

Flame-Retardant Poly(ethylene Terephthalate)*

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Synopsis

Poly(ethylene terephthalate) containing hexabromobenzene, tricresyl phosphate, or a combination of triphenyl phosphate and hexabromobenzene, pentabromotoluene, or octabromobiphenyl was extruded or spun at 280°C into monofilaments or low-denier yarn, respectively. Only combinations of the phosphorus- and halogen-containing compounds resulted in flame-retardant poly(ethylene terephthalate) systems, without depreciating their degree of luster and color quality. The melting temperature, the reduced viscosity, and the thermal stability above 400°C of these flame-retardant systems were in most cases comparable to those of poly(ethylene terephthalate) itself. Phosphorus-bromine synergism was proposed with flame inhibition occurring mostly in the gas phase.

INTRODUCTION

Recent studies of the flame retardation of polyesters including poly(ethylene terephthalate) (PET) have been the subject of many reports¹⁻²⁵ and reviews.²⁶⁻³² Halogen and/or phosphorus compounds were the most commonly claimed flame retardants.¹⁻¹⁴ Combinations of halogen compounds with oxides of Sb, Sn, Fe, Zn, Cu, and Ti were also described as flame retardants for polyesters.¹⁵⁻¹⁷ Other specific flame retardants included: (a) combinations of nylon 6 and triphenyl phosphine²¹; (b) tetrabromophthalic anhydride with or without Sb_2O_3 ²²; and (c) zinc borate and hydrated alumina (for partially chlorinated polyesters).²⁴ Most of the systems which were claimed in the literature as flame-retardant additives for polyesters cannot be used for direct spinning of flame retarded PET fibers or monofilaments. These flame retardants were not suitable for incorporation in the polymer melt at 280°C since they did not meet the following general criteria: (a) thermal stability; (b) small particle size; (c) causing no degradation or crosslinking; and (d) producing no undesirable side effects such as discoloration, unsatisfactory dyeability, loss of luster, and nonpermanency under normal end-use conditions. In this communication, examples of flame retardants for PET satisfying most of these criteria are reported.³³

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EXPERIMENTAL

Materials

Hexabromobenzene (HBB), triphenyl phosphate (TPP), tricresyl phosphate, pentabromotoluene, and octabromobiphenyl were purchased from Aldrich Chemical Co., Monsanto Corp., Great Lakes Chemical Corp., and Michigan Chemical Corp., respectively.

Analytical Methods

Reduced viscosity (η_{red}) was determined on a polymer solution in a 1:1 mixture of phenol and tetrachloroethylene (0.5 g/100 solvent). A du Pont-900 DTA apparatus was used to obtain the differential thermal analysis (DTA) data, in both air and nitrogen using a heating rate of 20°C/min and about 15 mg of sample. The thermogravimetric analysis (TGA) data in both air and nitrogen were recorded on an Ainsworth balance, using a heating rate of 10°C/min and about 50 mg of sample. The oxygen index test, ASTM D-2863, was used to evaluate the limiting oxygen index (LOI) of molded polymer bars (1/2 in. wide, 5 1/2 in. long, and 1/4 in. thick) or fabric specimens (2 in. × 10 in.) prepared from knitted sleeves and mounted on a U-frame holder. The Department of Commerce flammability standard test, DOC FF-1-70, was used for testing rugs with a pile height of 1 1/2 in. and yarn density about 28 oz/yd².

Polymer Extrusion and Spinning

Prior to extrusion or spinning, the PET powder (35 mesh) was mixed with the flame-retardant additives and tumbled for 0.5 hr at room temperature in a twin-shell blender with a mixer blade. The powder blend was then dried at 95°C under vacuum for 16 hr.

A 3/4-in. Brabender extruder was used for the extrusion of monofilaments (which can also be used for molding bars), and the polymer was extruded at 280°C through a die having a 0.125 in. diameter. In a typical run, 400 g of the polymer was extruded at a rate of 20 g/min, and the extrudate was collected after the first 10 min of extrusion (to allow for 10 min of purging) in preheated (~100°C) brass molds, or air cooled to solid monofilaments.

A spinning head, consisting of a 1-in. extruder and a metering pump with a 14-hole spinnerette (hole diameter = 20 mil) was used to produce the yarn. In a typical run, 170 parts hexabromobenzene, 265 parts triphenyl phosphate, and 5000 parts PET were mixed and dried as described above and then spun at 280°C into 210-denier, 14-filament yarn.

Preparation of Carpets and Knits

In order to prepare cut pile carpets, a construction known in the trade as a cross between the shag and plush, the 210-denier yarn was first plied to form 2100-denier yarn (140 filaments), texturized with a steam jet, and then tufted into the carpet primary backing. After the proper shearing, the

pile height and yarn density of typical carpets were 1 $\frac{1}{2}$ in. and 28 oz/yd², respectively.

A Banner circular knitting machine was used for knitting the 210-denier, 14-filament yarn into sleeves.

RESULTS AND DISCUSSION

The thermal analysis data on the main flame-retardant additives, hexabromobenzene (HBB) and triphenyl phosphate (TPP) (Table I), indicated good thermal stability at the PET processing temperatures. The weight loss values of TPP when heated in air were less than those obtained in nitrogen and are probably related to a concurrent conversion of TPP to a less volatile product in the oxygen atmosphere. Because of its low melting temperature ($T_m = 49^\circ\text{C}$), TPP was present as a liquid, while HBB ($T_m = 325^\circ\text{C}$) probably remained as a solid during the processing of PET at 280°C . However, upon mixing these two compounds in the polar PET matrix, it was likely that the T_m of HBB decreased somewhat in the presence of TPP and underwent substantial deformation and/or partial solubilization during melt spinning or extrusion.

The DTA data on PET extruded at 280°C with HBB and/or TPP (Table II) indicated that these flame retardants had no significant degradative effect on the polymer at that temperature. This is indicated by comparing the reduced viscosities and melting temperatures of the flame-retarded compositions with a PET control sample. Samples IV and XII exhibited somewhat lower viscosity values than the rest of the blends, which could be associated with the relatively high additive concentrations.

The TGA and LOI data of PET samples containing variable concentrations of HBB and TPP (Table III) can be summarized as follows:

1. At $\sim 500^\circ\text{C}$, all samples containing the additives exhibited weight loss values in nitrogen and air which were comparable to those of PET itself.

2. Near the critical decomposition temperature of PET,^{34,35} about 450°C , the data were scattered, and no definite conclusions could be drawn regarding the effect of additives on the polymer's thermal stability. However,

TABLE I
Thermal Analysis Data of Hexabromobenzene and Triphenyl Phosphate

	Hexabromobenzene (HBB)				Triphenyl phosphate (TPP)			
DTA Data								
T_m in nitrogen, $^\circ\text{C}$	325				49			
T_m in air, $^\circ\text{C}$	320				49			
TGA Data								
Temperature, $^\circ\text{C}$	200	300	350	400	200	300	350	400
Wt. loss in nitrogen, %	0	3	19	64	0	8	28	92
Wt. loss in air, %	0	3	16	66	0	6	23	80

TABLE II
Differential Thermal Analysis and Viscosity Data of Poly(ethylene Terephthalate)
Extruded with Hexabromobenzene and/or Triphenyl Phosphate

Sample no.	HBB		TPP		Reduced viscosity	T_m in nitrogen, °C	T_m in air, °C
	% Compound	% Br	% Compound	% P			
I	0.0	—	0.0	—	0.57	249	250
II	2.3	2.0	—	—	0.55	249	248
III	5.6	5.0	—	—	0.56	248	248
IV	11.3	10.0	—	—	0.39	247	247
V	2.3	2.0	2.6	0.25	0.53	248	248
VI	2.3	2.0	5.2	0.50	0.53	247	247
VII	5.6	5.0	1.1	0.10	0.55	247	247
VIII	5.6	5.0	2.6	0.25	0.53	247	247
IX	5.6	5.0	5.3	0.50	0.55	247	245
X	11.3	10.0	1.1	0.10	0.50	245	245
XI	11.3	10.0	2.6	0.25	0.50	240	245
XII	11.3	10.0	5.2	0.50	0.46	240	240

at 400°C, differences between the PET control sample and those having one or both additives were observed. In both oxygen and nitrogen, the PET control sample showed lower weight loss values than those having one or both additives. The weight loss values increased with the increasing PET additive concentration and was ascribed to accelerated PET depolymerization to low molecular weight species that volatilized at 400°C.^{34,35} The endothermic depolymerization and volatilization processes could have resulted in decreasing the thermal energy content of the polymer melt and, thus, led to delayed ignition or burning, especially if the low heat of combustion of PET was considered.^{21,36} Alternatively, the flame-retardant additives may have volatilized with or without decomposition at 400°C in the PET matrix and thus released active flame retardant species into the gas phase. This is consistent with the TGA data of HBB and TPP (Table I) which indicated high weight loss values at 400°C.

3. If the volatile fractions at 400°C decreased the polymer flammability, one could expect an increase of the LOI values with the increase of volatilization at 400°C. This was indeed the case in most of the systems described in Table III, with the fraction of volatile components also increasing with increased additive concentration. This implies gas-phase mechanism for these flame retardants, with the likelihood of a minimal condensed phase contribution.

The effect of the type and concentration of flame retardants on the LOI, luster, and color qualities of PET were studied on both extruded monofilaments, molded bars, or melt spun yarns and led to the following observations (Table IV):

1. HBB at an 11.2% concentration resulted in monofilaments with high LOI but poor luster and color qualities (sample IV). Comparable LOI values were obtained by decreasing the HBB concentration and adding

TABLE III
 Thermogravimetric Analysis and Limiting Oxygen Index Data of Poly(ethylene terephthalate) Extruded with Hexabromobenzene and/or Triphenyl Phosphate

Sample no.	HBB		TPP		LOI*	Wt. loss in nitrogen, %, °C							Wt. loss in air, %, °C												
	% Com-pound	% Br	% Com-pound	% P		200	300	350	400	450	500	550	600	700	800	200	300	350	400	450	500	550	600	700	800
						0	2.3	5.6	11.3	2.3	2.3	5.6	11.3	0	1	2	3	4	5	6	7	8	9	10	11
I	0	—	0	—	27.5	0	0	1	1	30	77	79	80	81	82	0	0	1	3	40	77	81	89	96	96
II	2.3	2.0	—	—	28.6	0	0	1	2	21	72	75	77	78	79	0	1	2	4	38	80	82	90	98	—
III	5.6	5.0	—	—	29.6	0.5	1.5	2	5	22	75	78	79	79	—	0	1	2	6	31	76	79	88	96	96
IV	11.3	10.0	—	—	33.9	0	1	3	7	26	73	77	78	78	79	0	1	4	11	46	77	81	90	96	—
V	2.3	2.0	2.6	0.25	32.8	0	1	2	4	20	72	75	76	78	80	0	1	3	8	36	80	83	90	98	—
IV	2.3	2.0	5.2	0.50	31.8	0	1	3	6	35	73	75	76	77	78	0	1	3	9	40	76	79	88	97	98
VII	5.6	5.0	1.1	0.10	32.8	0	1	2	6	30	76	78	79	80	—	0	1	2	7	30	75	79	85	95	95
VIII	5.6	5.0	2.6	0.25	33.3	0	2	3	6	26	78	76	77	80	—	0	2	5	12	45	79	83	92	98	98
IX	5.6	5.0	5.3	0.50	33.3	0	1	4	8	31	73	75	77	79	80	0	2	5	11	40	79	83	90	97	—
X	11.3	10.0	1.1	0.10	33.9	0	1	3	8	30	72	75	77	79	80	0	2	5	13	49	79	82	93	97	—
XI	11.3	10.0	2.6	0.25	35.4	0	1	4	9	28	73	77	78	81	82	0	2	6	15	53	81	85	92	98	—
XII	11.3	10.0	5.2	0.50	36.0	0	2	4	9	27	73	77	78	79	82	0	2.5	6	15	50	80	83	90	96	—

* Samples were tested as bars.

TABLE IV
Effect of Type and Concentration of Flame Retardants on the Properties of PET

Sample no.	Flame-retardant system				LOI			Color quality
	Components	% Compound	% Br	% P	Processing	Sample shape	Value	
I	None	0	—	—	extrusion	bar	26.9	good
VI	Hexabromobenzene	11.3	10.0	0	extrusion	bar	33.9	poor
V	Hexabromobenzene + triphenyl phosphate	2.3	2.0	—	extrusion	bar	32.8	good
		2.6	—	0.25				
VIII	Hexabromobenzene + triphenyl phosphate	5.6	5.0	—	extrusion	bar	33.3	good
		2.6	—	0.25				
XIII	Tricresyl phosphate (TCP)	5.9	—	0.45	extrusion	bar	30.9	poor
XIV	Pentabromotoluene + triphenyl phosphate	4.4	3.0	—	extrusion	bar	33.3	good
		5.3	—	0.50				
XVI	None	0	—	—	spinning	knit	20.8	good
XVII	Hexabromobenzene + triphenyl phosphate	3.1	3.5	—	spinning	knit	28.0	good
		4.9	—	0.45				

TPP as a coadditive. With 4.9% and 8.2% total concentrations of both additives, the extrudates were shown to have good luster and color qualities (samples V and VII vs. I).

2. Melt-spun yarns tested as PET fabric containing both HBB and TPP at a total concentration of 8% showed a considerable LOI improvement and retention of luster and color qualities as compared with a PET control sample (sample XVII vs. XVI).

3. Replacement of HBB with pentabromotoluene (PBT) or octabromobiphenyl (OBB) in the flame-retardant systems containing TPP (as in samples XIV and XV, respectively) resulted in PET extrudates with high LOI values and good luster and color qualities.

4. The use of tricresyl phosphate alone at 5.9% concentration in PET improved its LOI, but the extrudate was characterized by poor luster and color qualities (sample XIII).

5. The FR carpets tested by the Department of Commerce flammability standard test, DOC FF-1-70 (the "pill" test), passed but the control failed. No direct correlation between the LOI and pill test can be made.

6. The FR polymer sample (XVII) was tested as a knitted sleeve and gave an LOI of 28.0 as compared to a PET control (XVI) of 20.8 (Table IV).

The flame retardation of PET monofilaments or melt-spun yarns using combinations of a halogenated aromatic compound and TPP without depreciation of their luster or color qualities could be ascribed to (a) possible solubilization of the halogen compound in PET in the presence of TPP leading to luster retention, and (b) an apparent synergistic flame-retardant effect of the phosphorus and bromine moieties. Based on the TGA data alone, it was likely that the phosphorus-bromine synergism was displaced via a gas-phase flame retardation mechanism.

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