

THE EFFECT OF HEXACHLOROCYCLOPENTADIENE AND CHLORINE-CONTAINING CYCLIC ORGANIC DERIVATIVES OF DICARBOXYLIC ACID ON THE STRUCTURE OF THE BUTADIENE-NITRILE RUBBER SKN-40 UNDER THE INFLUENCE OF HEAT AND γ -IRRADIATION

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Abstract: The effect of Organo-Chlorine Compounds (OCC) on the radiation structuring of SKN-40 was investigated in filled model systems with 5 mass. h. of ZnO. The content of gel was determined at various dosages of OCC after irradiation with doses from 5 to 40 MRad. With increasing dosages of OCC, it takes part in the formation of rubber. After radiation exposure, the optimal conditions for the content of gel systems are 62-65%, and the activity in the processes of radiation structuring of OCC is located in the same row that was composed of the composition of the heating. The effective concentration of cross-links at optimal dosages of OCC ($n \cdot 10^{-19}, \text{cm}^{-3}$) in the optimum vulcanization constitute model systems with HCCP-5,3, adduct 1-5,3, adduct 2-6,3, adduct 3-6,5. In the presence of OCC, the optimal dose of radiation is reduced, so they can be considered as sensitizers of radiation structuring. Thus, it was found that the investigated OCC are effective structuring agents for SKN-40 both during heating and exposure to λ irradiation.

Key words: Elastomer, NBR, Radiation Vulcanization, Chlorogenic compound

1. Introduction

The use of haloid-containing organic substances as agents for the thermal vulcanization of elastomers is most prevalent in the rubber industry. Vulcanization structures formed in this case contain mainly C-C bonds, but in addition, they can contain a set of cross-links of various energies, and therefore allow producing rubber with the necessary statistical and dynamic characteristics. [1, 2]

It is known that haloid-containing substances are often introduced into the composition of rubber compounds as sensitizers of radiation vulcanization, which allows achieving the optimal properties of rubber at lower irradiation doses. [3]

The need to obtain vulcanizates with high resistance to aggressive media, high heat resistance, wear resistance, dynamic endurance, suggests the appropriateness of using halogen-containing compounds in the composition of rubber mixtures based on butadiene-nitrile rubber of the SKN-40 brand by the thermal-vulcanization method. [4]

The type of organohaloid compounds has been chosen, guided by information known from the literature: the highest activity is observed in chlorine-containing substances and increases with an increase in the number of its atoms in the molecule: simultaneous, the absence of other polar groups in the molecule strengthens the effect of rubber structuring.

2. Results and discussion

Herein, it has been studied the vulcanizing and sensitizing effect of an organochlorine compound (OCC) containing six chlorine atoms in a molecule, as well as one of the active functional groups: anhydride, atoximide, propionitrile.

The data presented in Table 1 allowed us to arrange that OCC in a series in accordance with their vulcanization activity: HCCP <Adduct 1 <Adduct 2 <Adduct 3.

Based on the results shown in Table 1, a series of oxide activity was also made during the vulcanization of SKN-40 using OCC:



Thus, the most active vulcanizing agent for SKN-40 at elevated temperature in the presence of activators is Adduct 3 among the considered OCC. The remaining compound studies can also quite effectively organize mixtures based on SKN-40 containing zinc, magnesium and cadmium oxides.

Table 1. The influence of the type of OCC and metal oxide on the structuring of SKN-40 processes heated by Mooney viscometer at 423 K.

OCC 3 wt. h.	Oxide, amounts, equimolar 5 wt. h.	Start structuring τ_5 , min	Speed characteristic Structuring $\tau_{35} - \tau_5$, min
1	2	3	4
HCCP	ZnO	3,8	4,2
	MgO	4,0	6,0
	CdO	4,4	6,6
	Al ₂ O ₃	5,6	6,7
Adduct 1	ZnO	3,6	4,4
	MgO	3,8	6,0
	CdO	3,6	6,2
	Al ₂ O ₃	10,0	7,0
Adduct 2	ZnO	3,5	3,4
	MgO	3,8	5,6
	CdO	3,7	5,4
	Al ₂ O ₃	10,0	6,4
Adduct 3	ZnO	2,4	2,2
	MgO	3,0	5,6
	CdO	3,2	5,6
	Al ₂ O ₃	4,0	6,0

It has been determined the relative amount of gel formed by unfilled model mixtures based on SKN-40 during heating in order to select the effective dosage of OCC (Figure 1.)

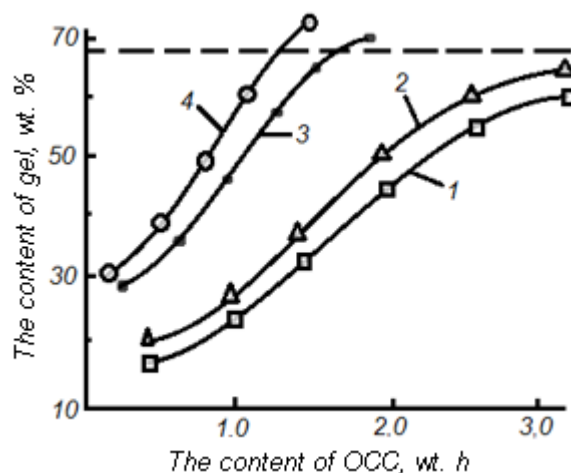


Fig. 1. The effect of the content of organochlorine compounds of Nagel formation in rubber mixtures based on SKN-40 wt. h. ZnO during heating (423 K, 40 min.): 1-HCCP; 2-adduct 1; 3-adduct 2; 4-adduct 3;

Data on the gel formation confirmed a number of OCC activity and allowed to choose effective dosages of OCC:

HCCP– 3 wt. h.; Adduct 1- 3 wt. h.; Adduct 2 - wt. h.; Adduct 3- 1.7 wt. h.

The effective concentration of cross-links in unfilled rubber has been determined using vulcanizing agents. (Table 2)

Table 2. The effective concentration of cross-links in unfilled vulcanizer based on SKN-40 with 5 wt. h. ZnO (423K optimum for a mixture of each composition)

Vulcanizing agent	HCCP 3 wt. h.	Adduct 1 3 wt. h.	Adduct 2 2 wt. h.	Adduct 3 1.7 wt. h.	Sulfuric vulcanizing group in a standard mixture
$n_c \cdot 10^{-19}, \text{cm}^{-3}$	5.2	5.4	6.7	6.8	7.6

The value of n_c for model vulcanizates was slightly lower than for a standard mixture with a sulfur vulcanizing group. Indeed, it is known that with vulcanization at the optimum, the value of n_c in rubber with polysulfide bonds is higher than in rubber with a predominant content of C - C bonds. The concentration of cross-linking of the vulcanizates with the studied OCC increases in accordance with a number of activities of the latter.

It can be assumed that [5], the vulcanization activity of OCC is directly related to their chemical structure (see Table 1). Each of the studied compounds contains six chlorine atoms in the molecule, and as well as adducts, and other active functional groups enhance the effect of rubber structuring. Since the nitrogen-containing compound is sometimes successfully used together with organohaloid compounds in the processes of vulcanization of elastomers as activators, and some effective vulcanizing agents simultaneously contain chlorine and nitrogen molecules. It is acceptable to assume that adducts 2 and 3 are the most active due to nitrogen-containing functional groups. It is possible that the high structuring ability of adduct 3 is due to the presence of two nitrogen atoms, one of which is in the -CN group. It can be assumed that in

this case the chemical affinity from Adduct 3 to nitrile-butadiene rubber also manifests itself, which facilitates the distribution of the vulcanizing agent in the elastomer.

3. Conclusion

The effect of OCC on the radiation structuring of SKN-40 was investigated in filled model systems with 5 wt. h. ZnO. The gel content was determined at various dosages of OCC after irradiation with doses from 5 to 40 Mrad. OCC takes part in the formation of rubber with increasing dosages. The optimal conditions for the content of the gel in the systems after radiation exposure is 62-65%, and the activity in the processes of radiation structuring of OCC is located in the same row that was composed of the heating composition. The effective concentration of cross-links at optimum dosages of OCC ($n \cdot 10^{-19} \text{cm}^{-3}$) in the optimum vulcanization consists of model systems with HCCP-5.3, adduct 1-5.3, adduct 2-6.3, adduct 3-6.5.

In the presence of OCC, the optimal dose of radiation decreases, so they can be considered as sensitizers of radiation structuring.

Thus, it was found that the investigated OCC are effective structuring agents for SKN-40 both during heating and exposure to λ irradiation.

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ВЛИЯНИЕ ГЕКСАХЛОРЦИКЛОПЕНТАДИЕНА И ХЛОРСОДЕРЖАЩИХ ЦИКЛИЧЕСКИХ ОРГАНИЧЕСКИХ ПРОИЗВОДНЫХ ДИКАРБОНОВЫЙ КИСЛОТЫ НА СТРУКТУРОВАНИЕ БУТАДИЕН-НИТРИЛЬНОГО КАУЧУКА SKN-40 ПОД ДЕЙСТВИЕМ ТЕПЛА И γ -ИЗЛУЧЕНИЯ

Г.Н. Ахундзаде

Резюме: Структурирующее действие гексахлорциклопентадиена (ГХЦП) и хлорсодержащие производных дикарбоновые кислоты (ХДК) на SKN-40 исследовали при воздействии повышенных температур, γ -облучения.

Показано что, при 423К рассматриваемые ХОС эффективно структурируют SKN-40 в присутствии оксидов металлов.

Ключевые слова: Эластомер, БНК, Радиационная вулканизация, Хлороганические соединения

HEKSAXLORTSİKLOPENTADIENVƏ XLORTƏRKİBLİ TSİKLIK ÜZVİ DİKARBONTURŞUSUNUNBUTADIEN_NİTRİLKAUÇUKUNUNTERMÖVƏ RADİASİONVULKANLAŞMASINATƏSİRİ

H.N. Axundzadə

Xülasə: Xlor-üzvi Birləşmələrin (XB) SKN-40-ın radiasion tikilməsinə təsiri ZnO-in 5 küt. hissə doldurulmuş model sistemlərində tədqiq edilmişdir. ZnO. XB-nin müxtəlif dozalarında 5 MRad-dan ilə 40 MRad-a qədər şüalanmadan sonra gelin tərkibi müəyyən edilmişdir. XB-lərin artan dozaları rezinin formalaşmasında iştirak edir. Radiasiyaya məruz qaldıqdan sonra gel sistemlərinin tərkibinin optimal şərtləri 62-65%-dir, beləki XB-nin radiasiya tikilməsinə aktivliyə əsasən təsiri onun istilik tərkibi ilə eynilik təşkil edir. Optimal vulkanlaşmada XB-nin optimal dozalarında ($n^{\circ} 10^{-19}$, sm^{-3}) tikici agentlərin effektiv konsentrasiyası HCCP-5.3, addukt 1 -5.3, addukt 2 -6.3, addukt 3 -6, 5 kimi müəyyən edilmişdir. XB-nin iştirakı ilə şüalanmanın optimal dozası azaldılır, buna görə də onları radiasiya tikilməsinin sensibilizatorları kimi qəbul edə bilərik. Beləliklə, tədqiq edilən XB-lərin istilik və λ radiasiyasına məruz qalması zamanı SKN-40 üçün effektiv tikilmə agentləri olduğu aşkar edilmişdir.

Açar sözlər: Elastomer, BNK, Radiasion vulkanlaşma, Xlor-üzvi birləşmələr