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THE THERMAL BEHAVIOUR OF CIS-1,4-POLYISOPRENE IN THE PRESENCE OF COBALT SALT

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The effects of synthetic fatty acids ("Versatic 10", average formula $C_{11}H_{22}O_2$) and the cobalt salts of these acids (cobalt siccative) on the thermal properties of cis-1,4-polyisoprene were examined, using a rheometer and a derivatograph. It was found that both Versatic 10 and the cobalt siccative accelerate the peroxide vulcanization of the isoprene rubber considerably, simultaneously decreasing the cross-linking density and increasing the sol fraction content in the vulcanizates. This is brought about by parallel radical and ionic decomposition of the peroxide initiator in the presence of these compounds. The addition of Versatic 10 or the cobalt siccative to the polyisoprene rubber does not alter the general character of its thermal changes, but decreases the temperatures of these processes and the degradation degree of the elastomer.

Studies carried out in our institute led to the conclusion that thermal processes in elastomers in an atmosphere of air are controlled by the rate of diffusion of oxygen into the reaction zone. These processes are initiated by the formation of unstable peroxide groups, whose decomposition gives rise to the degradation and thermal destruction or cross-linking of the macromolecules [1–3]. The role of initiator in these processes can also be played by a low-molecular peroxide added to the elastomer [1]. It is known from the theory and practice of radical polymerization that peroxides show particular activity in the presence of salts of metals with variable valency (in redox systems). Thus, we decided to establish whether this mechanism of peroxide activation also operates in the case of reactions taking place at a considerably elevated temperature in the elastomer system. Therefore, we have examined the effects of the cobalt salts of organic acids in the form of a siccative on the thermal properties of cis-1,4-polyisoprene.

Experimental

Materials

Studies were made on cis-1,4-polyisoprene (IR, Cariflex IR–307) with molecular weight M_v = 589,000 and its peroxide vulcanizates containing either a cobalt siccative or a mixture of organic acids (Versatic 10, average

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formula $C_{11}H_{22}O_2$). The cobalt siccative (cobalt salts of the acids $C_{11}H_{22}O_2$) contains 3.04% of metal with oxidation number 2, and 80% of a solvent mixture containing toluene and petrol in 1:1 proportion. These solvents are also contained in the same amount and proportion in Versatic 10. Both the cobalt siccative and Versatic 10 are commercial products of the "Hajduki" Coke Chemistry Works, Chorzów, Poland.

Table 1 gives the compositions of the rubber mixtures used in the study.

Methods

The molecular weight of IR was measured by viscosimetry [2]. Rubber mixtures were prepared by means of a laboratory rolling mill. Versatic 10 and the cobalt siccative were processed in with no difficulties.

Table 1 Rubber mixture compositions

Components	Content in weight parts per 100 weight parts of rubber		
	Mixture		
	I1	I2	I3
Cis-1,4-polyisoprene	100.00	100.00	100.00
dicumil peroxide, 98% (Merck-Schuchardt)	0.90	1.50	1.50
Versatic 10	–	6.40	–
siccative	–	–	6.60
Total	100.90	107.90	108.10

The vulcanization rates for rubber mixtures were determined with a Monsanto rheometer. The optimal vulcanization times, t_{09}, for mixtures I1, I2 and I3 were 74, 37 and 27 min., respectively. The rubber mixtures were vulcanized in an electric press at 4 MPa and 150°. The cross-linking density was calculated from measurements of the equilibrium swelling [2].

Thermal analysis of IR vulcanizates was performed with a derivatograph [2]. Samples for the analysis were prepared from non-extracted vulcanizates in a disintegrated form. The experimental conditions of thermal analysis always were the same as follows: atmosphere air, sample mass 90 mg, heating rate 7.9 deg/min, temperature range 25–800°.

IR vulcanizates were extracted in a Haanen apparatus for 24 h, with acetone as solvent. After extraction, the excess of solvent was evaporated off and the concentrated extract was analysed by thinlayer chromatography.

Results and discussion

Addition of the cobalt siccative of Versatic 10 brings about a considerable acceleration of vulcanization and, at the same time, a reduction of the cross-linking density of IR. To obtain comparable cross-linking densities of vulcanizates I1, I2 and I3, it was necessary to add a higher amount of the cross-linking agent to mixtures I2 and I3 than to mixture I1 (Table 1). The IR vulcanizates containing Versatic 10 or the cobalt siccative are characterized by an increased content of sol fraction. Because of the slightly acidic reaction of Versatic 10 and of the siccative, it seemed most probable that the increase in the cross-linking rate, and consequently the reduction in the cross-linking density of the isoprene rubber, is due to partial ionic decomposition of dicumyl peroxide in the presence of these substances. This is confirmed by the results of chromatographic analysis (Table 2).

Table 2 Results of qualitative thin-layer chromatography of acetone extracts of the examined vulcanizates

Extract	R_f	Identified compounds
I1	0.46	cumyl alcohol
	0.69	acetophenone
	0.84	unreacted dicumyl peroxide
I2	0.46	cumyl alcohol
	0.77	reaction product of Versatic 10, and dicumyl peroxide
	0.69	acetophenone
	0.84	unreacted dicumyl peroxide
I3	0.41	phenol
	0.46	cumyl alcohol
	0.56	cumyl hydroperoxide
	0.69	acetophenone
	0.73	reaction product of the siccative and cumyl peroxide
	0.84	unreacted dicumyl peroxide

It is known that in an acidic system the ionic decomposition of dicumyl peroxide is facilitated, the following compounds being formed: phenol, acetone and the dimer of α-methylstyrene [4], with cumyl hydroxide as starting material, according to Brinkman and Damen [5] and Rado [6]. Phenol was found in the extract of vulcanizate I3, but not in that of I2. This leads to the conclusion that the ionic decomposition of dicumyl peroxide is brought about not by the organic acid contained in Versatic 10, but by reactions resulting in the formation of hydrogen ions. An observation of great importance is that dicumyl peroxide reacts with organic acids in Versatic 10 and is therefore consumed non-effectively. This may well be one of the reasons for the increase of the sol fraction content in vulcanizates.

Figure 1 shows the TA curves of Versatic 10. The endothermic change starting at 110° in the DTA curve is due to the evaporation of solvents contained in this agent; the weight loss resulting from this change is 78.8%. The two endothermic changes at 280° and 390° are associated with the evaporation of organic acids, accompanied by their decomposition.

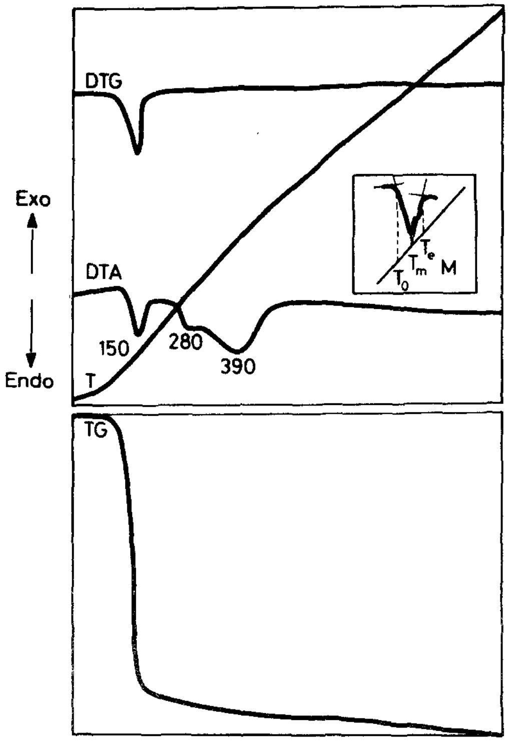


Fig. 1 TG, DTG and DTA curves of Versatic 10. Insert: the method of transition temperature evaluation, T_o, T_m, T_e – temperatures of the onset, maximum and end of the transition.

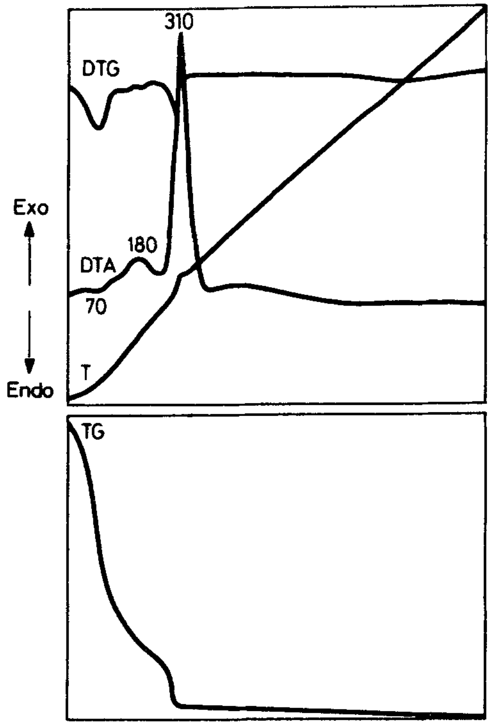


Fig. 2 TG, DTG and DTA curves of the cobalt siccative.

Figure 2 shows the TA curves of the cobalt siccative. At 70° a small endothermic DTA peak is observed, caused by the evaporation of solvents; the loss of weight is 53.3%. The exothermic process at 180°probably consists in oxidation of the remaining solvents and acids under the catalytic influence of cobalt. At 250°, after evaporation of the solvents, a very intensive thermooxidative destruction of organic acid radicals commences, also catalyzed by cobalt.

The thermal changes in the peroxide vulcanizate of IR are shown in Fig. 3. The first exothermic reaction starts at 160°, its beginning being associated with a slight but distinct increase in sample weight, due to the formation of peroxide groups in the heated vulcanizate. The decomposition of these groups brings about degradation and thermooxidative destruction of the rubber [1, 2]. At 210°, weight loss begins after completion of the first change, the loss is 17.8%. Decomposition of the isoprene vulcanizate begins at 320°. The large exothermic peak at T_{max} = 500° is associated with combustion of the solid residue after the decomposition of the cross-linked rubber [2].

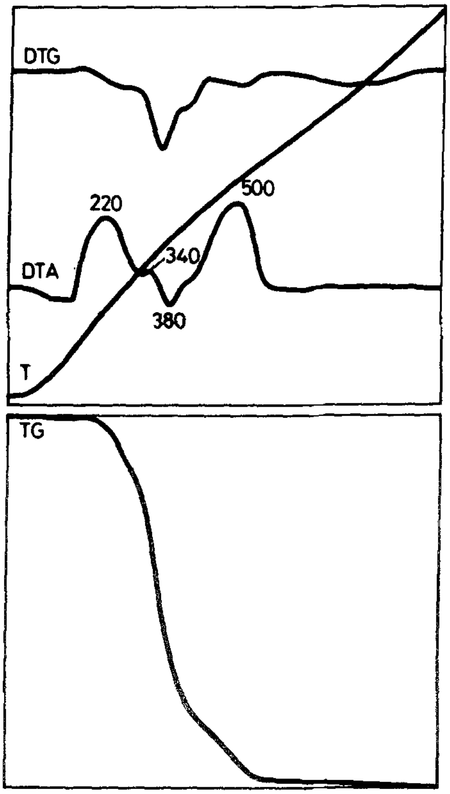


Fig. 3 TG, DTG and DTA curves of cis-1,4-polyisoprene cross-linked with dicumyl peroxide.

The presence of Versatic 10 in the peroxide vulcanizate of IR does not change the character of its thermal processes, but brings about their shift towards lower temperature (Fig. 4). In the range 70–110°, the weight loss of 3.3% is associated with the evaporation of residual solvents. The first exothermic change in IR cross-linked with dicumyl peroxide in the presence of Versatic 10 already begins at 130°. At the T_{max} of this exotherm, degradation and thermooxidative destruction begin. The additon of Versatic 10 to the rubber mixture considerably decreases the thermal degradation coefficient of polyisoprene (Table 3). Thus, it may be assumed that the role of the degradation inhibitor of cross-linked IR is played by the small amount of organic acid mixture remaining at the temperature of its first exothermic process.

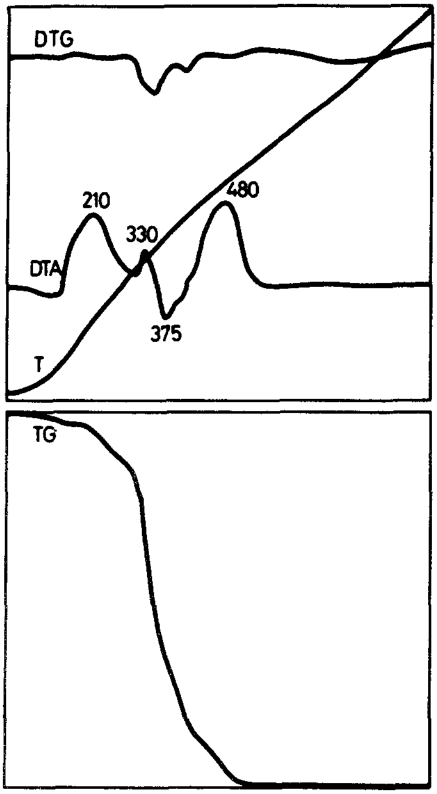


Fig. 4 TG, DTG and DTA curves of cis-1,4-polyisoprene cross-linked with dicumyl peroxide in the presence of Versatic 10.

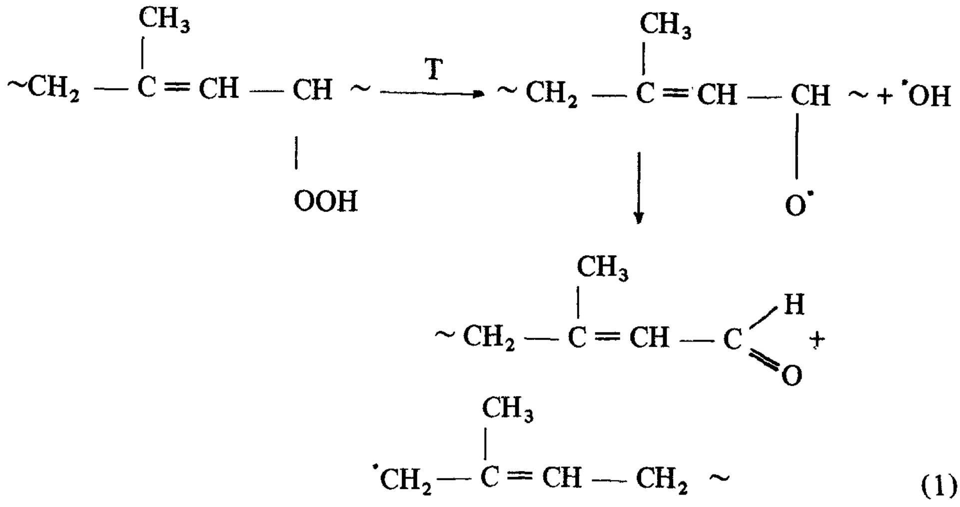
Table 3 Results of cis-1,4-polyisoprene vulcanizate analysis

Sample	Cross-linking density, $\nu_0\cdot 10^4$ mol cm^{-3}	Cross-linking density after heating to 200 °C* $\nu_t\cdot 10^4$ mol cm^{-3}	Degree of degradation $K=\nu_0/\nu_t$	Sol content %**	
				Unheated vulcanizate	Vulcanizate heated to 200 °C*
I1	0.87	0.43	2.0	1.9	23.9
I2	0.92	0.71	1.3	5.9	23.3
I3	0.91	0.83	1.1	2.9	10.7

* Vulcanizates were heated in the furnace of the derivatograph under the conditions of thermal analysis.

** Checked on the basis of mass loss during measurements of swelling.

The heating of IR in air causes an increase in the content of peroxide groups [1], whose decomposition gives rise to the elastomer degradation:



$$\sim CH_2-\overset{CH_3}{\overset{|}{C}}=CH-\underset{\underset{OOH}{|}}{CH}\sim \xrightarrow{T} \sim CH_2-\overset{CH_3}{\overset{|}{C}}=CH-\underset{\underset{O^\bullet}{|}}{CH}\sim+{}^\bullet OH$$

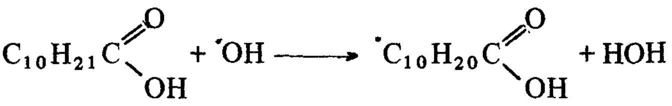
$$\downarrow$$

$$\sim CH_2-\overset{CH_3}{\overset{|}{C}}=CH-C\!\begin{smallmatrix}\diagup H\\ \diagdown\!\!\diagdown O\end{smallmatrix}+$$

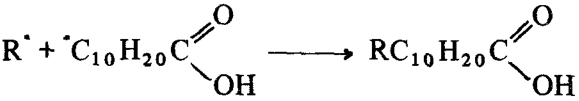
$${}^\bullet CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2\sim \qquad (1)$$

The hydroxyl radicals formed can react with the elastomer molecule as well as with organic aldehyde:

$$RH+{}^\bullet OH \longrightarrow R^\bullet+HOH \qquad (2)$$



$$C_{10}H_{21}C\!\begin{smallmatrix}\diagup\!\!\diagup O\\ \diagdown OH\end{smallmatrix}+{}^\bullet OH \longrightarrow {}^\bullet C_{10}H_{20}C\!\begin{smallmatrix}\diagup\!\!\diagup O\\ \diagdown OH\end{smallmatrix}+HOH \qquad (3)$$



$$R^\bullet+{}^\bullet C_{10}H_{20}C\!\begin{smallmatrix}\diagup\!\!\diagup O\\ \diagdown OH\end{smallmatrix} \longrightarrow RC_{10}H_{20}C\!\begin{smallmatrix}\diagup\!\!\diagup O\\ \diagdown OH\end{smallmatrix} \qquad (4)$$

$$R^\bullet+R^\bullet \xrightarrow{\text{cross-linking}} R-R \qquad (5)$$

Exothermic oxidative reactions of IR cross-linked with dicumyl peroxide in the presence of the cobalt siccative start at 60° (Fig. 5). The presence of metal with variable valency probably facilitates the formation and decomposition of peroxide groups considerably [7]. This results in both degradation and destruction of IR, which is confirmed by the considerable weight loss of the sample (Fig. 5) and by its cross-linking, shown by the low

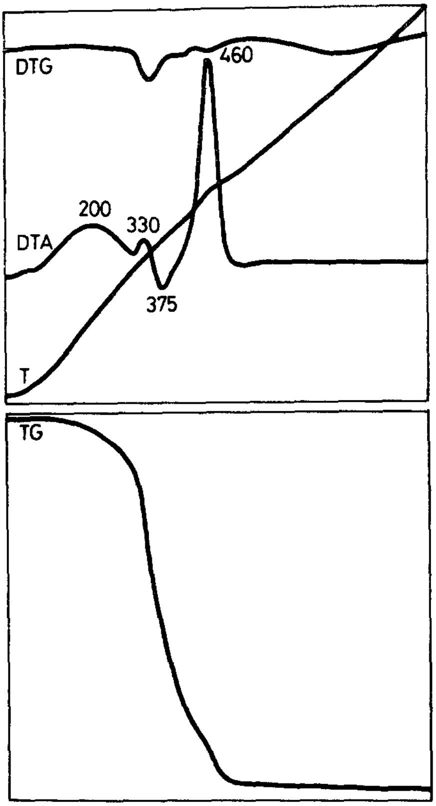


Fig. 5 TG, DTG and DTA curves of cis-1,4-polyisoprene cross-linked with dicumyl peroxide in the presence of cobalt siccative.

coefficient of degradation and relatively low sol content (Table 3). The low value of the degradation coefficient in this case may be caused by the presence of phenol (Table 2), acting as an oxidative destruction inhibitor for IR. At 310°, the thermooxidative destruction begins with the evolution of low-molecular oxidized fragments of macromolecules. The endothermic decomposition starts at 340°, due to the oxygen shortage in the reaction zone. The decomposition rate of strongly cross-linked IR is in this case considerably lower than those of I1 and I2 (DTG curves in Figs. 1–3). At the moment when the oxygen diffusion rate is equal to the decomposition rate of the residual elastomer, its combustion commences. The thermal effect of this reaction is very intensive, due to the catalytic action of cobalt.

The simultaneous TG-DTA results suggest that the presence of the cobalt siccative will facilitate the combustion of polyisoprene.

Conclusions

1. On the example of cis-1,4-polyisoprene, it was shown that simultaneous TG-DTA is a useful tool for the examination of slight differences in the thermal stabilities and rates of thermal changes in elastomers catalyzed by salts of metals with variable valency.
2. It was found that the unsaturated organic acids contained in siccatives as well as cobalt ions, take part in the radical processes in cis-1,4-polyisoprene.
3. The cobalt siccative simultaneously catalyzes the degradation and thermo-oxidative destruction, as well as the cross-linking of cis-1,4-polyisoprene.

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Zusammenfassung — Der Einfluss synthetischer Fettsäuren ("Versatic 10", mittlere Summenformel $C_{11}H_{22}O_2$) und ihres Kobaltsalzes ("Kobalt-Sikkativ") auf die thermischen Eigenschaften von cis-1,4-Polyisopren wurde mittels Rheometer und Derivatograph untersucht. Sowohl Versatic 10 als auch das Kobaltsikkativ beschleunigen die Peroxid-initiierte Vulkanisation des Isoprenkautschuk, gleichzeitig wird die Vernetzungsdichte verringert und der Gehalt an löslichen Stoffen in den Vulkanisaten erhöht. Ursache dafür ist der parallelle Ablauf der radikalischen und ionischen Zersetzung des Peroxids in Gegenwart der Zusätze. Die Beimengung von Versatic 10 oder Kobaltsikkativ zum Polyisoprenkautschuk ändert nicht den allgemeinen Charakter der thermischen Umwandlungen, aber die Temperatur dieser Reaktionen und der Abbau des Elastomeren werden verringert.

РЕЗЮМЕ — Используя реометр и дериватограф, изучено влияние синтетических жирных кислот среднего общего состава $C_{11}H_{22}O_2$ (Версатик 10) и их кобальтовой соли на термические свойства цис-1,4-полиизопрена. Найдено, что как Версатик 10, так и его кобальтовая соль значительно усиливают перекисную вулканизацию изопренового каучука, одновременно уменьшая степень его перекрестного сшивания и увеличивая содержание растворимых фракций в продуктах вулканизации. Это вызвано параллельно протекающими процессами радикального и ионного разложения перекиси в присутствии упомянутых соединений. Введение Версатик 10 и его кобальтовой соли в полиизопреновый каучук, не приводит к нарушению общего характера его термических изменений, но уменьшает температуру вышеуказанных процессов и степень разрушения этого эластомера.