

A Comparative Evaluation of a Novel Flame Retardant, 3-(Tetrabromopentadecyl)-2,4,6-tribromophenol (TBPTP) with Decabromodiphenyl oxide (DBDPO) for Applications in LDPE- and EVA-Based Cable Materials

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ABSTRACT: Flame retardation of polymeric materials for cables is becoming a statutory requirement due to governmental regulations to protect life and property from damages caused by fire. This and other factors such as the ever-increasing cost of existing flame retardants (FRs) have given rise to the search for better FRs. In this article, the suitability of an FR, 3-(pentadecyltetrabromo)-2,4,6-tribromophenol (TBPTP) developed from cardanol was evaluated for use in cable insulating and jacketing materials based on low-density polyethylene (LDPE) and ethylene vinyl acetate (EVA). The processability, mechanical properties, compatibility and miscibility, thermal behavior, flammability behavior, smoke generation, acid emission, aging characteristics etc., of the blends of the FR with LDPE and EVA were studied in comparison to those of decabromodiphenyl oxide (DBDPO), which is a standard FR used by the cable industry. Although TBPTP is found to be less thermally stable than is DBDPO, it exhibited better flame retardancy and has comparable thermal stability when blended with LDPE and EVA. Both LDPE-TBPTP and EVA-TBPTP blends produced less smoke than did the corresponding blends of DBDPO. In the case of the EVA-TBPTP blend, the percentage emission of smoke was almost negligible, placing EVA-TBPTP under the low smoke grade. Formulations containing a synergistic agent, promoter, and filler with the corresponding FR and polymer polymer along with an antioxidant were extruded out into wire and tested for cable properties. At 20% loading, the LOI values of the blends were 34.6 and 32.5, respectively, for the TBPTP-EVA and DBDPO-EVA blends. Vertical burning tests carried out with EVA-TBPTP cable showed that it is self-extinguishable. The processability of the compositions containing TBPTP were better than those of DBDPO. The improved processability was found to be due to the plasticising effect of TBPTP. SEM pictures of the blend showed excellent distribution of TBPTP in the polymer, indicating good compatibility and miscibility. Comparatively, DBDPO did not exhibit uniform distribution. The mechanical properties of the blends were within specifications of standard cable materials except that the % elongation of the DBDPO-LDPE blend was far too low. Aging studies also gave better properties for the TBPTP system than for those of the DBDPO system. The overall results show that the properties of EVA-TBPTP cable fall within specifications for the FARLS grade, whereas the

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EVA–DBDPO cable did not. In the case of LDPE, both TBPTP and DBDPO did not satisfy specifications for the FRLS grade, but the data indicate that they can be used as FRs. The superiority in properties of the TBPTP system over DBDPO is explained in terms of the structure of TBPTP characterized by the distribution of the flame-retardant element, bromine, almost evenly between the aliphatic and aromatic moieties of the molecule, which can, in contrast to the fully aromatic DBDPO, provide halogen over a wide range of temperatures to the combustion zone of the decomposing polymer. Moreover, the presence of the aliphatic segment assures improved processability and compatibility. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 3057–3073, 1997

INTRODUCTION

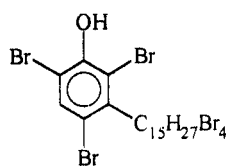
The susceptibility of polymeric materials to fire continues to be of great concern all over the world. Cable materials are of no exception. The stringent conditions set by statutory governmental regulations for the use of flame retardants (FRs) for cable materials demand development of newer and better FRs. Although brominated FRs are the most effective FRs on the market, there has been, in recent times, much concern worldwide over their use because they give rise to toxic gases and smoke.^{1,2} The inability to find effective substitutes to replace them has resulted in their use being continued even today as a large volume FR additive in polymeric materials.^{2,3–8} Although this cannot be a reason for inventing new brominated FRs, a novel brominated FR, 3-(pentadecyltetra-bromo)-2,4,6-tribromophenol (TBPTP) (**I**), which made the ethylene vinyl acetate (EVA) low smoke flame-retardant (FRLS) grade in a formulation for cable sheathing material containing flame suppressants needs mention because of its interesting structure and properties.^{8–15} The most significant characteristic of TBPTP is the distribution of bromine almost evenly between aliphatic and aromatic moieties of the same mole-

cule.^{9–11,16–17} This assures the availability of bromine or hydrogen bromide for flame retardation over a wide range of temperatures covering the decomposition range of the polymer. Additionally, the presence of both hydrophobic and hydrophilic groups in the same molecule makes it compatible with a wide range of polymers. This aspect has already been demonstrated with low-density polyethylene (LDPE) and EVA by way of improvements in processability.^{10,11} TBPTP has been shown to effect a plasticising action on both LDPE and EVA.^{10,11} The wide-spectrum capability of FRs having similar structures (hydrophobic and hydrophilic groups in the same molecule) for use in a numbers of polymers such as LDPE, phenolics, PVC, cellulose, and polyurethane has been demonstrated.^{8,18–21}

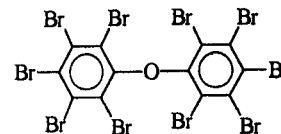
Thus, TBPTP was found to possess a number of positive attributes and this prompted us to study the properties of TBPTP in comparison with an all-aromatic brominated FR such as decabromodiphenyl oxide (DBDPO) (**II**) for flame retardation of LDPE- and EVA-based cable materials and the results are presented in this article. DBDPO was chosen for comparison because of the recent restrictions on its use and, hence, the need for an alternate FR:

Table I Specifications of LDPE

Property	Value
Grade	Indothene 20 CA 002
Density (gm/cc)	0.920
mp	110°C
Tensile strength (MPa)	15.68
Percentage elongation	600
Dielectrical constant	2.4
Dissipation factor (ASTM D 150)	3×10^{-4}
Dielectrical strength (kV/mm) (IS 255584)	29
Volume resistivity (ohm cm) (IS 3396)	1×10^{17}



I



II

The FRs generally used commercially in PE and similar polyolefins are the following^{1,22–23}: chlorinated paraffins, dechlorane plus (alicyclic chlorine), DBDPO (aromatic bromine), and 1,2-bis(tetrabromophthalimido)ethane (Saytex BT-93, aromatic bromine).²² The preferred FR for wire and cable insulation and jacketing is the acy-

Table II Specifications of EVA

Property	Value
Grade	Pilene EVA 2806
Vinyl acetate (%)	28
MFI (g/10 min)	6
Tensile strength (MPa)	14
Percentage elongation	800
Hardness (Shore A)	85
Density (g/cc)	0.95

clic chlorine-containing FR Dechlorane Plus.²³ While aromatic bromine-containing FRs such as DBDPO and Saytex BT-93 are more effective FRs than is Dechlorane plus, when coated wire is tested by the UL-44 V.0 flammability test, the latter passes the test, although this compound has the problem of blooming whereas the other two aromatic compounds do not.¹

It has lately been pointed out that brominated compounds with bromine attached to both aromatic and aliphatic moieties would serve as better FRs as they can provide an uninterrupted supply of HBr over a wider temperature range.^{16,17} As the aromatic brominated compounds have melting points almost nearer to the decomposition (T_i) temperature of PE, it is possible that the effect

of the FR will not be felt at the initial stages of decomposition. This problem could be overcome by the use of compounds having bromine attached to both aromatic and aliphatic moieties. It is also known that for an FR to be effective, it should decompose at a temperature 60°C less than that of the decomposition temperature of the polymer.²⁴ It has been shown in this laboratory that wide-spectrum FRs containing bromine attached to both aromatic and aliphatic moieties can function as effective FRs for PE.^{25,26} The significance of wide-spectrum FRs will be evident when one notes that although there are more than 25 brominated FRs on the market they are mostly used as one FR for a particular application, whereas the former can be used for a range of polymers. Additionally, wide-spectrum FRs will have better miscibility and compatibility and less reduction in mechanical properties. It is also reported that halogen attached to the aliphatic moiety gives better flame retardancy than that attached to the aromatic ring.^{1,27}

As brominated FRs even today excel in the efficiency of FR action³⁻⁵ and (because of this) they cannot be replaced simply overnight,² much work is being done to develop smoke suppressants.¹⁶ The use of alumina trihydrate^{1,28} as an FR cum smoke suppressant in wire and cable insulation

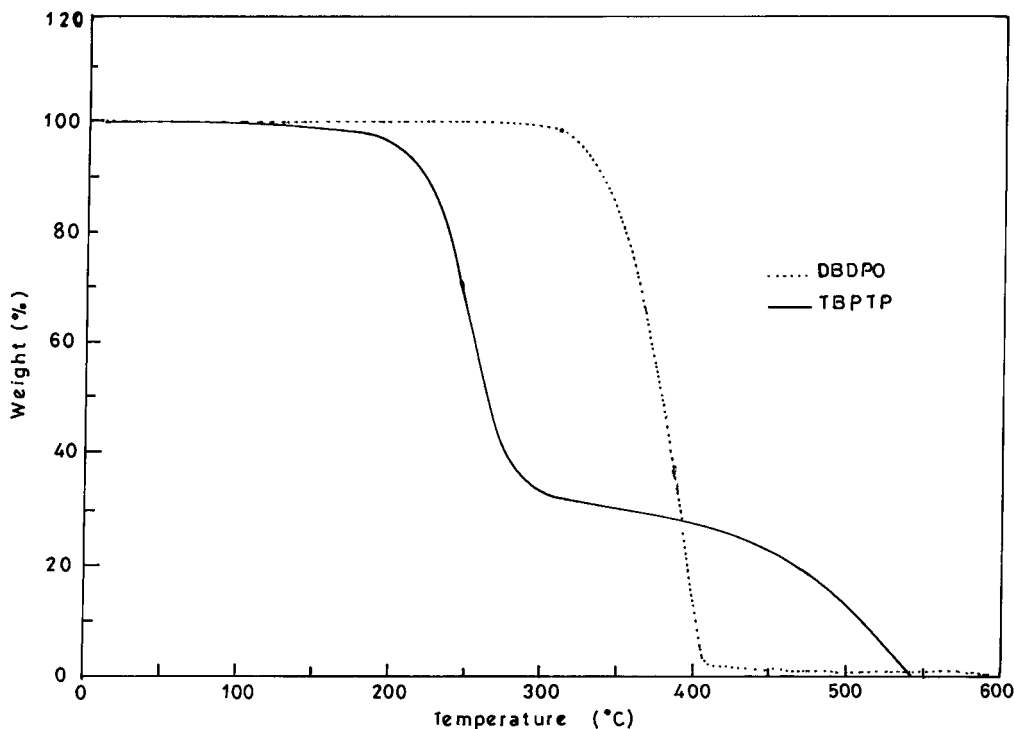


Figure 1 TGA of (a) TBPTP and (b) DBDPO (10°C/min in air).

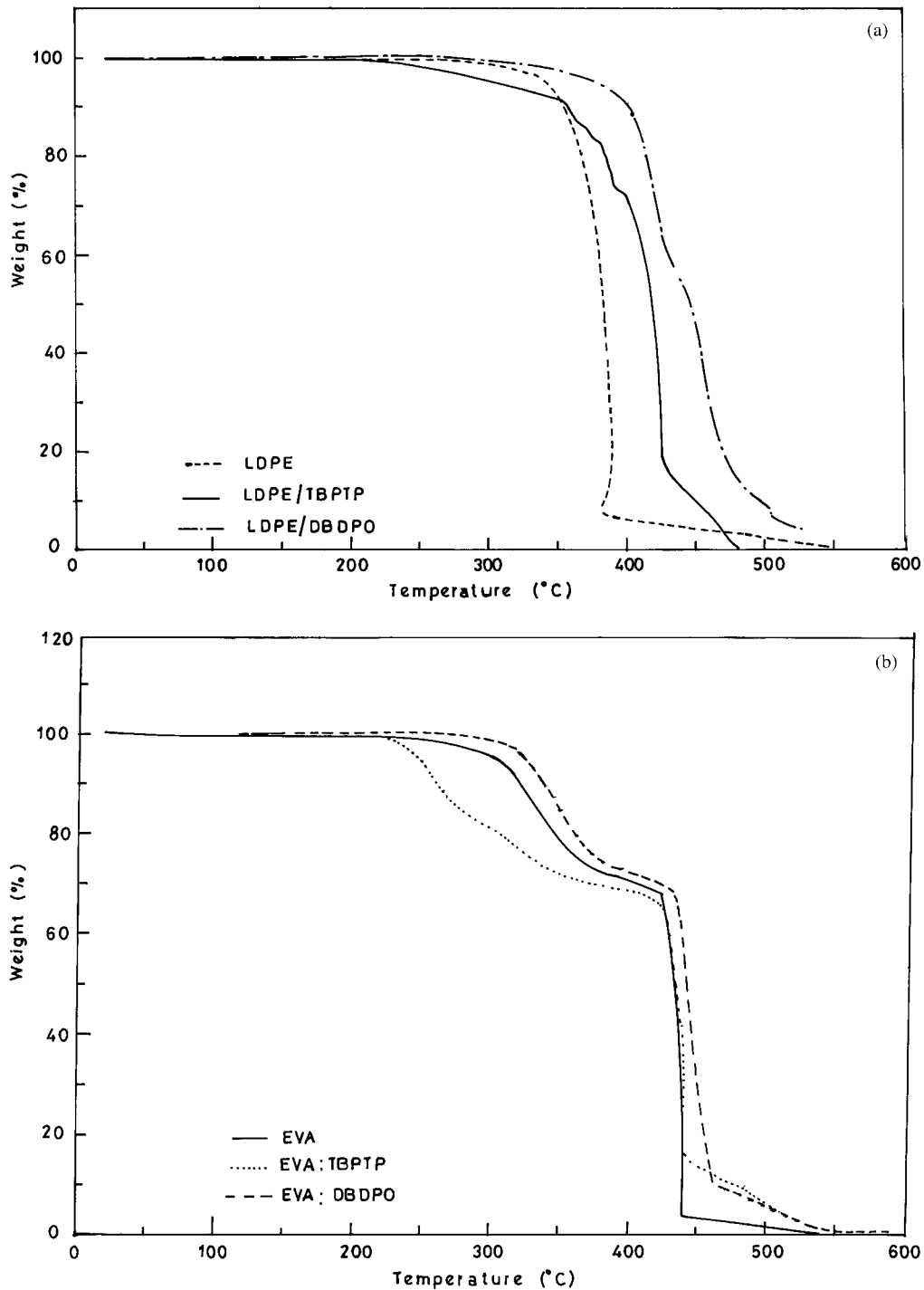


Figure 2 (a) TGA of LDPE, LDPE/TBPTP, and LDPE/DBDPO. (b) TGA of EVA, EVA/TBPTP, and EVA/DBDPO.

and jacketing is now well recognized. It has further been shown that when used along with organic FRs the problem of the drastic reduction in mechanical properties could be overcome. It was also shown that progressive replacement of anti-

mony trioxide (which is known to increase smoke) by talc (in the presence of ferric oxide) reduces the smoke density in Dechlorane Plus containing a polyolefin FR formulation from the D_{\max} 600 to 200 level.²³ However, the value of the LOI has

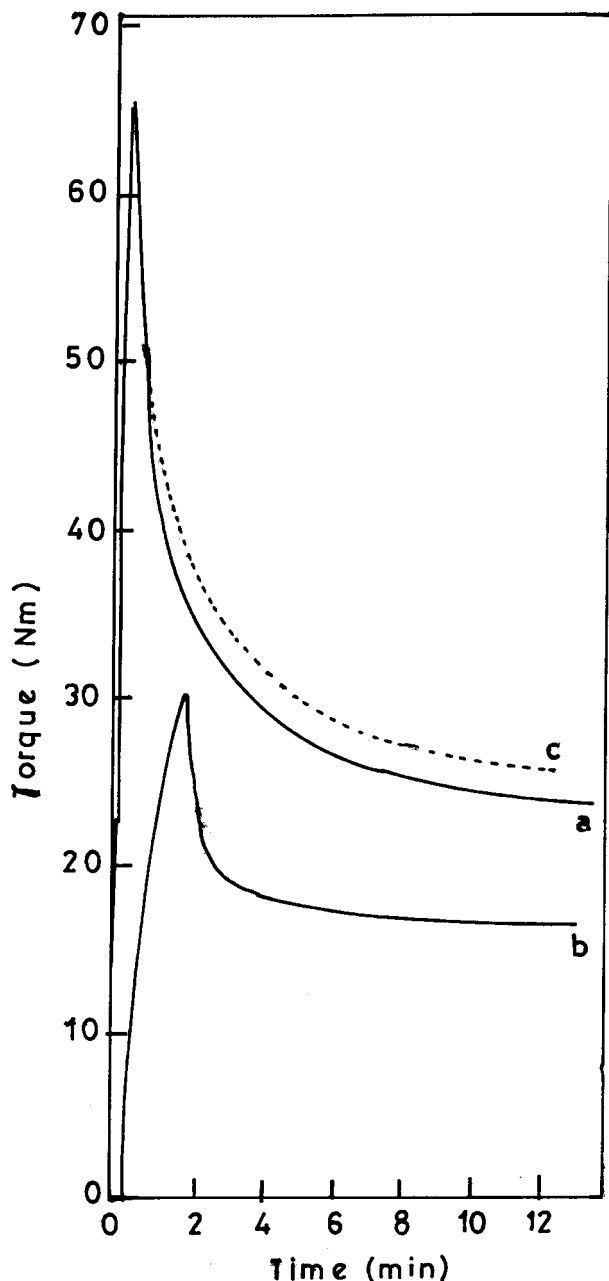


Figure 3 Brabender plasticorder torque profile: (a) LDPE only; (b) LDPE + 30% TBPTP; (c) LDPE + 30% DBDPO.

suffered, which could be expected. It was further shown that the halogenated additive need not be abandoned due to its having high smoke for what is required for the right selection of the FR and appropriate formulation of the FR product.^{5,23} In a recent study, magnesium hydroxide was also shown to be effective as a nonhalogen FR.²⁹ Zinc borate was indicated to be used as a partial replacement for antimony trioxide for smoke reduc-

tion.²³ Although the flame retardation of cables is becoming a prime requirement in almost all countries of the world, R&D studies on the flame retardation of cable materials have not been given the necessary emphasis. As of today, published data on FR cable materials are limited.^{23,28-36}

EXPERIMENTAL

Materials

Cardanol (37330-39-5) was obtained by double vacuum distillation of Cashew Nut Shell Liquid (8007-24-7) of IS specification IS: 840(1964) (purchased from the Kerala State Cashew Development Corp., Kollam, India) at a pressure of 3–4 mmHg and the fraction coming at 230–235°C that gave a refractive index of 1.509 and a Brookfield viscosity of 450–520 cps at 30°C was used. Low-density polyethylene (LDPE) was obtained from Indian Petrochemicals, Vadodara, India, and was of cable grade, Indothene 20 CA 002. Ethylene vinyl acetate (EVA) resin of cable-grade Pilene EVA 2806 was purchased from Polyolefins, Bombay. The specifications are given in Tables I and II.

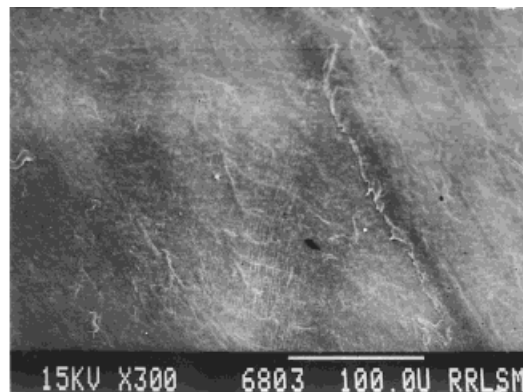
Bromine was purchased from E. Merck India. Antimony trioxide (Sb_2O_3) was obtained from BDH. Ferric oxide (red) (Fe_2O_3), LR grade, was obtained from SD Fine Chemicals, Bombay. Molybdenum trioxide (MoO_3) was a product of Riedel-Haas, Germany. Tin oxide (SnO_2), LR grade, was obtained from the Central Drug House (P), Bombay. Alumina trihydrate (ATH) was a product of Bayer India, Calcutta, available under the trade name "Apyral-B 60." Calcined clay was supplied by NICCO Corp., Calcutta. However, samples from English Indian Clays, Trivandrum, were also used and the results were tallied.

Decabromodiphenyloxide (DBDPO) was obtained from the NICCO Corp. as a free sample. Tetrabromobisphenol was a product of Ameribrom. A number of other solvents, fine chemicals, monomers, and polymers were also purchased in connection with this work, particularly for conducting the basic research; all are standard products of BDH, E. Merck, Aldrich, or Fluka.

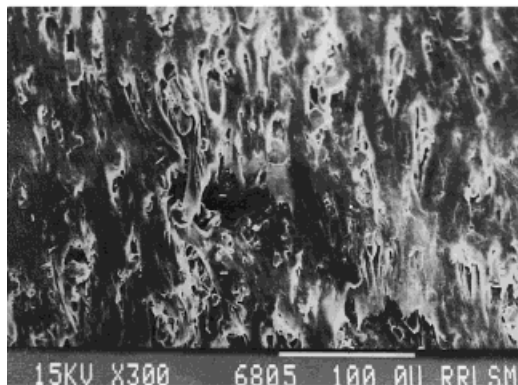
Methods

Preparation of Blend Compounds

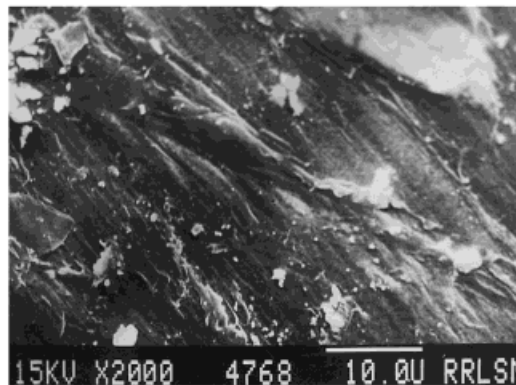
Blending was carried out by melt mixing in a Brabender plasticorder Model PLE 651. Unless other-



(a)



(b)



(c)

Figure 4 SEM of: (a) LDPE; (b) LDPE/TBPTP blend; and (c) LDPE/DBDPO blend.

wise specified, blending for normal operations was carried out at 120°C and at a rotor speed of 30 rpm. The overall mixing schedule was as follows: The polymer was charged directly to the mixer and the sample melted. A premix of the FR with the oxide additives was added and mixed for 5–8 min. The filler was added finally and mixing continued for another 5–12 min until an equilibrium torque was obtained. This was taken as a measure of the uniformity of the blend. Initially, TBPTP was varied between 10 and 30% with 5% Sb_2O_3 . The formulations were improved upon taking data from further experiments until FR or FRLS formulations as per ASTM or as followed by a standard industry such as the NICCO Corp., Calcutta, were obtained. At NICCO, EVA compounds were blended in a steam-heated two-roll mill at 40 rpm.

Compression Molding

Compression molding of the blended material was carried out as follows: The blended mass was pelletized and molded in the form of a sheet in an Indudyog Hydraulic Press Model DS-SD-HWP/25 in an open mold at a pressure of 50 kg per cm^2 and a temperature of 130°C. Blends were preheated for 2 min and then pressure was applied. Specimens of varying thickness were made depending on the requirement (electrical, mechanical, flammability tests, etc.)

Rheological Studies

Processing for rheological studies were carried out by using the Brabender Plasticorder Model PLE 651 fitted with a roller mixer measuring head at 30 rpm and at 120°C. The torque responses of 30

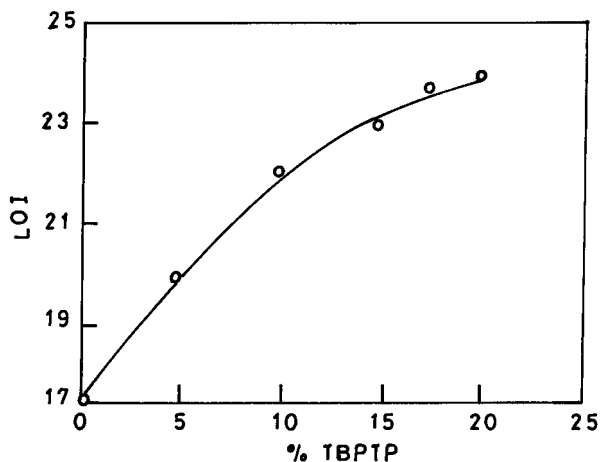


Figure 5 Effect of dosage of TBPTP on LOI of LDPE.

g each of the samples containing zero and 10% TPBTP were measured at 120 and 130°C at preset rotor speeds of 30, 60, and 90 rpm.

Curing

Curing characteristics were studied using a Wallace-Shawberry curometer with a temperature setting at 150°C.

Morphology and Miscibility

The morphology and miscibility of the blend were studied by using a scanning electron microscope, Model Jeol 35C.

Extrusion into Wires

Extrusion (extrusion coating) onto the conductor was carried out using a Haake Rheocord System

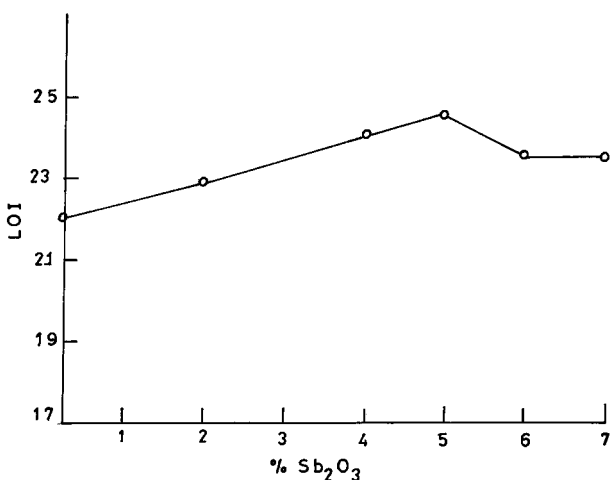


Figure 6 Effect of addition of Sb₂O₃ on LOI of LDPE/TBPTP (10 : 1) blend.

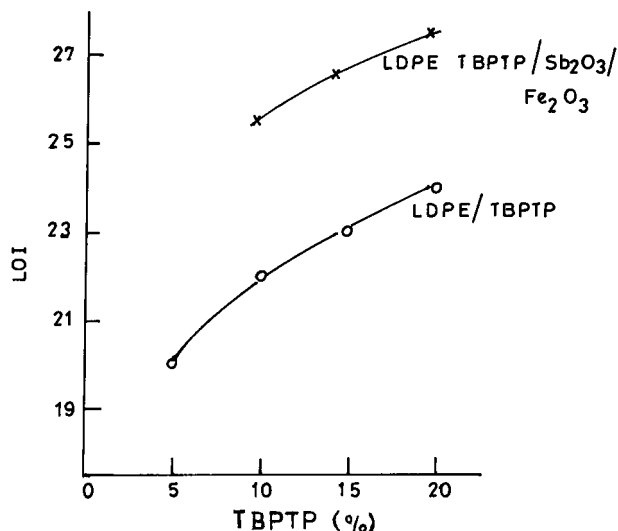


Figure 7 Combined effect of Sb₂O₃ + Fe₂O₃ on the LOI of LDPE/TBPTP blend.

40 rubber extruder at 20 rpm with an ATC conductor of 0.85 mm diameter.

Hardness

Compression-molded samples were prepared and hardness determined as per ASTM Standard D 2240-86 at 28°C.

Tensile Properties

Tensile properties were measured using an universal testing machine, Instron 1190, according to ASTM Standard D 412-87 (ASTM D 638) at 28°C.

Electrical Properties

Thin circular disc-shaped samples of 1 mm thickness and 10 mm diameter were prepared by compression molding. Thin rectangular sheets were

Table III Flammability Behavior of EVA-TBPTP Blend

Composition	LOI
EVA	18
EVA + 5% TBPTP	21
EVA + 10% TBPTP	23.5
EVA + 5% TBPTP + synergist	24.5
EVA + 10% TBPTP + synergist and promoter	27.0
EVA + 10% TBPTP + synergist and filler	30.0
EVA + 20% TBPTP + synergist and filler	34.5
EVA + 20% DBDPO + synergist and filler	32.5

Table IV Mechanical Properties of Unfilled LDPE-TBPTP Blends

	Tensile Strength (MPa)	% Elongation at Break
TBPTP content (%)		
0.0	15.70 ± 1.2	630 ± 12
10	13.8 ± 1.4	625 ± 17
20	12.55 ± 1.2	605 ± 19
30	12.05 ± 1.1	585 ± 15
Standard specification		
(a) ASTM D 1251-78 (Cable Jacketing)	12.00	500
(b) ASTM D 2633 (Cable Insulation)	9.7	350

molded and then circular samples were punched out using a metallic die. After measuring the diameter and thickness of the samples, they were treated with silver paste on both sides and copper electrodes were fitted. The volume resistivity, dielectric constant, and dissipation factor were measured using an impedance analyzer Model 4192 A LF (Hewlett-Packard) or using a Davenport volume resistivity apparatus and were calculated from the values obtained using the sample dimensions. All the measurements were carried out at four frequencies of 100 kHz, 300 kHz, 1 MHz, and 10 MHz. The average value of three to four measurements were taken as the final data.

Thermogravimetric Analysis (TGA)

TGA of blends and pure compounds were carried out by using a DuPont 951 thermogravimetric analyzer coupled with a thermal analyst 2000 in both nitrogen and air atmospheres (purge rate of 50 mL/min) at a heating rate of 20°C per min. About 5–10 mg of the samples was used for each experiment.

Air Oven Aging

Air oven aging was carried out at 100 ± 5°C for 168 h.

Table V Mechanical Properties of Unfilled EVA-TBPTP Blends

TBPTP Content (%)	Tensile Strength (MPa)	% Elongation at Break
0.0	8.83 ± 1.02	1324 ± 15
10	8.02 ± 1.2	1238 ± 12
20	7.81 ± 1.1	1158 ± 14
30	7.56 ± 1.3	1126 ± 15

Limiting Oxygen Index (LOI)

The LOI was measured using a limiting oxygen index apparatus of the model Stanton Redcroft FTA flammability Unit No. 710 as per ASTM D 2863-77 at 30°C.

Temperature Index and Oxygen Index at 250°C

The effect of temperature on the LOI was measured using a Stanton Redcroft high-temperature flammability unit (HFTA).

Smoke Density

Measurements on smoke evolution were carried out using a Stanton Redcroft smoke density tester. The percentage smoke density rating, percentage smoke absorption, percentage smoke transmission, etc., were evaluated as per ASTM D 2843-77.

Infrared Spectra

IR spectra were recorded on a Perkin-Elmer Model 882 spectrophotometer.

NMR

¹H-NMR spectra were run on a Hitachi R-24 high-resolution NMR spectrometer in CCl₄ using TMS as an internal reference.

Viscosity

Viscosity measurements were carried out using a Brookfield viscometer of Model HBT with spindle No. 3.

Synthesis of TBPTP

TBPTP was synthesized by the method of bromination of cardanol using bromine according to a

Table VI Effect of Addition of Fillers to Unmodified LDPE and EVA

Polymer	Filler	Percentage	TS (MPa)	% Elongation
LDPE	ATH	100	8	25
	Mg(OH) ₂	30	8	500
	Calcined clay	80	8	30
EVA	ATH	120	6	400
	Mg(OH) ₂	80	8.8	525
	Calcined clay	120	4.5	400

patent filed by Pillai et al.¹² Yield: 91%; bromine content: found, 63%; calculated, 65%. IR (cm⁻¹): 780 C-Br; NMR: δ 4.2 CHBr, δ 7.8 1 ArH; the peak at δ 5.5 due to unsaturated protons disappeared and a corresponding increase in the integral of the saturated protons at δ 0.9–2.7 was observed.

RESULTS AND DISCUSSION

Thermal Stability

The TGAs of TBPTP and DBDPO are given in Figure 1. Being fully aromatic, DBDPO obviously has a higher thermal stability than that of TBPTP. Figure 1 shows that TBPTP is stable up to 230°C and afterward it decomposes in two stages. In comparison, DBDPO is stable up to 320°C and decomposes in a single-stage reaction. The observed difference in thermal stability between the two FRs can be understood on the basis of their structural difference. The presence of the labile C₁₅ aliphatic moiety in TBPTP accounts for its lower thermal stability. It was, however, encouraging to observe that preliminary studies on

the effects of TBPTP and DBDPO on the thermal stability of LDPE/EVA indicated that TBPTP did not affect adversely their thermal stabilities. It was further noted that the thermal stabilities of both TBPTP–LDPE and DBDPO–LDPE blends are comparable. This finding paved the way for carrying out further studies on TBPTP with a view to developing it as a suitable FR for cable materials. Figure 2(a) and (b) give the TGAs of TBPTP–LDPE and TBPTP–EVA blends in comparison to those of DBDPO. The enhancement in thermal stability of both LDPE and EVA was thought to result from the improved dispersion of the FR in the polymer matrix. This effect is particularly pronounced for the TBPTP-containing blends.

Processability

The torque responses obtained from the Brabender plasticorder on mixing LDPE with TBPTP and DBDPO (30%) are given in Figure 3. It is clear from these traces that the TBPTP-modified blends attain a lower level of equilibrium torque at a faster rate than do the unmodified samples. A reduction in the bandwidth of the blend with TBPTP

Table VII Specifications for FRLS Cable Materials

Property	Insulation	Jacketing
Volume resistivity (ohm cm)	3×10^{15}	—
Dielectric constant at 50 Hz	3.15	—
Tensile strength (MPa)	11 min	6 min
Elongation (%)	600 min	150 min
Aging at 100°C, 168 h	% Variation \pm 30	% Variation \pm 30
Limiting oxygen index	30 min	30 min
Temperature index at 250°C	21 min	21 min
Smoke density, % transmission	80	80
Halogen content (%)	2 max	2 max

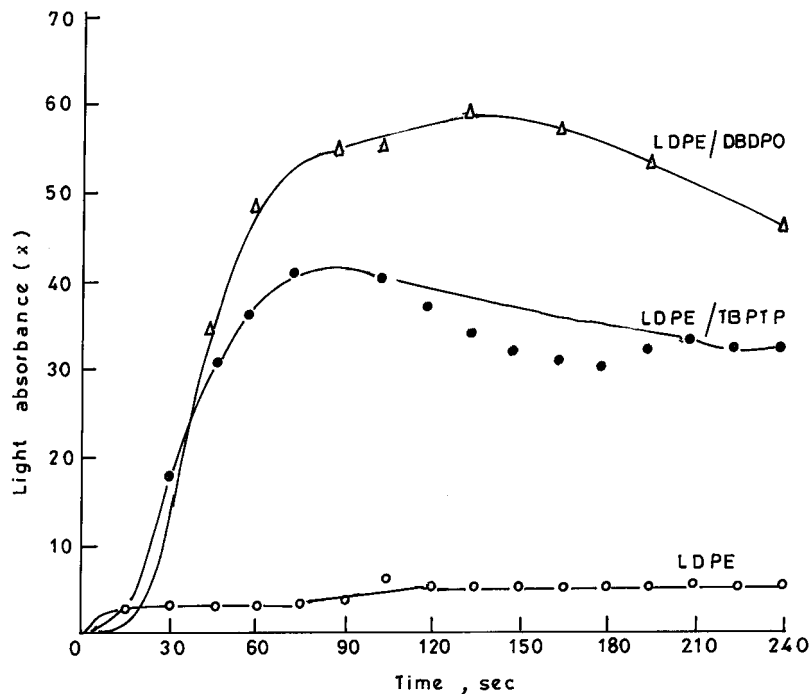


Figure 8 Smoke density curves of LDPE, LDPE/TBPTP, and LDPE/DBDPO.

can also be noticed. In contrast, the blend with DBDPO shows an increase in the equilibrium torque of LDPE and no decrease in the bandwidth. The bandwidth of the torque trace has been considered as an index of melt elasticity and a reduction in melt elasticity is considered to indicate a plasticizing action and, hence, improvements in processability.³⁷ Similarly, the viscosity index also registered a decrease from 75 to 50 and the power consumption from 70 to 47 (see also Table VIII). These data thus suggest that the processability of TBPTP-LDPE is better than that of the DBDPO-LDPE system. The processability characteristics of TBPTP-modified LDPE and EVA were discussed in detail in an earlier article.^{10,11} The difference in the behavior of TBPTP and DBDPO blends can be understood from the SEM photographs (Fig. 4) of the cross section of the blends. It is evident that TBPTP gives a uniform and intimate mixing possibly at the molecular level, whereas DBDPO gives a nonuniform distribution. This difference in the behavior of the two systems can be attributed to the difference in the structure of the two molecules. TBPTP possesses a long aliphatic side chain which, on blending, possibly aligns with the structurally similar segments of polyethylene, thus making the system compatible and miscible. Addition of additives such as alu-

mina has been found to increase the equilibrium torque value only marginally.

Flammability

Figure 5 shows that with the addition of TBPTP there is a steady increase in the LOI of LDPE. A leveling off of the LOI was observed above 30% of the FR. The maximum LOI observed was 23.5. In the case of DBDPO, the maximum LOI obtained was only 22.5 at the same loading. A higher value could naturally be expected for DBDPO having a bromine content of 83% against 53% for TBPTP. It, therefore, appears that the mechanism of flame retardation of LDPE by TBPTP differs from that of DBDPO. There are two possibilities: (1) The melting point and decomposition temperatures of DBDPO are higher than those of LDPE and, hence, the available bromine to effectively function as a radical quencher in the free radical-mediated decomposition of LDPE might be lower than that of TBPTP whose decomposition temperature is lower than that of LDPE. This meets the requirement that the decomposition temperature of an FR might be lower by a factor of 50°C to be effective in bringing about flame retardation.²⁴ (2) DBDPO is a fully aromatic compound whereas TBPTP has both aliphatic and aromatic moieties

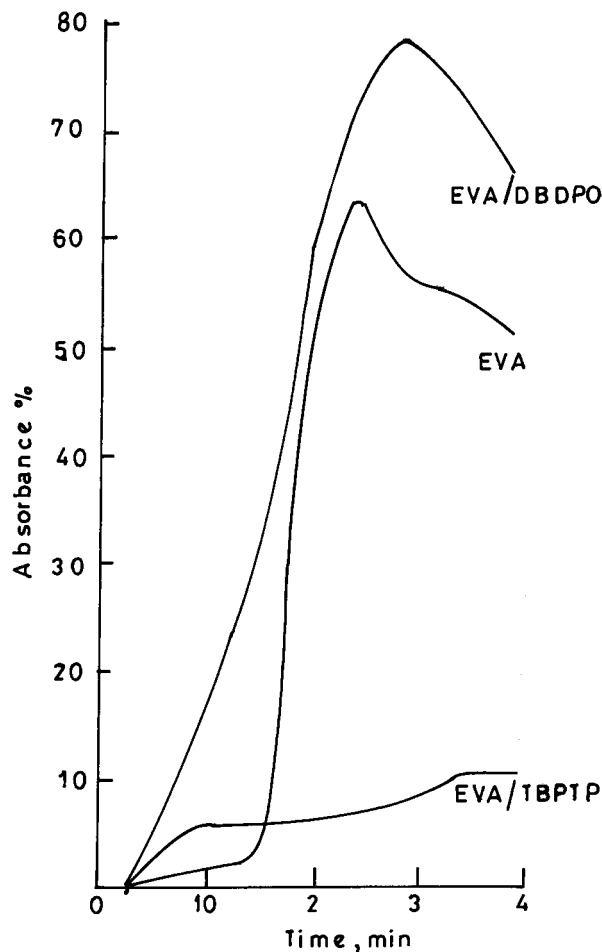


Figure 9 Smoke density curves of EVA, EVA/TBPTP, and EVA/DBDPO.

in its structure. As bromine in TBPTP is bound to both the aliphatic (30.5%) and aromatic (22.5%) moieties and as their thermal stabilities differ, bromine will be available over a wide range of temperature during the thermal decomposition of LDPE. The advantage of having bromine built in the same molecule whose structure has both aromatic and aliphatic moieties has been observed in other systems as well.^{16,17} (However, it has been observed that at higher concentration DBDPO has been found to give higher values of LOI than that of TBPTP.) Similar experiments were carried out with another commercially available FR: tetrabromobisphenol A (TBBP). The bromine in this case also is attached to the aromatic moiety. The results show that the behavior of TBPTP is superior to that of TBBP. It is well known that antimony trioxide (Sb_2O_3) acts as a synergistic agent for brominated FRs.^{1,6-8,22} Figure 6 gives the effect of the addition of antimony trioxide to the LDPE/

TBPTP blend. The LOI of the blend was found to increase up to 5 phr of the oxide and then decrease. A total of only 2.5 units of increment in the LOI value of the blend was observed. It is established that an Sb : Br ratio of 3 : 1 is generally used in halogenated FR systems.²² However, in the present system, Sb : Br ratio of 5 : 1 was required for effective performance. An analysis of the pyrolysis products is required to understand the reason. It is possible that, in the present case, antimony pentabromide is formed rather than antimony tribromide. Substitution of Sb_2O_3 by SnO_2 gave similar results.

It is reported that certain metal oxides such as ferric oxide influence the action of antimony trioxide positively to further enhance the LOI value. They act possibly by lowering the disproportionation temperature of antimony oxybromide intermediates, making available halogen at a lower temperature for radical scavenging action.^{6,7,22} Figure 7 shows the combined effect of antimony trioxide and ferric oxide on the LDPE-TBPTP blend. The value of LOI has increased to 27.5. Table III provides the flammability behavior of the EVA-TBPTP blend. At a 10% level, TBPTP makes EVA self-extinguishing with a final LOI of 27.5. It shows that TBPTP is more effective with EVA than with LDPE. However, in the case of DBDPO, the enhancement in the value of LOI was similar in both EVA and LDPE. To meet the flammability criteria for cables, a minimum LOI value of 30 is required. So, further increases in the LOI of the blends were achieved by manipulations with additives such as alumina or calcined clay.

Mechanical Properties

Table IV provides the tensile properties of the LDPE-TBPTP blend. The ASTM standard for the cable material is also given in Table IV for comparison. The data show that incorporation of TBPTP slightly reduces the tensile properties of LDPE, but it was found that even up to a 25% addition of TBPTP the strength values are within the ASTM standard. Table V gives the strength values of the EVA-TBPTP system. The results indicate that the addition of TBPTP does not affect the mechanical properties adversely. Table VI shows that the addition of fillers reduces the % elongation drastically. In the presence of the FR, it was, however, noted that the a higher loading of the filler could be achieved without much decay in mechanical properties. ATH and $Mg(OH)_2$ could raise the LOI values of these for-

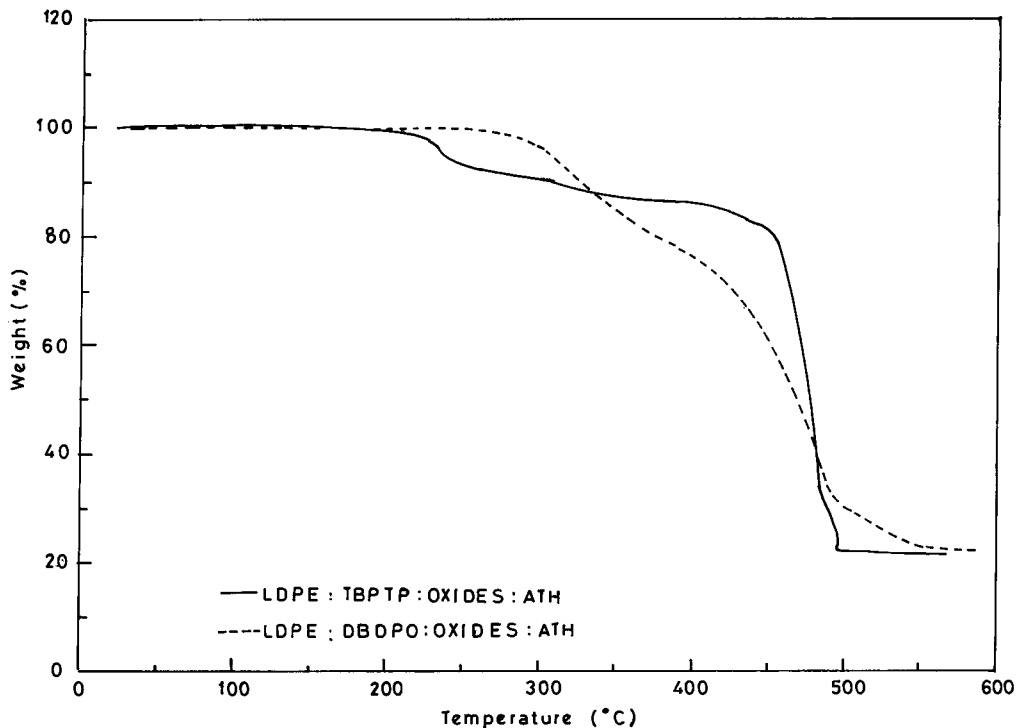


Figure 10 TGA of LDPE/TBPTP and LDPE/DBDPO.

mulations to and above 30, whereas calcined clay could not. Based on the relative performance including better processability, ATH was selected as the filler for further studies. ATH was recently reported to be used in low smoke compositions.³⁸ [With minor variations in compositions, it is possible to use both $Mg(OH)_2$ and calcined clay as a filler.] The properties of the ATH-filled blends were within the specifications for cable materials for jacketing applications as given in Table VII. In the case of LDPE, the reduction in percentage elongation was quite pronounced and, hence, a lower loading than that in EVA has to be used if the percentage elongation is to be maintained at the specification level. The deterioration in mechanical properties in the case of LDPE-DBDPO blends was much higher than that of TBPTP blends, but in the case of the EVA-DBDPO blend, the corresponding values were similar to those of the EVA-TBPTP blend.

Smoke Density Measurements

Evolution of smoke and toxic gases is a serious problem in the use of FRs, particularly in the case of halogenated FRs.^{1-8,22} Halogens, particularly bromine, give rise to profuse fumes which them-

selves may endanger life-saving endeavors. However, brominated FRs, because of their effectiveness and the inability of other systems to fully substitute them, continue to dominate the FR scene.² The amount of smoke generated is measured using a smoke density meter. Figures 8 and 9 give the smoke density data for LDPE-TBPTP and EVA-TBPTP blends in comparison to the DBDPO blends. The evolution of smoke generated by TBPTP was much less than that of DBDPO. Moreover, Figure 9 further shows that the smoke evolution for the EVA-TBPTP blend is much less than that of EVA alone. This observation was tested repeatedly to obtain the same results. As a brominated compound should produce a certain level of smoke, the present data suggest the possibility of some unknown mechanism operating to reduce the level of smoke in the case of the EVA-TBPTP blend. This is a finding which has not been reported so far and it requires further study to understand the mechanism. There are a few rare reports⁷ that suggest a role for bromine operating in the char rather than in the vapor phase. In such a situation, the formation of a stable char-forming bromo compound is indicated. However, char data from TGA show only < 1% char, which cannot account for the extremely low reduction in

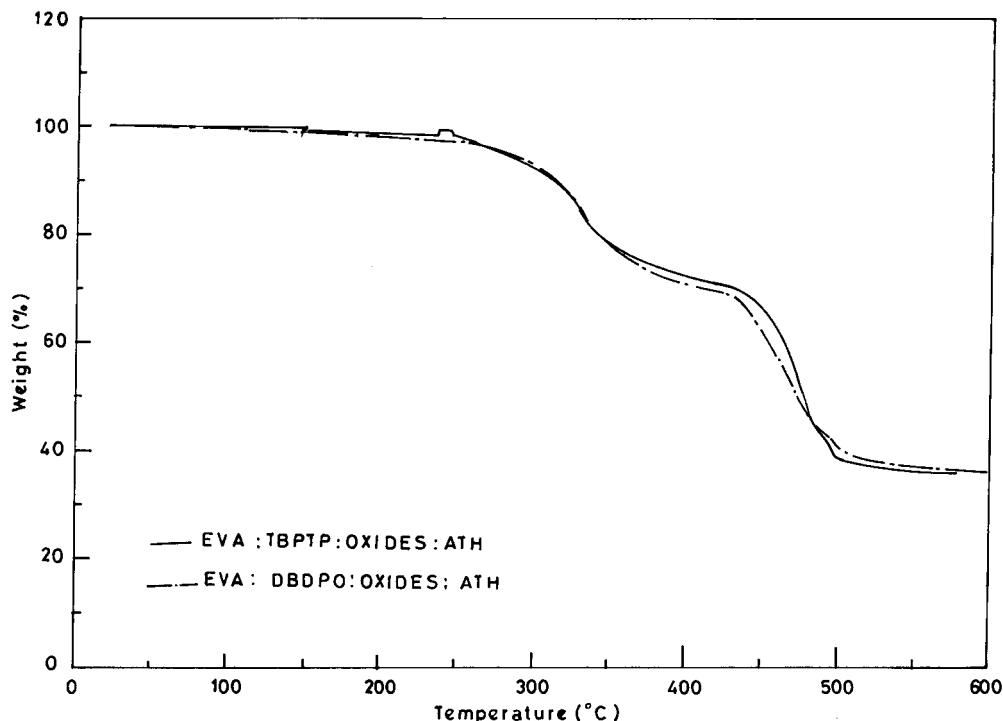


Figure 11 TGA of blends of EVA and TBPTP and EVA/DBDPO.

smoke. So, the other possible explanation might center around the formation of a stable volatile bromo compound that might evaporate without producing smoke-generating species. This aspect is not further studied. The percentage light absorption, percentage light transmission, and smoke density rating of the final formulations measured as per ASTM D 2843-77 are given in a later section.

Thermal Behavior of the Filled Compositions

The effect of TBPTP on the thermal stability of LDPE and EVA was discussed earlier. The addition of fillers and oxides are expected to increase the thermal stability and the results are given in Figures 10 and 11, respectively, for the LDPE-TBPTP and EVA-TBPTP systems. As expected, the thermal stability of the filled compositions are much superior to the unfilled compositions. Similar results were observed for the DBDPO blends as well.

Comparative Evaluation of Power Consumption for TBPTP and DBDPO Blends During Mixing

Table VIII provides a comparative evaluation of rheological properties and power consumption for

LDPE(90) : EVA(10) systems containing TBPTP and DBDPO. The torque profiles are given in Figures 12 and 13. The processability characteristics of the two mixes (filled) containing TBPTP and DBDPO were measured on the Brabender plasticorder at 120 and at 140°C at a rotor speed ranging from 30 to 90 rpm. Rheological parameters such as the melt-viscosity, flow behavior index (n), and power consumption were estimated from the equilibrium values of the torque after 10 min of processing in each case. The comparatively lower values of melt-viscosity and power consumption for the TBPTP-modified formulation along with its higher value of the flow behavior index at 120°C indicate its improved processability over that of the unmodified polymer. It should also be noted that the TBPTP-modified samples exhibit better processability than that of the DBDPO-modified samples.

Evaluation for Cable Properties

Based on the above findings, formulations containing TBPTP as an FR and ATH as a filler and a Sb_2O_3 synergist along with an antioxidant and a mold-release agent (by experience, it was noted that this system does not require a curing agent such as dicumyl peroxide which is invariably

Table VIII Comparative Evaluation of Rheological Properties of Filled LDPE-TBPTP and LDPE-DBDPO Blends Containing 10% EVA

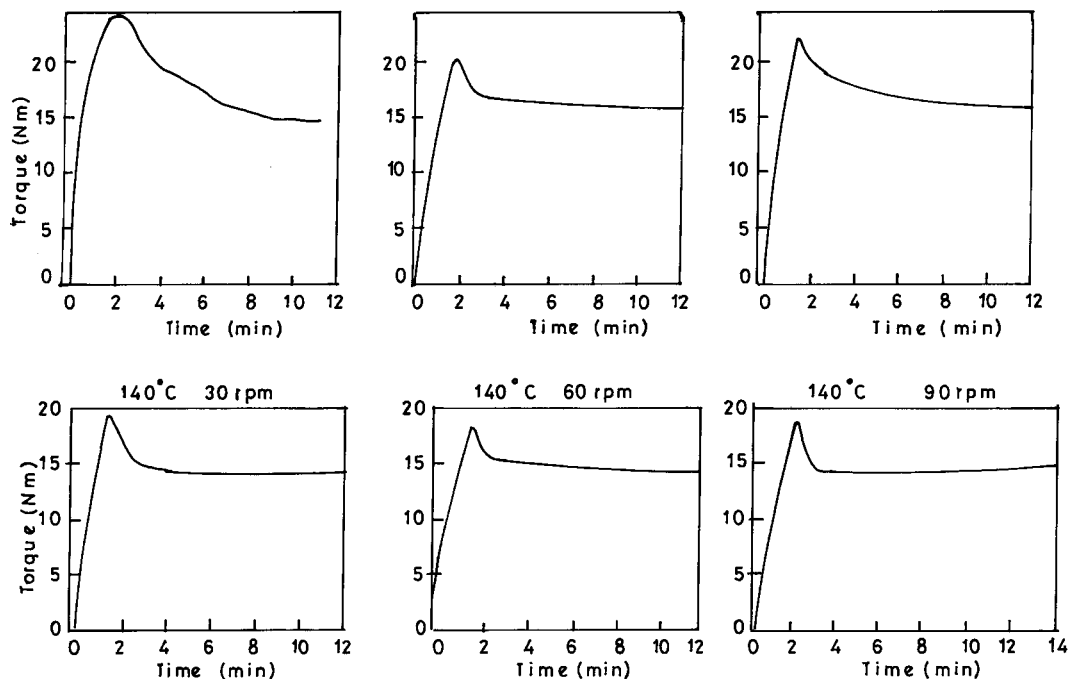
Parameter	LDPE-TBPTP Blend			LDPE-DBDPO Blend		
Rotor speed, S (rpm)	30	60	90	30	60	90
Equilibrium torque, M (Nm)	10	11	12	14	15	16
Melt viscosity (mg/rpm)	33.99	18.70	13.60	47.59	25.49	18.13
Flow behavior index (n)	0.17	0.17	0.17	0.12	0.12	0.12
Power consumption, P (W)	31.34	69.08	113.04	43.96	94.20	150.7

added to formulation containing LDPE and EVA) were compounded and extruded into wire and the properties of the cable were measured. Table IX provides the final properties of the cable made from EVA.

A comparative evaluation of the properties with the values of a standard specification for the FRLS grade shows that the EVA-TBPTP system containing 10% TBPTP (composition A) was found to meet the requirements for the FRLS grade. Composition A obeys the entire specification range for FRLS cable material for jacketing. The LDPE-TBPTP system did not meet the criteria for FRLS cable materials and so the data are not provided here. This, however, should not be explained to mean that TBPTP cannot be used as an FR for LDPE.

Composition A of the EVA-TBPTP system ex-

hibited self-extinguishable behavior when burnt by a vertical burning test. Figure 14 shows the experimental sample (b) with a control (a) after firing for 10 s. The flame on the FRLS cable material became extinguished immediately after the removal of the flame, indicating that it is behaving as a self-extinguishable material. Although the test was not conducted strictly as per UL 94 (Standards for Tests for Flammability of Plastic Materials for Parts in Devices and Appliances, Subjects 94, Underwriters Laboratories, Northbrook, IL, September 17, 1993), the present experiment does indicate that it can be placed under the grade UL 94 V-0. The EVA control sample burnt out completely with dripping. The data for DBDPO-EVA are also shown in Table IX. It can be noted that the values for TBPTP-EVA are far superior to those of the DBDPO-EVA system.

**Figure 12** Brabender torque profiles of filled LDPE (90)/EVA (10)/DBDPO blends.

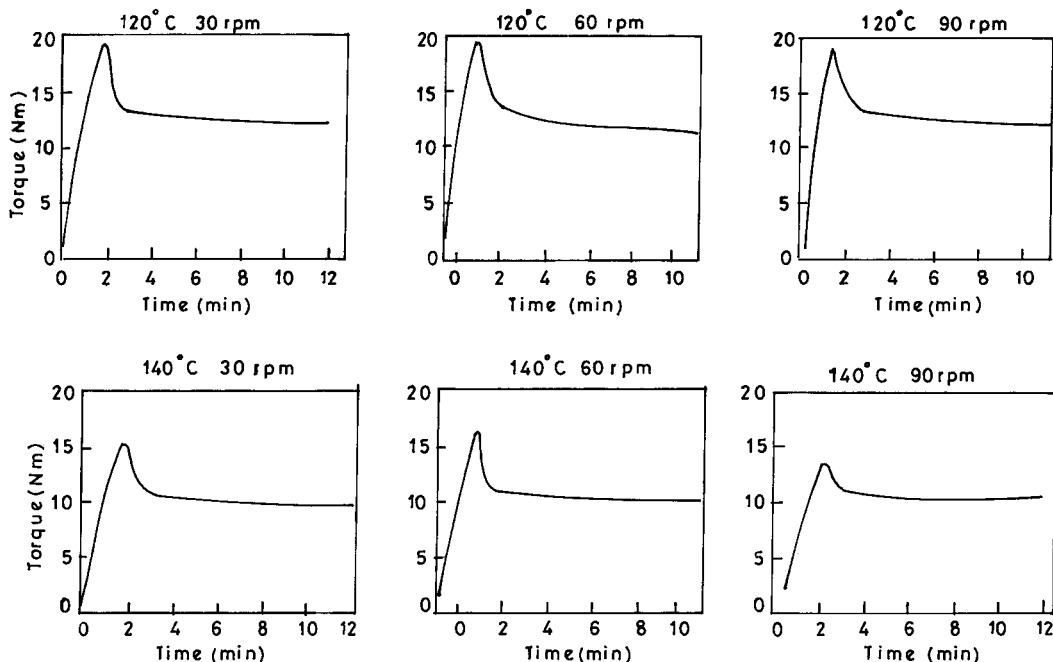


Figure 13 Brabender torque profiles of filled LDPE (90)/EVA (10)/TBPTP blends.

The possible explanation for the superior behavior of TBPTP compared to that of DBDPO was given in the earlier sections. The overall performance of a wide-spectrum FR having bromine distributed between aromatic and aliphatic moieties has thus been found to be better than fully aromatic brominated FRs. A blend of 50 : 50 LDPE and EVA was also tested and this also gave an FR composition with TBPTP that meets the specifications for ca-

ble-jacketing materials that did not meet the FRLS grade.

CONCLUSIONS

TBPTP, a new brominated FR (having bromine distributed between aliphatic and aromatic moieties) was found in combination with a synergistic

Table IX Properties EVA-TBPTP and EVA-DBDPO Cables

Property	EVA-TBPTP Cable		EVA-DBDPO Cable (20%)
	10-15% (A)	20% (B)	
LOI	30.0	34.6	32.5
Oxygen index at 250°C	21	27.1	25.5
Smoke density rating (%)	3.0	7.0	48.5
Light transmission (%)	96	82	20
Light absorption (%)	4	18	80
Acid gas emission (%)	2	7.7	10.5
Volume resistivity (ohm cm)	1.11×10^{10}	1.8×10^{10}	1×10^{10}
Dielectric constant at 100 kHz	2.01	2.08	5.76
Tensile strength (MPa)	6.8	6.2	6.8
Elongation at break (%)	450	400	450
Aging at 100°C 168 h TS/Eb	7.8/370	7.8/300	7.7/350

^a TS = tensile strength; Eb = elongation.



Figure 14 Vertical burning test. (b) Experimental sample with (a) a control after firing for 10 s.

agent, promoter, and filler to be an effective FR for EVA, permitting it to achieve the FRLS grade. A vertical burning flammability test showed that the composition is self-extinguishable.

The smoke density values of the system were almost negligible, permitting it to achieve the FRLS grade and the percentage of acid emission was below 2. This is possibly the first instant of a bromo compound to be classed under this grade. The extremely low smoke density values of the TBPTP-EVA system needs further study to understand the mechanism.

Comparative evaluations of the performance of various factors such as processability, compatibility, and mechanical properties of the blends of TBPTP and DBDPO with EVA and LDPE show that the overall performance of TBPTP was superior to that of DBDPO and this was true up to a percentage addition of 20%. In the case of thermal stability, the blends of both systems gave comparable results although DBDPO alone gave a higher value than that of TBPTP alone. The superior performance of TBPTP over DBDPO was explained on the basis of the structure of TBPTP

having bromine distributed between aliphatic and aromatic moieties of the same molecule. When compared to the fully aromatic bromine, a distribution of bromine between aliphatic and aromatic moieties assures the availability of bromine over a long temperature range for effective flame retardation. It would be interesting here to note that some experiments conducted with SnO_2 substituting Sb_2O_3 gave promising results, indicating possibilities for completely eliminating Sb_2O_3 .

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