Journal of Thermal Analysis, Vol. 36 (1990) 901-914

EFFECT OF METAL WITH VARIABLE VALENCE ON THE THERMAL PROPERTIES OF POLYBUTADIENE

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(Received April 25, 1989)

The effect of mixed synthetic saturated acids and of cobalt salt of these acids on the thermal properties of peroxide vulcanizates of *cis*-1,4-polybutadiene, Europrene cis, has been studied by derivatography.

The thermal curves of the samples under investigation have been interpreted on the basis of complementary examinations. It has been found that the introduction of a metal with variable valence into the rubber compound alters the optimum vulcanization time and brings about degradation of the elastomer during its crosslinking.

The presence of the cobalt salt facilitates the crosslinking of polybutadiene heated to the temperature of the second exothermic transition, resulting at the same time in an increase in the thermal decomposition rate and a decrease in the temperature of this process.

Studies carried out at the Institute of Polymers, Technical University of Lódz, have shown that the initation of thermal changes in elastomers is brought about by the decomposition of peroxide groups formed on heating in air [1, 2, 3].

The role of an initiator for these processes can also be played by a low molecular peroxide added to the elastomer [1]. According to the theory and practice of radical polymerization, peroxides show increased activity in the presence of a metal salt with variable valence, namely in redox systems. Such salts, in the form of catalyst residues, are highly probable to occur in elastomers, particularly in those synthesized by ionic polymerization. They can also be introduced accidentally into the elastomer, e. g. as impurities with fillers. Such cases have occurred in the industry with the very troublesome consequences of a considerably accelerated ageing of rubber products. This has also been confirmed by the results of our studies on the effect of cobalt and copper sulphates on the thermal properties and ageing of *cis*-1,4-polybutadiene [4]. The mentioned sulphates, however, form a heterogeneous

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system with the elastomer, which could lower their activity. In order to ensure higher homogeneity of the mixture, we have decided to use a cobalt salt of organic acid in the form of a siccative. It is used in the industry as an agent for increasing the adhesion between rubber and metal, but the mechanism of its action has not been fully explained as yet. It has been chosen for the study also because of the highest activity of cobalt in the series of metals with variable valence [5, 6]:

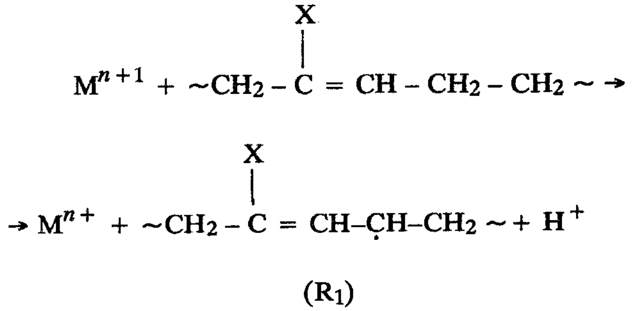
$$Co > Mn > Pb > Ni > Cu > Fe > Cd > Cr > Zn > Ca > Mg$$

The crosslinking of butadiene rubber with organic peroxide or hydroperoxide, in the presence of a metal of variable valence, is a typical redox polymerization process. The initiator, in the presence of an activator, decomposes into free radicals, initiating the radical polymerization of the unsaturated elastomer chain, and organic or hydroxyl anions. The activator cation at the same time assumes its higher state of oxidation. It can be reduced in a reaction with hydroperoxide or α-methylene group of the elastomer, which is accompanied by deprotonation. The reactions proceed as follows [7, 8, 9]:

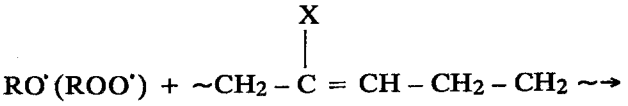
$$M^{n+} + ROOR \rightarrow M^{n+1} + RO^{\cdot} + RO^{-} \tag{1}$$

$$M^{n+} + ROOH \rightarrow M^{n+1} + RO^{\cdot} + OH^{-} \tag{2}$$

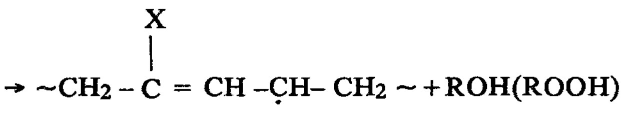
$$M^{n+1} + ROOH \rightarrow M^{n+} + ROO^{\cdot} + H^{+} \tag{3}$$



$$\begin{gathered} M^{n+1} + \sim CH_2-\overset{\overset{\displaystyle X}{|}}{C} = CH-CH_2-CH_2\sim \rightarrow \\ \rightarrow M^{n+} + \sim CH_2-\overset{\overset{\displaystyle X}{|}}{C} = CH-\underset{\cdot}{C}H-CH_2\sim + H^{+} \\ (R_1) \end{gathered} \tag{4}$$

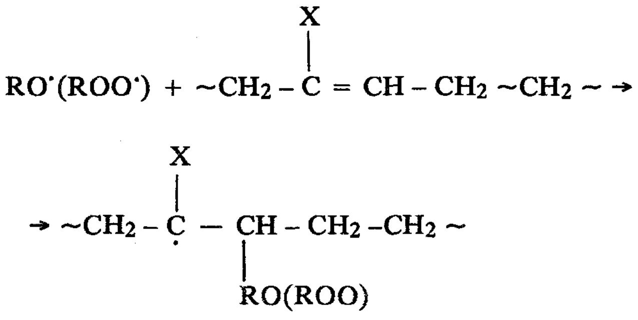


$$RO^{\cdot}(ROO^{\cdot}) + \sim CH_2-\overset{\overset{\displaystyle X}{|}}{C} = CH-CH_2-CH_2\sim \rightarrow$$



$$\rightarrow \sim CH_2-\overset{X}{C}=CH-\underset{\cdot}{C}H-CH_2\sim + ROH(ROOH) \tag{5}$$

or



$$RO^{\cdot}(ROO^{\cdot}) + \sim CH_2-\overset{X}{C}=CH-CH_2\sim CH_2\sim \rightarrow \sim CH_2-\underset{\cdot}{\overset{X}{C}}-\underset{RO(ROO)}{CH}-CH_2-CH_2\sim \tag{6}$$

$(R^{\cdot}_2)$

where : X ≡ H, CH_3

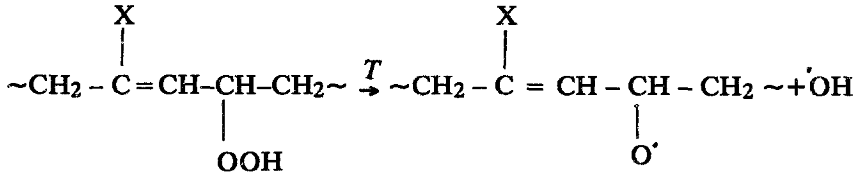
The macroradicals formed in the above reactions react between themselves or with double bonds of other molecules of the elastomer, resulting in C–C cross-links. The crosslinking processes are accompanied by cyclization and chain degradation processes as well as by macroradical deactivation as a result of addition of the radicals formed by peroxide decomposition.

$ROO^{\cdot}$ or $RO^{\cdot}$ radicals can also react with the metal ion M^{n+} which leads to the formation of anions:

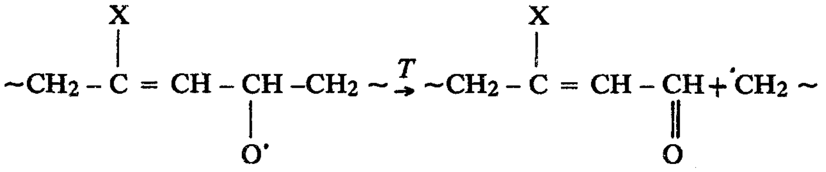
$$RO^{\cdot}\,(ROO^{\cdot}) + M^{n+} \rightarrow RO^{-}\,(ROO^{-}) + M^{n+1} \tag{7}$$

In order to ensure radical decomposition of the organic initiator, very low quantities of a metal salt with variable valence are used, i. e. about 0.001 % in relation to the monomer. By introducing a reducing agent into the reaction mixture along with the initiator (oxidizer), the activation energy of the free radical formation in redox systems, e. g. in the presence of iron ions, is lowered to 42-50 kJ/mole, being 2-3 times lower than that of the thermal decomposition of peroxides [10]. This allows to reduce the process temperature and to avoid undesirable side reactions negatively affecting the polymerization.

The decomposition of peroxide groups contained in the elastomer proceeds as follows [1, 11, 12]:

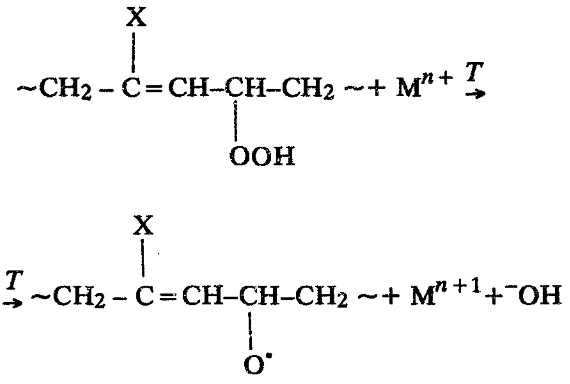


$$\sim CH_2-\overset{X}{C}=CH-\underset{OOH}{CH}-CH_2\sim \xrightarrow{T} \sim CH_2-\overset{X}{C}=CH-\underset{O^\bullet}{CH}-CH_2\sim + {}^\bullet OH \quad (8)$$



$$\sim CH_2-\overset{X}{C}=CH-\underset{O^\bullet}{CH}-CH_2\sim \xrightarrow{T} \sim CH_2-\overset{X}{C}=CH-\underset{\overset{\|}{O}}{CH}+{}^\bullet CH_2\sim \quad (9)$$

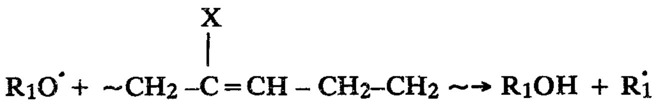
The presence of a metal with variable valence facilitates the thermal decomposition of the mentioned groups:



$$\sim CH_2-\overset{X}{C}=CH-\underset{OOH}{CH}-CH_2\sim + M^{n+} \xrightarrow{T}$$

$$\xrightarrow{T} \sim CH_2-\overset{X}{C}=CH-\underset{O^\bullet}{CH}-CH_2\sim + M^{n+1} + {}^-OH \quad (10)$$

Further course of the processes can be as follows:

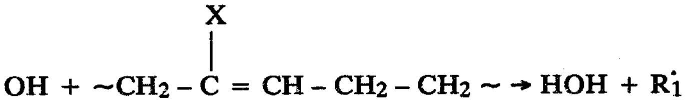


$$R_1O^\bullet + \sim CH_2-\overset{X}{C}=CH-CH_2-CH_2\sim \rightarrow R_1OH + R_1^\bullet \quad (11)$$

$$R_1O^\bullet + R_1^\bullet\ (R_2^\bullet) \rightarrow R_1OR_1 \qquad (R_1OR_2) \quad (12)$$

$$R_1^\bullet + O_2 \rightarrow R_1OO^\bullet, \text{ etc.} \quad (13)$$

The hydroxyl radicals are also active against the elastomer macromolecules:



$$OH + \sim CH_2-\overset{\overset{X}{|}}{C}=CH-CH_2-CH_2\sim \rightarrow HOH + R_1^{\bullet} \qquad (14)$$

Some macroradicals $R_1^{\bullet}$ are deactivated in the reaction with the metal of variable valence [9]:

$$R_1^{\bullet} + M^{n+} \rightarrow R^- + M^{n+1} \qquad (15)$$

Salts of metals with variable valence have been used for the modification of elastomers [13] and their effect on the thermal oxidation and crosslinking of butadiene-styrene rubber has been studied [20].

The present study was aimed at elucidating the effect of a cobalt siccative on the thermal changes in polybutadiene initiated by peroxides.

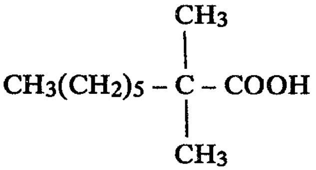
Experimental

Materials

The object of the study was *cis*-1,4-polybutadiene, Europrene *cis*, with a molecular weight M_v = 372 700 and its peroxide vulcanizates, some of which contained a cobalt siccative and others a mixture of organic acids under the trade name Versatic 10.

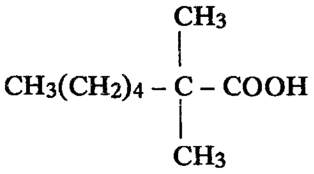
Both the cobalt siccative and Versatic 10 are commercial products manufactured by Zaklady Koksochemiczne "Hajduki" at Chorzów. The cobalt siccative is a salt of cobalt and synthetic saturated acids with the summary formula $C_{11}H_{22}O_2$.

The composition of the acids is as follows:

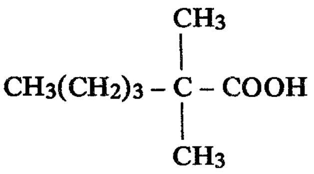


$$CH_3(CH_2)_5-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-COOH$$

—— 42 - 53 % by wt.



$CH_3(CH_2)_4-\underset{CH_3}{\overset{CH_3}{C}}-COOH$ —— 24 - 40 % by wt.



$CH_3(CH_2)_3-\underset{CH_3}{\overset{CH_3}{C}}-COOH$ —— 16 % by wt.

The cobalt siccative contains 3.04 % by wt. of metal in the higher state of oxidation and 80 % by wt. of toluene-petrol mixture in a proportion of 1:1. These solvents are also present in Versatic 10 in the same quantity and proportion. Table 1 shows the compositions of rubber compounds used for the study.

Table 1 Compositions of the rubber compounds

	Parts by wt. per 100 parts by wt. of the rubber		
Components	Symbols of compounds		
	B_1	B_2	B_3
cis-1,4-polybutadiene	100.00	100.00	100.00
dicumyl peroxide	0.17	0.27	0.24
Versatic 10	-	6.40	-
Siccative	-	-	6.60
Total:	100.17	106.67	106.84

* 98 %, Merck-Schuchardt

Methods

The molecular weight of cis-1,4-polybutadiene was determined by viscometry. The following conditions were used: temperature 32 ±0.5°, benzene as solvent, constants $K = 10^{-4}$, $\alpha = 0.77$ [14].

The rubber compounds were prepared using a laboratory rolling mill with rolls of 200 x 400 mm. The rotational speed of the front roll was 16 rpm, friction 1:1.1, roll temperature 25°. Compounding of Versatic 10 and the cobalt siccative was performed without any difficulties.

The vulcanization rate of the rubber compounds was determined with a Monsanto rheometer. The optimum vulcanization times are given in Table 2.

Table 2 Optimum vulcanization times of the rubber compounds, t_{09}, at temperature of 150°

Compound Symbol	t_{09}, min
B_1	65
B_2	57
B_3	75

The rubber compounds were vulcanized in an electrically heated press at 150° under a pressure of 4 MPa within the optimum time t_{09} corresponding to the increase in the rheometer torque by 90 % of the maximum value.

The crosslinking density of *cis*-1,4-polybutadiene vulcanizates was determined by the method of equilibrium swelling [15, 16] and the results were calculated using the interaction parameter between *cis*-1,4-polybutadiene and benzene $X = 0.314$ from the paper of Sheehan and Bisio [17].

The thermal stability of the vulcanizates was examined with a Hungarian derivatograph under the following conditions:
medium air; standard substance Al_2O_3; temperature range 25-800°; sample size 90 mg; heating rate 7.9 deg/min; sensitivity DTA 1/5; DTG 1/20; TG 100. For the derivatographic analysis samples of non-extracted vulcanizates were disintegrated.

Extraction of the vulcanizates was carried out for 24 h in Haanen extractors using acetone as solvent. After extraction, excess acetone was evaporated and the residue was examined by thin-layer chromatography, using plates coated with Kieselgel G type 60. The plates were activated by heating at a temperature of 120° for 20 min. Benzene solutions of cumylhydroperoxide, cumyl alcohol, acetophenone, dicumyl peroxide, phenol, the cobalt siccative and Versatic 10 were used as standards. Products of reaction between the cobalt siccative or Versatic 10 and dicumyl peroxide at the vulcanization temperature were also analysed.

Both the standards and acetone extracts of the polybutadiene vulcanizates were applied onto the chromatographic plates. Chromatograms were developed at room temperature in a mixture of hexane, chloroform, carbon tetrachloride and methanol in a volumetric proportion of 2:1:1:0.25. The following developers were used as required: 2 % (by wt.) methanol solution of 2,4-dinitrophenylhydrazine sulphate, 20 % (by wt.) solution of antimony pentoxide in carbon tetrachloride, 1 % (by wt.) aqueous solution of ferric chloride or potassium permanganate in concentrated sulphuric acid. After the development was completed, the plates were heated for 5 min in an oven at a temperature of 120°.

Results

The use of equal amounts of dicumyl peroxide to crosslink *cis*-1,4-polybutadiene in the presence of Versatic 10 or the cobalt siccative results in the formation of vulcanizates with different crosslinking densities. Thus, in order to obtain polybutadiene vulcanizates with predetermined density of crosslinking corresponding to the crosslinking density of *cis*-1,4-polyisoprene [12], various amounts of the crosslinking agent were introduced (Table 1). Both Versatic 10 and the cobalt siccative change the optimum vulcanization time of *cis*-1,4-polybutadiene, namely Versatic 10 brings about its shortening, while the siccative - its prolongation (Table 2). The presence of each of these products causes also a considerable increase in the sol fraction of the vulcanizate, the effect being particularly clear in the case of Versatic 10 (Table 4). The same effect has been found in vulcanizates of *cis*-1,4-polyisoprene [11, 12]. The results of chromatographic analysis show that the reduction of the crosslinking density of the polybutadiene rubber in the presence of Versatic 10 or the cobalt siccative is partially due to the ionic decomposition of dicumyl peroxide in slightly acidic medium of the mentioned compounds (Table 3).

In the extract of vulcanizate B_3 cumyl hydroperoxide was found which, according to Brinkman and Damen [18] and Rado [19], is an intermediate of the ionic decomposition of dicumyl peroxide in acidic system. Similarly as in the case of *cis*-1,4-polyisoprene [11, 12], one of the causes of increased sol content in the polybutadiene vulcanizate is the reaction of dicumyl peroxide with organic acids contained in Versatic 10, which brings about non-effective consumption of the crosslinking agent.

Figure 1 shows a derivatogram of the *cis*-1.4-polybutadiene vulcanizate with symbol B_1. The first exothermic peak on the DTA curve occurs at 210°. Similarly as in the case of *cis*-1,4-polyisoprene [11, 12], the beginning of the first thermal transition in the butadiene rubber is associated with a small weight increase recorded in the TG and DTG curves. At this temperature, degradation of the crosslinked *cis*-1,4-polybutadiene takes place (Table 4). This is an unexpected result since polybutadienes such as Taktene 1220, Cariflex BR 1220 and SKD II, studied previously at our Institute, showed a considerable susceptibility to thermal crosslinking within the range of the first exothermic transition temperature. It cannot be excluded that the

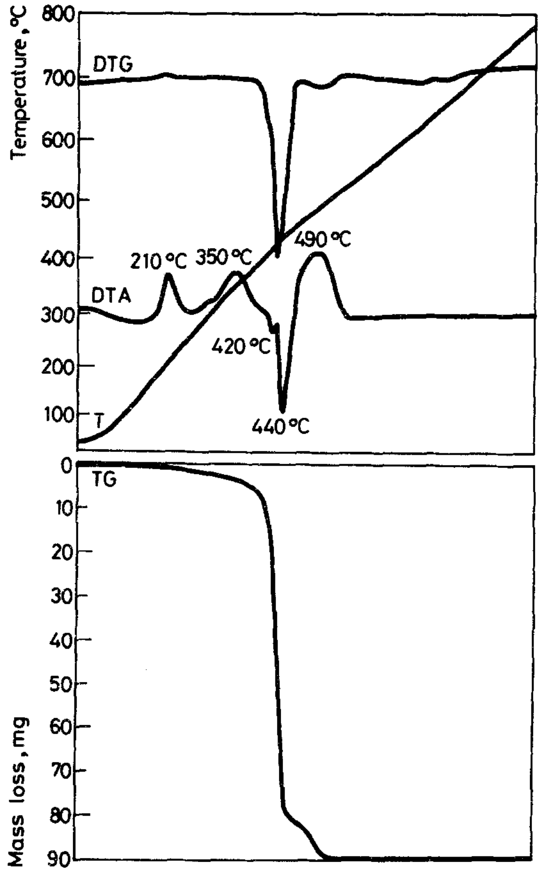


Fig. 1 TG, DTG and DTA curves of *cis*-1,4-polybutadiene cross-linked with dicumyl peroxide

degradation of *cis*-1,4-polybutadiene, Europrene *cis*, at the first transition temperature is due to the residues of the titanium catalyst contained in the polymer. The second transition of the crosslinked polybutadiene recorded at 350° is accompanied by a 6 % weight loss, which is associated with a considerable increase in the crosslinking of the sample (Table 4). Thus, the crosslinking of Europrene *cis* at its second transition temperature is accompanied by thermooxidative destruction. The thermal decomposition of the strongly crosslinked sample starts at 410°. It takes place with a deficiency of oxygen within the reaction zone, bringing about a 95 % weight loss. The final exothermic peak observed at 490° is due to the combustion of small residues of the decomposed polymer.

Table 3 Results of the qualitative thin-layer chromatography of acetone extracts of the examined vulcanizates

Extract symbol	R_f, identified compounds
B_1	R_f = 0.46 - cumyl alcohol
	R_f = 0.69 - acetophenone
	R_f = 0.84 - unreacted dicumyl peroxide
B_2	R_f = 0.46 - cumyl alcohol
	R_f = 0.69 - acetophenone
	R_f = 0.77 - reaction product of Versatic 10 and dicumyl peroxide
	R_f = 0.84 - unreacted dicumyl peroxide
B_3	R_f = 0.46 - cumyl alcohol
	R_f = 0.56 - cumyl hydroperoxide
	R_f = 0.69 - acetophenone
	R_f = 0.84 - unreacted dicumyl peroxide

Versatic 10 introduced into *cis*-1,4-polybutadiene lowers the beginning of both the first and second exothermic transition by 20^0 (Fig. 2). The sample weight loss starting at 90^0 is associated with the evaporation of solvents present in Versatic 10 [11, 12]. The heating of the peroxide vulcanizate of the butadiene rubber containing Versatic 10 up to 200^0 brings about its degradation and the degradation coefficient k_1 is considerably higher than that of vulcanizate B_1.

The presence of Versatic 10 increases also the sol fraction of the heated sample (Table 4). Thus, the presence of saturated synthetic acid mixture with a summary formula $C_{11}H_{22}O_2$ facilitates the degradation of the peroxide vulcanizate of *cis*-1,4-polybutadiene. Further heating of polybutadiene causes its crosslinking with a crosslinking coefficient of 30.8 at 350^0 (Table 4). The beginning of decomposition of the crosslinked polybutadiene is shown by a small exothermic peak at 400^0, while the main fraction of volatile products of decomposition is formed at $410\text{-}440^0$ with deficiency of oxygen - the endothermic peak at 430^0. As it follows from the DTG curve, both the decomposition rate and combustion rate of the residue after decomposition are considerably higher than those of vulcanizate B_1 (Figs 1 and 2), which was not shown by the derivatographic analysis of cis-1,4-polyisoprene [11, 12].

The presence of the cobalt siccative shows no significant effect on the two first transitions of *cis*-1,4-polybutadiene (Fig. 3), but, similarly as in the case of vulcanizate B_2, causes its decomposition temperature to decrease; the beginning of this decomposition is associated with the participation of oxygen: the exothermic peak at 400^0. The main fraction of the volatile decomposition products of the strongly crosslinked polybutadiene, ν =

42.05 x 10^{-4} [mole/cm^3] (Table 4), is evolved within the temperature range 410-460°. In this case, the decomposition and combustion rates are also higher than those of vulcanizate B_1. Besides, an additional peak at 450° is observed in the arm of the main peak recorded at 430° associated with the thermal decomposition of the strongly crosslinked polybutadiene. The elucidation of the reasons for its presence requires further research.

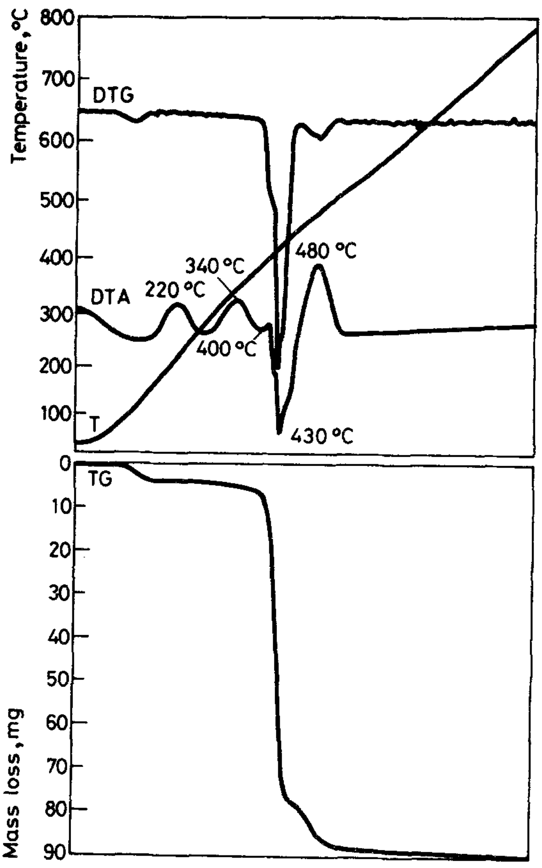


Fig. 2 TG, DTG and DTA curves of *cis*-1,4-polybutadiene cross-linked with dicumyl peroxide in the presence of Versatic 10

The examination of the effect of the cobalt siccative on the thermal properties of polybutadiene and polyisoprene which was studied previously [11, 12], leads to a conclusion that the susceptibility of the isoprene rubber to the action of a metal with variable valence at elevated temperature is

Table 4 Results of analysis of the vulcanizates of *cis*-1,4-polybutadiene

Vulcanizate	Density of crosslinking	Density of crosslinking after heating		Degradation coefficient	Crosslinking coefficient	Sol content, ** %		
symbol	$\nu_o \times 10^4$/mol/cm^3	at 200°C ν_{200}	at 350°C ν_{350}	$k_1 = \frac{\nu_o}{\nu_{200}}$	$k_2 = \frac{\nu_{350}}{\nu_o}$	unheated vulcanizate	vulcanizates 200°C	heated at 350°C
B_1	0.90	0.45	27.01	2.0	30.0	5.0	26.9	9.6
B_2	0.88	0.26	27.08	3.4	30.8	9.8	33.9	2.2
B_3	0.97	0.48	42.05	2.0	43.3	6.1	15.7	-

* the vulcanizates were heated in the oven of the derivatograph under conditions corresponding to the derivatographic analysis

** determined from the weight loss of the samples during their swelling higher. The cobalt siccative, initiating at the same time the degradation and thermooxidative destruction as well as the crosslinking of both polydienes, decreases considerably the temperatures of these processes in the case of cis-1,4-polyisoprene. It may be concluded that the process of peroxide activation in the presence of cobalt salts becomes more difficult in the butadiene rubber than in isoprene.

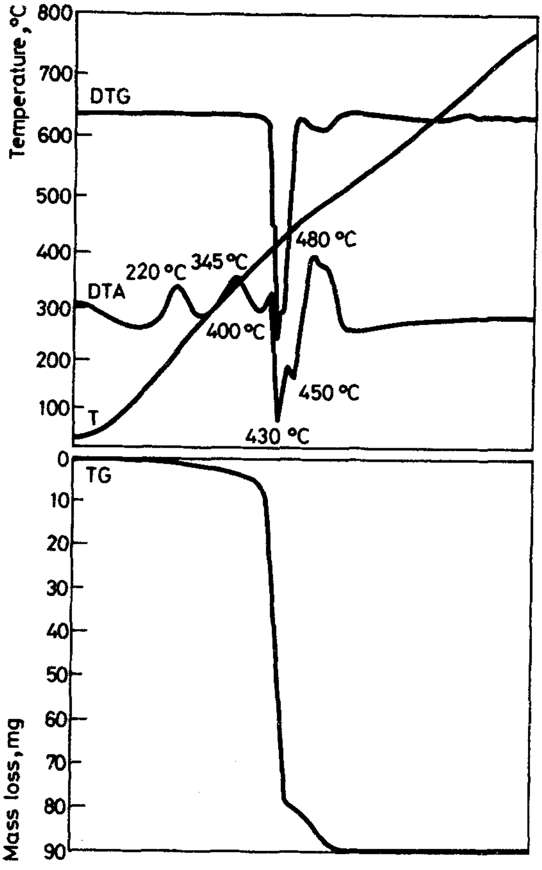


Fig. 3 TG, DTG and DTA curves of *cis*-1,4-polybutadiene cross-linked with dicumyl peroxide in the presence of cobalt siccative

The presence of a metal with variable valence shows no effect on the degradation coefficient of polybutadiene at its first exothermic transition temperature, but brings about considerable crosslinking of the polymer at the temperature of its second transition (Table 4), so facilitating reactions [12].

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Zusammenfassung — Mittels Derivatographie wurde der Einfluß von synthetischen gesättigten Säuregemischen und der Kobaltsalze dieser Säuren auf die thermischen Eigenschaften von peroxidvulkanisiertem *cis*-1,4-Polybutadien (Europrencis) untersucht.

Die thermischen Kurven der untersuchten Proben wurden auf der Basis ergänzender Betrachtungen interpretiert. Man fand, da die Einbringung eines Metalles mit verschiedenen Bindigkeiten in die Kautschukmischung die optimale Vulkanisierungsheit erhöht und eine Zerlegung des Elastomers während der Vernetzung verursacht.

Die Gegenwart von Kobaltsalzen erleichtert bei der Temperatur der zweiten exothermen Umwandlung die Vernetzung von Polybutadien und hat gleichzeitig eine gesteigerte thermische Zersetzungsgeschwindigkeit sowie eine Abnahme der Temperatur dieses Prozesses zur Folge.