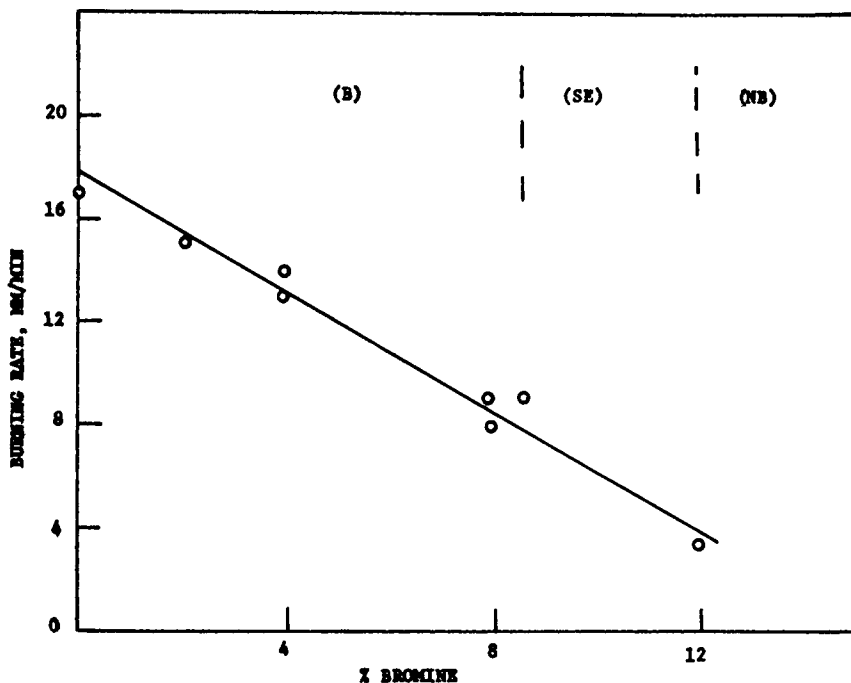


Fig. 5. Dependence of burning rate on bromine content.

Only a few samples were analyzed for tensile properties, due to difficulties in obtaining perfect dumbbells by direct casting. Qualitatively, the trend is similar to that found for the flexural properties (including the plateau above the 12% level), except that in this case increase with bromine content is much slower. (Tensile strengths of 538 and 626 kg/cm² were found for 0 and 8% bromine content, respectively.)

Viscometric analysis showed Newtonian behavior, with viscosities of 6 to 10 poise. No correlation was found between viscosity and bromine content.

Burning rates are plotted in Figure 5. Classification according to ASTM D635 is given in Table I, which shows that the 0-8% bromine

TABLE II
Flexural Properties of Laminates

Bromine in styrenated resin, %	Glass content, %	Burning properties (D635) ^a	Flexural strength, kg/cm ²	Flexural modulus, kg/cm ²
8.6	45.0	NB	2260	102,000
12.0	52.0	NB	2570	131,000
15.0	51.0	NB	2760	124,000
18.7	46.0	NB	3290	135,000

^a See Table I.

range comes within the "burning" (B), 8–12% within the "self-extinguishing" (SE), and above 12% within the "non burning" (NB) category. The values shown in Figure 5 are not significantly different from Nametz's results obtained by the D757 method and given in Table 7 of his review.¹ Table II shows that glass-polyester laminates are classified as nonburning at lower bromine contents.

To sum up, it was shown that the mechanical properties of polyester resin based on tetrabromophthalic anhydride vary only over the 0 to 12% range above which level the resins may be classified as nonburning according to ASTM D635.

References

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