Studies on the Flammability of Short Kevlar® Fiber-Thermoplastic Polyurethane Composite

SUNIL K. N. KUTTY
Department of Polymer Science and Rubber Technology
Cochin University of Science and Technology
Kochi 682 022
India

GOLOK B. NANDO*
Rubber Technology Centre
Indian Institute of Technology
Kharagpur 721 302
India

(Received June 1, 1992)
(Revised August 11, 1992)

ABSTRACT: The flammability of short Kevlar® aramide fiber-thermoplastic polyurethane (TPU) has been investigated with respect to fiber loading and various flame retardant additives such as halogen containing polymers, antimony oxide/chlorine donor combination, zinc borate, and aluminum hydroxide. Smoke generation was reduced drastically, while the oxygen index was reduced marginally in the presence of short fibers. The best improvement in the oxygen index was obtained with antimony oxide/chlorinated paraffin wax combination, in the weight ratio 1:6. A 70 phr loading of aluminum hydroxide improved LOI and reduced smoke generation.

INTRODUCTION

IT IS NOW well established that it is the smoke and the toxic gases (STG) that are more dangerous than the hazards due to the fire itself. Principal hazards resulting from the generation of STG are obscuration and poisoning. Obscuration is caused by particulate materials suspended in the air. Poisoning depends on the quality and quantity of the toxic materials in the combustion products. In this context reducing smoke generation in fire calls for as much attention as for improving the flame resistance of materials.

Thermoplastic polyurethane is a high performance thermoplastic elastomer and is widely being used in cable industries as well as in applications like automobile parts, belting, tires, etc. Despite very attractive mechanical properties TPU is handicapped by its low fire resistance and high smoke generation during combustion. Grassie et al. studied the effect of ammonium polyphosphate on the thermal degradation of polyurethanes [1,2]. A composite with short Kevlar® fiber was found to have better mechanical properties [3]. The composite has also been evaluated for its rheological and stress relaxation properties [4,5]. Kutty and Nando have reported the thermal degradation behavior of Kevlar®-TPU composite recently [6]. A systematic study to improve the flammability of this composite is lacking. Attempts to produce fire resistant urethane were mainly confined to polyurethane foams [7]. In this study an attempt has been made to optimize various fire retardants for short Kevlar®-TPU composite. Fire retardant additives such as halogen containing materials, antimony oxide/halogen donor combination, zinc borate, and aluminum hydroxide were compared. The effect of fiber content on the flame resistance of the optimized fire retardant composition also is reported.

EXPERIMENTAL

Ether-based thermoplastic polyurethane (Estane 58311, molecular weight = 1.5×10^5 and $T_g = -21$°C) used in this study was obtained from Urethane India and Kevlar® staple fibers (T-970) of approximately 6 mm length were obtained from E. I. du Pont de Nemours and Co., USA.

Formulation of the mixes is given in Tables 1 and 2. Kevlar® fibers and TPU were dried at 105°C for 2 hours in an air oven. The mixing was carried out in a Brabender plasticorder attached with a cam type mixing head at 180°C and a rotor speed of 60 rpm for six minutes. The mixing sequence is shown in Table 3. The molten mass from the plasticorder was sheeted out immediately on a two roll open mixing mill at tight nip. Sheets of 2 mm thickness were molded at 180°C for 3 minutes and quench cooled by immersing the mold in water. Test pieces

---

®Kevlar is a registered trademark of DuPont.
*To whom all correspondence should be addressed.

0734-9041/93/01 0066–14 $06.00/0

Table 1. Formulation of the mixes.

	PW	SPW	SPE	SPV	SPV(S)	SP1	SP2	AL	ZB
TPU	100	100	100	100	100	100	100	100	100
Antimony oxide[1]	—	5	5	5	5	5	5	—	—
CPW	a	a	—	—	—	—	—	—	—
CPE	—	—	a	—	—	—	—	—	—
PVC	—	—	—	a	—	—	—	—	—
PV(S)	—	—	—	—	a	—	—	—	—
P1	—	—	—	—	—	a	—	—	—
P2	—	—	—	—	—	—	a	—	—
$Al(OH)_3$	—	—	—	—	—	—	—	b	—
Zinc borate	—	—	—	—	—	—	—	—	c

[1] Manufactured by Cookson Ceramics and Antimony Ltd., USA.
CPE—chlorinated polyethylene, 42% chlorine content, obtained from Hoechst, Germany.
CPW—chlorinated paraffin wax, 40% chlorine content, obtained from NICCO Corporation, India.
ZB—zinc borate, manufactured by U.S. Borax, California.
PVC—rigid PVC, Ka = 60, obtained from Bata, India Ltd.
a—5, 10, 20 and 30 phr.
b—30, 50 and 70 phr.
c—2, 5, 10 and 20 phr.
P1 and P2 are given in Table 2.

Table 2. Formulation of the mixes.

Ingredient	PV	PV(S)	P1	PV2
PVC	100	100	100	100
TBLS[1]	—	6	6	6
DOP[2]	—	—	40	—
Santicizer® 148[3]	—	—	—	40

[1] Tribasic lead sulfate.
[2] Dioctyl phthalate.
[3] Isodecyl diphenyl phosphate, obtained from Monsanto Co., USA.

Table 3. Mixing sequence.

Ingredient	Time, min	RPM	Ram
1/2 TPU	0	30	up
Fiber + fire retardants	1.5	30	up
1/2 TPU	3.0	60	down
—	9.0	—	dump

were cut out along and across the milling direction. Fiber orientation in test samples is shown schematically in Figure 1. Limiting oxygen index (LOI) was determined on a Stanton Redcroft FTA flammability unit. Smoke density measurement was carried out in a smoke density test chamber as per ASTM D 2843-77.

RESULTS AND DISCUSSION

Figure 2 shows the LOI and smoke density of TPU filled with 10 to 40 phr short Kevlar® fibers. Smoke density is reduced from 90 to 32 at 40 phr Kevlar® short fiber. The drop is very steep initially–up to 10 phr–beyond which the change is less significant. LOI values show a marginal reduction in the presence of short fibers. LOI is reduced from 20.3 and remains in the range 17.2–17.8 for the fiber content up to 40 phr. The shift in LOI to the lower side is unexpected, as it has been reported from the degradation studies that the thermal stability of TPU is improved in the presence of short Kevlar® fibers [6]. The reduction in LOI with fiber loading may be attributed to the following. Vertically kept neat TPU sample drips down during burning, thus depleting the burning head of the fuel. For a flame to sustain, a continuous supply of fuel and oxygen is needed. In the presence of fibers, the dripping is arrested completely even at a fiber loading of 10 phr. The burnt samples with and without fibers are shown in Figures 3(a)–3(d). The degradation of polyurethane takes place by first decomposing into its components, namely polyols and isocyanates which undergo further degradation at

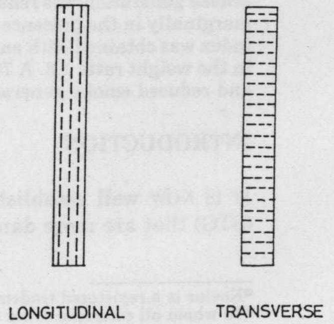

Figure 1. Schematic representation of fiber orientation in the flammability test samples.

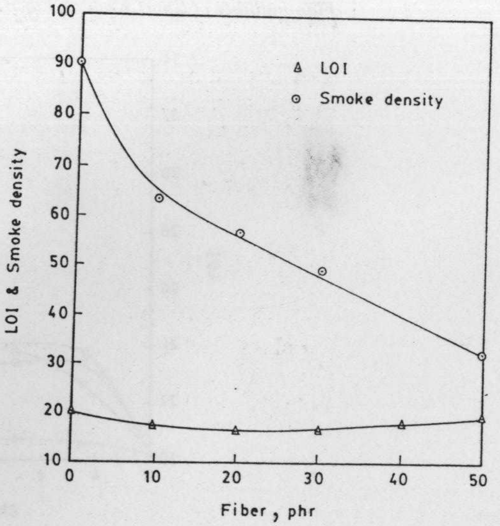

Figure 2. LOI and smoke density of short Kevlar® fiber–TPU composite (TPU-100 and Kevlar® varies from 10–40 phr).

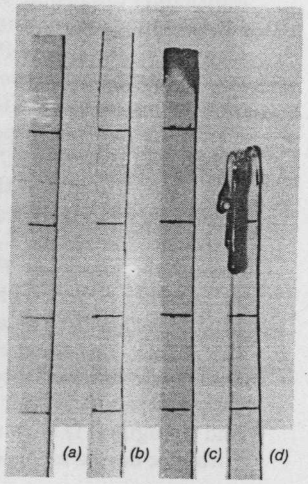

Figure 3. LOI test samples before and after testing (a) 10 phr fiber-filled TPU before burning, (c) after burning, (b) neat TPU before burning, and (d) after burning.

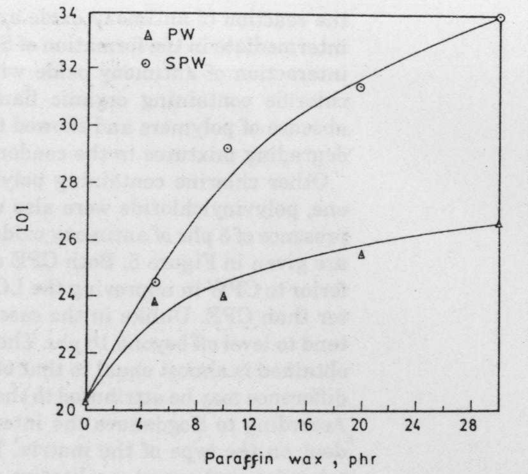

Figure 4. LOI vs. the amount of CPW with and without antimony oxide.

high temperature [8]. In the absence of dripping, the primary degradation products are available for further burning, thus resulting in lower LOI.

Low smoke formation in the presence of short fibers points to the formation of less volatile products during combustion leading to high char formation [7]. Thermogravimetric analysis of 0–40 phr Kevlar® TPU showed that the char residues of the fiber-filled samples at 800°C were higher than the values calculated from the residues of the individual components at the same temperature [6].

Halogen containing polymers are known for their fire retardancy. The halogens are gas phase flame retardants, as they react with other free radical species in the flame. Chlorinated paraffin wax (CPW) was used in different proportions in TPU and the flammability and smoke generation were estimated. Figure 4 shows the LOI values at different CPW loading (Mix PW). LOI registers an improvement from 20.3 to 26.6 at 30 phr loading. In another series, CPW was varied in the same range, in the presence of 5 phr of antimony oxide (Mix SPW). The presence of antimony oxide improves the oxygen index significantly, as is seen in Figure 4. This indicates a synergistic effect of the antimony oxide/CPW combination. It has been reported that SbOCl formed by reaction of antimony oxide and the halogen donor, during combustion, is the fire retardant species [9]. Pitts [10] reported that $SbCl_3$ formed by the reaction of antimony oxide and halogen donor and SbOCl was an intermediate in the formation of SbCl$_3$. Bogdanova et al. [9] studied the interaction of antimony oxide with hydrogen chloride vapor and the chloride containing organic flame retardants in the presence and absence of polymers and showed that SbOCl was formed in thermally degrading mixtures in the condensed phase.

Other chlorine containing polymers such as chlorinated polyethylene, polyvinylchloride were also used in the same proportions, in the presence of 5 phr of antimony oxide and the LOI was determined. These are given in Figure 5. Both CPE and rigid PVC are found to be far inferior to CPW in improving the LOI. Of the two, PVC is marginally better than CPE. Unlike in the case of CPW, the effect of CPE and PVC tend to level off beyond 10 phr. The maximum value of the oxygen index obtained is almost equal to that obtained at 5 phr loading of CPW. The difference may be attributed to the difference in their thermal stability. According to Bogdanova the intermediate SbOCl formation is dependent on the type of the matrix. He showed that the flame retardant mixtures underwent qualitative and quantitative transformations in the pre-flame zone of the condensed phase and these differences influenced the fire retarding efficiency. PVC was stabilized with TBLS [Mix SPV(S)] and plasticized with dioctyl phthalate (Mix SP1) and Santicizer® (Mix SP2). These were used along with antimony oxide and the OI and smoke density were determined. Figure 6 shows the effect of these modifications of PVC on its flame retardant effect. SP1 and SP2 series samples give the oxygen index (OI) values close to that of the SPV series. Compared to dioctyl phthalate, Santicizer® 148-plasticized PVC exhibits a better performance. This indicates that, of all the chlorinated polymer used, CPW in the presence of antimony oxide gives the best improvements in the flame resistance of TPU.

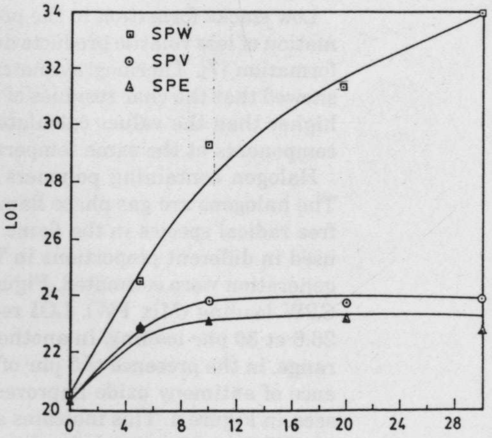

Figure 5. LOI vs. chlorine donor concentration.

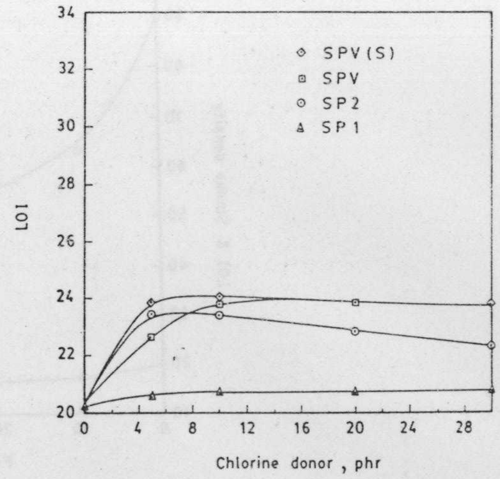

Figure 6. Effect of modification of PVC on the LOI.

Al(OH)$_3$ was incorporated in the range 30–70 phr (Mix AL) and zinc borate in the range 2–20 (Mix ZB) into TPU and the resultant OI values are shown in Figure 7. Al(OH)$_3$ improves the oxygen index values only above 30 phr. At 70 phr loading, OI is raised to 22.7 from 20.3 of neat TPU. The action of Al(OH)$_3$ is mainly physical dilution of the matrix. The water released by Al(OH)$_3$ cools the flame, thereby reducing the flammability.

Zinc borate is a good flame retardant and smoke suppressor. Shen and Sprague [11] have reported that replacing part of antimony oxide with zinc borate reduced smoke and improved flame resistance of PVC.

®Santicizer is a registered trademark of Monsanto Co.

The effect of zinc borate on OI of TPU is shown in Figure 7. The LOI is improved gradually up to about 6 phr and then tends to level off to 21.6 at higher loading. Zinc borate is a condensed phase fire retardant [11]. During combustion zinc borate separates into nearly pure boric oxide phase and one-to-one zinc borate [12], and boric oxide is a good inhibitor for the oxidation of carbonaceous material [13]. Table 4 gives the smoke generation of different samples. As expected, the smoke density is increased with increasing loading of chlorine containing fire retardants. Presence of 5 phr antimony oxide further increases the smoke generation in the case of chlorinated paraffin wax containing samples. CPE and PVC cause higher smoke generation than chlorinated paraffin wax at all proportions studied. Stabilization of PVC does not reduce the smoke generation. Plasticization of PVC does not affect the smoke generation. Plasticization of PVC by dioctyl phthalate and Santicizer® 148 results in almost the same smoke generation.

With increasing zinc borate content, the smoke is reduced gradually from 90 to 78 at 20 phr loading. For $Al(OH)_3$-filled samples, the smoke generation is reduced from 90 to 62 at 70 phr loading.

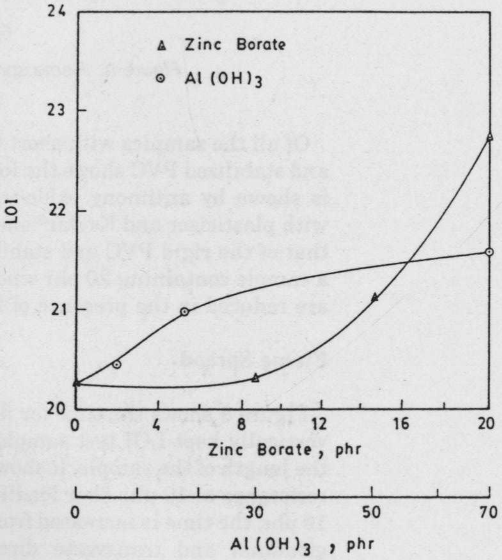

Figure 7. Effect of aluminum hydroxide and zinc borate on the LOI.

Table 4. Smoke generation characteristics of different mixes.

	Smoke Density (% absorbance)			
	Halogen Donor, phr			
Mix	5	10	20	30
PW	81	80	83	92
SPW	90	94	92	92
SPE	100	100	98	98
SPV	99	100	100	99
SP(S)	99	99	100	100
SP1	90	90	98	98
SP2	90	92	98	100
ZB[1]	85	80	78	78
AL[2]	74	70	62	—

[1] Zinc borate loading 2, 5, 10 and 20 phr.
[2] Aluminum hydroxide loading 30, 50 and 70 phr.

Effect of incorporating 20 phr short Kevlar® fibers on the OI and smoke density of different flame retardant TPU compositions is shown in Figure 8. The OI values and smoke generation are reduced in the presence of short fibers. The highest reduction in OI (40%) is for antimony oxide/CPW combination (Mix SPW)—it is reduced from 34 to 20.2, followed by sample containing only CPW. For this composite (mix CPW) the OI is reduced from 26.6 to 17.6 (33%). The minimum reduction of 1.4 unit (6%) is shown by both antimony oxide/CPE (Mix SPE) and antimony oxide/PVC (Mix SPV) combinations. For the sample with Santicizer® 148-plasticized PVC (Mix SP2) the reduction is by 14% and for sample with stabilized PVC [Mix SPV(S)], the reduction is about 8%. It is clear that the reduction in OI in the presence of 20 phr short Kevlar® fibers is different for different fire retardant combinations. The OI values of the Kevlar® fiber-filled samples show that the highest OI of 22.3 is given by rigid PVC followed by antimony oxide/CPE. OI is not changed by stabilization of PVC. A comparison of the OI values of Kevlar® fiber-filled CPW and Kevlar® fiber-filled antimony oxide/CPW shows that OI is higher in the presence of antimony oxide.

Smoke density of the fire retardant formulation is reduced in the presence of short Kevlar® fibers. The highest reduction in smoke is for antimony oxide/stabilized PVC combination. Antimony oxide/plasticized PVC and antimony oxide/stabilized PVC give a smoke density of 60 or less.

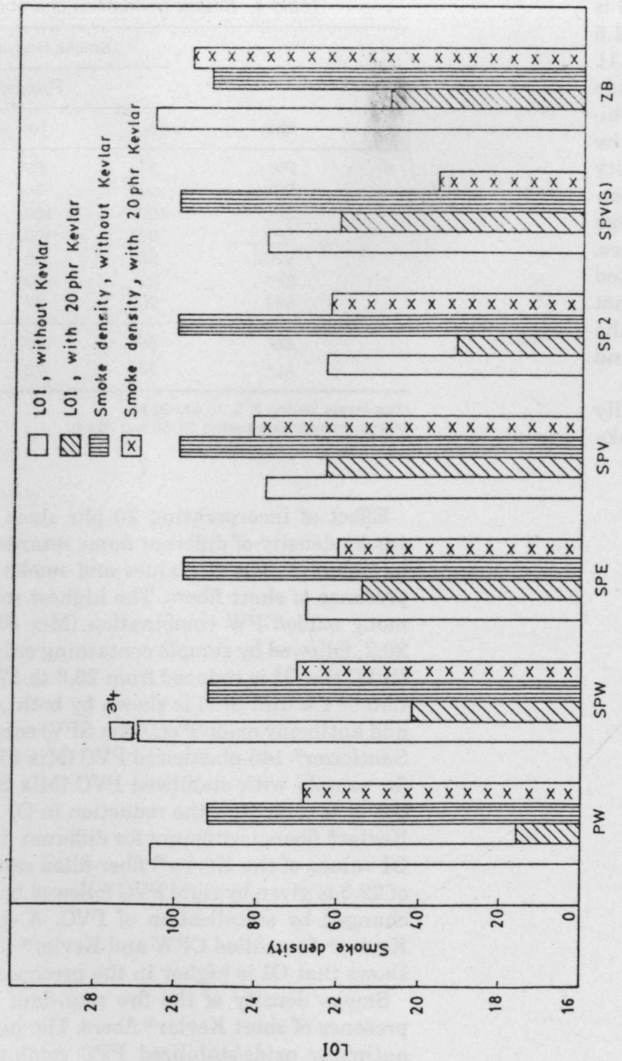

Figure 8. Effect of fiber loading on LOI and smoke density.

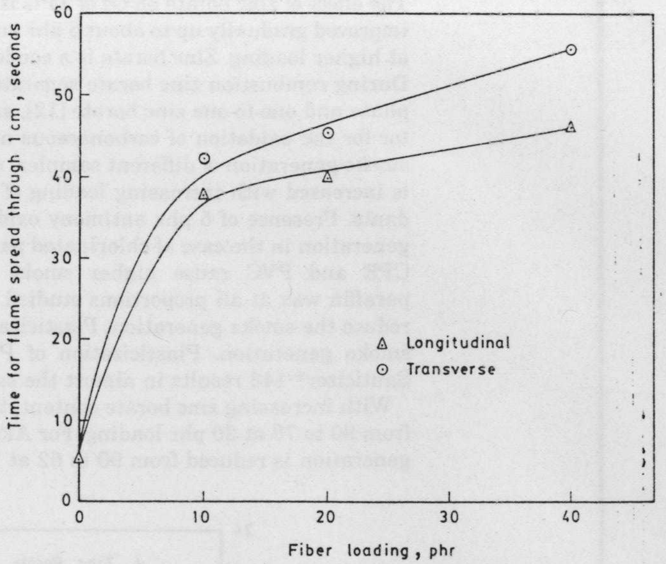

Figure 9. Flame spread at different fiber loading.

Of all the samples with short fibers, a combination of antimony oxide and stabilized PVC shows the lowest smoke generation and the highest is shown by antimony oxide/rigid PVC combination. Stabilized PVC with plasticizer and Kevlar® shows a smoke generation intermediate to that of the rigid PVC and stabilized PVC/antimony oxide/Kevlar®. For a sample containing 20 phr zinc borate, the LOI and smoke generation are reduced in the presence of 20 phr of Kevlar® fibers.

Flame Spread

Figure 9 shows the time for flame propagation through 1 cm down a vertically kept LOI test sample with fibers oriented along and across the length of the sample. It shows a sharp improvement in flame spread resistance at 10 phr fiber loading beyond which the effect levels off. At 10 phr, the time is increased from 5 seconds to 36 and 44 seconds in longitudinal and transverse direction, respectively. The faster flame spread in the case of TPU is due to dripping. In the presence of short fibers the dripping is totally avoided and the sample undergoes charring. The TPU samples with and without fibers after 1 min of burning are shown in Figures 3(c) and 3(d). The difference in height of the filled and unfilled samples indicates the relative ease of flame propagation in neat TPU. The total absence of dripping in the case of fiber-filled sample is evident from the figure. At all fiber loadings, the resistance to flame spread is higher when the fibers are oriented across the sample length than when they are oriented along the sample length. When the fibers are oriented longitudinally, the molten matrix below the burning head can ooze to the flame through the inter-fiber space comparatively easier than when they are in the transverse direction, thereby resulting in a faster flame spread.

CONCLUSION

From this study the following conclusions may be drawn:

- The flammability of TPU is increased marginally and smoke generation is reduced significantly in the presence of short Kevlar® fibers. The smoke generation is suppressed by high char formation. The rate of flame spread is reduced tremendously with short fibers. The flame spread resistance is higher when the fibers are oriented preferentially across the direction of flame propagation.
- Chlorinated paraffin wax along with antimony oxide improves the flame resistance of TPU to a higher extent than PVC and chlorinated polyethylene. The smoke generation is high in the halogen containing compositions. Zinc borate and aluminum hydroxide reduces the smoke generation.

REFERENCES

1. Grassie, N. and G. A. P. Mendoza. 1985. *Polym. Deg. Stab.,* 11:359.
2. Grassie, N. and G. A. P. Mendoza. 1985. *Polym. Deg. Stab.,* 11:145.
3. Kutty, S. K. N. and G. B. Nando. 1991. *J. Appl. Polym. Sci.,* 43:1913.
4. Kutty, S. K. N., P. P. De and G. B. Nando. 1991. *Plast. Rubber Comp. Proc. Appl.,* 15:23.
5. Kutty, S. K. N. and G. B. Nando. 1991. *J. Appl. Polym. Sci.,* 42:1835.
6. Kutty, S. K. N., T. K. Chaki and G. B. Nando. In press. *Polym. Deg. Stab.*
7. Grayson, S. J., J. Hume and D. A. Smith. 1982. *Plast. Rubber Proc. Appl.,* 2:111.
8. Yang, W. P., C. W. Macosko and S. T. Wellinghoff. 1986. *Polymer,* 27:1235.

9. Bogdanova, V. V., S. S. Fedeev, A. I. Lesnikovich, I. A. Klimovtsova and V. V. Sviridov. 1985. *Polym. Deg. Stab.,* 11:205.
10. Pitts, J. 1972. *J. Fire and Flammability,* 3:51.
11. Shen, K. K. and R. W. Sprague. 1982. *J. Vinyl Tech.,* 4:120.
12. Harrison, D. E. and F. A. Hummel. 1956. *J. Electrochem. Soc.,* 103:496.
13. Rakszawski, J. F. and W. E. Parber. 1964. *Carbon,* 2:53.