Design of Multiple Flame-Retardant Polymers

SABITABRATA ROY, SUKUMAR MAITI

Materials Science Centre, Indian Institute of Technology, Kharagpur, 721302, India

ABSTRACT: Two polyphosphonates having multiple flame-retardant actions were synthesized by interfacial polycondensation of a bisphenol and dichlorophenylphosphine oxide using cetyl trimethyl ammonium chloride as a phase transfer catalyst (PTC) at 0°C. The polyphosphanates thus prepared were characterized by viscometry, elemental analysis, IR, ^{1}H-NMR, ^{31}P-NMR, and X-ray diffraction studies. These polymers are highly soluble in polar solvents such as DMF, DMAc, DMSO, etc., as well as in chlorinated hydrocarbon solvents such as CH_2Cl_2, $CHCl_3$, etc. The thermal study of polymers was carried out by TGA and DTA analyses. The flammability of the polymers was studied by the limiting oxygen index measurements. The polymers are self-extinguishing, and begin to lose weight at around 252°C. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 785–792, 2001

Key words: polyphosphonate; fluorescence; thermal stability; flammability

INTRODUCTION

Aromatic polyphosphonates are well-known flame-retardant materials, and are generally prepared from the polycondensation of phosphonic dichloride with bisphenols.[1] In these polymers, flame retardancy arises mainly due to the presence of phosphorus in the polymer chain. The flame retardancy of these polymers may be further improved if their bisphenol moiety is such that this can also contribute to flame retardancy. Phenolphthalein, which can act as a bisphenol, based polymers are well-known flame-retardant polymers because of their ability to produce higher crosslinking density during pyrolysis, which subsequently leads to the greater yield of char.[2] Besides, they also produce carbon dioxide during thermal degradation, which acts as a flame-extinguishing agent and a diluent to combustible gases.

In this investigation an attempt has been made to modify the structure of phenolphthalein by incorporating bromine. The polyphosphonate based on the brominated phenolphthalein is expected to act as a flame-retardant polymer by three actions, viz. the condensed phase due to phosphorus, vapor phase due to liberated hydrogen bromide, and physical dilution due to liberated carbon dioxide during burning. A polyphosphonate from fluorescein having almost similar structure to that of phenolphthalein has also been synthesized to compare its thermal and flame-retardant behavior with the polyphosphonate prepared from brominated phenolphthalein.

EXPERIMENTAL

Materials

Phenolphthalein (S.D.Fine Chem.) was recrystallized from a mixture of methanol–water (m.p. 261–263°C). Fluorescein (S.D.Fine Chem.) was purified by refluxing with a concentrated HCl for 4 h, followed by recrystallization from a mixture

of methanol–water. Dichlorophenyl phosphine oxide (Lancaster) was purified by vacuum distillation before use. Bromine (S.D.Fine Chem.) was used as received. Dichloromethane was dried according to the reported procedure.[3] Acetic acid, acetone (BDH, India), and cetyl trimethyl ammonium chloride (Fluka) were used as received.

Monomer Synthesis

3,5,3′,5′-Tetrabromophenolphthalein

It was prepared according to the reported procedure.[4] In a two-necked 1000-mL reaction flask fitted with a thermometer pocket and a dropping funnel, 25 g (0.078 mol) of phenolphthalein was dissolved in 500 mL solution of 60 wt % of aqueous acetic acid. The temperature of the mixture was raised to 70°C with stirring until the clear solution was obtained. Next, 51.2 g (0.315 mol) bromine solution was added dropwise through a dropping funnel at this temperature. The addition was continued until the yellow color of bromine persisted. To ensure the completeness of the reaction, the reaction mixture was further stirred for another 2 h at this temperature and then cooled to room temperature. The white product was filtered, washed repeatedly with water to remove the excess bromine, and then further washed with aqueous sodium bicarbonate solution to remove the hydrobromic acid formed during the course of the reaction. The product was dried and recrystallized from acetone, yield 88%, m.p. 275°C (lit. 273–276°C).[5]

Polymer Synthesis

In a 250-mL reaction flask fitted with a stirrer were placed 2.5 mmol tetrabromophenolphthalein or fluorescein and 20 mL of aqueous KOH solution containing 0.29 g KOH (5.1 mmol). The solution was stirred and then 0.16 g (0.5 mmol) of cetyltrimethylammonium chloride (CTMAC) as PTC was added. The solution was then cooled to 0°C, and a solution of 2.5 mmol dichlorophenylphosphine oxide in 10 mL dichloromethane was added dropwise with vigorous stirring. The stirring was continued at this temperature for another 1 h. After this, the aqueous layer was decanted and the polymer solution was washed repeatedly with water. The polymer was precipitated by pouring the solution into excess hexane. The product was collected and dried at 50°C under vacuum.

Characterization

Inherent viscosity of the polymer solution in $CHCl_3$ was determined at 30°C using a Ubbelhode suspended level viscometer. Elements carbon and hydrogen of the monomer and polymer were analyzed by a Heraeus elemental analyzer. Elemental phosphorus and bromine were analyzed by the Schoniger combustion method.[6] The IR spectrum was recorded with a Perkin-Elmer Model 837 infrared spectrophotometer with KBr pellets. The ^{1}H-NMR spectra of monomer and polymer were recorded with a 200-MHz Varian EM 390 spectrometer in DMSO-d_6 and $CDCl_3$, respectively, using TMS as internal standard. The ^{31}P-NMR spectrum was recorded with a Brucker 270 MHz FT NMR spectrometer with $CDCl_3$ as solvent and H_3PO_4 as internal standard. TGA and DTA of the polymers were carried out with a Shimadzu DT 40 instrument in air at a heating rate of 10°C/min. Flame retardancy study of the polymer blends with chloroprene rubber (CR) and styrene butadiene rubber (SBR) was carried out by the limiting oxygen index (LOI) test. The test sample having 15 cm length, 0.8 cm width, and 0.2 cm thickness was burnt in a Flammability tester under controlled nitrogen–oxygen environments. The powder polyphosphonate samples were tested in a glass cup under similar test procedure with the same flammability tester. Because the powder samples were different from the standard test specimens, the results have been indicated by the Modified Oxygen Index (OI)$_m$.[7]

RESULTS AND DISCUSSION

Monomer Synthesis and Characterization

3,5,3′,5′-Tetrabromophenolphthalein was synthesized by reacting phenolphthalein with bromine in aqueous acetic acid medium at 70°C. Bromination is an electrophilic reaction, and it is very difficult to introduce bromine in the benzene ring, but the presence of an electron-donating —OH group makes it easier because of the environment of higher electron density at the two *o*-positions with respect to the phenolic —OH group of the benzene ring. The reaction of bromination can be represented as shown in Figure 1.

The tetrabromophenolphthalein was characterized by melting point determination, elemental analysis, and IR. The compound shows a sharp melting point at 275°C, and this value coincides
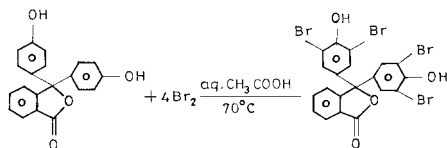
Figure 1   Reaction scheme for the preparation of tetrabromophenolphthalein.

with that of literature value.[5] The elemental analysis of the compound was done by chemical analysis. The results of elemental analyses agree well with the theoretical values obtained from chemical structure shown in Figure 1. The results of elemental analysis are as follows (the theoretical values are shown in parentheses): C: 37.19% (37.85%); H: 1.24% (1.57%); Br: 49.86% (50.44%).

The IR spectrum of the compound is shown in Figure 2. The spectrum shows absorption peaks at 3300 cm^{-1} due to the —OH group and at 1460 cm^{-1} and 1700 cm^{-1} due to the brominated aromatic ring[8,9] and the carbonyl group of the lactone ring, respectively. ^{1}H-NMR spectrum of the compound is shown in Figure 3. It shows a sharp singlet at 7.1 ppm for the proton (type "a") of the brominated benzene ring[10] and two doublets at 7.5 and 7.7 ppm for the protons "b" and "c," respectively and a quartret at around 7.4 ppm for the protons of type "d." The spectrum does not show any peak for the proton of the —OH group because of the high exchangable nature of these protons. This arises due to the high acidity of the compound because of the presence of electron withdrawing bromine group.
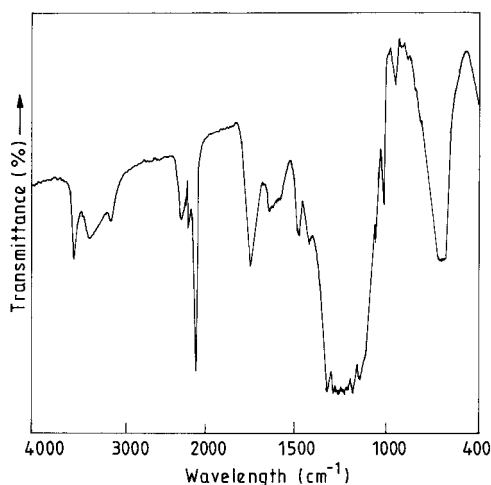

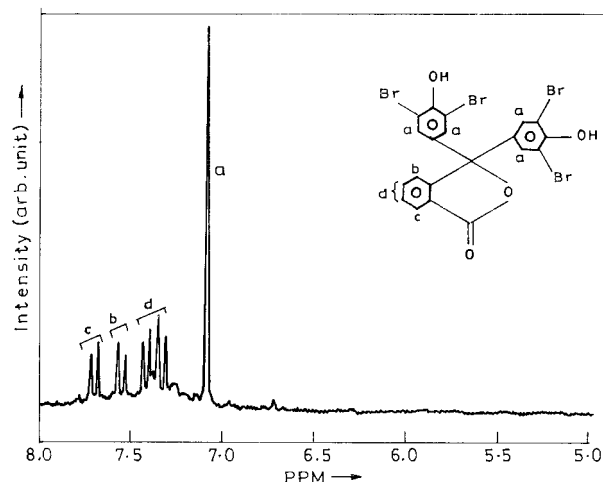**Figure 2**   IR spectrum tetrabromophenolphthalein.

Figure 3 ^{1}H-NMR spectrum of tetrabromophenolphthalein.

Polymer Synthesis and Characterization

Polyphosphonates were synthesized according to the following scheme (Fig. 4). Initially, the solution polycondensation was used to prepare polyphosphonates using different chlorinated hydrocarbon solvents with increasing boiling points such as CH_2Cl_2, $CHCl_3$, and $CHCl_2$–$CHCl_2$. The reaction was carried out in reflux condition in presence of triethylamine as acid acceptor. But in every case, polymer with very low inherent viscosity ($\eta_{inh} \leq 0.05$ dL/g) was obtained, and the yield in every case was more or less same (~75%). Imai et al.[11] reported that interfacial polycondensation using PTC offers a better method for the preparation of polyphosphonates using CTMAC as PTC.

In presence of alkali, tetrabromophenolphthalein produces a deep violet color rather than the usual pink color of phenolphthalein. This is due to the introduction of bromine, which shifts the absorption frequency from that of phenolphthalein, although color, in both cases, arises because of the
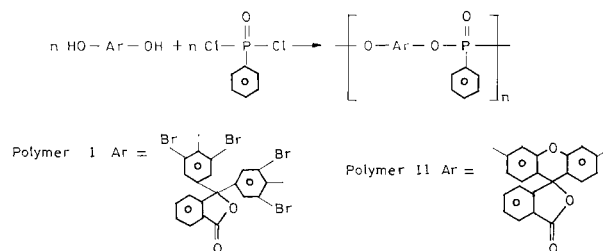

Figure 4   Reaction scheme for the synthesis of polyphosphonates.

Table I   Yield and Physical Properties of Polyphosphonates I and II

Polymer Code	Color	Yield, %	η_{inh},[a] dL/g Interfacial Method	Modified Method[b]
I	Light yellow	80	0.11	0.18
II	Brown	82	0.16	

[a] Measured in $CHCl_3$ (0.5 dL/g) at 30°C.
[b] Method developed by Morgan.[12]

formation of quinomethine structure. During polycondensation, there occurs a rapid loss of violet color, but complete loss of color does not necessarily mean that the reaction was complete because the pH becomes lower for the color change. Even this method of polymerization also results in very low molecular weight polymers.

To increase the molecular weight, the method adopted by Morgan[12] was used. After the initial color of the reaction mixture was discharged, fresh amount of alkali (three to four drops of 20% KOH) was added to bring back the color, stirring was continued, and a small portion of dichlorophenylphosphine oxide in dichloromethane was added. These steps were repeated twice. The inherent viscosity of the product was markedly increased. This procedure is suitable only where the sharp change of color occurs. Although fluorescein has the same type of structure that phenolphthalein has, and it also forms the quinomethine structure in the presence of alkali, the above method of polymerization cannot be used in this case due to lack of sharp change of color. The results of synthesis and the physical characteristics of polymers are summarized in Table I.

The low inherent viscosity of polymer I is due to the lower reactivity of the tetrabromophenol-phthalein because of the presence of electron withdrawing bromine atom. The low inherent viscosity of polymer II is due to low reactivity of fluorescein and lack of rapid and complete conversion of quinomethine structure to benzenoid, i.e., bisphenol structure. Such difficulty does not arise in the case of tetrabromo phenolphthalein, and as a result, Morgan's method cannot be used for the polymerization of fluorescein.

Both the polymers are highly soluble in polar solvents like DMF, DMAc, DMSO, and NMP as well as chlorinated hydrocarbon solvents like CH_2Cl_2, $CHCl_3$, but these are insoluble in hexane, acetone, methanol, etc. The chemical structure of polymers I and II was authenticated by elemental, IR, and NMR analyses. The elemental analysis of polymers was done by chemical analyses (Table II). The results of elemental analyses confirm the structure of the polymers shown in Figure 4. The IR spectra of the polymers are presented in Figures 5 and 6. The IR spectra shows characteristic absorption peaks around 1425 (P—Ph), 1270 (P=O), 1200 cm^{-1} (P—O—C).[13,14] The spectra also show peak at around 1790 cm^{-1} and a small plateau around 3300 cm^{-1} due to the carbonyl group of lactone ring and the —OH end group of the bisphenol, respectively.

The ^{1}H-NMR spectra of the polymers are presented in Figure 7. The spectra show no peak due to the proton of the —OH group present in the monomers confirming the formation of polyphosphonates. The aromatic protons of polymer I appear as a broad multiplet in the region 7.2–8.1 ppm, and the same for polymer II appear in the region 6.5–7.9 ppm.

Polymers I and II were further characterized by ^{31}P-NMR analysis. The spectrum of ^{31}P-NMR for the polymer I is shown in Figure 8. The spectrum shows a sharp singlet at 12 ppm. The ^{31}P-NMR spectra of dichlorophenylphosphine oxide [$PhP(O)Cl_2$] shows peak at 33.7–34.5 ppm.[15,16]

Table II   Results of Elemental Analysis and Characteristic IR Peaks of the Polyphosphonates I and II

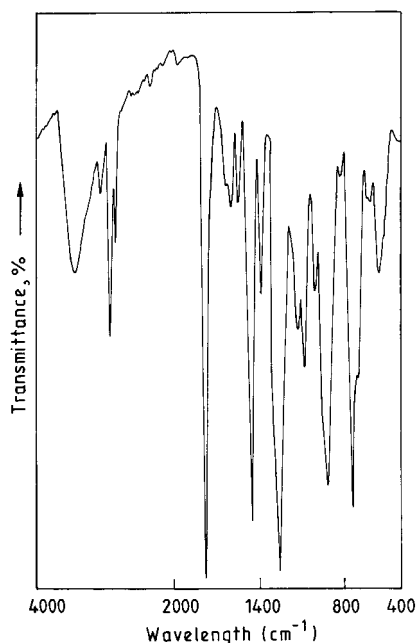| Polymer Code	Elemental Analysis, % Found (Calcd)				IR (cm^{-1})			
	C	H	P	Br	$\bar{\gamma}_{P=O}$	$\bar{\gamma}_{P—Ph}$	$\bar{\gamma}_{P—O—C}$	$\bar{\gamma}_{C=O}$
I	40.58 (41.29)	1.43 (1.72)	3.98 (4.10)	41.81 (42.29)	1267	1428	1180	1790
II	68.14 (68.72)	2.97 (3.30)	6.54 (6.82)	— —	1255	1420	1190	1785

Figure 5 IR spectrum of polymer I.

This shielding on the phosphorus atom is caused by the substitution of the electronegative chlorine atoms by —OPh groups in the polymers. The extent of shielding is comparable with 4,4'-diphenoxyphenyl phosphine oxide [PhP(O)(OPh)$_2$], in which the chemical shift in the ^{31}P-NMR spectra appears at 11.8 ppm.[17] Maiti et al. also reported the ^{31}P-NMR peaks for polyphosphonate at 12 ppm.

The fluorescein behavior of polymer II has also been investigated. When the excited molecule reaches a lower vibration state, it may then emit radiation and revert to the ground state; the radiation emitted, causing the fluorescence, is normally of lower frequency than that of the initial absorption. It is generally found that the most intensely fluorescent aromatic molecules are characterized by rigid, planer structures. For example, fluorescein exhibits very intense fluorescence in liquid solution, whereas phenolphthalein
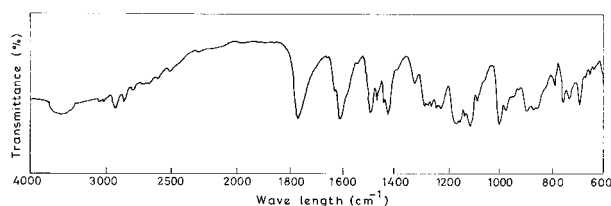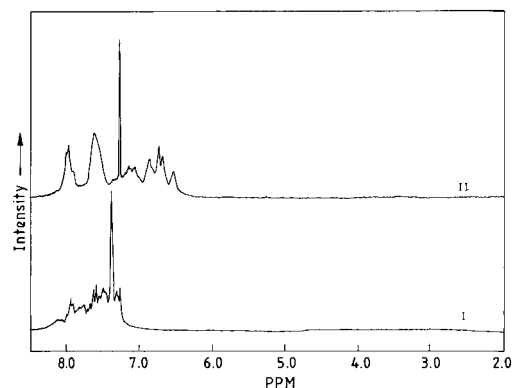

Figure 6 IR spectrum of polymer II.

Figure 7 ^{1}H-NMR spectra of polymer I and II.

does not, despite its structural similarity to fluorescein.[18] The principal effect of increasing molecular rigidity is to decrease vibrational amplitudes, which in turn, usually reduces the efficiency of intersystem crossing and internal conversion which competes with fluorescence.[19] For polymer II, the spectrum (Fig. 9) was recorded in DMAc solvent. The wavelength for excitation was 460 nm, and the spectrum shows a broad emission spectra, having a maxima at wavelength of 526 nm. This wavelength corresponds to the wavelength of the emission energy of polymer II.

X-ray Diffraction Study

X-ray diffraction patterns of the polymers I and II are presented in Figure 10. It shows that the polymers are completely amorphous in nature. This is expected, because polymers do not have a rigid moiety, and due to the bulky structure of the bisphenols, polymers are not able to arrange in definite pattern so that they can originate the crystalline region.

Thermal Behavior

The thermal behavior of the polymers was investigated and evaluated by TGA and DTA. The TGA
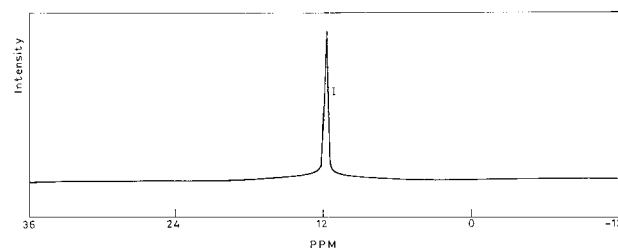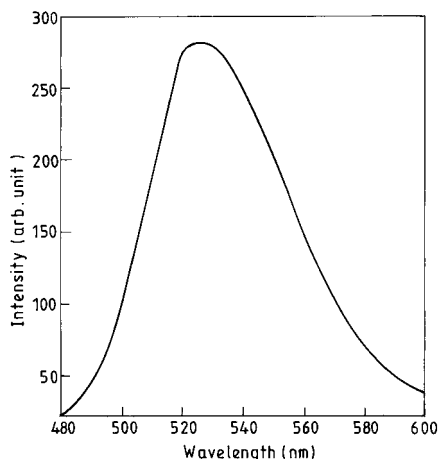

Figure 8 ^{31}P-NMR spectrum of Polymer I.

Figure 9   Fluorescence spectrum of polymer II.

Figure 11   TGA and DTA curves of polymers I and II.

curves for polymers I and II are presented in Figure 11. It shows that polymer I begins to lose weight at around 252°C, whereas the same for polymer II starts at 305°C. The temperature, corresponding to 10 and 50% weight loss for polymers I and II, are given in Table III. The TGA curve of polymer I shows that the polymer degrades in two steps. The first step ends at 331°C, and the weight loss in the first step of degradation is about 43.3%, which is very close to the theorretical weight loss of four bromine atoms (42.3%). From the weight loss data (Table III), it is evident that polymer II is more thermally stable than that of polymer I. This is expected, because the repeat unit of polymer II is a higher condensed polynuclear structure than that of polymer I, which confers extra stability to the former. The presence of a C—Br bond may also be attributed to the lower thermal stability of polymer I, because the C—Br bond is weak (66 k cal/mol), which undergoes dissociation very readily.

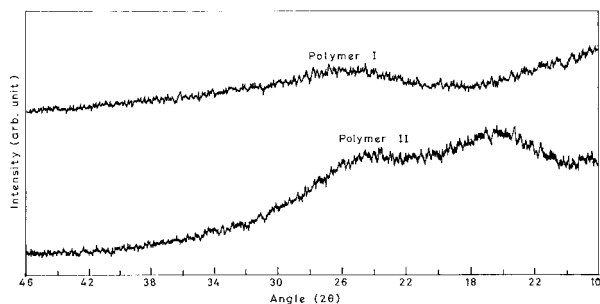The char residue of polymers I and II at 600°C are about 27.1 and 55%, respectively. The lower

char yield of polymer I is due to the presence of weak C—Br bonds. The loss of bromine accounts for the higher weight loss because weight percentage of bromine contributes significantly to the weight percentage of the entire polymer structure. It also may be due to the fact that a part of phosphorus is lost as volatile phosphorus bromide compounds; thereby, the availability of phosphorus is less for char formation. These two possibilities do not arise for polymer II, and thus give rise to a higher char yield than polymer I.

The DTA curves of polymers I and II (Fig. 11) show a discontinuous shift along the temperature axis. The DTA curve of polymer I shows an exothermic peak at about 260°C. This temperature falls within the first step of degradation, so this peak may be due to the dissociation of C—Br bonds. Finally, it gives a broad peak at 524°C due to the decomposition of the polymer. The DTA curve of polymer II shows a broad peak at around 540°C due to the decomposition of the polymer backbone. The higher decomposition temperature of polymer II than polymer I is due to the higher thermal stability of it, which is offered by the extra cycle ring of the bisphenol moiety.

Flame-Retardant Behavior

Both the polymers are self-extinguishing in nature like other phosphorus-containing polymers.[20,21] The $(OI)_m$ values of powder samples of polymers I and II are 51 and 42, respectively. The higher $(OI)_m$ value of polymer I may be due to the synergistic effect of phosphorus and bromine. Liberation of CO_2 during decomposition may also contribute somewhat to the flame retardancy. The phosphorus halogen compounds have been considered to be flame retardant due to either free radical quenching or by some other manner. According to some other workers, hydrogen halide

Figure 10   X-ray diffraction pattern of polymers I and II.

Table III   Thermal Behavior of Polymers I and II

Polymer Code	Temperature (°C) Corresponding to		Peak Temperature (°C) for Decomposition	Char Residue at 600°C, (%)
	10% wt. Loss	50% wt. Loss		
I	273	362	524	27.1
II	372	>600	540	55.0

splits off, which acts in the vapor phase, whereas phosphorus still modifies the condensed phase processes. There are some other cases where both phosphorus and bromine in the same compound are expected to increase flame-retardant activity. It is doubtful whether such combination really gives rise to synergism.[22–25] Polymer II has moderately high value of $(OI)_m$. Its char yield is also very high, and as a result, it prevents the flammable product to diffuse through the char layer. Beside this, the liberation of CO_2 during decomposition also promotes the flame retardancy of the polymer.

To see the effectiveness of the improvement of flame retardancy of polymer I, this polymer was mixed with chloroprene rubber (CR) and styrene butadiene rubber (SBR). The formulation of the blends is given in Table IV. Mixing of 8 phr of polymer I (which corresponds to 3.38 g bromine and 0.328 g phosphorus) increases the LOI of CR by five units, i.e., from 36 to 41. In the case of

Table IV   Stock Formulations for Fabrication of Blend Samples for LOI Testing

Stock/Ingredient (phr)	1	2	3	4
Zinc oxide	5.0	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0	2.0
Magnesium oxide	4.0	—	4.0	—
Na-22	0.5	—	0.5	—
CBS	—	1.0	—	1.0
S	—	1.7	—	1.7
Polymer I	—	—	8.0	18
SBR	—	100	—	100
CR	100	—	100	—
Vulcanization time (min.)	48	32	43.3	17.5
Vulcanization temp. (°C)	150	150	150	150

SBR, no reduction of flammability occurs at lower phr. At 18 phr (which corresponds to 7.61 g bromine and 0.73 g phosphorus) the LOI of SBR is increased by three units, i.e., from 18 to 21. The LOI values of the blends indicate that polymer I is not as effective as a flame-retardant additive, particularly for SBR, although the $(OI)_m$) value of the powder sample is reasonable.

There are three possible reasons for this observation. One reason is the bonding of bromine to aromatic carbon. The liberation of bromine does not occur at the right time, i.e., at the time of decomposition of the base polymer, because the decomposition of CR or SBR begins above 330°C, whereas liberation of bromine from polymer I ceases at around 331°C. The second reason may be the less effectiveness of the phosphorus-containing additive towards such saturated hydrocarbon polymer. Pearce et al.[26] pointed out that in polymers containing no oxygen groups such as polystyrene or polypropylene, the acid-catalyzed char-forming mode of action of phosphorus plays a less effective role, and in fact, phosphorus is not as effective in such polymers as it is in oxygenated polymers. Third, the expected P—Br synergism is not operative in this case. This is because of the fact that the bromine phosphorus compounds such as PBr_3 or $POBr_3$, which are the effective fire retardants, are possibly not formed in this case due to the lack of conducive condition for their formations during burning.

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