

# Phosphorus Modification of Epoxidized Liquid Natural Rubber to Improve Flame Resistance of Vulcanized Rubbers

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## SYNOPSIS

The use of phosphorus for improving flame retardancy of natural rubber vulcanizates was attempted by incorporating a modified form of natural rubber. By reacting epoxidized liquid natural rubber (ELNR) with dibutylphosphate it was possible to chemically modify the polymer. On a 25% epoxidized LNR, 5.2–6.8% w/w of phosphorus could be fixed on the polymer backbone. The reaction carried out in bulk and solution resulted in products with different  $T_g$  values probably due to the varying crosslink levels in the resultant products. Chemical analysis of the modified polymers prepared by two sets of reactions under identical conditions proved the reproducibility of the reactions in bulk and in solution. Incorporation of the phosphorus-modified ELNR in a natural rubber formulation decreased the flammability behaviors of the vulcanizate. On the other hand, a decrease of the rate of curing and mechanical properties was observed. The phosphorus addition could also be carried out by mixing ELNR and dibutylphosphate at the time of mixing the compounds and resulted in equally good flame retardance with relatively better processing and mechanical properties. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Annual consumption of natural rubber (NR) is about 5 million tonnes. It has some unique advantages over competitive synthetic rubbers such as properties required for special applications like manufacture of aerotires, suspension elements, various latex products, etc. Above all, its natural photosynthetic origin is of great interest for the environmentalists and the material is important as a renewable source for different polymeric materials. Extracted from the hevea *Brasiliensis* as latex, it is used in a variety of applications for the manufacture of products from latex phase as well as dry elastomer. However, as synthetic rubbers, it has one considerable drawback: it is combustible. The problem of controlling the fire hazard of polymeric materials

has become a subject of worldwide concern in recent years due to the increased usage of these products.

One way to improve the flammability of polymer materials is chemical modification by using phosphorus-containing reagents or monomers.<sup>1,2</sup> The advantage of this method is the inclusion of active species in the polymer structure. Then, they cannot diffuse toward the polymeric material surface and remain more efficient longer.<sup>3</sup> Another way of improvement is to introduce as a flame-retardant additive, a phosphorus-containing oligomer having good compatibility with the flame-sensitive material.<sup>4,5</sup> Phosphorus-containing polymers are well known for their flame-retardant properties, and they are increasingly gaining popularity over their halogen counterparts since they generally give off non-toxic and noncorrosive volatile combustion products. Phosphorus is supposed to act as a flame-retardant by a variety of mechanisms, the most important being probably its ability to increase distinctly the organic matter conversion to char during burning, which thus decreases the amount of flammable vol-

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atile gases reaching the flame zone and reduces the heat transfer from the flame to the polymer.<sup>6</sup>

Modification of epoxidized liquid natural rubber (ELNR) by fixing phosphorus atoms on the natural rubber backbone using dibutylphosphate reaction was attempted to prepare a flame-retardant polymer additive for rubber vulcanization by a sulfur vulcanizing agent. The present study is an investigation of the critical conditions for polymer combustion as well as for reduction of the flammability of natural rubber vulcanizates. The thermal stability and flammability of the synthesized vulcanizates have been evaluated by thermogravimetry and limiting oxygen index (LOI), respectively.

## EXPERIMENTAL

### Raw Materials Used

Toluene and dichloromethane (99.5% of purity) were used as received. Dibutylphosphate was a Fluka product (purity > 97%). Latex used as starting rubber material for modification was collected from hevea plantations in the Ivory Coast, centrifuged to 60% dry rubber content (drc) and preserved with ammonia. ELFAPUR-N150, nonylphenylethoxylate, was provided by Akzo Chemie (100% paste). Gases used for thermal analysis were of 99.99% purity.

### Synthesis of ELNR Bearing Dibutylphosphate Groups

#### Natural Rubber Depolymerization

Latex was diluted with water to bring down drc to 30% and was deammoniated by mechanical stirring at room temperature (the pH was reduced to 10). It was then stabilized with 3 phr of a nonionic stabilizer (ELFAPUR-N150) and stored for 24 h for maturation. The depolymerization reaction was conducted on 1 L of latex into a double-jacketed reactor with provisions for stirring, temperature control, and air inlet. The temperature was maintained at 60°C with continuous stirring and bubbling of air (3 L/min) during the reaction. Phenylhydrazine (26 g) was slowly added into the reactor. After 24 h, a sample was drawn from the reaction mixture and dried as thin film to obtain liquid natural rubber (LNR), which was used for characterization. In infrared spectroscopy, absorption at 830 cm<sup>-1</sup> is due to C=C *cis*, at 1380 cm<sup>-1</sup> to CH<sub>3</sub>. A weak peak at 1710 cm<sup>-1</sup> indicated the formation of small amounts of carbonyl groups during the depolymerization

process. A broad one in the range 3400–3500 cm<sup>-1</sup> shows the presence of —NH— phenylhydrazone groups in the depolymerized rubber. The number-average and weight-average molecular weights measured by SEC are  $\bar{M}_n = 8000$ ,  $\bar{M}_w = 21000$ ,  $\bar{M}_w/\bar{M}_n = 2.6$ .

### Epoxidation

Epoxidation was carried out by reacting LNR in latex phase with *in situ* formed performic acid. The theoretical level of epoxidation chosen was 25%. The reaction mixture containing the depolymerized rubber in latex form was diluted with water to bring down the drc to 20%. The lower drc helps to reduce the extent of side reactions that can happen during the course of reaction. Then, 30.5 g of formic acid were poured into 1.5 L of latex with efficient stirring. Then, 240 g of 37.5% aqueous solution of hydrogen peroxide was slowly added into the reactor. Stirring was continued and the temperature was maintained at 60°C for 24 h. At the end, the reaction mixture was neutralized with sodium hydroxide. The latex was destabilized by heating at 85°C, and the polymer was separated, washed with water, and dried at 110°C.

### Purification of ELNR

The ELNR was extracted with dichloromethane for 24 h in a Soxhlet apparatus. It was extracted almost completely, leaving behind traces (0.7% w/w) of solid residue on the paper cone. The extract containing the polymer in dichloromethane was partially evaporated and slowly poured into methyl alcohol agitated vigorously by a magnetic stirrer. The mixture was allowed to settle for distinct separation of the layers. Methyl alcohol phase was decanted, and the polymer dissolved in dichloromethane was reprecipitated in methyl alcohol. It was then dried on rotary evaporator and finally under vacuum at 40°C.

The epoxidation level was evaluated from the <sup>1</sup>H-NMR spectrum by comparison of the integration value corresponding to proton on the carbon-carbon double bonds with epoxide ring ones. The 25% level measured is in agreement with the theoretical selected value. The side reaction of furanization of epoxide linkages has proceeded only to a very small extent.

### Phosphorus Modification

The reaction between dibutylphosphate and ELNR was carried out by two methods, in bulk and in so-

lution. For the bulk reaction, ELNR and dibutylphosphate in stoichiometric quantity with the epoxide units existing in ELNR were taken in a glass reactor equipped with a water condenser and mechanical stirrer. The reactor was immersed into an oil bath maintained at 100°C. The mixture was well stirred for 24 h. The formed gel mixture was transferred into a filter paper cone and extracted with dichloromethane in a Soxhlet extraction apparatus for 8 h. NMR analysis of the extract shows principally unreacted starting phosphorus compound mixed with very small quantities of modified ELNR.

For conducting the reaction in solution, ELNR was dissolved in toluene in a 500-mL round-bottomed flask and stoichiometric quantity of dibutylphosphate was added. The mixture was well stirred using a magnetic stirrer and heated into an oil bath at 100°C for 24 h. The homogeneous resulting solution was slowly poured into well-agitated methyl alcohol so that the polymer precipitated. After distinct separation of the layers, methyl alcohol phase was decanted, and the polymer dissolved in dichloromethane was reprecipitated in methyl alcohol. It was collected, dried on a rotary evaporator, and finally under vacuum.

All these samples were subjected to chemical analysis.

### Preparation of Natural Rubber Vulcanizates

Gum formulations were chosen according to a standard recipe (NFT 43-001) specified by the Agence Française de Normalisation (AFNOR). Mixing of the ingredients were carried out on a laboratory two roll mills with 150 mm rolls. The friction ratio between the rolls was 1 : 1.4. Mixing procedure and sequence of addition of the ingredients were according to the AFNOR specification. The processing characteristics (Mooney viscosity  $ML_{1+4}$  at 100°C, optimum cure time and scorch time) were measured.

Vulcanizates were prepared by compression moulding of the rubber compounds for  $t_{90}$  time at 140°C. Sheets 2 mm thick, 120 mm length and 80 mm breadth were made and test specimens for studies were prepared from the sheets by punching with suitable dies.

### Chemical Characterization of Products

The products were characterized by infrared and NMR spectroscopies. Infrared analyses were carried out on film samples of the polymers on NaCl cells, using a Fourier transform Perkin-Elmer 1750 spec-

trometer.  $^{13}\text{C}$ -NMR and  $^1\text{H}$ -NMR measurements were carried out on deuterated chloroform solutions containing tetramethylsilane as an internal standard by using a Brücker AC 400 (400 MHz) spectrometer equipped with a Brücker QNP multinucleus cell.

Molecular weights ( $M_n$ ) were determined by steric exclusion chromatography (SEC) in THF on a Waters 1500 instrument fitted with 5  $\mu$ Styragel columns (0.7  $\times$  120 cm) of different pore sizes (100, 3  $\times$  500, and 1000 Å), calibrated with polystyrene standards.

Elemental analyses were made by the Central Service for Analysis of CNRS (Vernaison, France).

### Evaluation of the Technological and Flammability Properties of Vulcanized Natural Rubber Incorporating PLNR

Physical properties of the vulcanizates under tension, tensile strength, elongation at break, modulus at different elongations, and tear strength (die C) of the samples were determined using an electronic dynamometer with coupled extensometer. Hardness of the samples were measured using a Shore A hardness tester.

$T_g$  values of the samples were measured using a Perkin-Elmer 7 differential scanning calorimeter (DSC). Scanning rate was 10°C/min.

Thermogravimetric analyses of the vulcanized rubber compounds were carried out using a Perkin-Elmer 7 TGA thermal analyzer, in oxygen and air, at constant heating rate of 20°C/min, with about 10-mg samples. Measures were made from ambient up to 600°C. In the case of mix F, the study was extended to 800°C for recording the complete ignition of the char. The inlet gas pressure was adjusted to 3 kg/cm<sup>2</sup> and the flow rate measured was 42.8 mL/min.

Flammability behavior of vulcanizates was carried out using an AIS oxygen index test equipment. Studies were conducted on test specimens 70–150 mm long, 6.5 mm wide, and 2 mm thick, cut from vulcanized sheets and clamped in the specimen holder vertically in the approximate center of the glass cylinder with the top of the specimen at least 100 mm below the top of the open column. The overall flow rate was adjusted to 17 L/min for all the tests. The top of the specimen was ignited using a butane gas burner. To compare the inflammability behaviors of the different samples, advancement of the flame downward was measured in seconds over a 3-cm length. Lengths of the flame for the samples were also measured.

**Table I Analysis of Phosphorus-Modified Polymers (Temperature 100°C, Duration 24 hr)**

Product Reference	Elemental Analysis Results				Yield of Addition <sup>c</sup> (%)
	C %	H %	O %	P %	
PLNR 1 <sup>a</sup>	64.54	9.42	16.30	6.77	89.8
PLNR 2 <sup>b</sup>	69.53	9.40	13.73	5.21	62.9
PLNR 3 <sup>a</sup>	67.45	9.58	16.21	6.66	87.7
PLNR 4 <sup>b</sup>	68.74	9.60	14.88	5.58	68.9

<sup>a</sup> In bulk (gel part).<sup>b</sup> In solution.<sup>c</sup> Calculated from initial epoxyde unit content, for a reaction leading to dioxaphospholane structures.

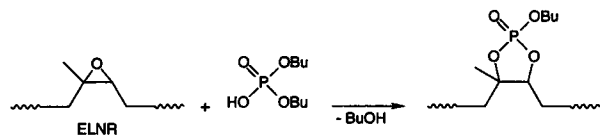
## RESULT AND DISCUSSION

### Synthesis of Phosphorus-Modified LNR

Liquid natural rubber used in this study was produced in the latex phase through a combined action of phenylhydrazine and atmospheric oxygen.<sup>7,8</sup> Phenylhydrazine with oxygen gives phenyl radicals that attack the polyisoprene chain to form allylic radicals by hydrogen transfer reactions. Oxygen is grafted onto the macromolecular radicals to form peroxy groups that cause polymer chain scissions, leading to smaller macromolecules.

Epoxidation was carried out by reacting LNR in latex phase with *in situ* formed performic acid.<sup>9</sup> Hydrogen peroxide reacts with formic acid to form performic acid, which then reacts with the hydrocarbon. Formic acid is generated during the reaction and is recycled. These mild reaction conditions were chosen to yield ELNR free from secondary reaction products.

The anticipated reaction between ELNR and dibutylphosphate is as follows:



The epoxide ring is opened and a five-membered ring is formed with elimination of one molecule of butanol.<sup>10</sup> Crosslinking is another possible reaction. The phosphorus atom is fixed on the polymer in either case.

The reaction between stoichiometric quantity of dibutylphosphate with the ELNR epoxide units was carried out by two methods, in bulk and in toluene solution. By using the 25% epoxidized LNR ( $M_n = 8000$ ), 5.2–6.8% w/w of phosphorus can be in-

troduced on the polymer backbone (Table I). Results are consistently different for the preparations in bulk and in solution. The former retains a higher percentage of phosphorus. The reactions carried out in bulk and solution result in products with different crosslink levels. Contrary to the reaction in solution, gel formation is noticed in bulk. Analysis of the modified polymers prepared by two sets of reactions under identical conditions shows a reproducibility of the reactions in bulk and in solution.

Addition of dibutylphosphate in the case of PLNR2 or PLNR4 was characterized in <sup>1</sup>H-NMR by a signal between 4.1 and 4.2 ppm, which corresponds to the H fixed on the tertiary carbon in the  $\beta$  position of the phosphorus atom. On <sup>31</sup>P-NMR spectrum, three different peaks close to each other and different from the signal of dibutylphosphate, which appears at 1.74 ppm, are observed around 15 ppm corresponding to three different states of phosphorus atom (stereoisomers of 2-butoxy-2-oxo-1,3,2-dioxaphospholane) in the modified compound.

DSC plots of the two modified polymers in bulk (PLNR3) and in solution (PLNR4) show that  $T_g$  values recorded are  $-34^\circ\text{C}$  for PLNR3 and  $-18^\circ\text{C}$  for PLNR4. The shift in  $T_g$  may be due to different extents of crosslinking.

**Table II Control Compound A [AFNOR Recipe (NFT 43-001)]**

Components	Parts by Weight
Natural rubber	100
Zinc oxide	5
Stearic acid	2
HAF black	35
TBBS <sup>a</sup>	0.7
Sulfur	2.25

<sup>a</sup> *t*-Butyl benzothiazylsulfenamide.

**Table III Mix Formulations (Parts by Weight for 100 Parts of NR)**

Mix	A	B	C	D	E	F
LNR	—	13.3	—	—	—	—
ELNR	—	—	13.3	—	—	13.3
PLNR III (bulk)	—	—	—	25	—	—
PLNR IV (solution)	—	—	—	—	25	—
Dibutylphosphate	—	—	—	—	—	11.3

### Preparation of Natural Rubber Vulcanizates

The standard recipe of formulation specified by the AFNOR (NFT 43-001) is summarized in Table II. Mixes containing LNR, ELNR, PLNR (bulk), PLNR (solution), and ELNR/dibutylphosphate were prepared by mixing each one with standard compositions A (Table II) and compared to A. Mix formulations are given in Table III.

Phosphorus content in the resultant vulcanizates was selected as 1% w/w approximately. To achieve the above phosphorus content 25 phr of PLNR were added to mix A. Mix F contains ELNR and dibutylphosphate in stoichiometric quantity with oxirane rings. The above ingredients were added expecting an *in situ* fixing of phosphorus on the polymer during vulcanization.

The processing properties of the rubber compounds are given in Table IV. The Mooney viscosity values show a reducing trend with LNR and ELNR compounds (B and C) in comparison with control compound A. This may be due to their plasticizing action. Same effect was not shown with compounds D and F, while E showed a much higher viscosity value. Modification of ELNR by dibutylphosphate reagent reduces its plasticizing properties. With E, a reaction during mixing between natural rubber and the dioxolane phosphorus groups of PLNR can occur. In both cases D and F, where the used PLNR is obtained in bulk conditions, the structures are probably different. With respect to the cure char-

acteristics LNR and ELNR compounds are close to the control compound A, while decreasing of the crosslinking reaction is observed with the phosphorus-modified polymers. The retarding action is prominent for E but comparatively small for compounds D and F. The cure rate index of compound E is considerably low. This is due to higher retarding effect of the modified ELNR. Maximum torque values also show a reduction. The rate of crosslinking of E is lowered as evidenced by the cure rate index values. Vulcanization is greatly affected by phosphorus units. The  $T_g$  values of the compounds obtained from the DSC measurements are in close limits.

The properties of the vulcanized rubber compounds are given in Table V. A general decrease in tensile strength values is observed in compounds containing the phosphorus-modified ELNR, with maximum deviation for compound E. Among the phosphorus-modified compounds, F shows the highest value. No remarkable change has been observed in the elongation at break values. So is the case with modulus at 100, 200, and 300% elongations. Shore A hardness measured on the samples are in the range 57–61, the highest being in the case of compound with ELNR and dibutylphosphate added on the mill. This may be attributed to the possible additional crosslinks established by the phosphorus atom between the macromolecules. For vulcanizate incorporating ELNR (C), remarkable improvement in tear strength is observed.

### Thermal and Flammability Behaviors of Vulcanized Natural Rubber Incorporating PLNR

#### Thermogravimetric Studies

Thermogravimetric analysis of the vulcanized rubber compounds was carried in oxygen and air for all the samples.

In oxygen atmosphere (Fig. 1), two transition stages are observed in all the cases, the first due to decomposition of the hydrocarbon with flame emis-

**Table IV Properties of Rubber Compounds**

Physical Characteristic	A	B	C	D	E	F
Mooney viscosity $ML_{(1+4)}$ , 100°C	34	26	28	39	58	37
Scorch time, $ts_2$ at 140°C (min)	10.00	10.75	11.75	12.00	35.00	9.00
Cure time, $t_{90}$ at 140°C (min)	30.5	28.5	28.5	65.0	85.0	46.0
Max torque (dNm)	79	65	62	37	30	49
Cure rate index	86	85	86	68	16	57
$T_g$ (°C)	-61.8	-60.9	-62.3	-61.8	-61.7	-61.7

**Table V Mechanical Properties of Vulcanizates**

Physical Test	A	B	C	D	E	F
Tensile strength (MPa)	30.0	28.1	27.1	11.78	7.16	13.19
Elongation at break (%)	527	600	590	514	473	472
100% Modulus (MPa)	2.01	1.68	1.81	1.55	1.56	2.10
200% Modulus (MPa)	4.53	3.86	3.95	3.38	2.62	3.95
300% Modulus (MPa)	8.94	7.63	7.47	5.46	4.11	6.51
Hardness Shore (A)	59	57	58	57	58	61
Tear strength (N/mm)	65.5	61.0	76.8	35.5	25.6	35.0

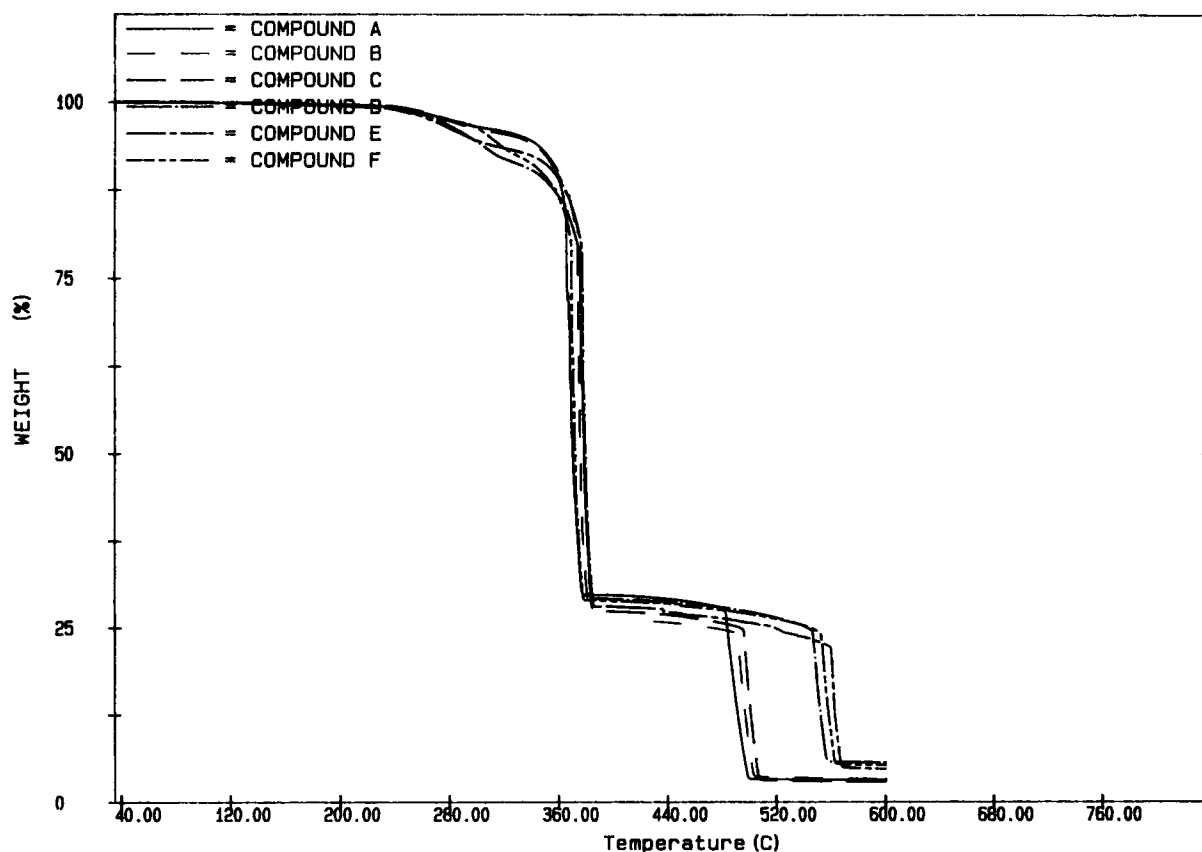
sion and the second due to burning of the char. The first change of all compounds occurs in the temperature range 363–373°C. But in the case of the second transition, loss in weight for compounds without phosphorus occurs around 490°C, while for the phosphorus-containing compounds it is at a higher temperature around 540–570°C. This can be assigned to the protection by the charred mass formed during burning by the phosphorus oxide from contact with the surrounding air.

In air (Fig. 2), the same effects are observed. Compounds A, B, and C are completely reduced to ashes when temperature reaches 605°C, while for

the other the corresponding temperature is 692°C, although oxidation of the charred mass starts around 410–420°C in all cases.

#### Limiting Oxygen Index

Flammability behaviors of the compounds were studied on test specimens as described in the experimental part. To compare the inflammability behaviors of the different samples, the advancement of the flame downward was measured in seconds on a 3-cm length. Length of the flame for the samples were also measured.

**Figure 1** TGA thermograms for compounds A to F in oxygen.

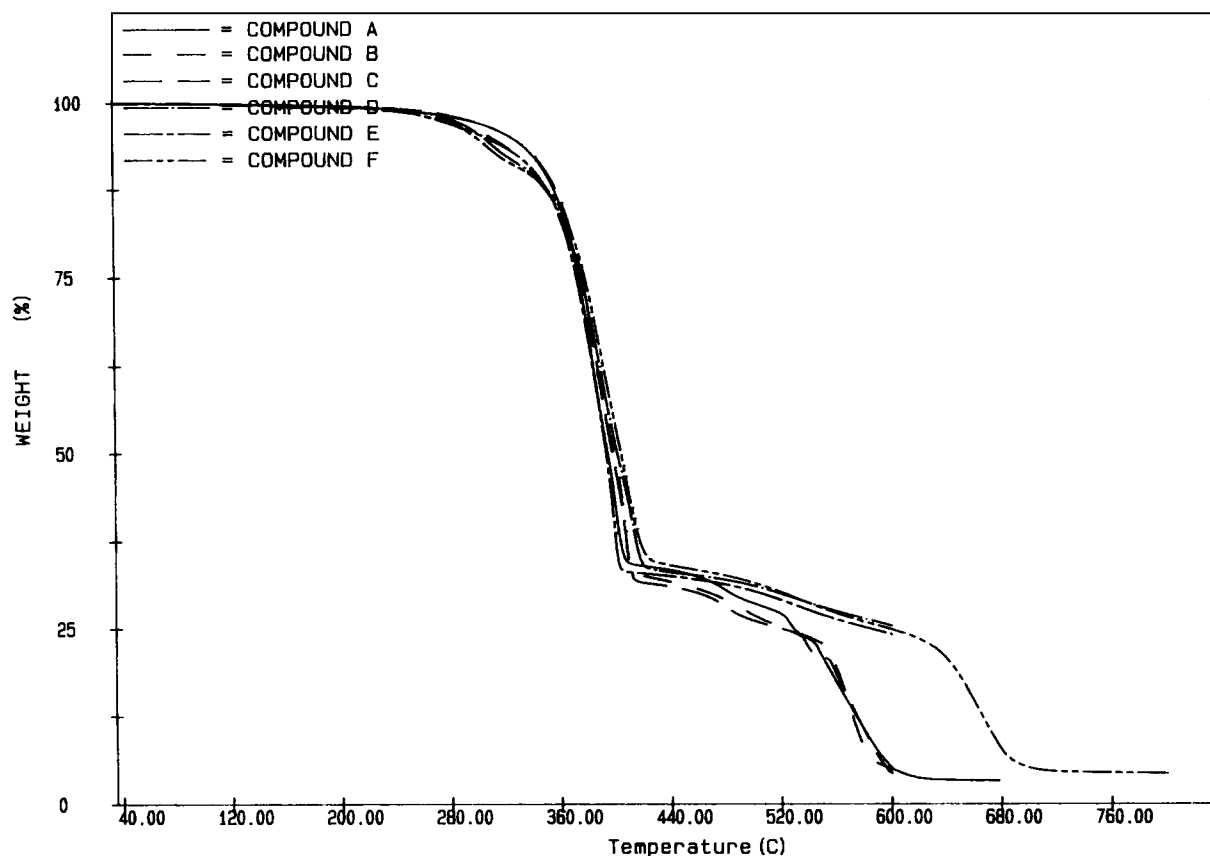


Figure 2 TGA thermograms for compounds A to F in air.

The burning behaviors of the samples by measuring burning times in different atmospheres with varying oxygen content are given in Table VI. Burning properties of compounds A, B, and C without phosphorus are comparable. However, a small increase in burning time for LNR and ELNR compounds is noticed. Compounds D, E, and F with phosphorus showed similar burning times. The differences in burning times noticed between phosphorus- and nonphosphorus-containing compounds were significant and showed the same trend at all oxygen levels. Figure 3 gives the flame length for the compounds at various concentrations of oxygen. For each vulcanizate, the flame length depends on

oxygen concentration: two distinct groupings of constant values are noted and flame length change occurs always at the same oxygen concentration (between 18.5 and 19%). On the other hand, at the same oxygen concentration, a decrease in flame length is noticed as follows:  $A > B > C > D \gg E > F$ . The great difference in flame length observed between the phosphorus incorporating vulcanizate D with the two others, E and F, is surprising.

## CONCLUSION

By reacting epoxidized liquid natural rubber (ELNR) with dibutylphosphate it is possible to

Table VI Burning Times(s) of the Samples

% of Oxygen	A	B	C	D	E	F
21	80	84.5	86	102	101	103
19.5	102	106	108	138	137	139
19	123	125	128	180	175	178
18.5	164	166	170	187	190	195
18	180	190	192	230	225	230
17.5	217	219	218	270	280	Extinguished

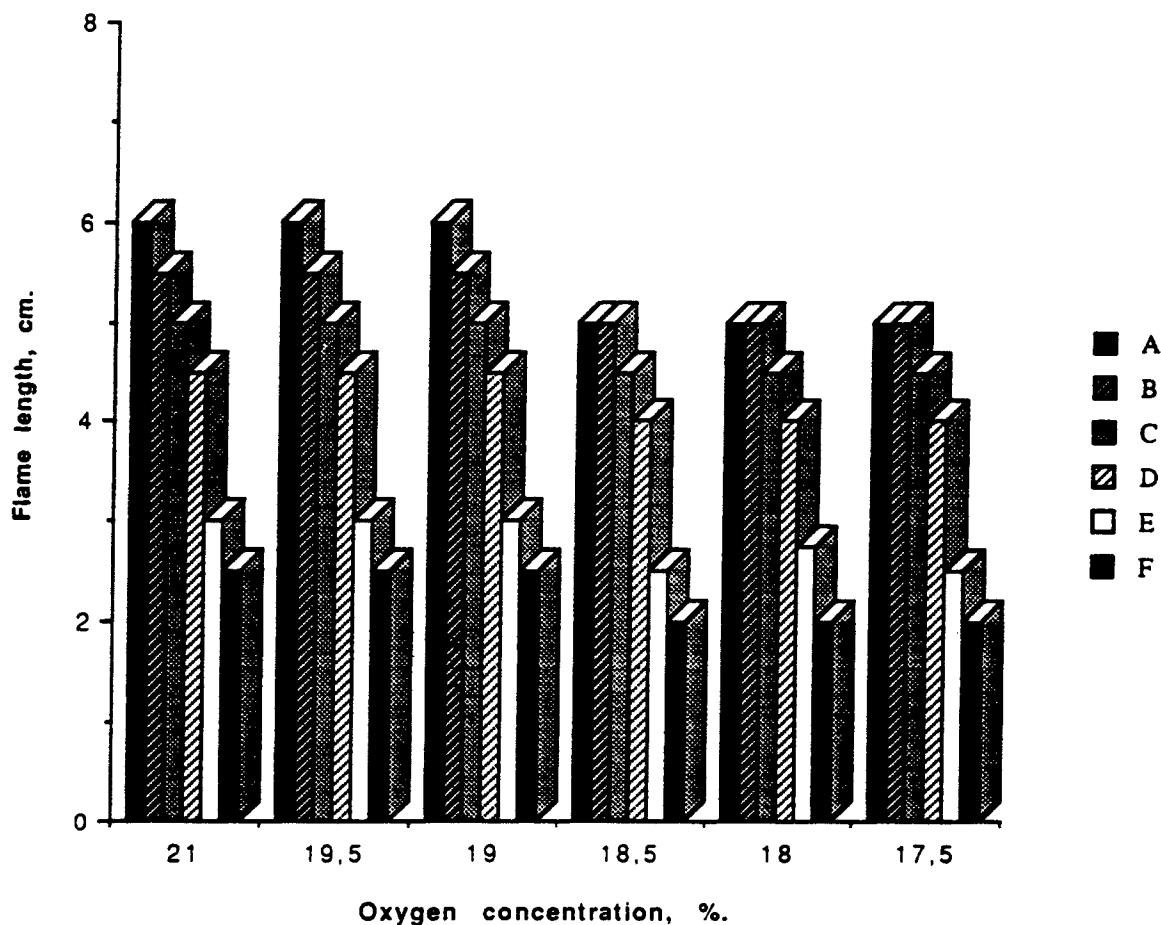


Figure 3 Flame length for different concentrations of oxygen.

chemically modify the polymer. Incorporation of the phosphorus-modified polymers in a natural rubber formulation decreases the flammability behaviors of the vulcanizates, but also decreases the mechanical properties because vulcanization is greatly affected by phosphorus units. On the other hand, the phosphorus addition can also be carried out by mixing ELNR and dibutylphosphate at the time of mixing the compounds, resulting in equally good flame retardance with relatively better processing and mechanical properties.

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