

Flame-Retardant Polyester

H. GALIP,¹ H. HASIPOĞLU,¹ G. GÜNDÜZ²

¹ Eastern Mediterranean University, Department of Chemistry, G. Magosa-T.R.N.C.

² Orta Doğu Teknik Üniversitesi, Kimya Mühendisliği Bölümü, Ankara, Türkiye

Received 6 May 1998; accepted 9 March 1999

ABSTRACT: Halogenation and addition of some heavy metallic oxides have been in use for a few decades to impart flame-retarding properties to polymers. In this study bromine was added to the polymer (polyester of propylene glycol + phthalic anhydride) by means of decabromodiphenyloxide (DBDPO) at varying concentrations. In addition to bromine, 2% antimony oxide (Sb_2O_3) was also added. In predicting the flame-retarding properties of the polymeric samples prepared, the oxygen index test and the burning rate tests were applied. The results of these tests indicate that the oxygen index values of brominated polyester increase linearly as bromine content increases, and that the polyester containing 2% Sb_2O_3 in addition to 10–12% Br has a marked flame-retarding property. The mechanical properties were also studied, and some improvement has been observed in mechanical properties by adding acrylonitrile to the polyester. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2906–2910, 1999

Key words: Flame retardating properties; polymers; DBDPO

INTRODUCTION

Plastics, synthetic fibers, and other polymeric materials are being extensively used in many areas of daily life. The low-density, fairly high mechanical strength, and the lack of susceptibility to corrosion in polymers constitute their main advantage over metals and alloys as materials of construction. But this advantage of polymeric materials is shadowed by the fact that polymeric materials catch fire easily or do not withstand as high temperatures as do the metals and other materials of construction. The demand for non-burning or flame-retardant polymers is strong in various manufacturing industries.

The mechanism of flame retardancy is not yet well understood. Radical scavenging is the main reaction for flame retardance. Bromine-bearing compounds are effective agents as radical scaven-

gers for a variety of polymers.^{1–10} The brominated aromatic compounds are supposed to be more effective as retardants of polyethyleneterephthalate (PET) fabric flammability than aliphatic compounds.¹¹ Several comparative studies of the effectiveness of aromatic vs. aliphatic brominated compounds have been published.^{12–14} The superiority of the aromatic compounds in flame-retardant capability is now well established.

The burning characteristics of unsaturated polyester can be modified by the addition of inorganic fillers or organic fire retardants, by chemical modification of the acid, alcohol, or unsaturated monomer component, and by the chemical combination of organometallic compounds with the resin.^{15–17} It is the common practice to add an inert filler to polyester composition to reinforce the cured composite, lower its cost, and improve its fire retardance.

Fire-retardant chemicals available commercially for plastics can be divided into two general classes—unreactive additives, and reactive monomers or crosslinking agents.¹⁸ The unreactive ad-

Correspondence to: H. Galip.

Journal of Applied Polymer Science, Vol. 74, 2906–2910 (1999)

© 1999 John Wiley & Sons, Inc.

CCC 0021-8995/99/122906-05

ditives are generally added to the polymer during processing, but do not react with the other constituents of the composition. The reactive types, on the other hand, are generally reacted chemically with the polymer structure at the same processing stage. Additive retardants are generally incorporated by compounding. High molecular weight halogenated polymers can also be used as fire retardants.¹⁹

It is worthwhile to point out the difference between a "flame retardant" and a "fire retardant." According to Sanders,^{20,21} a flame-retardant chemical enables a material to resist burning when exposed to a relatively low-energy source such as a cigarette, match flame, candle flame, etc. A fire retardant, on the other hand, causes a material to resist burning when exposed to a high energy source such as a large flame produced by burning gasoline or something similar.

EXPERIMENTAL

Materials Used and Procedure

The initial polyester used in this study was the polymer product obtained by polymerizing phthalic anhydride, maleic anhydride, and propylene glycol. The flame-retarding agent was DBDPO, and the other additive used to impart flame retardancy was Sb_2O_3 . DBDPO and Sb_2O_3 were added to the polymer synthesized. With the aim of improving the mechanical properties of the polymer, later on acrylonitrile was added to it, constituting up to 40% of the total mass.²²

To start the curing reaction methylethylketone peroxide (MEKP) was added as the initiator and Co-naphthanate was added as the promoter. The initiator constituted about 2% of the whole mass, while the promoter would make about 0.4%. The polyester containing the initiator and promoter was poured into molds having the dimensions of $12 \times 10 \times 0.6$ cm and left to polymerize at room temperature for about 24 h, although it hardens within a few hours. The polymer samples were then taken off from the molds and kept in an oven at 50°C for another 24 h to get rid of the unreacted monomer present. Polyester samples of four different compositions were prepared. These samples consisted of: polyester + DBDPO; polyester + DBDPO + Sb_2O_3 ; polyester + DBDPO + AN; polyester + DBDPO + AN + Sb_2O_3 .

Tests Applied

Oxygen Index Test

The oxygen index, often referred to as limiting oxygen index (LOI), is defined as the minimum concentration of oxygen in a flowing mixture of oxygen and nitrogen that is necessary to support a flame for at least 3 min under specified test conditions. The test was carried according to ASTM 2863-77. The gas mixture flows upwards in a test column, and the vertically positioned specimen in the column is exposed to an ignition flame at its top. The column is supported and held vertically by a small holding assembly at its base. The glass beads placed in the column up to a height of 100 mm help the nitrogen and oxygen gas mix well. The gas flow rates were measured and controlled separately to adjust the desired oxygen concentration in the column. The ignition source having a 1-cm diameter, would provide a standard 3-cm blue flame. Ten test specimens were used for each polymer sample prepared, and the average value was noted. The specimens tested were 10 cm long, 0.6 cm wide, and 0.4 cm in thickness. When the burning of a sample lasted for 3 min, the oxygen concentration inside the column was taken as the oxygen index of the sample. Polymeric materials are said to be flammable if $\text{LOI} \leq 20$, slowly burning if LOI is between 20 and 25, and self-extinguishing if $\text{LOI} \geq 25$ –26.²³

Burning Rate

The burning rate test compares the relative rate or extent of burning of self-supporting plastics in the form of bars held in a horizontal position. The burning rate also was determined according to ASTM D-635-77. The free end of the specimen was exposed to a gas flame having a height of 2.5 cm, for 30 s. The flame was produced by a Bunsen burner, which was fixed at a position 10 mm below the free end of the specimen. If the specimen did not burn within 30 s, the flame was kept for another 30 s under the same conditions.

If the specimen burned completely, it was labeled as "burning," and the rate of burning was calculated as $600/t$ (cm/min), where t is the burning time in seconds.

If the specimen did not burn completely, but it burned to some extent, it was labeled as "self-extinguishing."⁹ Here the extent of burning and self-extinguishing time (SET) was calculated. Equations (1) and (2) show the calculation of SET and extent of burning, respectively.

Table I Burning Rate Test Results

Substance	B.T (s)	E.B. (cm)	B.R. (cm/min)	SET (s)	Classification
P + 0% DBDPO	145.4	all	4.13	—	burning
P + 2% DBDPO	178.9	all	3.35	—	burning
P + 5% DBDPO	216.9	all	2.77	—	burning
P + 8% DBDPO	349.1	all	1.72	—	burning
P + 10% DBDPO	148.4	2.27	—	118.4	self-extinguishing
P + 12% DBDPO	94.89	0.87	—	72.1	self-extinguishing
P + 2% DBDPO + 2% Sb ₂ O ₃	152.3	1.5	—	122.3	self-extinguishing
P + 5% DBDPO + 2% Sb ₂ O ₃	71.7	0.43	—	41.7	self-extinguishing
P + 8% DBDPO + 2% Sb ₂ O ₃	—	—	—	—	nonburning
P + 10% DBDPO + 2% Sb ₂ O ₃	—	—	—	—	nonburning
P + 12% DBDPO + 2% Sb ₂ O ₃	—	—	—	—	nonburning
P + 0% DBDPO + 20% AN	106.4	all	5.64	—	burning
P + 2% DBDPO + 20% AN	107.6	all	5.58	—	burning
P + 5% DBDPO + 20% AN	161.2	all	3.72	—	burning
P + 8% DBDPO + 20% AN	265.3	all	2.26	—	burning
P + 10% DBDPO + 20% AN	73.2	1.79	—	48	self-extinguishing
P + 12% DBDPO + 20% AN	47.0	1.24	—	18.9	self-extinguishing
P + 2% DBDPO + 2% Sb ₂ O ₃ + 20% AN	147.9	all	4.06	—	burning
P + 5% DBDPO + 2% Sb ₂ O ₃ + 20% AN	53.9	1.3	—	23.9	self-extinguishing
P + 8% DBDPO + 2% Sb ₂ O ₃ + 20% AN	—	—	—	—	nonburning
P + 10% DBDPO + 2% Sb ₂ O ₃ + 20% AN	—	—	—	—	nonburning
P + 12% DBDPO + 2% Sb ₂ O ₃ + 20% AN	—	—	—	—	nonburning

P: polyester.

B.T.: burning time.

E.B.: extent of burning.

B.R.: burning rate.

SET: self-extinguishing time.

$$\text{SET} = \frac{\Sigma(t - 30) \text{ s}}{\text{Number of specimens}} \quad (1)$$

Extent of burning EB

$$= \frac{\Sigma(10 \text{ cm} - \text{unburned length})}{\text{Number of specimens}} \quad (2)$$

If the specimen did not burn after the two ignition trials, then the specimen was labeled as “non-burning.” For each group of modified polyester at least 10 specimens were tested, all having the same dimensions of $12.5 \times 1.25 \times 0.3$ cm.

RESULTS AND DISCUSSION

The OI values of polyester start increasing upon the addition of bromine to the polymer. The increase in OI values indicates that bromination of the polyester imparts flame-retarding properties.

However, this gain in flame retardance is not much.

The addition of 2% DBDPO did not raise the OI value of the polyester by one unit; the increment was only 0.9 (OI of plain polyester = 18.50, OI of polyester + 2% DBDPO = 19.40). But the addition of antimony oxide to the polyester caused a much higher rise in the OI value of the polyester. The addition of 2% Sb₂O₃ raised the OI value of plain polyester from 18.50 to 20.60. The addition of 2% Sb₂O₃ to brominated polyester gave better results than adding either bromine or 2% Sb₂O₃ alone. This is the synergistic effect of this chemical on the flame-retardant properties of the polymer.

To see the effect of acrylonitrile AN on the mechanical properties of polyester, 10 samples that contained 20% AN and progressively increasing amounts of DBDPO were prepared and tested. When the results of this group were compared with the results of the polyesters that contained the corresponding amounts of DBDPO only, it

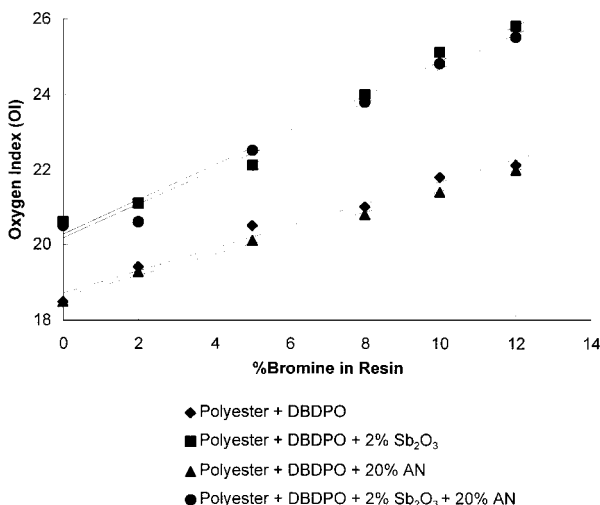


Figure 1 Oxygen index test results.

was observed that the OI values of the polyester have decreased. This shows that addition of AN had a negative effect on the flame-retarding properties of the brominated polyester.

Finally, the effect of AN was studied on brominated polyester filled with Sb₂O₃. Twenty percent AN was added to each of the polymer samples brominated progressively and filled with 2% Sb₂O₃. The OI values showed a small decrease compared to the previous ones, thus indicating a slight negative effect on the flame retardancy of the polyester. For example, while the OI value of polyester + 10% DBDPO + 2% Sb₂O₃ was measured as 25.10, that of polyester + 10% DBDPO + 2% Sb₂O₃ + 20% AN was found to be 24.80.

The results of all OI measurements are plotted in Figure 1. Apparently, there is a linear relationship between the OI and percent DBDPO in the polymer. As the percent DBDPO increases, the OI values increase linearly. However, the best results are obtained when the brominated polyester is filled with Sb₂O₃ as well.

The addition of AN has a negative effect on the flame retardancy of the polymer, but it does have a positive effect on some of its mechanical properties. Samples of polyester, containing increasing amounts of AN, were tested for hardness and impact strength. The results show that (Table II and Fig. 2) Brinell hardness and impact strength values of the polyester containing AN are greater than those of plain polyester. Brinell hardness and impact strength increase as the percent of the AN increases in the polyester. They reach a maximum point and then start declining.

Table II Mechanical Test Results

% Acrylonitrile (AN) in Polyester	Brinell Hardness Number (BNH)	Impact Strength (IS) J/m · width
0	12	13.5
5	22	16
10	25	23
20	23	39.5
30	20	34
40	17	32

Burning Rate Test Results

As mentioned before, according to the rate of burning the polyester samples were classified as “burning,” “self-extinguishing,” and “nonburning.” For the samples that were classified as

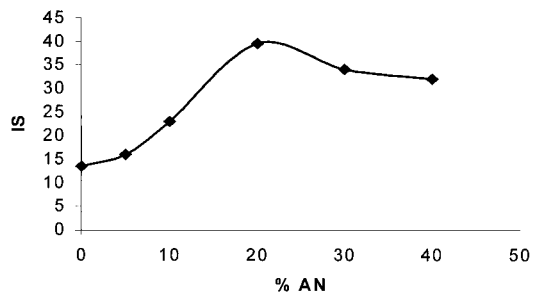
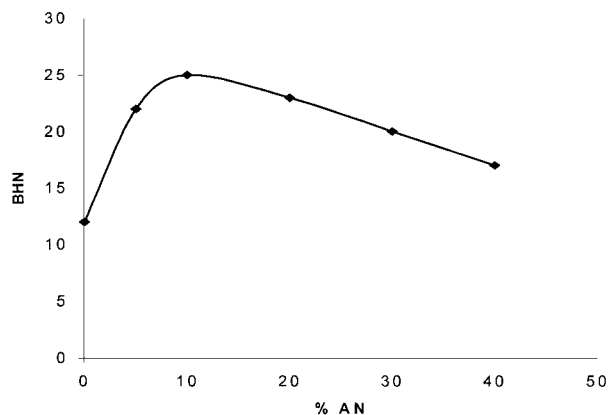


Figure 2 (a) Effect of AN on the hardness of the polyester. (b) Effect of AN on the impact strength of the polyester.

“burning,” the burning rate was calculated. For the samples that were characterized as “self-extinguishing,” the extent of burning and the self-extinguishing time were both calculated. The results of the burning rate tests are given in Table I.

CONCLUSIONS

The oxygen index of the polyester increases linearly as the bromine content increases. But this increase in OI is rather small. When Sb_2O_3 is added to the brominated polymer, there is a sharper increase in the OI and flame retardancy of the polymer. The addition of acrylonitrile to the brominated polyester causes a decrease in OI values, thus exhibiting a negative effect on the flame retardancy of the polymer, but the addition of AN improves the hardness and impact strength of the polyester. The addition of bromine increases the burning time of the polymer. Brominated polyester containing more than 8% DBDPO becomes nonburning upon the addition of 2% Sb_2O_3 . The effect of Sb_2O_3 on flame retardancy of the polyester is much more evident than the effect of bromine.

REFERENCES

- Mey-Marom, A.; Rajbenbach, L. A.; Levy, M. *J Appl Polym Sci* 1983, 28, 2411.
- Aminabhavi, T. M.; Cassidy, P. E. *Polym Plast Technol Eng* 1989, 28, 717.
- Camino, G.; Costa, L. *Polym Degrad Stabil* 1988, 20, 271.
- Camino, G.; Costa, L.; Cortemiglia, M. P. L. *Polym Degrad Stabil* 1994, 33, 131.
- Dauengauer, S. A.; Utkina, O. G.; Sazanov, Y. N. *J Therm Anal* 1988, 33, 1213.
- Gachter, R.; Müller, H. *Plastics Additives Handbook*; Hanser Publishers: Munich, 1987.
- Gündüz, G.; Öztürk, S. *Polym Plast Technol Eng* 1994, 33, 245.
- Hastie, J. W. *Combust Flame* 1973, 21, 49.
- Luijk, R.; Govers, H. A. J.; Eijkel, G. B.; Boon, J. J. *J Anal Appl Pyrol* 1991, 20, 303.
- Prins, M.; Marom, G. *J Appl Polym Sci* 1976, 20, 2971.
- Barker, R. M.; Drews, M. J. *NBS-GCR-ETIP*, 1976, 76, 430.
- McNeill, W. C.; Drews, M. J.; Barker, R. H. *J Fire Retard Chem* 1977, 4, 222.
- Einsele, U. *Melliand Textilber Int* 1976, 57, 64.
- Liepins, R.; Surless, J. R.; Morosoff, N.; Stannet V. T. *J Appl Polym Sci* 1977, 21, 2529.
- Nametz, R. C. *I/EC Ind Eng Chem* 1967, 59, 99.
- Ram, A.; Calahora, A. *J Appl Polym Sci* 1979, 23, 797.
- Ravey, M.; *J Polym Sci Polym Chem* 1983, 21, 375.
- Hindersinn, R. In *Encyclopedia of Polymer Science and Technology*; Wiley-Interscience: New York, 1977, p. 270, vol. 1.
- Novikov, S. N.; Gitina, R. M.; Antonov, A. V. *Int J Polym Mater* 1993, 20, 19.
- Landrock, A. H. *Handbook of Plastic Flammability and Combustion Toxicology*; Noyes Publications: Park Ridge, NJ, 1983.
- Sanders, M. J. *Chem Eng News* 1978, 56, 22.
- Gündüz, G.; Deniz, A.; *Polym Plast Technol Eng* 1992, 31, 221.
- Van Krevelen, D. N. *Polym J* 1976, 16.