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THE INFLUENCE OF FLAME RETARDANTS ON THE THERMAL STABILITY OF *CIS*-1,4-POLYISOPRENE

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Abstract

The effect of flame retardants such as chloroparaffin, antimony trioxide, mixtures of antimony trioxide and chloroparaffin, melamine cyanurate and pentabromotoluene on the thermal properties of *cis*-1,4-polyisoprene peroxide vulcanizate has been studied. The thermoanalytical curves of elastomers were interpreted. The flame retardants used, except Sb_2O_3 were found to change the characteristic thermal transitions of polyisoprene and to cause a decrease in its thermal stability. From among the investigated flame retardants only pentabromotoluene favoured the degradation of the elastomer in the range of its first exothermic transition.

Keywords: *cis*-1,4-polyisoprene, decomposition, degradation, destruction, flame retardants, peroxide vulcanizates, thermal analysis

Introduction

Cis-1,4-polyisoprene is one of the elastomers most commonly used in rubber industry. Our earlier investigations have proved that both the thermal properties and flammability of *cis*-1,4-polyisoprene depend on its crosslink density, network structure, content and type of fillers and the presence of metals with variable valence [1–7]. In this work the effect of flame retardants on the thermal properties of *cis*-1,4-polyisoprene has been demonstrated.

Experimental

Materials

The objects of my investigations were peroxide vulcanizates of *cis*-1,4-polyisoprene, Cariflex IR 307, containing the following flame retardants: chloroparaffin (70.4% Cl), antimony trioxide, 1:1, 1:2, 1:3, 2:1, 3:1 mixtures of antimony trioxide and chloroparaffin, melamine cyanurate and pentabromotoluene. I have prepared rubber mixtures with the following composition: *cis*-1,4-poly-

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isoprene 100 parts by mass, zinc oxide 5 phr, (parts per hundred rubber) stearic acid 1 phr, dicumyl peroxide 1 phr, flame retardants 10, 20, 30, 40 and 50 phr. The content of chloroparaffin and antimony trioxide mixture in all cases was 30 phr.

Methods

The rubber mixtures were vulcanized in an electrical press at 150°C for the optimum vulcanization time determined with a Monsanto rheometer.

Thermal analysis was carried out with a Paulik, Paulik, Erdey Derivatograph in an air atmosphere and a Perkin-Elmer thermobalance TGS-1 in inert gas atmosphere. The conditions of thermal analysis in an air atmosphere were: standard reference substance Al_2O_3, temperature range 25–800°C, sample mass 90 mg, heating rate 7.9°C min^{-1}. The conditions of thermal analysis in a nitrogen atmosphere were: temperature range 25–800°C, sample mass 7 mg, heating rate 10°C min^{-1}. Thermal stability indexes T_5 and T_{50} corresponding to 5 and 50% loss of mass, respectively, were determined from the TG curves.

Degree of crosslinking of *cis*-1,4-polyisoprene vulcanizate, before and after heating to 200°C was determined by means of the equilibrium swelling method in toluene at 25°C using microsamples of about 30 mg. In the calculation of equilibrium swelling values the content of flame retardant in the vulcanizate was taken into account.

Table 1 Results of thermal analysis of flame retardants

Flame retardant	T_5/ °C	T_{50}/ °C	Residue at 800°C/ wt%
Antimony trioxide	–	–	101.7*
Chloroparaffin	240	310	0
Mixture of Sb_2O_3 and chloroparaffin (1:1)	270	300	22.2
Pentabromotoluene	190	250	35.6
Melamine cyanurate	320	365	18.3

* The increase in mass is caused by oxidation of Sb_2O_3

Results and discussion

The results of thermal analysis of flame retardants are given in Table 1. From among the investigated flame retardants antimony trioxide has the highest thermal stability. In the temperature range of 480–530°C an increase was observed in the mass of Sb_2O_3 caused by oxidation. The lowest values of thermal stability index were found for pentabromotoluene although its solid residue at 800°C was relatively large. Heating of chloroparaffin to 800°C leads to its total decomposition. A considerable mass loss of a mixture of chloroparaffin and Sb_2O_3 was caused by chemical reactions of the components in the temperature range of 265–565°C [9, 10].

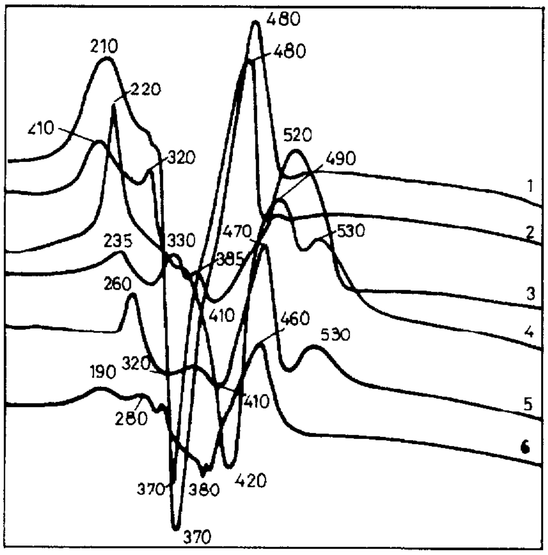
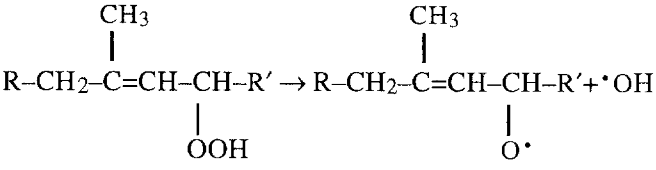
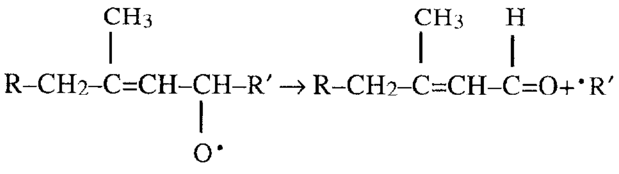


Fig. 1 DTA curves of *cis*-1,4-polyisoprene vulcanizates: 1 – free of flame retardant, 2 – containing 40 phr of Sb_2O_3, 3 – 0 phr of chloroparaffin, 4 – 30 phr of a mixture of chloroparaffin and Sb_2O_3 (1:1), 5 – 40 phr of pentabromotoluene, 6 – 40 phr of melamine cyanurate

Figures 1 and 2 show DTA and TG curves of *cis*-1,4-polyisoprene peroxide vulcanizates in an air atmosphere. The results of their thermal analysis are presented in Tables 2, 3 and 4. The first exothermic transition of polyisoprene at 210°C is connected with scission and crosslinking reactions caused by decomposition of peroxide groups present or formed in the polymer during its heating (Table 2):



$$R{-}CH_2{-}\overset{\overset{\textstyle CH_3}{|}}{C}{=}CH{-}\underset{\underset{\textstyle OOH}{|}}{CH}{-}R' \rightarrow R{-}CH_2{-}\overset{\overset{\textstyle CH_3}{|}}{C}{=}CH{-}\underset{\underset{\textstyle O^\bullet}{|}}{CH}{-}R' + {}^\bullet OH$$



$$R{-}CH_2{-}\overset{\overset{\textstyle CH_3}{|}}{C}{=}CH{-}\underset{\underset{\textstyle O^\bullet}{|}}{CH}{-}R' \rightarrow R{-}CH_2{-}\overset{\overset{\textstyle CH_3}{|}}{C}{=}CH{-}\overset{\overset{\textstyle H}{|}}{C}{=}O + {}^\bullet R'$$

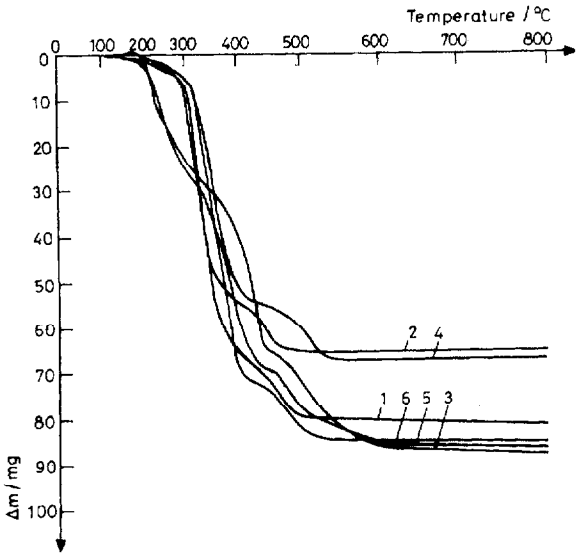


Fig. 2 TG curves of *cis*-1,4-polyisoprene vulcanizates: 1 – free of flame retardant, 2 – containing 40 phr of Sb_2O_3, 3 – 40 phr of chloroparaffin, 4 – 30 phr of a mixture of chloroparaffin, and Sb_2O_3 (1:1), 5 – 40 phr of pentabromotoluene, 6 – 40 phr of melamine cyanurate

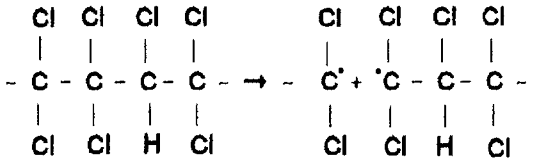
The homolytic cleavage of polyisoprene can also take place in the range of the first exothermic transition, favouring modification, cyclization of the macromolecules and depolymerization [3].

Sb_2O_3 probably hinders the formation of peroxide groups in the range of the first transition of *cis*-1,4-polyisoprene vulcanizate but does not affect its thermal characteristics. The other flame retardants cause a change in the thermal transitions of polyisoprene and prevent formation of peroxide groups (Figs 1 and 2). Addition of flame retardants, except Sb_2O_3, causes a decrease in the T_5 value of the sample. Evaporation of a part of the additive may be the reason for the effect (Table 3). For pentabromotoluene, the degradation of the vulcanizate is observed at 200°C (Table 4). On the other hand, chloroparaffin and melamine cyanurate favour elastomer crosslinking at this temperature. Chloroparaffin reduces the degree of crosslinking of polyisoprene during its vulcanization at 150°C, probably

Table 2 Results of elemental analysis of *cis*-1,4-polyisoprene vulcanizates before and after heating to 170 and 200°C

Temperature/°C	25	170	200
Content of C, H and O/ wt%	C=81.77 H=10.94 O= 7.29	C=81.09 H=10.81 O= 8.10	C=80.60 H=10.75 O= 8.65
Total	100.00	100.00	100.00

caused by the HCl released, which reduces the activity of dicumyl peroxide as a crosslinking agent. At 200°C free radicals can be formed as a result of the homolytic cleavage of chloroparaffin molecules:



$$-\underset{Cl}{\overset{Cl}{C}}-\underset{Cl}{\overset{Cl}{C}}-\underset{H}{\overset{Cl}{C}}-\underset{Cl}{\overset{Cl}{C}}- \rightarrow -\underset{Cl}{\overset{Cl}{C^{\bullet}}} + {}^{\bullet}\underset{Cl}{\overset{Cl}{C}}-\underset{H}{\overset{Cl}{C}}-\underset{Cl}{\overset{Cl}{C}}-$$

These radicals are capable of crosslinking the elastomer [11] which, at somewhat higher temperature, 210–220°C, undergoes thermal destruction in two stages.

Table 3 Results of thermal analysis of *cis*-1,4-polyisoprene vulcanizates

Flame retardant/ Content [phr]	T_5/ °C	T_{50}/ °C	Residue at 800°C/ wt%
–	290 340*	370 390*	7.8 4.9*
Sb_2O_3			
10	280	360	7.8
20	285	365	15.0
30	295	370	18.9
40	305	370	27.2
50	310 335*	390 395*	32.2 30.2*
Chloroparaffin			
10	295	370	4.4
20	250	380	4.1
30	230	390	3.9
40	220	395	3.5
50	210 231*	395 415*	3.3 7.5*
Mixture of Sb_2O_3 and chloroparaffin, 30			
1:1	295	390	30.5
1:2	240	390	31.1
1:3	235	385	31.1
2:1	300	400	17.8
3:1	300 338*	385 412*	25.0 27.0*

Table 3 Continued

Flame retardant/ Content [phr]	T_5/ °C	T_{50}/ °C	Residue at 800°C/ wt%
Pentabromotoluene			
10	240	360	5.7
20	225	360	5.5
30	220	355	5.5
40	220	350	4.1
50	210 233*	345 413*	4.2 5.6*
Melamine cyanurate			
10	285	345	5.7
20	280	350	5.7
30	280	340	5.5
40	285	340	5.0
50	295 338*	350 395*	4.9 2.8*

* in inert gas atmosphere

Table 4 Effect of flame retardants on the degree of crosslinking of *cis*-1,4-polyisoprene vulcanizates $1/Q_w$, before and after heating in the furnace of a derivatograph to 200°C

Flame retardant/ Content [phr]	$\frac{1}{Q_w}$ at 25°C	$\frac{1}{Q_w}$ at 200°C
–	0.185	0.178
Sb_2O_3		
10	0.226	0.181
20	0.220	0.189
30	0.218	0.200
40	0.209	0.214
50	0.210	0.219
Chloroparaffin		
10	0.161	0.185
20	0.150	0.275
30	0.136	} *
40	0.126	
50	0.120	

Table 4 Continued

Flame retardant/ Content [phr]	$\frac{1}{Q_w}$ at 25°C	$\frac{1}{Q_w}$ at 200°C
Pentabromotoluene		
10	0.154	0.089
20	0.133	0.069
30	0.112	*
40	0.109	
50	0.105	
Melamine cyanurate		
10	0.193	0.239
20	0.199	0.243
30	0.211	0.258
40	0.206	0.275
50	0.190	0.281

* crumbling samples
** sticky samples

The thermal decomposition of *cis*-1,4-polyisoprene vulcanizate proceeds with deficiency of oxygen in the reaction zone. Halogen-containing flame retardants also favour an endothermic decomposition of the elastomer. In the presence of other flame retardants, the thermal decomposition of the vulcanizate is initiated by exothermal reactions (Fig. 1). Above 430°C, in an air atmosphere, the burning of the residue after thermal decomposition of *cis*-1,4-polyisoprene vulcanizate takes place. In the presence of halogen-containing flame retardants, a two-stage combustion of the residue is observed.

Conclusions

1. The flame retadants studied, except pentabromotoluene, favour crosslinking of *cis*-1,4-polyisoprene when heated in an air atmosphere to 200°C.
2. All the investigated flame retardants, except Sb_2O_3 reduce the rate of thermal destruction of *cis*-1,4-polyisoprene.
3. The results of studies on the thermal properties of flame retardants and their effect on the thermal stability of *cis*-1,4-polyisoprene provide an insight into processes taking place during the burning of the elastomer.

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