

Flame-resistance and Thermal Stability of 1,4-polydienes Modified by Dialkyl(or aryl) Phosphates

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The chemical modification of 1,4-polydienes by dialkyl(or aryl) phosphates was considered in order to improve their flame-resistance. Chemical introduction of phosphorus onto polydienes was carried out by a two-step process: partial epoxidation of unsaturated units and introduction of the dialkyl(or aryl) phosphate using the reactivity of the P-OH acidic bond towards oxirane rings of epoxidised 1,4-polydienes (synthetic polybutadiene, polyisoprene and liquid natural rubber). Incorporation of phosphorus (around 1.1-1.2 weight percent) in crosslinked polydienes is generally sufficient to produce air fire-resistant materials. The best limiting oxygen indices (LOI) are obtained with diphenyl phosphate. Degradation kinetics of modified polydiene networks at moderate temperatures (from 200°C to 400°C) are more and less similar to those of unmodified specimens but the weight losses are weaker after 400°C. The residual masses after 600°C are relatively important compared to the unmodified specimens which are entirely decomposed at this temperature.

Elastomers present a commercial interest because of their own properties (elasticity, electric insulation, etc.) required for special applications in various industrial sectors (tyres, adhesives, habitat, etc.). However, they have one considerable drawback: they are combustible. By burning, they decompose into volatile breakdown products and radicals which combine with the surrounding air to sustain the combustion.

One way to improve the flammability of polymeric materials is chemical modification by using phosphorus-containing reagents or monomers¹. An advantage of this method is that active species cannot diffuse toward the polymer surface, and thus, it stays more efficient for a long time². Phosphorus-containing polymers are well known for their

flame-retardant properties and, moreover, their use is on the increase over their halogen counterparts because they generally produce less toxic and corrosive volatile combustion products³.

The chemical introduction of phosphorus onto polydienes was carried out by a two-step process (*Figure 1*). In the first step, partial epoxidation of 1,4-polyisoprene or 1,4-polybutadiene units produced functionalised intermediate polydiene. The second step of the chemical modification was the introduction of the dialkyl(or aryl) phosphate using the reactivity of the P-OH acidic bond towards oxirane rings.

A preliminary study on model molecules of epoxidised polydiene units allowed the

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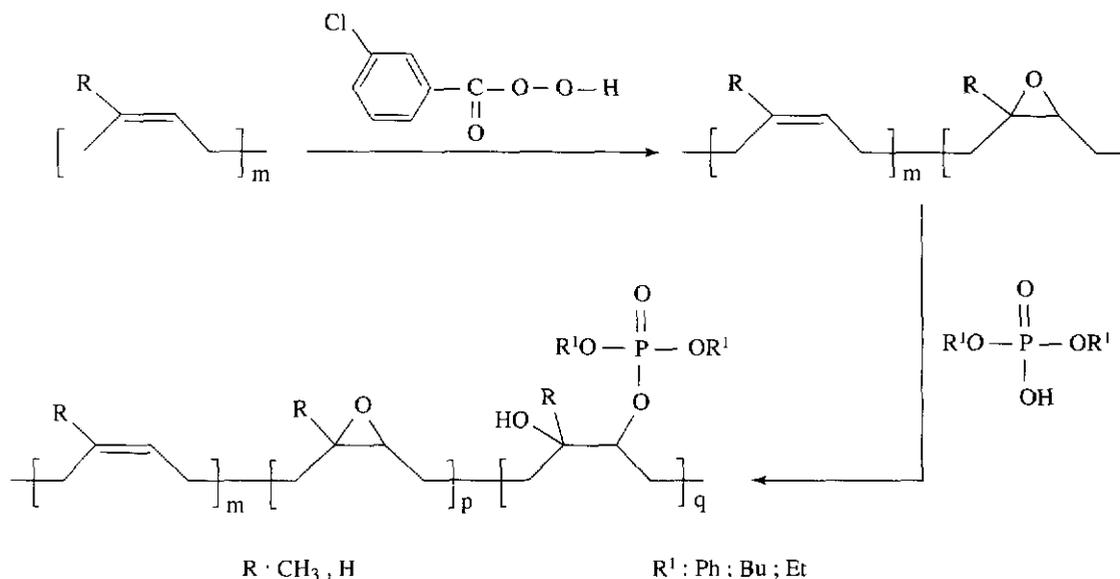


Figure 1. Principle of the synthesis of 1,4-polydienes containing phosphorus chemically bonded onto the chains.

characterisation of adducts obtained with respect to each type of polymer [epoxidised 1,4-polybutadiene or 1,4-polyisoprene; epoxidised liquid natural rubber (ELNR)], and with respect to the ester substituent nature of dialkyl(or aryl) phosphate reagent⁴. In all cases, the oxirane ring is opened. For epoxidised polyisoprene unit (natural or synthetic), a five-membered ring (2-alkoxy-2-oxo-1,3,2-dioxaphospholane) is formed with elimination of one molecule of alcohol and for polybutadiene, a non-cyclised phosphate triester is formed.

The chemical modification of epoxidised 1,4-polydienes confirmed partially the results obtained by using model molecules⁵. Secondary microstructures obtained with the polybutadiene

correspond to diol units which have been already observed in the case of model studies. On the contrary, secondary products obtained with 1,4-polyisoprene model (ketone, diol, allylic ether and allylic alcohol)⁴ are not observed with the epoxidised polyisoprene. Secondary microstructures correspond to the formation of ether linkage between two polydiene chains or diol. It was also shown that partial modification of oxiranes by dialkyl(or aryl) phosphates left unreacted epoxides without change in their structure. This result is very important because a latter crosslinking of the systems can be considered to prepare rigid tri-dimensional networks by using polyfunctional reagents able to react with residual epoxides. The present study is an investigation of the critical conditions for polydiene combustion and for reduction of the

flammability of such crosslinked polydienes. The flammability and thermal stability of the synthesised specimens were evaluated respectively by limiting oxygen index (LOI test) measures and thermogravimetric analysis.

EXPERIMENTAL

Solvents and Reagents

The solvents were purified by classical methods⁶ and the following was also used:

- Methylnadid anhydride (Methylbicyclo [2.2.1]hept-5-ene-2,3-dicarboxylic anhydride) (Janssen; purity 95%, was used as received)
- Dialkyl(or aryl) phosphates
- Dibutyl phosphate (Fluka) (was distilled before use).

Synthesis of diethyl phosphate. The chloride derivative, diethyl chlorophosphate (Janssen; purity 95%), was introduced into an excess of distilled water and the solution was stirred for 1 h. The aqueous phase was extracted with dichloromethane, then the organic solution was dried with anhydrous sodium sulphate. After filtration and removing the dichloromethane, diethyl phosphate was distilled under reduced pressure (b.p. at 0.3 mmHg = 36°C – 37°C).

Synthesis of diphenyl phosphate. The chloride derivative, diphenyl chlorophosphate (Janssen; purity 98%), was hydrolysed for 12 h at room temperature into an excess of distilled water. The aqueous phase was extracted with dichloromethane, then the organic phase was dried with anhydrous sodium sulphate. After filtration and removal of dichloromethane, the product was crystallised. The diphenyl

phosphate was purified by re-crystallisation from hexane (m.p. = 59°C).

Polydienes. Synthetic liquid 1,4-polyisoprene (LIR 30) was supplied by Japan Kuraray Company. It was purified by re-precipitation from benzene to methanol, then dried *in vacuo*. It consists of 94% of -1,4 (64% *cis*, 36% *trans*) and 6% of -3,4 units.

Synthetic liquid 1,4-polybutadiene was supplied by Aldrich. It was purified by re-precipitation from benzene to methanol, then dried *in vacuo*. It consists of 86% of -1,4 (50% *cis*, 50% *trans*) and 14% of -1,2 units.

Epoxidised Polydienes

ELNR was supplied by the Institut de Recherche Appliqué des Polymères (IRAP) of Le Mans. It is prepared from LNR which is a natural rubber derivative (100% *cis*-1,4-polyisoprene units) obtained by degradation of natural rubber in the latex phase, by using the phenylhydrazine/oxygen system^{7,8}. LNR was epoxidised directly also in the latex phase by performic acid prepared *in situ* by reaction between formic acid and hydrogen peroxide. ELNR is recovered by thermocoagulation. It consists of 41% epoxidised units.

Epoxidation of 1,4-polyisoprene and 1,4-polybutadiene. Partial epoxidation of polydienes was carried out by metachloroperbenzoic acid⁹ (predetermined amount in relation to the required yield of epoxidation). The metachloroperbenzoic acid solution in dichloromethane was added slowly to the biphased system: polydiene in dichloromethane and aqueous solution with 5% of sodium bicarbonate, cooled at 0°C and magnetically stirred. After reaction, the mixture was stirred for 3 h. The two phases were separated and the

organic phase was washed with a 0.1 M sodium hydroxide solution, then with water. Epoxidised polymers were isolated by precipitation into methanol, purified by re-precipitation from dichloromethane to methanol, then dried *in vacuo*.

Characteristics of the different basic epoxidised polydienes used during the study are summarised in Table 1.

TABLE 1 CHARACTERISTICS OF THE BASIC EPOXIDISED POLYDIENES

Polydiene	LIR	Polybutadiene	ELNR
\overline{M}_n	25 600	10 300	9 400
\overline{M}_w	33 800	12 700	29 100
Epoxidation yield	41%	39%	41%

Preparation of Specimens: Crosslinking of Epoxidised 1,4-polydienes by Methyl nadic Anhydride in the Presence of Dialkyl(or aryl) Phosphate

Liquid epoxidised polyisoprene (or liquid epoxidised polybutadiene, or ELNR) and dialkyl(or aryl) phosphate (predetermined amount in relation to the required percentage of modification) were heated to 90°C until the mixture become homogeneous. Methyl nadic anhydride (amount corresponding to 50% of the residual epoxidised units) was added and the mixture vigorously stirred at 90°C for 2 or 3 min. The blend was poured into a teflon mould so as to prepare specimens 126 mm × 6 mm × 5 mm. The crosslinking was obtained by treatment at 150°C for 5 h.

Characterisation of Products

NMR spectroscopy. ^1H and ^{13}C NMR spectra were recorded on Fourier transform

spectrometer, Bruker AC 400, in CDCl_3 solution, using tetramethylsilane (TMS) as internal standard. ^{31}P NMR spectra were recorded on Bruker AC 400 Fourier transform spectrometer in CDCl_3 solution, using phosphoric acid as external standard.

Molecular weight measurements. Size exclusion chromatography (SEC) was performed in THF on a Waters Associates 1500 apparatus fitted with 5 μ -styragel columns (100 Å, 3 × 500 Å and 1000 Å) with calibration from polystyrene standards.

Glass transition temperatures. The glass transition temperature (T_g) were determined using a Perkin-Elmer DCS 7 apparatus. All measurements were made in nitrogen at a heating rate of 20°C/min on samples weighing about 15 mg. T_g was taken at the inflexion point of the curve.

Thermogravimetric analysis. TGA measurements were carried out by using a Perkin-Elmer TGA 7 apparatus. Samples were heated from 40°C to 800°C, at 20°C/min under air flow. The air flow rate was 50 ml/min.

Limiting oxygen index (LOI). LOI measurements were performed using a AIS apparatus with a magnetodynamic oxygen analyser, according to the ASTM D-2863-70 specification. Both oxygen and nitrogen were connected to the equipment through pressure regulators (about 2 bars). The gas flow rate through the combustion chamber was 4 cm/s (17 l/min). Test specimens (126 mm × 6 mm × 5 mm) were clamped in the holder vertically in the approximate center of the combustion column with the top of the specimen at least 40 mm below the open column. The igniter with a butane cartridge was inserted into the conical opening of the column. The top of the

specimen was ignited with the ignition flame so that the specimen is well lit and the entire top is burning. The LOI of a specimen is the minimum percentage of oxygen in a slowly rising O_2/N_2 atmosphere which will just support combustion of the specimen. It corresponds to the minimum concentration of oxygen in the mixture just necessary so that the specimen burns for at least 3 min, or over a length of 50 mm.

RESULTS AND DISCUSSION

Preparation of Crosslinked Phosphorus-modified Polydienes

Crosslinked phosphorus-modified polydienes were prepared on two stages. At first, the chemical modification was realised by heating the mixture of liquid epoxidised polydiene and dialkyl(or aryl) phosphate at 90°C, and secondly, crosslinking was achieved at 150°C by using methyl nadic anhydride as crosslinking reagent. Crosslinking is initiated by reaction of an hydroxyle group from the polydiene backbone (for instance, the hydroxyle of a β -hydroxy phosphate unit formed after addition of the phosphorus reagent onto the oxirane) onto methyl nadic anhydride which leads to the opening of the anhydride ring (*Figure 2*).

Theoretical modification percentages of epoxidised units by dialkyl(or aryl) phosphates (dibutyl phosphate : DBP, diethyl phosphate : DEP, diphenyl phosphate : DPP) were settled to 5%, 10% and 20%, that corresponded to theoretical yields of phosphorus building units between 2% and 8%, and theoretical contents of phosphorus between 1% and 2% (*Table 2*).

Phosphorus contents in the crosslinked specimens were determined by Elemental Analysis. The proportions of phosphorus incorporated onto crosslinked polydienes were

deliberately limited in order to facilitate the moulding of specimens used to measure the fire-resistance behaviour. Indeed, the increase of dialkyl(or aryl) phosphate concentrations leads to an acceleration of the crosslinking rate, making the moulding operation more difficult, indeed impossible. The crosslinking kinetics does not only depend on the dialkyl(or aryl) phosphate concentration, but also, at one and the same time on the nature of the phosphorus reagent (it decreases in the direction : DEP > DPP > DBP) and on the polydiene structure (it decreases in the direction : epoxidised PBu \cong epoxidised LIR > ELNR). For instance, in the case of epoxidised polybutadiene modified by DEP and crosslinked by methyl nadic anhydride, the crosslinking kinetic is so fast that it was impossible to realise the moulding of the specimens.

T_g of samples were performed by DSC. The T_g measurements were made on the crosslinked unmodified polydienes and those incorporating diphenylphosphate groups (10% in relation to the epoxidised units) (ELNR 10 DPP) (*Table 3*). The chemical modification of polydiene chains by DPP brings out changes in T_g . It is known that epoxidation and crosslinking increase the T_g values^{10,11}. In the present case, the unmodified epoxidised polydiene/methyl nadic anhydride networks have very close T_g , between -59°C and -62.5°C. By introduction of diaryl phosphate substituents onto the networks, significant increases in T_g values are noticed : 20°C to 25°C in the case of ELNR and polybutadiene, and 6°C in that of LIR.

Limiting Oxygen Index Measurements

The LOI test allows one to determine the relative flammability of materials by measuring the minimum concentration of oxygen in an oxygen/nitrogen mixture that will just support continuing combustion of the ignited material.

TABLE 2 COMPOSITION OF PREPARED SPECIMENS

Specimen reference	ELNR 5 DBP	ELNR 10 DBP	ELNR 20 DBP	LIR 10 DBP	PB 10 DBP	ELNR 10 DEP	LIR 10 DEP	PB 10 DEP	ELNR 10 DPP	LIR 10 DPP	PB 10 DPP
Oxirane modification (%)	5	10	20	10	10	10	10	10	10	10	10
Theoretical phosphate units (%)	2.05	4.1	8.2	4.1	3.9	4.1	4.1	3.9	4.1	4.1	3.9
Theoretical phosphorus content (%)	0.54	1.10	2.03	1.10	1.21	1.12	1.12	1.24	1.08	1.08	1.19
Real phosphorus content (%)	0.52	1.13	2.07	1.16	1.23	1.09	1.09	1.23	1.03	1.06	1.24

TABLE 3. GLASS TRANSITION TEMPERATURES OF CROSSLINKED UNMODIFIED POLYDIENES AND THOSE INCORPORATING DIPHENYLPHOSPHATE GROUPS

Polydienes	ELNR	Polyisoprene (LIR)	Polybutadiene
Unmodified (T_g)	-59°C	-62°C	-62°C
10% DPP (T_g)	-35°C	-56°C	-39°C

Unmodified specimens. Figure 3 shows the limiting oxygen index of crosslinked unmodified specimens derived from ELNR, epoxidised 1,4-polyisoprene and epoxidised 1,4-polybutadiene. In atmosphere composed of low oxygen concentrations (<20%), specimens derived from ELNR burn more easily than those derived from epoxidised polybutadiene and polyisoprene. However, all crosslinked polydienes are combustible in surrounding air and require the introduction of fire-proofing agents to improve their fire resistant behaviour.

Modified specimens: influence of the incorporated dialkyl(or aryl) phosphate in function of the polydiene type. Compared to unmodified epoxidised polydienes crosslinked by methylnadic anhydride, specimens incorporating 10% of dialkyl(or aryl) phosphates (10% in relation to the epoxidised units) show an improvement in flame-resistance (Figure 4).

For specimens derived from ELNR, the limiting oxygen index of ELNR modified by the dialkyl phosphates are identical (LOI = 21). On the other hand, the combustion times (to burn a length of 50 mm) in the air are different: 189 s for ELNR modified by the dibutyl phosphate and 213 s for ELNR modified by the diethyl phosphate. An increase of the length of n-alkyle chains in the dialkyl phosphate reduces the combustion time, thus helping combustion. For ELNR specimens modified by

diphenyl phosphate, the limiting oxygen index is higher (LOI = 22) and an almost immediate self-extinguishment is observed in the air.

The epoxidised polyisoprene specimens modified by the dialkyl(or aryl) phosphates have limiting oxygen index of 22 to 23 and are better than those derived from ELNR. They are all self-extinguished in air. The best fire resistant behaviour is also obtained with polydiene networks incorporating diphenylphosphate groups.

Only three specimens were prepared from epoxidised polybutadiene because crosslinkage by methylnadic anhydride of this polydiene modified by diethyl phosphate occurs too quickly. Specimens incorporating DBP and DPP have LOI of 24.5 and 24.0, respectively. In this particular case, it appears that, contrary to the results obtained with the epoxidised polyisoprene derivatives, the best fire resistant behaviour is obtained with epoxidised polybutadiene modified by dibutyl phosphate. However, the fire resistant behaviour difference from the product incorporating the DPP is small.

Self-extinguishment is brought about by the formation of charred layer on the surface of polymer materials which inhibits heat transmission into the bulk and slows down diffusion of formed combustible products into

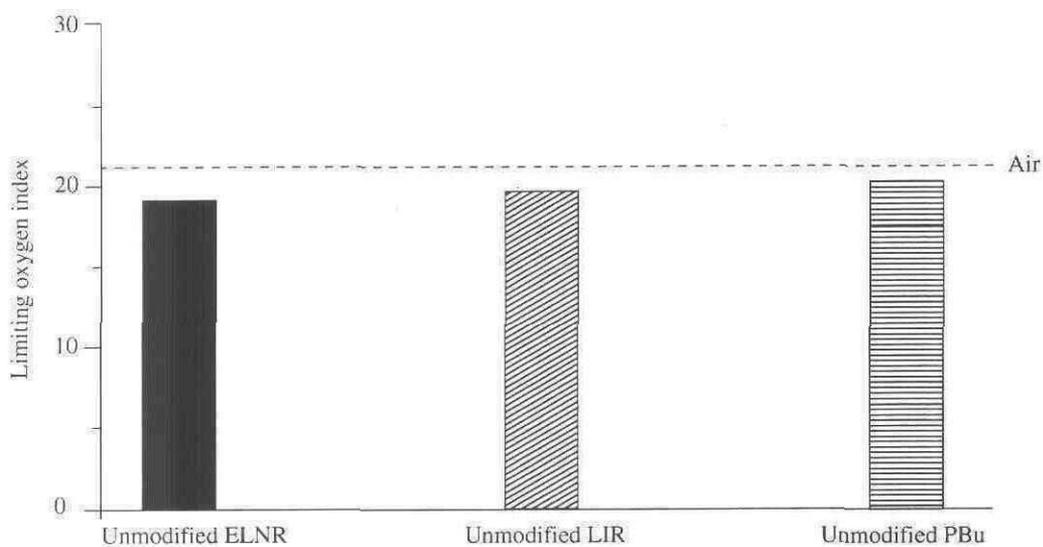


Figure 3. Limiting oxygen index of unmodified epoxidised polydienes crosslinked with methyl nadic anhydride.

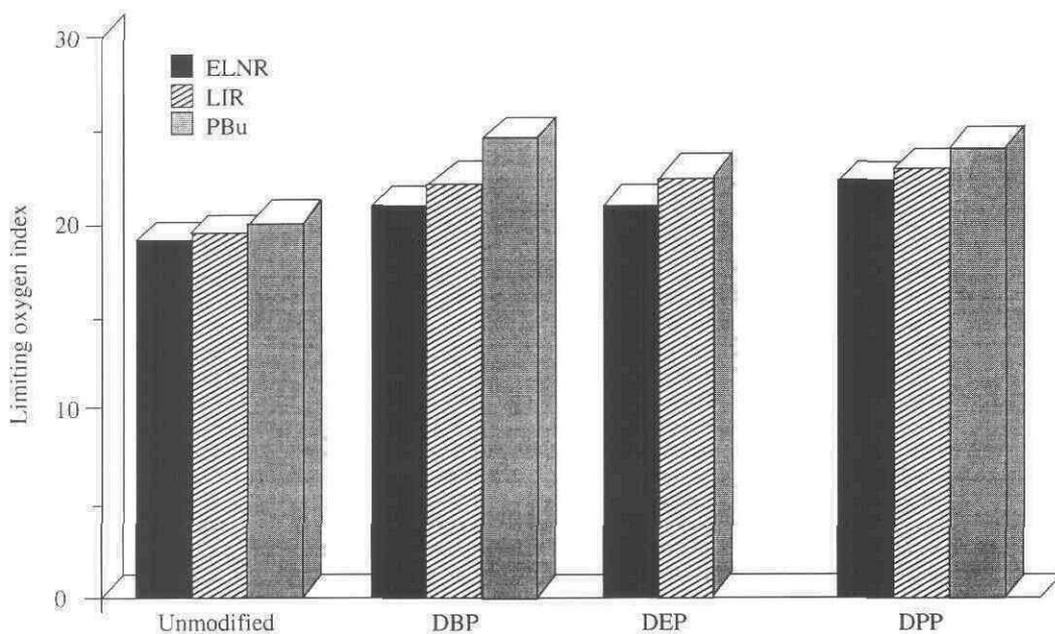


Figure 4. Limiting oxygen index of specimens, unmodified and modified by dialkyl (of aryl) phosphates.

atmosphere. Although a precursor of inorganic acid [dialkyl(or aryl) phosphate] and a carbon-rich polyhydric compound (presence of hydroxyl groups along the polydiene chain) are associated to fireproof the crosslinked polydiene, no intumescent behaviour is observed. This is probably due to the absence of organic amine functions which, by evolving gaseous products (ammoniac, for instance)³, can induce foaming of the char.

The fire-resistance of modified ELNR specimens is always lower than those of specimens derived from epoxidised polyisoprenes or polybutadienes, incorporating a same content of a same dialkyl(or aryl) phosphate. It decreases as follows: modified PBu specimens > modified LIR specimens > modified LNR specimens. The best fire resistant behaviour obtained with specimens incorporating diphenyl phosphate is understandable because of the presence of phenoxy groups which, instead of being totally degraded by heat, tend to form char by post condensation (crosslinking, cyclisation and aromatisation) and reduce the amount of volatile gases reaching the flame zone¹².

The global improvement of polydienes fire behaviour by chemical incorporation of di(alkyl or aryl) phosphate groups is modest, but is in part explained by the low contents of incorporated phosphorus (around 1.1% – 1.2%).

Modified specimens: influence of the amount of dialkyl(or aryl) phosphate incorporated onto specimens. The limiting oxygen index of ELNR crosslinked specimens whose epoxidised units were modified at 0%, 5%, 10% and 20% by dibutyl phosphate are given in *Figure 5*. The higher the modification yield, the higher is the LOI value. The flame-resistance of polydiene network increases with its dibutyl phosphate group content.

In a different state, the combustion times of ELNR crosslinked specimens modified at 5%, 10% and 20% by DBP were measured in a 22% oxygen atmosphere and compared with that of the standard unmodified ELNR (*Figure 6*). In comparison with crosslinked unmodified ELNR which burns very quickly, an increase of the combustion times of ELNR networks including DBP chemically bonded on the rubber backbone was noticed. The combustion time, as well as fire-resistance behaviour, increases with the DBP contents. Crosslinked ELNR including 20% of DBP (phosphorus content: 2.07%) or 10% of DPP (phosphorus content: 1.03%) do not burn in air. This result shows the importance of the nature of ester functional groups of $(RO)_2P(O)OH$. Phosphate group reagents with -O-aryle ester bonds are more efficient than the ones with -O-alkyle ester bonds.

Thermal Stability Studies

Unmodified specimens. The thermograms of crosslinked unmodified polydienes derived from ELNR, epoxidised polyisoprene (LIR) and polybutadiene are superimposed on *Figure 7*. Two transition stages are observed for each unmodified specimen: the first occurs around 230°C and the second around 460°C. The ELNR specimen decomposes more quickly than synthetic polyisoprene specimen. Moreover, its decomposition is total at 580°C, whereas crosslinked synthetic polyisoprene is complete only above 630°C. Unmodified synthetic polybutadiene specimen presents higher first and second decomposition temperatures than unmodified synthetic polyisoprene and ELNR. Its resistance to degradation and thermal oxidation appears to be better. These results are in agreement with those noticed on flammability behaviours.

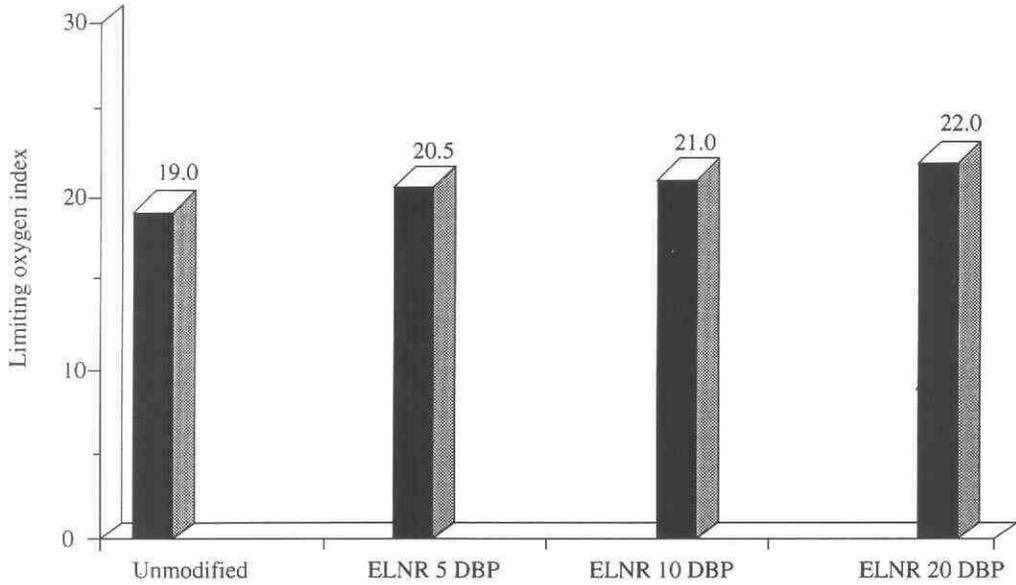


Figure 5. Limiting oxygen index of ELNR/methylnadic anhydride specimens in function of the amount of incorporated dibutyl phosphate.

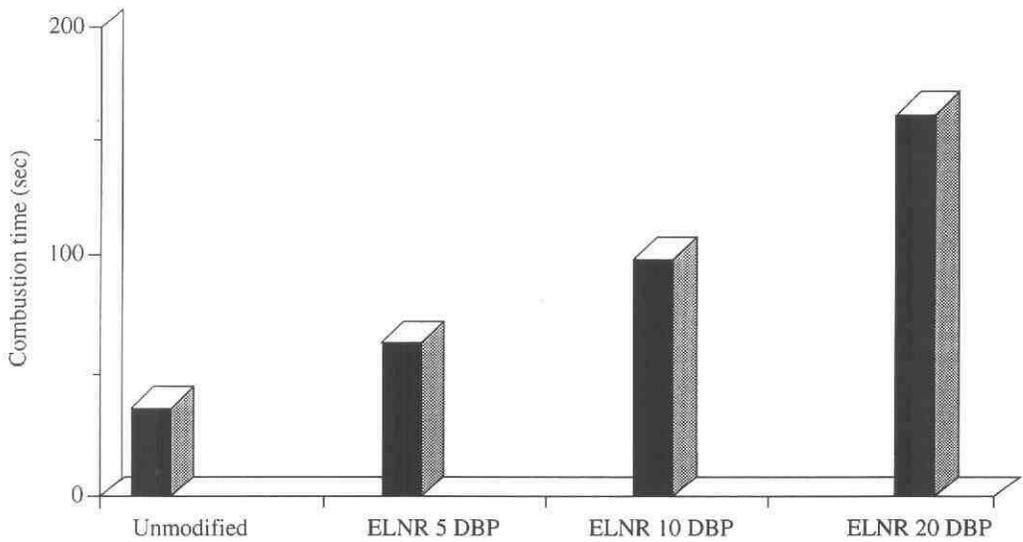


Figure 6. Combustion time in a 22% oxygen atmosphere of ELNR/methylnadic anhydride specimens in function of the amount of incorporated dibutyl phosphate.

Modified specimens: influence of dialkyl (or aryl) phosphate reagent. The specimens derived from polydienes modified by dialkyl (or aryl) phosphate (10% in relation to the epoxidised units) are compared with the unmodified ones. They also decompose in two stages (Figures 8-10).

ELNR derivatives (Figure 8). The first and second decomposition temperatures are close to that of unmodified ELNR network. On the other hand, in contrary to unmodified specimen which is completely reduced to ashes when the temperature reaches 550°C, a 15% to 20% residual mass is always noticed with ELNR networks including phosphorus.

Comparison of the thermogravimetric curves of materials fireproofed by various systems can be used as a way to characterise the intumescent fireproofing systems. Generally, the first decomposition temperature of a material fireproofed with a intumescent system, *i.e.* a system which leads during burning to the formation of a foaming carbonaceous coating^{13,14}, is lower in comparison with those of a similar material which cannot develop swollen char during its combustion. In the present study, unmodified and modified specimens have comparable first decompositions; this may indicate the absence of intumescent behaviour. This result is in accordance with the previous observations noticed during flammability tests.

Epoxidised LIR derivatives (Figure 9). On the whole, the remarks are the same as above. The thermograms of crosslinked specimens derived from epoxidised polyisoprene, unmodified and 10% modified by the dialkyl(or aryl) phosphates, are similar to the respectively corresponding crosslinked specimens derived from ELNR.

Epoxidised polybutadiene derivatives (Figure 10). Important differences were noticed in the thermograms of the specimens derived from epoxidised LIR and ELNR.

During the first decomposition, the weight loss of phosphorus modified polybutadiene specimens follows kinetics which, compared to those of the reference sample, seems in accordance with an intumescent system, but no intumescent char is formed during combustion of this category of polybutadiene samples (as reported above). Unexplained differences are also noticed during the first decomposition between the weight loss of specimens incorporating dialkylphosphate groups and that of the diphenyl phosphate-modified specimen. These particular results can be the consequence of the greatest difficulties encountered in the preparation of specimens from phosphorus-modified epoxidised polybutadiene, due to the particularly fast crosslinking kinetics of this product. So, these thermograms must be considered prudently because, in these conditions, the polydiene network is not perfectly homogeneous.

After 400°C, at the beginning of the second decomposition, thermograms of phosphorus modified polybutadiene networks are all superimposed. At 550°C, temperature of total decomposition of the unmodified specimen, the residual mass is still of the order of 10% to 15%.

Modified specimens: influence of the amount of dialkyl(or aryl) phosphate incorporated onto specimens. Figure 11 shows the thermograms of ELNR specimens whose epoxides were modified at 0%, 5%, 10% and 20% by dibutyl phosphate. The first decompositions are very similar whatever the modification level of ELNR by dibutyl phosphate may be. The results indicate the absence of a intumescence system

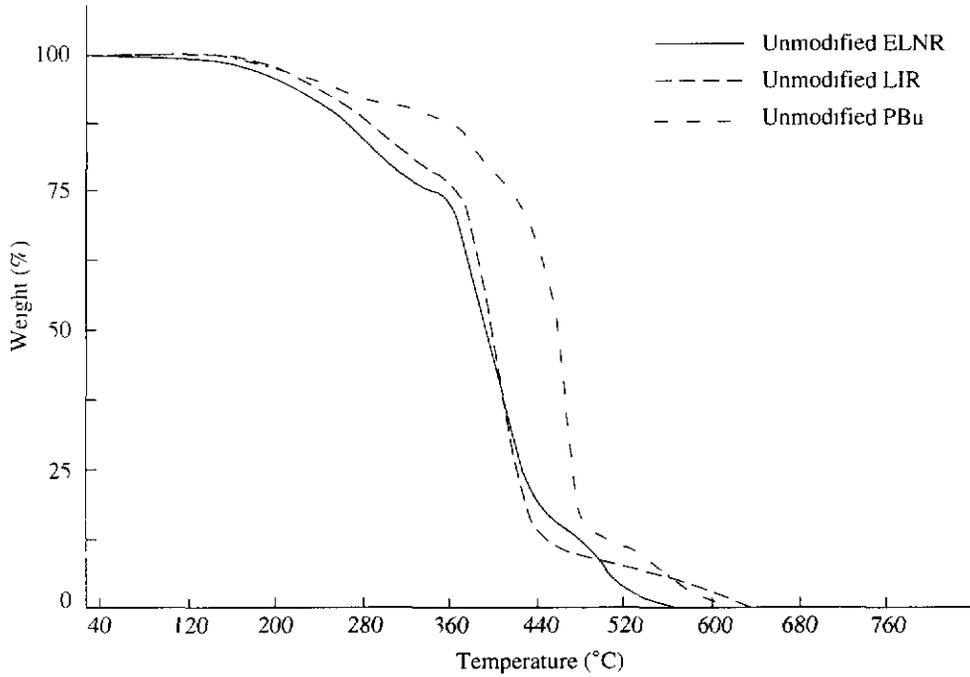


Figure 7 TGA thermograms for unmodified epoxidised rubber specimens

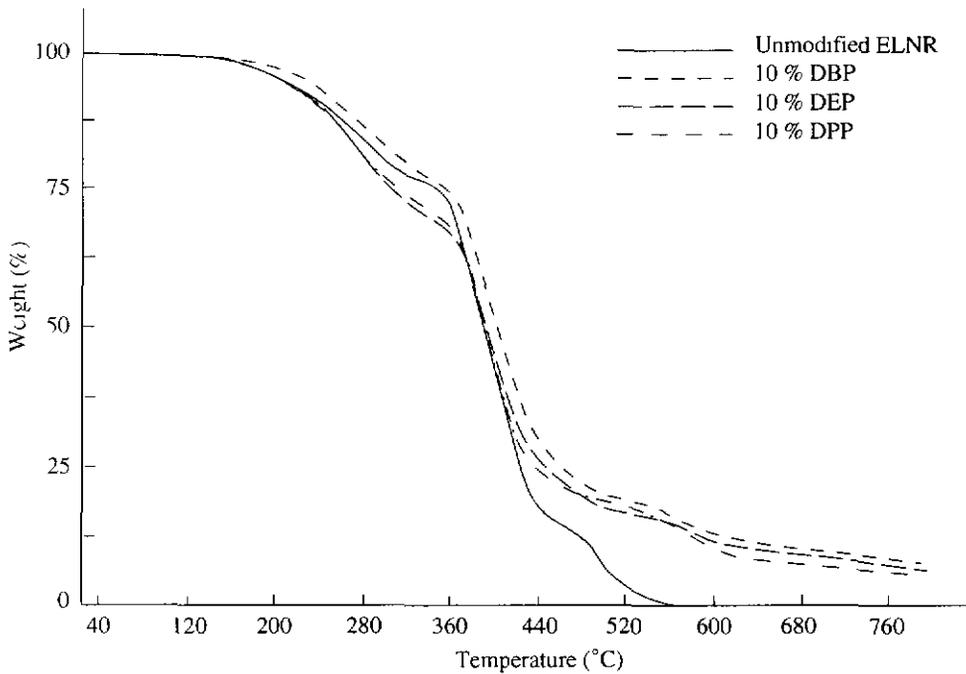


Figure 8 TGA thermograms for unmodified and phosphorus modified ELNR specimens

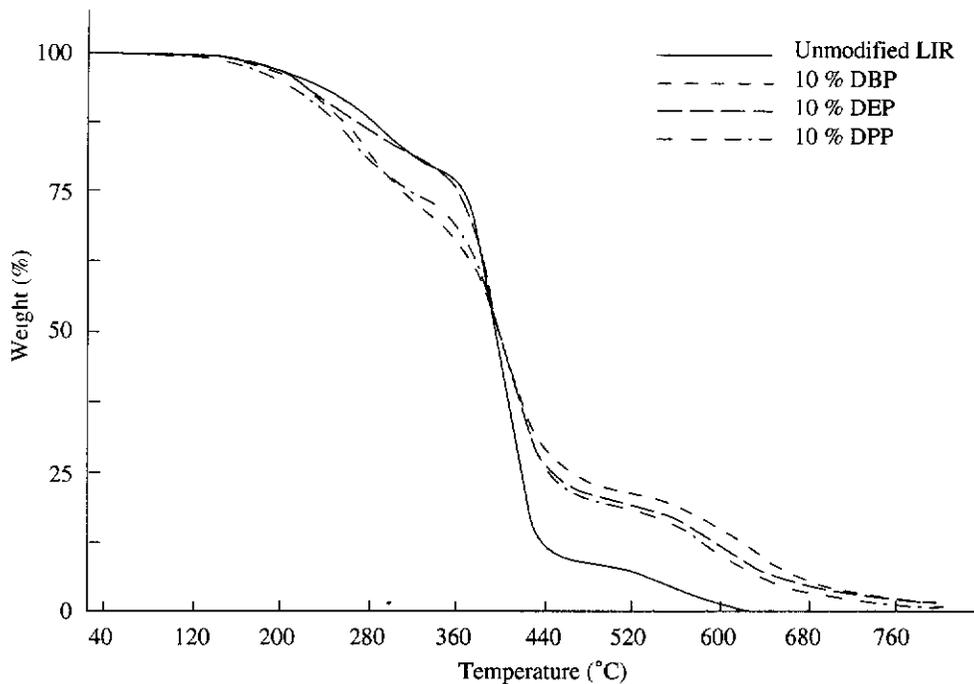


Figure 9. TGA thermograms for unmodified and phosphorus-modified epoxidised LIR specimens.

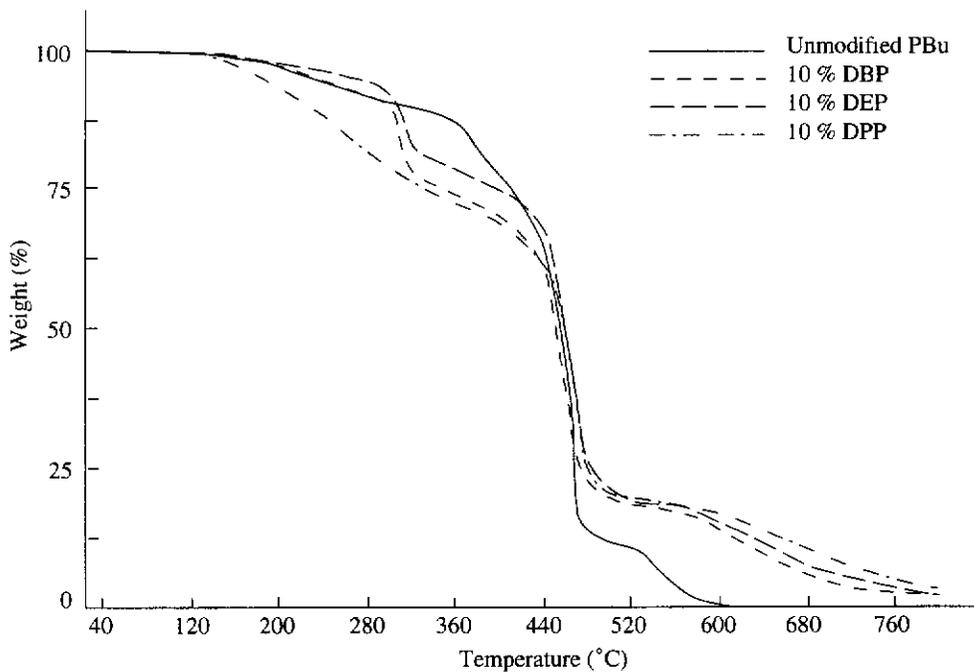


Figure 10. TGA thermograms for unmodified and phosphorus-modified epoxidised polybutadiene specimens.

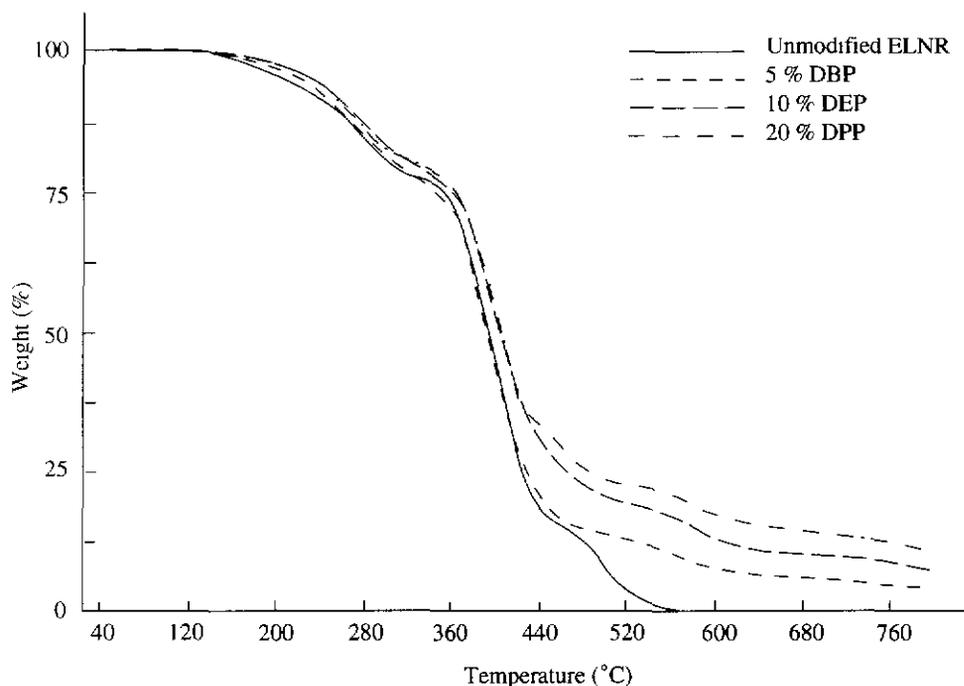


Figure 11. TGA thermograms of specimens derived from ELNR, unmodified and modified at different yields by dibutyl phosphate.

in which when the phosphorus concentration is increased the first decomposition temperature decreases^{14,15}. On the other hand, differences are noticed during the second decomposition (beyond 500°C) although the weight losses according to the temperature follow the same decrease for each phosphorus-modified specimen, the residual masses grow with the phosphorus content of the specimen.

CONCLUSION

Crosslinking by methylnadic anhydride of epoxidised 1,4-polydienes partially modified *in situ* by the dialkyl(or aryl) phosphates allowed the realisation of rigid tridimensional

systems, essential for the studies of flammability and thermal stability.

The incorporation of around 1.1–1.2 weight percent of phosphorus in crosslinked polydienes is generally sufficient to obtain fire-resistant materials in air with good rubber-elastic properties. The limiting oxygen indices obtained with specimens including diphenyl phosphate grafts (these groups tends to favour the formation of char and to reduce amount of active radicals which feed the combustion process) are better than those reached with specimens bearing dialkylphosphate groups. This shows the importance of the ester-group nature of phosphate groups chemically bonded onto polydiene network.

From the thermal stability viewpoint, degradation kinetics at low temperatures (from 200°C to 400°C) of modified specimens are more or less similar to those of the unmodified specimen. On the other hand, the residual masses are relatively large at about 600°C, compared to the unmodified specimens which entirely decompose at this temperature (the greater is the phosphorus content, the more the decomposition process is retarded at high temperature).

Fire-resistance properties of specimens incorporating di(alkyl or aryl) phosphate groups are achieved by the formation of a char layer on the polymer surface which retards the diffusion of combustible products toward the flame zone and impedes the heat transmission into the material bulk. The observations concerning the aspect of the carbonaceous layer formed during the combustion of specimens (formation of a non-foaming char in any case) and the information obtained from thermogravimetric analysis [specimens including chemically bonded dialkyl(or aryl) phosphate groups have a first decomposition temperature very similar to those of the unmodified reference specimens] can be associated to indicate the absence of intumescent behaviour.

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