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Crosslinking of *cis*-Polybutadiene by Co^{60} γ-Rays

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Synopsis

The radiation-induced vulcanization of *cis*-polybutadiene (Europrene Cis, 92% *cis*-configuration) was investigated. The crosslinking density of irradiated rubber was determined by two methods: equilibrium swelling and equilibrium compression modulus. The inhibition and acceleration of radiation-induced crosslinking by addition to Europrene Cis of sulfur, Thiurame, Elastopar, Arubrene, paraffin oil, or barium sulfate was studied. The chemical resistance of radiation vulcanizates to 10% nitric acid was determined.

Introduction

In recent years numerous publications have been devoted to the action of ionizing rays on plastomers and elastomers.[1–9]

Most representative of the above two groups of polymers are investigations on the radiation crosslinking of polyethylene and natural rubber, respectively.

The authors have decided to investigate radiation-induced vulcanization of *cis*-polybutadiene rubber, mainly because of its particularly regular structure.

The aim of the present work is to determine the influence of some additives accelerating the radiation crosslinking and to investigate the chemical stability of radiation vulcanizates.

Experimental

The *cis*-polybutadiene rubber used in the present experiments, Europrene Cis, consists of 92% *cis*, 2.2% *trans*, and 5.8% vinyl configuration. Its weight- and number-average molecular weights are 227,000 and 131,000, respectively.

Europrene Cis, purified by extraction with acetone, was pressed in slabs. Cylindrical samples, 10 mm. in diameter and 6.3 mm. in height were cut out.

The thus prepared samples were deaerated and irradiated in sealed glass tubes by γ-rays from a Co^{60} source at a dose rate of 0.2 Mrad/hr. The total doses ranged between 1 and 75 Mrad.

The irradiated specimens of *cis*-polybutadiene were subjected to swelling in toluene, equilibrium being reached after 4–6 days.

The density of crosslinking was determined by the method of equilibrium swelling of Flory and Rehner[10] and by the compression modulus method of Cluff, Glading, and Pariser.[11]

Certain samples were prepared by adding to Europrene Cis in the course of milling the following additives: sulfur, 2.9 wt.-%; Thiurame (tetramethylthiuram disulfide), 2.9 wt.-%; Elastopar (*N*-4-dinitroso-*M*-methylaniline), 2.9 wt.-%; Arubrene (chlorinated paraffin, 70%), 3.9 wt.-%; Paraffin oil, 5.7 wt.-%; or barium sulfate, 44.4 wt.-%. Samples containing the above listed ingredients were irradiated with doses of 1.7 and 20 Mrad. Crosslinking density was then determined by the equilibrium swelling method.

The chemical resistance of irradiated rubber was examined by gravimetric and volumetric investigations of samples immersed in 10% nitric acid at room temperature for periods of 72, 120, 168, and 216 hr.

Results and Discussion

The results obtained for radiation-induced crosslinking are listed in Table I.

TABLE I
Radiation Vulcanization of *cis*-Polybutadiene

Radiation dose, Mrad	Cross-linking density × 10^{-5}, mole/cm.^{3}	
	Swelling method	Method of compression modulus
0.96	0	0
7.2	2.82	4.36
23.4	9.92	8.72
35.0	11.2	10.6
46.5	15.9	13.3
63.0	21.0	16.6
74.5	28.6	21.3

The Huggins constant of interaction between *cis*-polybutadiene and toluene was determined by osmometric measurements as 0.39.

The dependence of the crosslinking density y on the absorbed dose x, as established by equilibrium swelling and compression modulus may be roughly expressed as

$$y = 0.358x \text{ and } y = 0.3x, \text{ respectively}$$

In the above formulas the crosslinking density is given in 10^{-5} mole/cm.^{3}, the doses in megarads.

Radiation yield for crosslinking of *cis*-polybutadiene equals 3.6 crosslinkages per 100 e.v. The formation of one crosslinkage requires 28 e.v. The corresponding value for natural rubber is 44 e.v.

TABLE II
Radiation Vulcanization of *cis*-Polybutadiene with Additives

Dose, Mrad	Crosslinking density × 10^{-5}, moles/cm.^{3} (method of swelling)					
	Sulfur (2.9%)	Thiurame (2.9%)	Elastopar (2.9%)	Arubrene (3.9%)	Paraffin oil (5.7%)	Barium sulfate (44.4%)[a]
1	0	0	0.18	0	0	0
7	0.757	0.741	3.68	6.22	2.81	2.8
20	7.19	11.0	12.6	18.6	5.75	15.0

[a] The data in this column refer only to the polymer fraction of the sample.

The inhibiting or accelerating influence of various additives on the radiation-induced vulcanization of *cis*-polybutadiene may be seen in Table II.

By comparing the data in Tables I and II one may conclude, that sulfur and Thiurame act as inhibitors. Similar phenomena have been already reported by Nikitina et al.[2] In contrast to this, Elastopar and barium sulfate cause moderate acceleration, whereas the presence of chlorinated paraffin leads to a very marked acceleration.

Probably the atoms of chlorine as acceptors of electrons create favorable conditions for ion formation.

On account of the high energy (64 kcal./mole) of the C–C linkage is radiation vulcanizates[12] we have examined the resistance to 10% nitric acid (Table III).

Taking into account the values of crosslinking density it may be seen that radiation vulcanizates of Europrene Cis are chemically more resistant than thermal vulcanizates with sulfur.

TABLE III
Chemical Resistance of Thermal and Radiation Vulcanizates

Type of *cis*-polybutadiene vulcanizate	Crosslinking density 10^{-5}, mole/cm.^{3}	Changes in weight after 168 hr. immersion in HNO_3, %	Changes in volume after 168 hr. immersion in HNO_3, %
Thermal vulcanizate with sulfur; 50 min., 143°C.	9.0	4.62	3.80
Radiation vulcanizate without additives, 23.4 Mrad	9.92	2.40	2.12
Radiation vulcanizate without additives, 74.5 Mrad	28.6	1.78	1.71
Radiation vulcanizate with $BaSO_4$, 7 Mrad	2.8	3.80	4.83
Radiation vulcanizate with Arubrene, 7 Mrad	6.22	3.80	3.22
Radiation vulcanizate with Elastopar, 7 Mrad	3.68	3.27	3.00

Further investigations on the radiation vulcanization of *cis*-polybutadiene are in progress.

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Résumé

On a examiné le processus de vulcanisation par radiation du *cis*-polybutadiène (Europren Cis, 92% de *cis*-configuration). La densité de pontage du caoutchouc irradié a été déterminée par deux methodes: gonflement à l'état d'équilibre et module de compression à l'état d'équilibre. On a examiné l'inhibition et l'accélération du pontage induit par irradiation par l'addition à l'Europren Cis des ingrédients suivants: soufre, Thiurame, Elastopare, Arubrène, l'huile de paraffine et le sulfate de baryum. On a examiné aussi la résistance chimique de radiovulcanisats dans l'acide de nitrique à 10%.

Zusammenfassung

Es wurde die strahlungsinduzierte Vulkanisation von *cis*-Polybutadien (Europren Cis, 92% *cis*-Konfiguration) untersucht. Die Vernetzungsdichte der in einer Kobaltbombe bestrahlten Kautschukproben wurde nach zwei Methoden: nämlich aus der Gleichgewichtsquellung und aus dem Druckmodul bestimmt. Die Autoren haben die Verzögerung und die Beschleunigung der strahlungsinduzierten Vernetzung durch Zusatz von Schwefel, Thiuram, Elastopar, Arubren, Paraffinöl und Bariumsulphat überprüft. Es wurde auch die chemische Beständigkeit der Strahlungsvulkanisate gegen 10%-ige Salpetersäure bestimmt.

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