EFFECT OF THE NETWORK STRUCTURE
ON THE FLAMMABILITY OF *CIS*-1,4-POLYISOPRENE
VULCANIZATES

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The combustibilities of *cis*-1,4-polyisoprene and its peroxide and sulphur vulcanizates have been investigated by means of the oxygen index method. The temperature distribution in the sample and the molecular weight of the liquid products formed as a result of elastomer destruction in the combustion zone have been measured. It has been found that the combustibility of *cis*-1,4-polyisoprene diminishes as its cross-link density increases. This effect is much stronger for sulphur than for peroxide vulcanizates. The investigations lead to the conclusion that a mechanism of network degradation and volatile sulphur compounds penetrating to the flame are responsible for this difference.

In previous studies we have shown that the thermal stability of *cis*-1,4-polyisoprene (PI) depends on its cross-link density and its network chemical structure [1]. We recently decided to find out whether such a correlation holds in the case of the flammability of the polymer. In principle one may except a correlation between the thermal stability and the flammability of polymers, as it is their low molecular weight destruction products which undergo burning. However, the above assumption does not have to be generally valid with respect to cross-linked elastomers. Due to the differences in energy of carbon-carbon, mono-, di- and polysulphide cross-links and the various reactivities of their homolysis products, we expected the effect of the network structure on the flammability of vulcanizates to be of a specific nature. This could be considered as a theoretical problem of some practical importance, not only for *cis*-1,4-polyisoprene, but also for other cross-linked elastomers.

Experimental

Materials

Synthetic cis-1,4-polyisoprene (IR) and its peroxide and sulphur vulcanizates of different crosslink densities were used in the studies. The compositions of the rubber mixtures are shown in Table 1. The rubber compounds were vulcanized for 60 min at 150° in an electric press. The samples for the thermal analysis were

Table 1 Compositions of mixtures, parts by weight per 100 parts by weight of elastomer

No.	Component	Symbol of mixture									
		1N	2N	3N	4N	5N	1S	2S	3S	4S	5S
1	cis-1,4-poly-isoprene[1]	100	100	100	100	100	100	100	100	100	100
2	zinc oxide, 1st grade						5	5	5	5	5
3	stearic acid						1	1	1	1	1
4	sulphur						1	2	3	4	5
5	N-cyclohexylo-benzothiazyl sulphenamide[2]						1.2	1.2	1.2	1.2	1.2
6	dicumyl peroxide[3]	0.5	1.0	2.0	4.0	8.0					
	together	100.5	101.0	102.0	104.0	108.0	108.2	109.2	110.2	111.2	112.2

[1] Cariflex IR–307, Shell Chem. Co
[2] Tioheksam, Poland
[3] 98% Merck–Schuchardt

prepared in the form of 0.5 ± 0.05 mm films, and the samples for the determination of flammability were in the form of blocks having dimensions $50 \times 10 \times 5 \pm 0.5$ mm. Both the unvulcanized elastomer and its vulcanizates were extracted with acetone at room temperature under an inert gas.

Methods

The molecular weight of cis-1,4-polyisoprene was determined using a Hewlett Packard Model 501 osmometer. 1.00, 0.50, 0.25 and 0.12 g/100 ml toluene solutions and 0.005 µg PG membranes were used for the measurements.

The cross-link densities of the PI vulcanizates were determined by the equilibrium swelling method in toluene at 25°. Samples of about 20 mg were weighed on a torsion balance. The swelling time was 48 hr. The calculations were

based on the Flory–Rehner equation [2, 3] and the polymer-solvent interaction parameter was taken from the paper published by Blanchard and Wotton [4]. The flammabilities of cis-1,4-polyisoprene and its vulcanizates were determined by the oxygen index method [5]. The measurements were carried out at room temperature, according to the ASTMD 2863–74 Standard. The samples were lit for 15 s using a gas burner at an oxygen content in the mixture with nitrogen sufficient to allow complete burning of a 50 mm sample length within 180 s. The arithmetic mean of at least ten independent measurements was taken as the measurement result. The cross-link density changes resulting from the degradation and destruction of the burning elastomer were examined. Samples were prepared as follows: a rubber block of the dimensions given above was lit for 15 s in a mixture of oxygen and nitrogen of composition corresponding to the vulcanizate oxygen index value. The sample was allowed to burn for a further 15 s and it was then rapidly extinguished and cooled down by cutting off the oxygen supply.

The cross-link density was determined at the sample edge and along its axis. Microsamples of about 20 mg were taken within a distance $l = 40$ mm from the top of the sample, according to the predetermined scheme shown in Figs 4 and 5. The measurements were carried out as mentioned above. The molecular weights of liquid degradation and desctruction products were determined by osmometry, after the burning of PI vulcanizates samples was completed.

The temperature distribution was measured along the axis of the sample burned in the oxygen and nitrogen mixture with composition corresponding to the sulphur vulcanizate oxygen index value, as illustrated in Fig. 1. The thermocouple was
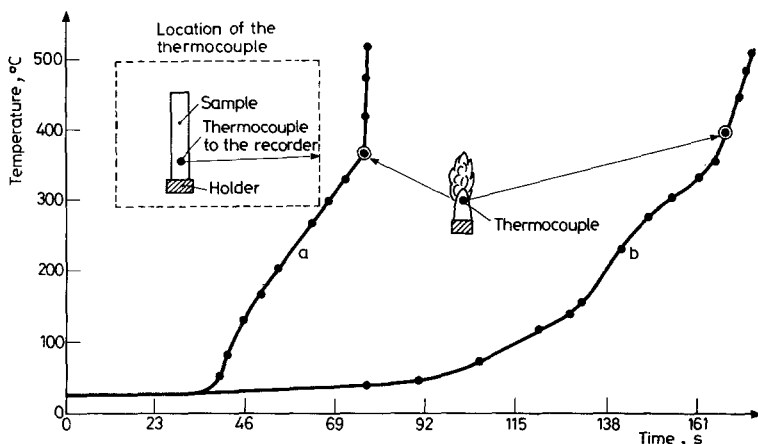

Fig. 1 Temperature distribution along the length of the burning sample axis in the oxygen and nitrogen mixture corresponding to the oxygen index of the sulphur vulcanizate. The moment at which the flame surrounds the end of the thermocouple is denoted by a circle. a) peroxide vulcanizate; b) sulphur vulcanizate

placed in the sample axis at a height of 10 mm from the holder. The sample was lit for 15 s using a gas burner. Thermal analysis was carried out using a Hungarian derivatograph of the Paulik–Paulik–Erdey system. The measurement conditions were given in our previous paper [1].

Calculations of the activation energies of destruction of cis-1,4-polyisoprene and its vulcanizates were based on the thermogravimetric curves obtained [6].

Results and discussion

The anticipated dependence between the network structure and the flammability of cis-1,4-polyisoprene vulcanizates was generally confirmed by our studies. We found that the cross-linking of IR with dicumyl peroxide slightly increases its oxygen index (OI), and the influence is fairly distinct in the effective chain concentration range up to $v_e = 3 \cdot 10^{-4}$ mol/cm³ (Fig. 2). Similar changes were
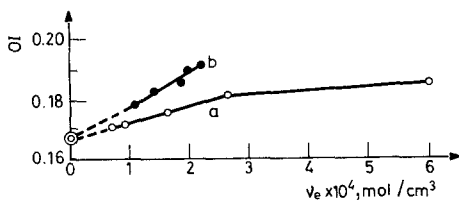

Fig. 2 Dependence of the oxygen index, IO, of cis-1,4-polyisoprene vulcanizates on their effective cross-link density, v_e. a) peroxide vulcanizates; b) sulphur vulcanizates; ○ uncross-linked rubber

observed in the thermal stability of IR as a function of its cross-link density [1]. It turned out, however, that the flammabilities of sulphur vulcanizates were lower than those of the uncross-linked IR and its peroxide vulcanizates. This was a rather unexpected result, because IR sulphur vulcanizates exhibit lower thermal stability than the peroxide vulcanizates [1]. The oxygen index values of vulcanizates of both types show a linear increase with the increase in activation energy of their destruction (E_a) (Fig. 3). The linear relationship between OI and E_a indicates that the heat transferred from the flame to the sample is mainly used for the destruction of the elastomer. Subsequently, the destruction leads to the formation of volatile products, which undergo burning. The burning rate of the sample was kept constant at $V = 0.28$ mm/s, according to the principle of the OI determination method. Therefore, in the discussed system, a kind of steady state exists, where the amount of heat entering the sample and the amount of volatile products formed during burning are approximately constant. A substantial part of the evolved heat is carried away by gas flowing around the sample and the apparatus chimney.
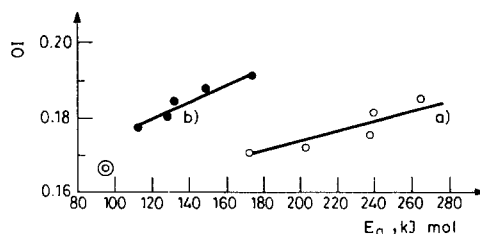
Fig. 3 Dependence of the oxygen index, OI, *cis*-1,4-polyisoprene vulcanizates on their destruction activation energy, E_a. a) peroxide vulcanizates; b) sulphur vulcanizates; ○ uncross-linked rubber

During burning, the sample essentially preserves its form and the evident signs of elastomer destruction and degradation can be observed above all in the region directly in contact with the flame. There is no doubt, however, that the above processes also occur in the slightly deeper layers of the sample. Thermal analysis reveals that the main fraction of volatile destruction products of vulcanizates is evolved in the temperature range 320–420°, and thus we expected that the temperature of the boundary layer between the flame and the sample would be given by that range; this was indeed confirmed by our measurements (see Fig. 1). Elastomers are poor thermal conductors; the thermal conductivity of IR and its unfilled vulcanizates is $\lambda = 0.155$ W/mK, and in the range up to 220° is almost independent of temperature [7, 8]. There is, then, a considerable thermal gradient in the burning sample. The results of cross-link density measurements are plotted as a function $(1/M_c = f/l)$, where l is the distance within 40 mm from the top of a sample measured after burning for 30 s (Figs 4 and 5). M_c is the molecular weight of the network chains. Thus, the value of $1/M_c$ corresponds to the concentration of the
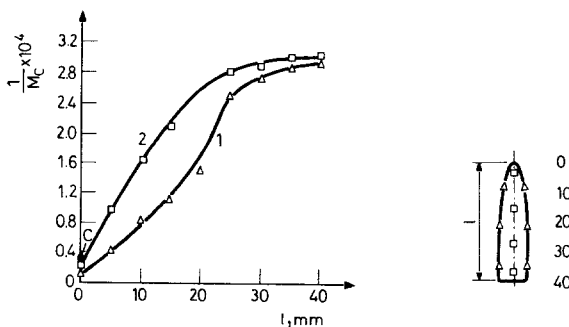

Fig. 4 Changes in cross-link density, $1/M_c$, of *cis*-1,4-polyisoprene peroxide vulcanizate along the length of the sample, l, after burning for 30 s. 1 at the periphery of the sample; 2 in the axis of the sample; Point C corresponds to the value $1/\bar{M}_n$
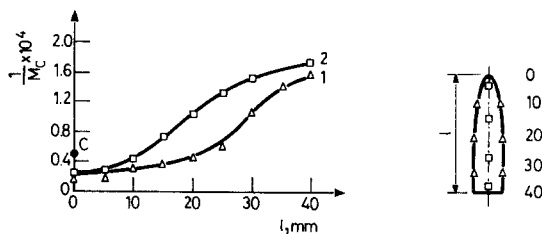
Fig. 5 Changes in cross-link density, $1/M_c$ of cis-1,4-polyisoprene sulphur vulcanizate along the length of the sample, l, after burning for 30 s. 1 at the periphery of the sample; 2 in the axis of the sample; Point C corresponds to the value $1/\bar{M}_n$

effective chains of cross-linked elastomer. The ordinate shows not only the values of $1/M_c$, but also the point C, resulting from osmometric measurements, corresponding to the value of $1/\bar{M}_n$. $\bar{M}_n$ is the number-average molecular weight of the liquid products of degradation and destruction, formed during burning of the PI vulcanizates. The value of $1/\bar{M}_n$ is therefore the concentration of chains of uncross-linked cis-1,4-polyisoprene given in moles per gram. The $1/M_c$ values determined from the curves at $l = 0$ are close to the respective values of $1/M_n$. The positions of the curves in Figs 4 and 5 show that the density decrease of the burned vulcanizate is greater at the periphery of the sample than in its axis. The difference is due to the flame propagation by the flowing liquid products of destruction, that also fulfil the role of heat transfer agent.

Consequently, the thermal gradient occurs not only along the sample axis, but also in the direction perpendicular to the axis. Distinct differences were revealed between the cross-link density distributions and the degrees of degradation along the sample axis for the two types of vulcanizates. For the peroxide vulcanizate, a very strong degradation occurs in the direct neighbourhood of the flame at $l = 0$ and the degree of degradation $k = \dfrac{M_c}{M_{c,0}} = 22$ (Fig. 6, curves 1 and 2), where M_c and $M_{c,0}$ denote the molecular weights of the network chains after degradation and initially, respectively.

However, even at a distance of 5 mm from the boundary layer, the degradation degree decreases strongly, reaching values of $k = 3$ and $k = 7$ in the sample axis and at the sample periphery, respectively. At a distance $l = 15$ mm from the boundary layer, measured in the sample axis, or $l = 25$ mm at the sample periphery, $k = 1$, indicating that there is in practice no degradation (Fig. 6, curve 2).

The picture is different in the case of the sulphur vulcanizate. Though the degree of degradation is relatively low ($k = 7.3$), at points of direct contact with the flame, that is at $l = 0$, the region of strong degradation extends to $l = 20$ mm and even to

$l = 30$ mm, in the sample axis and at the periphery, respectively (Fig. 7, curve 1). This points to the much higher thermal stability of the *cis*-1,4-polyisoprene peroxide vulcanizate than that of the sulphur one. This is of crucial importance, for, as can be seen in Fig. 1, during the OI determination the temperature of the peroxide vulcanizate sample increases faster than that of the sulphur vulcanizate sample. The difference is due to the formation of liquid products as a result of the degradation and destruction of the peroxide vulcanizate. These products, flowing down the sample, act as heat transfer agents.

On the other hand, during the sulphur vulcanizate pyrolysis, semi-solid products are formed and remain in the burning zone. The results show that the flammability of the elastomer is determined by the reactions taking place in the boundary layer a few mm thick, whereas the degradation occurring deep inside the elastomer sample
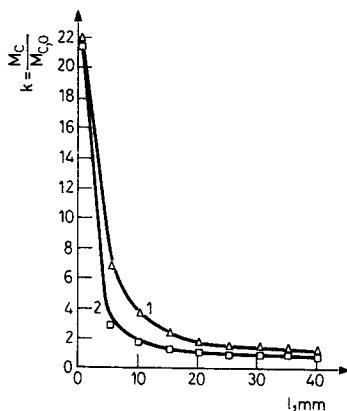

Fig. 6 Changes in degradation degree, k, of *cis*-1,4-polyisoprene peroxide vulcanizate along the length of the sample, l, after burning for 30 s. 1 at the periphery of the sample; 2 in the axis of the sample; M_c and $M_{c,0}$ denote the molecular weights of network chains after degradation and initially, respectively

Fig. 7 Changes in degradation degree, k, of *cis*-1,4-polyisoprene sulphur vulcanizate along the length of the sample, l, after burning for 30 s. 1 at the periphery of the sample; 2 in the axis of the sample; M_c and $M_{c,0}$ denote the molecular weights of network chains after degradation and initially, respectively
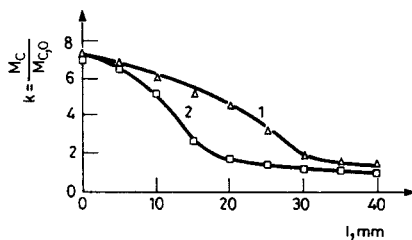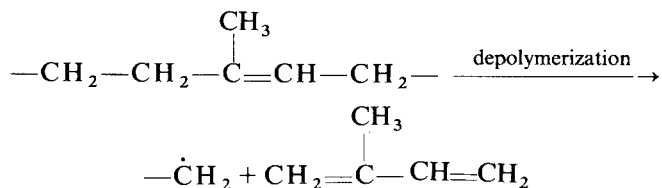
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does not play such an important role. This is a very general statement, however, and on the basis of a deeper analysis of the experimental data we present the following working hypothesis. In the case of the IR peroxide vulcanizates, having high-energy (285 kJ/mol) C—C cross-links [9], degradation occurs via chain-breaking. A single act like this is accompanied by the splitting-off of monomer molecules from both the macroradicals formed, so that depolymerization takes place:

$$-CH_2-CH_2-\overset{\overset{\displaystyle CH_3}{\displaystyle |}}{C}=CH-CH_2- \xrightarrow{\text{depolymerization}}$$

$$-\dot{C}H_2 + CH_2=\overset{\overset{\displaystyle CH_3}{\displaystyle |}}{C}-CH=CH_2$$

Thus, isoprene is the main volatile product of the decomposition of peroxide cross-linked IR. As a general rule, depropagation stops when a free radical centre is formed on a carbon atom linked to the adjacent chain [1]. This explains the negative effect of the peroxide cross-link density on the flammability of IR. On the other hand, the degradation of sulphur vulcanizates having low-energy di- and polysulphide cross-links, 269 and 138 kJ/mol, respectively [9–11], proceeds primarily by —S—S— bond cleavage. This does not favour the splitting-off of monomer units. The macroradicals terminated by sulphur are stabilized mainly by cyclization, modification and secondary cross-linking reactions, accompanied by strong cage effects. Consequently, a smaller amount of volatile inflammable products of low molecular weight enters the flame than in the case of the peroxide vulcanizate. In fact, we found earlier that the weight loss due to pyrolysis is smaller for PI sulphur vulcanizates than for the peroxide ones [1]. It is highly probable, however, that an additional cause exists for the lower flammability of sulphur vulcanizates. Under the conditions in the boundary layer, the sulphide cross-links undergo oxidation to sulphenic and thiosulphinic acids, and evidently further to SO_2 and SO_3. These volatile products enger the flame and can inhibit oxidative chain reactions, acting as free radical scavengers and catalysts of the ionic decomposition of peroxides. This assumption is fairly probable, as soot is formed in a much higher quantity during the burning of PI sulphur vulcanizates than in the burning of the uncross-linked elastomer and its peroxide vulcanizates. The mechanism of the PI vulcanizate burning is at present the object of our further studies.

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Zusammenfassung — Die Brennbarkeit des unvernetzten *cis*-1,4-Polyisoprens und seiner Peroxid- und Schwefelvulkanisate wurde mit der Sauerstoffindexmethode untersucht. Messungen der Temperaturverteilung im Prüfling wurden ebenfalls ausgeführt und das Molekulargewicht der infolge der Zersetzung der Elastomere in der Verbrennungszone entstehenden flüssigen Produkte mit der Methode der dynamischen Osmometrie bestimmt. Es wurde festgestellt, daß die Brennbarkeit des cis-1,4-Polyisoprens mit zunehmender Vernetzungsdichte abnimmt, und zwar viel ausgeprägter im Falle der Schwefel- als im Falle der Peroxidvulkanisate. Es wurde gefolgert, daß flüchtige, in die Flamme gelangende Schwefelverbindungen als Verbrennungsinhibitoren wirken.

Резюме — Методом кислородного индекса изучена горючесть цис-1,4-полиизопрена и его перекисных и серных вулканизатов. С помощью метода динамической осмометрии проведено определение молекулярного веса жидких продуктов, образующихся при распаде эластомера в зоне горения. Найдено, что горючесть цис-1,4-полиизопрена уменьшается при увеличении числа поперечных связей. Этот эффект более сильно выражен в случае сернистых вулканизатов. Сделано заключение, что механизм расщепления поперечных связей и проникновение летучих серных соединений в пламя обусловливает различие между двумя типами вулканизатов.