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THE EFFECT OF THE NETWORK STRUCTURE OF THE THERMAL PROPERTIES OF *cis*-1,4-POLYISOPRENE VULCANIZATES

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The thermal properties of *cis*-1,4-polyisoprene and its vulcanizates were investigated by means of thermal analysis and complementary methods. It was found that cross-linking generally increases the thermal stability of this elastomer, though distinct differences between peroxide and sulphur vulcanizates were observed. Polysulphide cross-links cleave readily at elevated temperature, and transform to cross-links of lower sulphidity, mainly disulphide. However, some of them are probably oxidized first to sulphoxides, and further to sulphenic or thiosulphoxylic acids. The products formed involve the ionic decomposition of the peroxides and thereby prevent the autocatalytic thermooxidative destruction of *cis*-1,4-polyisoprene.

The mechanical and relaxational properties of elastomers depend strongly on their network structure. It seemed that this dependence should also appear in the case of their thermal properties as investigated by DTA and TG methods. The goal of our work was to clarify the nature of the thermal transitions which occur in *cis*-1,4-polyisoprene (IR) vulcanizates with different cross-link densities and chemical network structures when these are heated in the furnace of a derivatograph. Although Sircar [1] has observed an effect of the sulphur level, and Brazier and Schwartz [2] that of an accelerator on the thermal profiles of IR, the results were not analyzed from the aspect of the network structure.

Experimental

Materials

Synthetic *cis*-1,4-polyisoprene (IR), Cariflex IR-307, produced by the Shell Chem. Co., and also its peroxide and sulphur vulcanizates with different cross-link densities, were the objects of our investigations. The composition of the rubber mixtures were as follows. Series I: the samples denoted 1P to 5P contained IR, 100 weight parts, and dicumyl peroxide, DCP (98%, Merk–Schuchard), in an amount of 0.5 to 8.0 phr. Series II: the samples denoted 1S to 5S contained IR, 100 weight parts, zinc oxide 5 phr, stearic acid 1 phr, sulphur 1 to 5 phr, and N-cyclohexyl benzothiazylsulphenamide (Tioheksam, Poland). The compounds were vulcanized for 60 minutes in an electric press at 150°. The samples were prepared in the form of plates 0.5±0.05 mm thick. Both the unvulcanized elastomer and its vulcanizates were throughly extracted with acetone in the dark at room temperature in an atmosphere of an inert gas.

Methods

The molecular weight of IR was determined by viscometry at 25 ±0.5°. Toluene solutions and Ubbelohde's viscometer were used. The number average molecular weight M_n was calculated according to the Bristow formula: $|\eta| = 9.00 \cdot 10^{-6} M_n^{-1.026}$ [3]. The cross-link densities of the IR vulcanizates were determined by the equilibrium swelling method in toluene at 25°. Microsamples of about 20 mg were weighed on a torsion balance. The calculations were made on the basis of the Flory–Rehner [4, 5] equation and the value of the polymer-solvent interaction parameter from the paper of Blanchard and Wotten was applied [6]. The bound sulphur was determined by the Schöniger method [7]. Sol-gel analysis was carried out in a Soxhlet apparatus. 3 g samples of disintegrated vulcanizates, placed in cells made of phosphor-bronze wire net, were extracted with toluene for 72 hours in an atmosphere of inert gas, and then dried to constant weight. In calculations of gel fractions, the weight of zinc oxide was subtracted from the sample weight. The chemical nature of the cross-links was determined with thiolamine reagents; two kinds were used, "soft" and "hard" [8]. The first kind cleaves only polysulphide cross-links, and the second kind both poly- and disulphide cross-links.

Thermal analysis was performed using a Hungarian derivatograph with the Paulik, Paulik and Erdey system. The conditions of analysis were as follows:

atmosphere	air
sample mass	90 mg
heating rate	7.9 degree/min
temperature range	25–800°
sensitivity	DTA 1/5, DTG 1/20, TG 100.

The samples for analysis were prepared by cutting out circular pieces of the elastomer, having a diameter equal to the diameter of the platinum plate of the apparatus. The thickness of the disks was 0.5 ±0.05 mm. In some cases samples prepared by disintegration of an elastomer into small cubes about 1 mm in size were also tested. The temperatures and heat effects of the IR transitions were determined from the thermal curves and their activation energies were calculated by the Freeman–Carroll [9] method.

Results and discussion

In the thermal curves of uncross-linked IR, the following five regions of thermal transitions could be recognized (Fig. 1). The first, endothermic event, in the region

AB, is connected with the desorption of gases and the volatilization of water and acetone, contained in trace amounts in the extracted elastomer.

This interpretation, based on results obtained by mass-spectrometry [10], is in accordance with a very small loss of sample weight. The second, exothermic transition, in the region BC, could be subdivided into two stages, before and after a peak temperature. The first stage is characterized by a slight increase in sample weight. From our earlier investigations it follows that in this stage peroxide groups are formed as a result of oxidation of isoprene units [10]. In the second stage the thermally initiated homolysis of these peroxide groups causes simultaneously the scission and cross-linking of elastomer chains. Thermooxidative scission follows via a free radical chain mechanism and has an autocatalytic character. The changes in the IR chemical composition and its $\bar{M}_n$ values after the completion of the second, BC transition are illustrated by the data in Table 1. An investigation of the strongly disintegrated IR

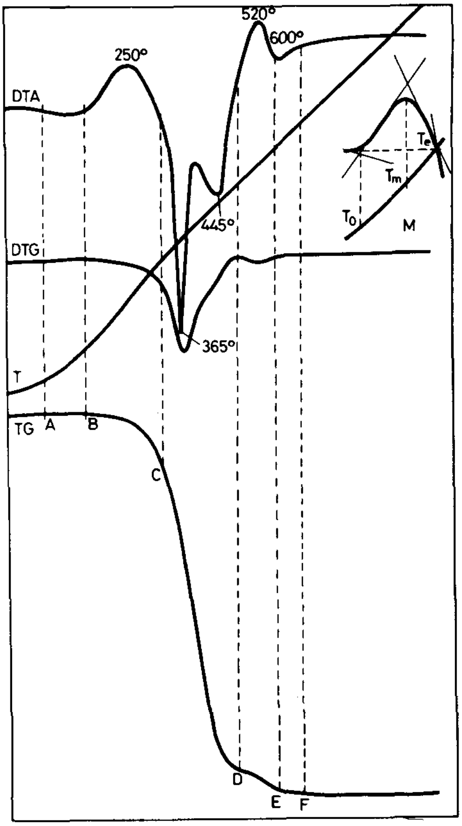


Fig. 1 Thermal curves for *cis*-1,4-polyisoprene (Cariflex IR-307). *M* – the method of transition temperature evaluation, T_0, T_m, T_e – temperatures of the onset, maximum and end of the transition

Table 1 Data relating to thermal transition of uncross-linked IR in region BC

Results of analysis	Initial	Sample	
		disk	disintegrated
Temperature range, °C	–	160–315	150–340
Peak temperature, °C	–	250	270
Weight loss, %	–	15	38
Heat of transition, J	–	92	198
Chemical composition *, w.%	C 88.35	87.86	85.57
	H 11.61	11.53	11.17
	O 0.04	0.61	3.26
Molecular mass, $\bar{M}_n \cdot 10^{-3}$	280.7	189.5	124.0

* Theoretical C = 88.2; H = 11.8% by wt.

sample revealed that in air atmosphere the diffusion of oxygen is the factor controlling the relative rate of the competitive reactions, i.e. degradation and cross-linking, favouring the former (Table 1). Chain scission is accompanied by evolution of the monomer (depolymerization) or other low molecular weight substances (desctruction). A contribution to the positive heat effect in the region BC is made by cyclization, and to some extent by *cis-trans* isomerization too [2]. The former reaction probably involves the residue of the catalytic system used for polymerization of the isoprene. In the region CD, as a result of a third, endothermic transition, decomposition of the elastomer occurs. This transition is also of composite character; two endothermic peaks are distinctly visible in the DTA curve. In the first stage, decomposition products with a high H/C ratio are formed. In the second, slower stage, mainly the cyclized and branched carbon skeleton of IR decomposes. The overall rate of evolution of low molecular weight substances is very high, as evidenced by a sharp peak in the DTG curve. As a consequence, a considerable oxygen deficiency occurs in the reaction zone. At the moment when the rate of oxygen diffusion balances the rate of decomposition, the flameless combustion of the solid, carbonaceous residues starts. This is the fourth thermal transition of IR, manifested in the region DE as an exothermic peak in the DTA curve. The above-mentioned residue is oxidized at a temperature 100–140° lower than for typical carbon black grades. The desorption of destruction and combustion products from the pot surface is the reason for the fifth, endothermic event, which appears in region EF. It should be emphasized that the temperature range of each region is not constant, but depends to some extent on the sample size and shape, the heating rate and other factors. In the following part of our work, only the results obtained with disk samples are discussed. Two kinds of IR vulcanizates, peroxide and sulphur, were the objects of our investigations. The use of DCP as a cross-linking agent leads to the formation of four functional cross-links, with nearly 100% efficiency. The chain length distribution is gaussian and their structure remains almost unmodified. The gel content above the value

$\nu_e \cong 0.9 \cdot 10^{-4}$ mol/cm^3 was 100%, which indicates that practically no degradation occurred during the vulcanization.

Peroxide vulcanization does not change the thermal IR profile essentially; the three main regions, i.e. BC, CD and DE, of fingerprint character are still present. Nevertheless, a quite distinct effect of the network structure could be recognized. The elastomer practically loses its typical properties in the region BC, which is why this transition was considered first. Transitions occurring above about 300°, i.e. in regions CD and DE, are of importance when the correlation between the thermal properties and the elastomer combustibility is of special interest. The events manifested in regions AB and EF are not closely connected with the properties of the elastomer, and their minor practical importance means that they can usually be neglected.

In the case of peroxide vulcanizates, as their cross-link density increased, the main parameters of the thermal transition in region BC, i.e. a heat effect and a sample mass loss, attained lower values (Figs 2a, 3a). Changes like these were expected, because a more dense chain packing diminishes the solubility and the rate of oxygen diffusion in an elastomer, and in addition enhances the efficiency of its cross-linking.

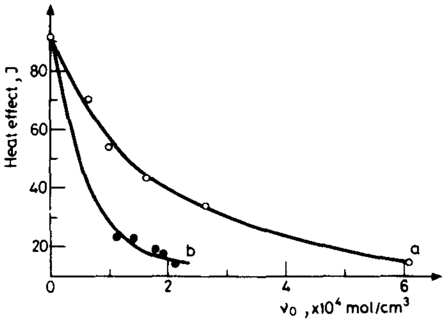


Fig. 2 The effect of the cross-link density of *cis*-1,4-polyisoprene vulcanizates on the transition heat. a) peroxide vulcanizates, b) sulphur vulcanizates

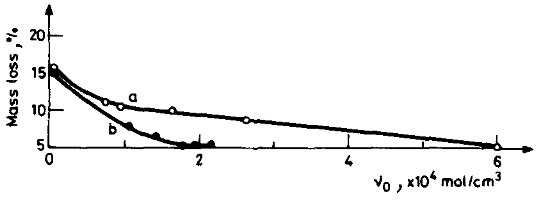
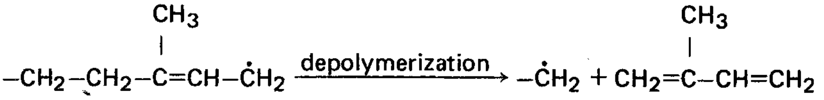


Fig. 3 The mass loss of *cis*-1,4-polyisoprene vulcanizates with different cross-link density. a) peroxide vulcanizates, b) sulphur vulcanizates

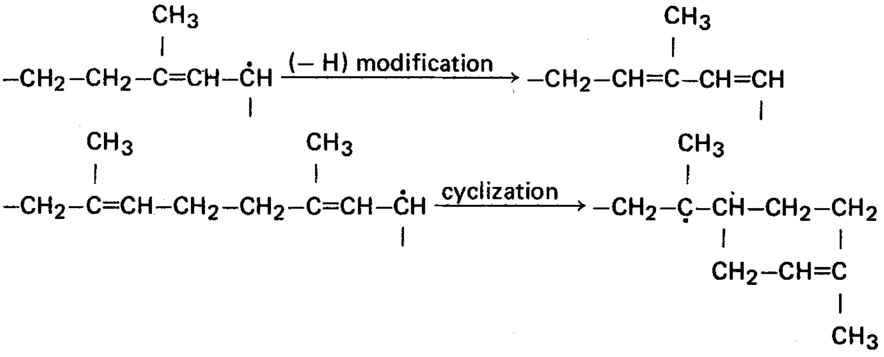
A useful measure of the resultant efficiency of reactions occurring in the region BC is the coefficient of degradation, $k = \bar{M}_0/\bar{M}_t$, where $\bar{M}_0$ and $\bar{M}_t$ denote the number average molecular mass of chains, uncross-linked, or their segments between cross-links, before and after thermal treatment, respectively. $\bar{M}_t$ was measured after heating of a sample in the furnace of the derivatograph to the point C (Fig. 1). A linear function $k = f(\nu_0)$ was found (Fig. 4a). During IR vulcanization by DCP, one C–C cross-link is formed as a result of the abstraction of two H atoms from methylene groups and the recombination of macroradicals. The overall concentration and energy of the chemical bonds in the system do not change essentially, since there is one such cross-link on average for tens or several hundreds of monomer units. The decrease of k with increasing cross-link density, therefore is rather a symptom of the cage effect, connected with the hindered translational and rotational mobility of the IR backbones. The cross-linking of IR by DCP also increases the activation energy E_A of its destruction (Fig. 5a). The applied method of E_A calculation does not differentiate between destruction and depolymerization. In our opinion, cross-linking of an elastomer prevents the second of the above reactions, favouring the modification and cyclization of the macromolecules. This supposition may be illustrated by the following schemes:

uncross-linked IR:



$$-CH_2-CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}}=CH-\dot{C}H_2 \xrightarrow{\text{depolymerization}} -\dot{C}H_2 + CH_2=\overset{\displaystyle CH_3}{\overset{|}{C}}-CH=CH_2 \tag{1}$$

cross-linked IR:



$$-CH_2-CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}}=CH-\underset{|}{\dot{C}H} \xrightarrow{(-\,H)\ \text{modification}} -CH_2-CH=\overset{\displaystyle CH_3}{\overset{|}{C}}-CH=\underset{|}{CH} \tag{2}$$

$$-CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}}=CH-CH_2-CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}}=CH-\underset{|}{\dot{C}H} \xrightarrow{\text{cyclization}} \begin{array}{l} -CH_2-\overset{\displaystyle CH_3}{\overset{|}{\underset{\bullet}{C}}}-\dot{C}H-CH_2-CH_2 \\ \qquad\quad\ \ | \qquad\qquad\quad\ | \\ \qquad\quad CH_2-CH=\underset{\displaystyle CH_3}{\underset{|}{C}} \end{array}$$

The dependence between E_A and ν_0 is not linear; the most marked effect is observed at a low degree of cross-linking. It seems that a high concentration of short network chains in overcured samples favours their destruction to some extent. In the case of IR vulcanization by sulphur in the presence of N-cyclohexyl-2-benzothiazyl sulphenamide, mainly polysulphide cross-links are formed. Besides the polysulphide, only disulphide cross-links are present in the network (Table 2). A comparison of the data

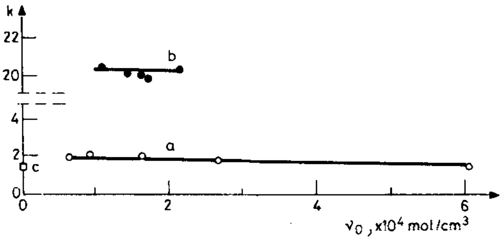


Fig. 4 The degree of degradation of *cis*-1,4-polyisoprene vulcanizates versus cross-link density. a) peroxide vulcanizates, b) sulphur vulcanizates, c) point C on the ordinate relates to the uncross-linked rubber

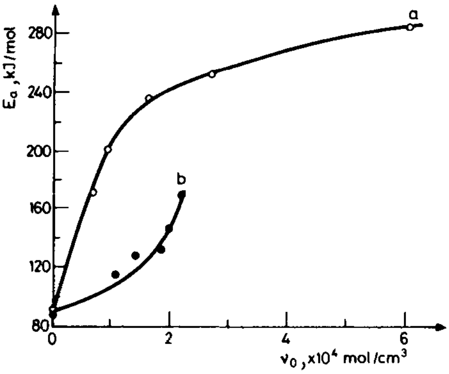


Fig. 5 The dependence of the destruction activation energy of *cis*-1,4-polyisoprene vulcanizates on their cross-link densities. a) peroxide vulcanizates, b) sulphur vulcanizates

concerning the cross-link density and the bound sulphur concentration leads to the conclusion that the IR chains are strongly modified by cyclic sulphides and side-groups containing sulphur atoms. From our calculations, it follows that on average about 16 S atoms are bound per cross-link. On the basis of the reaction stoichiometry, it could be accepted that no more than 8 or even 6 S atoms may form a cross-link. A relatively high sol content may be connected with a degradation of IR during the vulcanization or non-gaussian distribution of its network chains [11]. The thermal profile of vulcanizates with a high bound sulphur concentration is to some extent different from that of uncross-linked IR or its peroxide vulcanizates (Fig. 6). Small additional exothermic peaks appeared in regions BC and CD in the DTA curve. As in the case of peroxide vulcanizates, first of all the transition occurring in the region BC was analyzed. The cross-linking of IR with sulphur diminishes the heat effect of the transition (Fig. 2b), as well as the mass loss of the sample (Fig. 3b). Both effects are major ones in comparison to IR samples cross-linked with DCP. The coefficient of

Table 2 The network structure of sulphur IR vulcanizates

Symbol of sample	Cross-link density $\nu_0 \cdot 10^4$ mol/cm^3	Gel content, wt. %	Bound sulphur wt.%	S atoms per 100 monomer units	Cross-link content, %	
					C–S$_x$–C	C–S$_2$–C
1S	1.08	92.6	1.2	2.5	82.9	17.1
2S	1.40	96.9	1.9	4.1	76.4	23.6
3S	1.78	94.0	2.9	6.1	73.6	26.4
4S	1.84	91.7	3.5	7.4	72.9	27.1
5S	2.10	88.4	4.2	8.9	72.5	27.5

sulphur vulcanizate degradation is almost independent of the cross-link density (Fig. 4b). However, the absolute value of k is approximately one order higher than the k values for peroxide vulcanizates. The cross-linking of IR with sulphur increases its destruction activation energy E_A (Fig. 5b) to a far lower degree than the cross-linking with DCP. It should be noticed that a similar E_A value has been reported for sulphur IR vulcanizate in the work of Ono et al. [12], who also found the controlling effect of

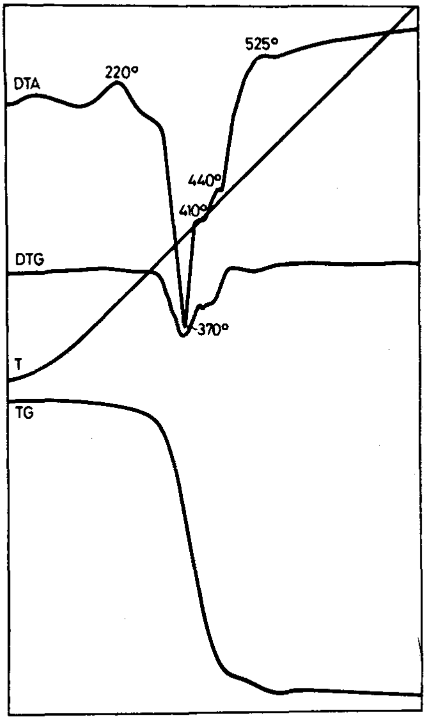


Fig. 6 Thermal curves of *cis*-1,4-polyisoprene sulphur vulcanizate, $\nu_0 = 1.08 \times 10^{-4}$ mol/cm^3

oxygen diffusion on the degradation rate. An analysis of our experimental data leads to the following conclusions. The thermal splitting of labile polysulphide cross-links leads to a network effective degradation:

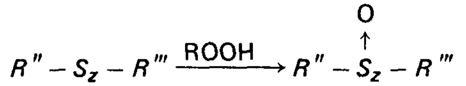
$$R' - S_x - R'' \xrightarrow{T} R'S_y^{\bullet} + {}^{\bullet}S_zR'' \qquad (3)$$

R is a rubber chain and indices x, y and z denote the number of sulphur atoms. The sulphide-free radicals may stabilize themselves as a result of IR modification, cyclization or cross-linking, e.g.

$$R'S_y^{\bullet} + R'''H \longrightarrow R - S_y - H + R_{\bullet}''' \qquad (4)$$

$$R'''S_z^{\bullet} + R_{\bullet}''' \longrightarrow R'' - S_z - R''' \qquad (5)$$

These or similar reactions correspond well with the small mass loss of the sample in the second stage of region BC. However, the rather low heat effect in this region indicated that a mechanism preventing the autocatalytic oxidation of IR plays an important role too. It seems very probable that, as Shelton and Harrington have stated [13], in the first step the oxidation of the sulphide groups occurs, and sulphenic or thiosulphoxylic acids are formed:



$$R'' - S_z - R''' \xrightarrow{\text{ROOH}} R'' - \overset{\overset{\text{O}}{\uparrow}}{S_z} - R''' \qquad (6)$$

If $z = 1$, the product decomposes the sulphenic acid, while if $z = 2$ thiosulphoxylic acid is formed. Both acids involve an ionic breakdown of hydroperoxides, and therefore act as active antioxidants.

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Zusammenfassung — Es wurden die thermischen Eigenschaften von *cis*-1,4-Polyisopren und dessen Vulkanisaten untersucht. Dabei wurden die Derivatographie und komplementäre analytische Methoden benutzt. Es wurde festgestellt, dass die Vernetzung im allgemeinen die thermische Stabilität von diesen Elastomeren erhöht, obwohl ein ausgeprägter Unterschied zwischen Peroxid- und Schwefelvulkanisaten beobachtet wurde. Die polysulfidischen Brücken wurden bei erhöhter Temperatur leicht gespalten und verwandeln sich in Brücken, die eine niedrigere Schwefelatomzahl besitzen und zwar hauptsächlich disulfidisch sind. Ein Teil der Schwefelatome wurde jedoch wahrscheinlich unter Bildung von Sulfin- und Thio-Sulfoxysäuren oxydiert. Diese Produkte verursachen ionische Zersetzung von Peroxiden und verhindern auf diese Weise die autokatalytische thermooxidative Zersetzung von *cis*-1,4-Polyisopren.

Резюме — С помощью термического анализа и дополняющих его методов исследованы термические свойства цис-1,4-полиизопрена и продуктов его вулканизации. Установлено, что, в общем, поперечные связы увеличивают термоустойчивость этого эластомера, хотя и наблюдались определенные различия между перекисными и серусодержащими продуктами его вулканизации. Полисульфидные поперечные связы легко разрываются при повышенных температурах, давая поперечные связы более низкой сульфидности, главным образом, дисульфидные связы. Однако, возможно, что некоторые из них сначала окисляются до сульфоксидов, давая затем сульфиновую или тиосульфоксиловую кислоты. Образующиеся продукты вызывают ионное разложение перекисей, предотвращая тем самым автокаталитическое термоокислительное разрушение цис-1,4 полиизопрена.