Synthesis and Characterization of Brominated Polyester Composites

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ABSTRACT: Two unsaturated polyesters containing a halogen (bromine) in the backbone of the polymer chain were synthesized and compared with a halogen-free polyester. The bromine content was measured by elemental analysis. The chemical structures of the polyesters were characterized by means of IR and ¹H-NMR spectroscopies. Feldspar was used as the filler to form the polyester composites. The effects of the halogen substituents, filler concentration, and crosslinking monomers and comonomers

on the electrical and mechanical properties of the polyester composites were studied. The flammability was also investigated. The styrenated polyesters and their composites achieved fire resistance and good mechanical and electrical properties. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 1356–1365, 2006

Key words: composites; crosslinking; dielectric properties; flame retardance; halogenated

INTRODUCTION

Advances in polymer science over the past 50 years have led to the introduction of a large number of polymers with different properties and applications in industry and domestic market. These kinds of materials can catch fire very easily and keep burning to propagate the flame so that a large amount of toxic gas and heavy smoke are generated. Therefore, in recent years, the development of polymer flame-retardant technology has been very important.^{1–5}

Unsaturated polyesters are widely used in the composite industry.⁶⁻⁸ They can provide excellent mechanical, electrical, and chemical properties and good chemical and weather resistance.8 Further advantages of unsaturated polyester resins over other thermosetting resins are that they are easy to handle, can be pigmented, and can be easily filled and fiber-reinforced in a liquid form. However, the major drawback of unsaturated polyester resins are their flammability and the large amount of smoke generated when they burn. The high flammability of any polymeric system presents a considerable hazard; for example, a general purpose polyester resin containing styrene has a limiting oxygen index (LOI) value of 19. This means that the resin will burn readily in an atmosphere containing 19% oxygen or more. Many methods have been used to combat this.9-11 Two common methods used

to make unsaturated polyesters flame retardant and safe for use in many applications are (1) the introduction of a halogen into the polyester structure and (2) the blending of flame-retardant materials with the unsaturated polyester resin.

The presence of a halogen in the polymer system in place of traditional resins greatly increases the fire retardancy of materials.^{12–16} The halogen may be put either as separate polyhalogenated compounds, such as a halogenated wax, or as a reactive halogenated monomer in the producing polymer. For example, vinyl chloride in making poly(vinyl chloride) and tetrabromophthalic anhydride is used in polyester resin synthesis.

Halogens are very effective in capturing free radicals and, hence, removing the capability of the flame propagate. All halogen atoms are effective in eliminating free radicals, and the trapping efficiency increases with the size of the halogen atom (i.e., I > Br > Cl >F). Therefore, all organohalogen compounds could be good forms for the storage and delivery of halogens to be used as flame retardants.^{17,18} Bromine is the major component of flame-retardant materials^{9,10} because there is no particular restriction on the structure of the backbone and the decomposition products are less volatile at high temperatures. Various fillers,^{19–22} such as silica, clay, and feld-

Various fillers,^{19–22} such as silica, clay, and feldspar, are used to reduce the cost, shrinkage, and cracking and to modify the physical properties and appearance of the polymers. Feldspar is an abundant group of rock-forming minerals that constitutes 60% of the earth's crust. It is a very useful industrial mineral,²³ which finds applications in glass-making,

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Glycol	Unsaturated anhydride	Other dibasic anhydride and acid	Polyester
Neopentyl glycol	Maleic anhydride	Phthalic anhydride and succinic acid	PE I
Neopentyl glycol	Maleic anhydride	Phthalic anhydride and dibromosuccinic acid	PE II
Neopentyl glycol	Maleic anhydride	Tetabromophthalic anhydride and succinic acid	PE III

TABLE I Monomers Used to Form the Polyesters

including containers and insulation for housing and building construction, plumbing fixtures, tile, and pottery. It can be replaced in some of its end uses by clays, electric furnace slag, feldspar–silica mixtures, or talc.

Halogenated polyester thermosets were chosen as suitable polymers for this study as their synthesis allows for the facile incorporation of different bromine contents as an integral part of their structure, and they were commercial products. In this investigation, the effects of bromine content, filler content, and type of crosslinking monomer on the physical, mechanical, and electrical properties of polyester composites were studied. LOI and flammability properties were also investigated.

EXPERIMENTAL

Materials

Neopentyl glycol, maleic anhydride, phthalic anhydride, succinic acid, dibromosuccinic acid, and tetrabromophthalic anhydride were obtained from Merck (Darmstadt, Germany). Styrene, methyl methacrylate (MMA), and acrylonitrile (AN) were also obtained from Merck and were used without further purification.

Fine-grade (0.1 mm, 100 mesh) red feldspar was obtained from El Nasr Phosphate Co. (Cairo, Egypt) with the following specifications: loss on ignition = 0.35%, SiO₂ = 64.98%, Al₂O₃ = 18%, Fe₂O₃ = 0.2%, CaO = 0.15%, MgO = 0.02%, TiO₂ = 0.1%, K₂O = 12.61%, and Na₂O = 2.50%.

Polyester prepolymer synthesis

The unsaturated polyester [polyester I (PE I)] was synthesized with a 2.2:0.5:0.5:1 molar ratio of neopentyl glycol, succinic acid, phthalic anhydride, and maleic anhydride, respectively, with a one-step melt condensation technique. The halogenated resins were prepared by the same method with the substitution of succinic acid by dibromosuccinic acid [polyester II (PE II)] and phthalic anhydride by tetrabromophthalic anhydride [polyester III (PE III)]. The mixtures were stirred under a continuous nitrogen flow for 6 h, and the temperature was increased from 150°C at the beginning of the reaction to 200°C at the end. Samples for end-group titration were collected every hour to monitor the progress of the reaction. The monomers used to form the unsaturated polyesters, along with the polyester codes, are shown in Table I.

Crosslinking of the prepared unsaturated polyesters

The resins were crosslinked with 30 wt % styrene monomer and a styrene mixture with MMA or AN in the ratios of 2 : 1 by weight with methyl ethyl ketone peroxide as the initiator (1.5% w/w) and cobalt naphthenate as the accelerator (0.5% w/w). Curing occurred after the mixtures were left at room temperature overnight followed by 2 h at 80°C in a thermostated oven. Samples from the cured product were prepared with appropriate molds for different testing. The coding of the samples is given in Table II.

Polymeric composites

Polymer composites were prepared by the mixture of different ratios of feldspar filler (60, 70, and 80%) with the polyester resin I/styrene (SS) or comonomers, styrene/methyl methacrylate mixture (SM), or styrene/acrylonitrile monomers mixture (SA). Curing occurred under the same conditions.

Techniques

IR spectra were recorded on a Jasco FT/IR 300 E Fourier transform infrared spectrometer (Tokyo, Japan). The nuclear magnetic resonance (¹H-NMR) spectrum was run at 260 MCPS on a Jeol Ex-270 NMR spectrometer (Tokyo, Japan).

Molecular weight determination was done by gel permeation chromatography. Gel permeation chro-

TABLE II Sample Codes

	•	
Code	Type of monomers	Type of polyester
SS	Styrene	PE I
SM	Styrene/MMA	
SA	Styrene/AN	
DS	Styrene	PE II
DM	Styrene/MMA	
DA	Styrene/AN	
TS	Styrene	PE III
ТМ	Styrene/MMA	
TA	Styrene/AN	

 TABLE III

 Physical Properties of the Prepared Polyester Resins

Property	PE I	PE II	PE III
Appearance	Pale yellow	Pale brown	Dark yellow
Specific gravity			-
at 20°C	1.2	1.3	1.5
Acid value			
(mg of KOH/g)	28	40	42
M_n	4,579	5,691	8,180
M_w	7 <i>,</i> 532	6,976	12,588
M_w/M_n	1.6	1.2	1.5
Bromine content (%)	0	17.27	33.98
Monomer content in			
resin (wt %)	30	30	30

matography was carried out with an Agilent Technologies (Walden Bornn, Germany) 1100 series instrument equipped with three Styragel columns $(10^2, 10^4, \text{ and } 10^5 \text{ Å})$ and a refractive index detector (Agilent G 1362). Tetrahydrofuran was used as the eluent with a flow rate of 1 mL/min. The columns were calibrated by means of polystyrene (an internal standard was used).

Bromine content was calculated with an elemental analysis method with a Vario-El (Hanau, Germany) elemental analyzer.

Apparent porosity and water absorption were calculated according to ANSI/ASTM C20-74.

The oxygen index (OI) measured by a LOI tester according to the ASTM D 2863-77 with ONI flammability (model Cs-178-B).

Compressive measurements were carried out according to ASTM D 695 with an Instron universal testing instrument (model 1178) (Norwood, MA) on cylindrical rods 2.5 cm long and 1.3 cm in diameter.

Dielectric measurements were carried out in the frequency range 100 Hz to 100 kHz with an LCR meter type AG-411 B (Ando Electric, Ltd., Tokyo, Japan). The capacitance, loss tangent, and resistance were obtained directly from the bridge from which the permittivity (ε'), dielectric loss (ε''), and direct-current conductivity (σ) were calculated. A guard ring capacitor type NFM/5T (Wiss Tech Werkstatten GMBH, Weilheim, Germany) was used as a measuring cell. The cell was calibrated with standard materials,²⁴ and the experimental error in ε' and ε'' was ± 3 and $\pm 5\%$, respectively. The temperature was controlled with an ultrathermostat. The experimental error in temperature controlling was 0.1° C.

RESULTS AND DISCUSSION

Characterization of the prepared polyesters

The polyesters under investigation were soluble in common organic solvents, such as chloroform, acetone, and tetrahydrofuran, at room temperature. The good solubility characteristics of the polymers were mainly attributed to the bulkiness of the bromine atom.²⁵ The solubility of the prepared polyesters increased in the order PE I < PE II < PE III. Various physical properties in addition to the number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersities (M_w/M_n 's) of the prepared polyester resins were determined and are listed in Table III.

The bromine contents for PE II and PE III were 17.27 and 33.98%, respectively.

The chemical structure of the prepared polyesters was characterized by means of Fourier transform infrared and NMR spectroscopies.

The IR spectra of the polyesters illustrated typical ester absorption characteristics and are shown in Figure 1. Strong C=O stretching absorptions occurred around 1725 cm⁻¹, and strong, broad C-O-C stretching vibrations appeared in the range from 1300 to 1000 cm⁻¹. The carbonyl frequency was somewhat greater for those polymers that had halogen substituents. It is known that these polar substituents can influence the stretching vibrational frequency of the C=O in both alkyl and aryl compounds.²⁶ In addition, PE II and PE III, containing halogen atoms, exhibited a strong vibration at 1040 and 1168 cm⁻¹, which could be assigned to the aryl and alkyl (C–Br) halide vibrations.



Figure 1 IR spectrum of the prepared polyester resins (PE I, PE II, and PE III).

Figure 2 shows the ¹H-NMR spectra of the prepared polyester resins. The spectrum showed an intense signal at δ 1.0 assigned to the methyl protons of the glycol parts. A group of signals appeared between δ 2.7 and 4.3, which seemed to be due to the methylene protons in aliphatic acid and glycol residue. The unsymmetrical signals at δ 6.2 and 6.8 seemed to be two ill-defined doublets for the olefinic protons in maleic and fumaric acid residues. The three polyester resins displayed almost identical proton spectra except for PE III. The signals at δ = 7.7 ppm of the four aromatic protons disappeared, which indicated the incorporation of the tetrabromophthalic



Figure 2 NMR spectrum of the prepared polyester resins (PE I, PE II, and PE III).

anhydride instead of phthalic anhydride in the PE III backbone.

Electrical properties

 ε' and ε'' of the prepared PE I samples cured with the three crosslinking monomers (SS, SM, and SA) with and without feldspar filler with different loadings were studied at different frequencies (100 Hz to 100 kHz) and at temperatures ranging from 30 to 70°C.

Figure 3 shows the variation of ε' and ε'' with the applied frequency for SS filled with 60, 70, and 80 wt % feldspar at 30 and 70°C. As shown in Figure 3, the values of ε' decreased with increasing applied frequency, showing an anomalous dispersion. In such range, ε' had a contribution from orientation polarization.²⁷ However, as the filler addition increased, a pronounced increase in ε' was obtained, whereas slight increase was noticed at the highest feldspar concentration. Also, ε' increased with increasing temperature. The increase in ε' with the addition of feldspar may have been due to the presence of polar groups in that filler. As the filler loading increased, the density of the system also increased, and the extent of orientation of dipoles was retarded; thus, ε' showed a slight increase at this concentration.

Figure 4 represents the variation of ε' and ε'' for the crosslinking PE I (SS, SM, and SA) and its composites versus the filler content at different temperatures and at a fixed frequency (f = 100 Hz). As shown in Figure 4, a pronounced increase in ε' and ε'' occurred with increasing temperature for all of the polyester composites.

Also, both ε' and ε'' increased in the order SS < SM < SA. This result seemed to be logical, as the dipole moments at 20°C in dilute carbon tetrachloride solution for styrene = 0.156 D,²⁸ MMA = 1.77 D,²⁸ and AN = 3.43 D,²⁹ respectively. The same trend was also observed when the temperature was increased. This increase was much more pronounced for the SA system due to the higher polarity of the system.

The absorption curves relating ε'' and the applied frequency shown in Figure 3 indicated that more than one relaxation mechanism was present. Also, the higher values of ε'' in the lower frequency range indicated the presence of σ . In addition to σ ,³⁰ analysis of the absorption curves was done in terms of superposition of two Fröhlich and one Havriliak–Negami functions according to an equation given elsewhere.³¹

An example of the analyses are given in Figure 5. The result of the analyses revealed three distinct absorption regions. A low-frequency region was fitted with the Fröhlich function³¹ with distribution parameter of 3, which was detected with the first relaxation time (τ_1) in the range of 5–6.5 × 10⁻⁴ s. This region was unaffected by either temperature or filler content. This region could be attributed to the



Figure 3 ϵ' and ϵ'' of SS filled with $(\diamondsuit) 0$, $(\Box) 60$, $(\bigtriangleup) 70$, and $(\times) 80$ wt % of feldspar.

Maxwell-Wagner effect,³² which was expected to be at a lower frequency range due to the multiconstituents of the investigated systems. The second absorption region with relaxation time (τ) in the order of 10^{-5} s, which was fitted by the Havriliak–Negami function with distribution parameters $\alpha = 0.35$ and $\beta = 0.7$, was attributed to the orientation of the large aggregates caused by the movement of the main chain, which were expected to be formed by the addition of different ingredients (crosslinking monomer, initiator, and accelerator). The third process with τ in the order of 10^{-7} s with the maximum frequency out of the available frequency range could be attributed to those for the smaller aggregates. Because of the uncertainty in this process, we concentrate our dissuasion on the second process.

The obtained τ 's associated with the second relaxation process, its relaxation strength (S_2), and σ are listed in Table IV for all of the investigated systems at different temperatures.

As shown in Table IV, the values of ε' and ε'' increased in the order SS < SM < SA, but they were still in the insulating range.³³ This would allow one to use these composites in insulating and antistatic applications, as the range of σ for such applications is 10^{-9} to $10^{-14} \Omega^{-1} \text{ cm}^{-1}$.³³ Also, σ increased with both increasing filler content and increasing temperature for all of the investigated composites. The data listed in Table IV indicated that the second relaxa-

tion time (τ_2) given in the case of SS was higher than that for both SM and SA. The steric hindrance due to the presence of phenyl ring in the side group of styrene may have been the reason for such an increase in SS. Figure 6 represents the variation of both σ and τ_2 versus filler content at 30°C for all of the systems (SS, SM, and SA). From this figure, it is clear that σ increased with increasing filler content. This increase was much more pronounced above 60 wt % feldspar content.

Also, the values of τ_2 increased above 60% feldspar for the three systems. This increase indicates some sort of interaction between the filler and the polymer matrix. This interaction may have increased the molecular volume of the rotating units and, consequently, increased τ . In general, the best results were obtained for PE I composites containing 70 wt % feldspar. For this reason, this concentration was used with PE II and PE III to prepare the composite samples.

 ε' and ε'' of PE II and PE III containing different bromine contents with different crosslinking monomers without filler and those loaded with 70 wt % feldspar were measured in the same way as mentioned previously. An example of these measurements is illustrated graphically in Figure 7 for the DS samples at different temperatures with and without feldspar.

Figure 8 represents the variation of ε' and ε'' versus temperature at f = 100 Hz for PE II and PE III with and without filler. It is clear that both values



Figure 4 Relation between ε' and ε'' of PE I composites at f = 100 Hz versus filler content at different temperatures: (\bigcirc) 30, (\square) 50, and (\triangle) 70°C.

increased with increasing temperature. Also, both values were higher for samples loaded with feldspar than those free from filler.

The obtained data for ε'' were analyzed in the same way discussed before and as given in Tables V and VI. It was concluded from these tables that

- τ of the crosslinking polyester samples increased with the incorporation of bromine in the PE II and PE III backbones when compared with those free from halogen.
- τ of the polyester composites increased with the addition of 70 wt % feldspar filler, which indicated some sort of interaction between the filler and the polyester matrix, which increased the volume of the rotating unit and, consequently, τ.
- τ was higher in PE III than in PE II, which was logical due to the larger size of the tetrabromophthalic anhydride molecule when compared with that of dibromosuccinic anhydride.
- σ of PE III was slightly higher than that of PE II.



Figure 5 Absorption curves of SS filled with 60% feldspar at 30°C. We fit the (\Box) experimental data after subtracting of the (\bigcirc) losses due to σ with two Froehlich terms and a Havriliak Negami function term.

Temperatures				
Filler content	Temperature (°C)	$\sigma imes 10^{12}\ (\Omega^{-1}~{ m cm}^{-1})$	$\tau_2 \times 10^5$ (s)	<i>S</i> ₂
SS				
0	30	4.06	3.20	0.094
	50	7.66	2.72	0.160
	70	10.30	2.05	0.214
60	30	6.06	3.20	0.167
	50	10.70	2.72	0.265
	70	20.81	2.05	0.380
70	30	8.86	5.11	0.249
	50	12.60	4.19	0.314
	70	27.20	3.20	0.453
80	30	11.10	5.60	0.215
	50	12.61	4.50	0.248
	70	21.50	3.40	0.382
SM				
0	30	4.26	2.38	0.174
	50	10.71	1.70	0.249
	70	13.10	1.22	0.328
60	30	9.09	2.38	0.208
	50	21.5	1.70	0.205
	70	27.2	1.22	0.309
70	30	11.10	3.00	0.23
	50	25.0	2.72	0.303
	70	32.20	2.15	0.400
80	30	16.00	5.11	0.255
	50	18.91	4.19	0.299
	70	26.31	3.2	0.48
SA				
0	30	5.86	2.38	0.180
	50	11.80	1.70	0.390
	70	23.80	1.22	0.600
60	30	9.55	3.2	0.229
	50	13.10	2.72	0.272
	70	26.30	2.05	0.354
70	30	13.50	3.66	0.250
	50	14.40	2.80	0.440
	70	30.10	2.40	0.552
80	30	16.50	5.11	0.269
	50	17.11	4.19	0.362
	70	31.11	3.20	0.577

TABLE IV σ , τ_2 , and S_2 for PE I Composites at Different Temperatures

Porosity and water absorption

The apparent porosity and water absorption of the polymeric composites (70%) were low, as is clear from Table VII. These low values suggest that they can prevent the intrusion of water salts that could cause the corrosion of any installation.

LOI

LOI was used for the evaluation of the flame retardation of a material. OI is the minimum concentration of oxygen to maintain a candle-like burning for a testing material under an environment with a slowly rising gas of nitrogen/oxygen mixture. The larger value of LOI is, the harder it is for the material to catch fire and to burn. Generally speaking, for the case of OIs below 21, the material is considered flammable; for OI = 22–25, the material is self-extinguishable; and for the case of OI > 26, the material is hard to burn.¹ Table VIII shows the effect of bromine content and filler on the LOI value of the thermoset polyesters with and without filler.

Clearly, LOI increased as the bromine content increased. As shown in Table VIII, LOI increased for the polyester composites containing 70 wt % feldspar as the filler. This may have been due to the ability of the filler to absorb the heat evolved during burning.

Mechanical properties

A comparative study was done on the three polyester resins (PE I, PE II, and PE III) with different crosslinking monomers, namely, the SS, SM, and SA mixtures, and the corresponding composites loading with 70 wt % feldspar. The compressive strength values were measured for such samples, as illustrated in Figures 9 and 10. Figure 9 shows that higher com-



Figure 6 Relation between σ and τ_2 versus filler content for PE I at 30°C: (\Box) SS, (×) SM, and (\triangle) SA.



Figure 7 ϵ' and ϵ'' of DS at different temperatures [(\bigcirc) 30, (\square) 50, and (\triangle) 70°C] (a) without filler and (b) filled with 70 wt % feldspar.



Figure 8 ϵ' and ϵ'' at 100 Hz versus temperature for PE II, PE III, and their composites: (—) without filler and (- -) composites (70% feldspar); PE II (\Box) DS and (\times) DM and DA; and PE III (\Box) TS and (\times) TM and TA.

σ_{1} , τ_{2} , and S_{2} for FE II Composites at Different Temperatures				
Filler content	Temperature (°C)	$\sigma imes 10^{12}\ (\Omega^{-1}\ \mathrm{cm}^{-1})$	$ au_2 imes 10^5$ (s)	<i>S</i> ₂
DS				
0	30	1.32	4.20	0.059
	50	3.80	3.72	0.064
	70	5.86	3.05	0.086
70	30	5.13	5.60	0.157
	50	5.86	4.50	0.173
	70	7.92	3.40	0.210
DM				
0	30	5.48	3.20	0.090
	50	6.70	2.72	0.111
	70	7.92	2.05	0.177
70	30	6.67	5.60	0.143
	50	6.93	4.50	0.187
	70	9.05	3.40	0.276
DA				
0	30	2.18	4.20	0.093
	50	8.46	3.72	0.111
	70	9.05	3.05	0.204
70	30	6.93	5.60	0.142
	50	7.66	4.50	0.205
	70	9.35	3.40	0.297

TABLE V •.. 10 0

pressive strength values were obtained when a styrene monomer was used as a crosslinking monomer rather than the other styrene comonomer mixtures. In general, as shown in Figures 9 and 10, the compressive strength values increased to different extents for all of the styrenated polyester resins and their composites A maximum value of 200 MPa was obtained for PE III.

TABLE VI σ_{1} , τ_{2} , and S_{2} for PE III Composites at Different Temperatures

Fillor	Tomporaturo	$ \pi \times 10^{12}$		
content	(°C)	$(\Omega^{-1} \text{ cm}^{-1})$	$\tau_2 \times 10^5 \; (s)$	S_2
TS				
0	30	2.60	5.11	0.062
	50	3.93	4.19	0.069
	70	7.66	3.20	0.110
70	30	1.6	7.04	0.100
	50	7.16	5.50	0.200
	70	12.20	3.80	0.320
TM				
0	30	5.67	5.11	0.110
	50	6.93	4.19	0.141
	70	13.10	3.2	0.303
70	30	9.48	7.04	0.180
	50	11.80	5.5	0.220
	70	18.21	3.8	0.370
TA				
0	30	6.35	5.11	0.110
	50	12.12	4.19	0.130
	70	21.50	3.20	0.330
70	30	8.92	7.04	0.200
	50	15.12	5.50	0.260
	70	25.23	3.80	0.390

TABLE VII Porosity and Water Absorption of the Thermoset **Polyesters and Their Composites**

Water absorption (%)		Apparent porosity (%)		
a	b	а	b	Polyester
0.49	0.64	0.60	0.72	PE I
0.4	0.67	0.50	0.75	PE II
0.27	0.68	0.41	0.77	PE III

a = thermoset polyester; b = composite.

The compressive strength values of the cured polyester resins were comparatively higher than the filled polyester composites. This was due the fact that the incorporation of the filler reduced the volume fraction of the matrix.

CONCLUSIONS

Two unsaturated polyesters (PE II and PE III) containing different bromine contents were synthesized, characterized, and compared with the free-halogen PE I. The solubility of these prepared polyesters increased with increasing bromine content. The electrical, mechanical, and flammability properties of the prepared polyester resin samples cured with the three crosslinking monomers (SS, SM, and SA) and loaded with different concentrations of feldspar filler were studied. It Both ϵ' and ϵ'' increased in the order SS < SM < SA and as the concentration of filler increased. The electrical σ was on the order of $10^{-12} \Omega^{-1} \text{ cm}^{-1}$, which suggests that the end product be used in insulating and antistatic applications (with a σ range of 10^{-9} to $10^{-14} \Omega^{-1} \text{ cm}^{-1}$).

The best results were obtained for PE I composites containing 70 wt % feldspar. For this reason, this concentration was used with PE II and PE III to prepare the composite samples.

 τ of the crosslinking polyester samples increased with the incorporation of bromine in the PE II and

TABLE VIII Effect of Bromine Content on the LOI Values of the **Polyester Thermosets and Their Composites**

LOI of the composite	LOI without filler	Sample
30	22	SS
30	22	SM
30	22	SA
32	23	DS
32	23	DM
32	23	DA
34	27	TS
34	27	TM
34	27	TA



Figure 9 Compressive strength values of the crosslinked polyesters.



Figure 10 Compressive strength values of the polyester composites.

PE III backbones when compared with those free from halogen. The LOI values of the thermoset polyesters with and without filler were higher for higher bromine content. The compressive strength values increased to different extents for all styrenated polyester resins and their composites.

References

- 1. Chiu, H.-T.; Chui, S.-H.; Jeng, R.-E.; Chung, J.-S. Polym Degrad Stab 2000, 70, 505.
- Atkinson (nee Moth), P. A.; Haines, P. J.; Skinner, G. A. Thermochim Acta 2000, 360, 29.

- Arias, P. In Proceedings of the Second International Workshop on Brominated Flame Retardants; Stockholm: AB Firmatryck, 2001; p 17.
- 4. Cusack, P. A.; Heer, M. S.; Monk, A. W. Polym Degrad Stab 1991, 32, 177.
- 5. Levchik, S. V.; Weil, E. D. Polym Int 2005, 54, 11.
- 6. Cao, X.; Lee, L. J. Polymer 2003, 44, 1893.
- Evans, S. J.; Haines, P. J.; Skinner, G. A. Thermochim Acta 1996, 278, 77.
- Tsai, S. W.; Hahn, H. T. Composite Design Guide; Center for Composite Materials, University of Delaware, Newark, 1983.
- 9. Haines, P. J.; Lever, T. J.; Skinner, G. A. Thermochim Acta 1982, 59, 1331.
- 10. Alaee, M.; Arias, P.; Sjodin, A.; Bergman, A. Environ Int 2003, 29, 683.
- 11. Cusack, P. A.; Monk, A. W.; Pearce, J. A.; Reynolds, S. J. Fire Mater 1989, 14, 23.
- 12. Cusack, P. A. Fire Mater 1993, 17, 1.
- 13. Cusack, P. A.; Heer, M. S.; Monk, A. W. Polym Degrad Stab 1997, 58, 229.
- 14. Kicko-Walczak, E. Fire Mater 1998, 22, 253.
- 15. Kicko-Walczak, E. J Appl Polym Sci 1999, 74, 379.
- 16. Kicko-Walczak, E. Macromol Symp 2003, 199, 343.
- 17. Lein, T.; Dieter, D. Fire Mater 2004, 28, 403.
- El-Nashar, D. E.; Abd-El-Messieh, S. L.; Eid, M. A. M. Polym Plast Technol Eng 2004, 43, 671.
- 19. Hepburn, D. M.; Kemp, I. J.; Cooper, J. M. Polym Degrad Stab 2000, 70, 245.
- 20. Mansour, S. H. J Elastomers Plast 2000, 32, 248.
- Mansour, S. H.; Abd-El-Messieh, S. L. J Appl Polym Sci 2001, 83, 1167.
- 22. Ikladious, N. E.; Doss, N. L.; Moussa, H. E.; Nassif, J. Polym Plast Technol Eng 1997, 36, 733.
- Kauffman, R. A.; Van Dyk, D. Industrial Minerals and Rocks, 6th ed.; Society for Mining, Metallurgy, and Exploration: Littleton, CO, 1994; p 473.
- 24. Abd-El-Messieh, S. L.; El-Sabbagh, S.; Abadir, F. I. J Appl Polym Sci 1999, 73, 1509.
- 25. Ballauff, M. Angew Chem Int Ed Engl 1989, 28, 253.
- Choi, E.-J.; Hill, D. J. T.; Kim, K. Y.; O'Donnell, J. H.; Pomery, P. J. Polym Adv Technol 1998, 9, 52.
- 27. George, S.; Varughese, K. T.; Thomas, S. J Appl Polym Sci 1999, 73, 255.
- 28. Abd-El-Messieh, S. L. J Mol Liq 1996, 68, 127.
- 29. Abd-El-Messieh, S. L. J Mol Liq 2002, 95, 167.
- 30. Abd-El-Messieh, S. L. Polym Plast Technol Eng 2003, 42, 153.
- Abd-El-Messieh, S. L.; Abd-El-Nour, K. N. J Appl Polym Sci 2003, 88, 1613.
- Abd-El- Messieh, S. L.; Mohamed, M. G.; Mazrouaa, A. M.; Soliman, A. J Appl Polym Sci 2002, 85, 271.
- 33. Huang, J.-C. Adv Polym Technol 2002, 21, 299.