UDC 678.742.4-136.23.01:678.023

VULCANIZATION OF BUTYL RUBBER IN THE PRESENCE OF 2-(2-OXA-6-THIADECYL)OXIRANE

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Received 22.06.2018

The vulcanization of rubber mixture of butyl rubber containing ether- or thioether-containing oxirane in its composition and physico-mechanical properties of the prepared vulcanizate have been determined. It has been revealed that its endurance in multiple stretching is higher than for vulcanizate prepared from rubber mixture not containing above-mentioned oxirane.

Keywords: vulcanization, butyl rubber, ingredient, 2-(2-oxa-6-thiadesil)oxirane, epichlorohydrin.

The rubbers on the basis of butyl rubber possess high heat- and ozone resistance, gas impermeability, resistance to aggressive media and swelling in the water, high dielectric properties. However, along with these positive properties, these rubbers possess also negative characteristics – low endurance at multiple stretching. Now there are scientific works devoted to elimination of this lack by application of new rubber mixtures. For ex., it was carried out the sulphur vulcanization of rubber mixture of butyl rubber having ingredient mixture of glycidyl-1-methoxy-1-cyclopentanecarboxylate (GMCP) [1]. The rubbers prepared by vulcanization of this mixture had also this lack. The investigations of other author [2–6] also did not bring tangible positive results.

The solution of this problem requires the carrying out of investigations with application of various classes of the compounds with strictly determined structure as an addition.

Taking into account above-mentioned one, this paper has been devoted to the preparation of vulcanizate on the basis of butyl rubber by vulcanization of the rubber mixture containing 2-(2-oxa-6-thiadesyl)oxirane (OTDO), sulphur and butyl rubber and also to the study of structure of OTDO.

Experimental part

For carrying out of vulcanization of butyl rubber in the presence of OTDO there have been made the rubber mixtures, a composition of which has been presented in Table 1. In Table the data of quantitative data of GMCP,

taken from literature [1] with the aim of comparison of the physico-mechanical parameters of vulcanizates prepared in the presence of GMCP with physical-mechanical parameters of vulcanizates prepared in the presence of OTDO and GMCP have been also presented.

The vulcanization was carried out by pressing for 20, 40 and 60 min at temperature 143°C.

OTDO has been prepared by interaction of 4-thia-1-octanol (TO) with epichlorohydrin (ECH). TO was synthesized by addition of *n*-butyl mercaptane to 2-propen-1-ol on methodology [8]. B.p. – 105–106°C/0.5 kPa, $d_4^{20} = 0.9660$, $n_D^{20} = 1.4832$.

Preparation of OTDO. The mixture 23 g (0.2 mol) of TO, 12.43 g (0.31 mol) of NaOH, 21.5 g (0.23 mol) of epichlorohydrin and 140 ml of toluene was heated at 85°C for 3 h. After neutralization, drying, filtration of organic layer, toluene sublimation and residue distillation it has been prepared 25.5 g (57%) of OTDO. B.p. – 112°C/0.2 kPa, $n_D^{20} = 1.4740$, $d_4^{20} = 0.9957$. Found, %: C 59.03, H 10.16, S 15.97. $C_{12}H_{16}O_2S$. Calculated, %: C 58.78, H 9.87, S 15.69.

OTDO, TO used at synthesis can consist of mixture of two isomers: 4-thia-1-octanol and 3-thia-1-heptanol. The prepared product should also consist of two similar isomers: OTDO (forming from 4-thia-1-octanol and ECH) and 2-oxa-5-thia-4-methylnonanyl oxirane (OTMNO) (forming from 4-thia-1-octanol and ECH).

Table 1. Optimal composition of mixture of ingredients in mass part (m.p.) for preparation of vulcanizate of butyl rubber

Composition of rubber mixture	Known mixtures		Suggested mixtures (samples) having OTDO in the composition		
	quantity of ingredients in mixture, not containing OTDO and GMCPC [1]	quantity of ingredients in mixture, containing GMCPC [2]	example 1	example 2	example 3
Butyl rubber of mark 2045	100	100	100	100	100
Steraic acid	3.0	3.0	3.0	3.0	3.0
Captax	0.65	0.65	0.65	0.65	0.65
Thiuram	1.3	1.3	1.3	1.3	1.3
Zinc oxide	5.0	5.0	5.0	5.0	5.0
Carbon black DG-100	50	50	50	50	50
Sulphur	1.5	2.0	2.0	2.0	2.0
GMCPC	—	3.0	—	—	—
OTDO	—	—	1.0	3.0	8.0

The determination whether the product consists only of OTDO or OTMNO or from mixture of these isomers, makes it possible to accurately determine the physico-mechanical properties of the rubber prepared after vulcanization. The structure of the synthesized product has been investigated by spectroscopic methods, GLC and elemental analysis.

In the IR spectrum of the prepared product there are frequencies 3060, 1255, 850, 920 cm^{-1} , characteristic for C–S–C group. There have been also found the bands at 1120, 1240 and 1375 cm^{-1} , characteristic for ether bond, oxirane and methyl groups, respectively. The intensive bands at 2874–2961, 1485 cm^{-1} belong to $-\text{CH}_2-\text{C}$,

In the spectrum ^1H NMR there are appeared the following signals of protons (CD_3COCD_3 , δ , ppm): 0.84 s (3H, $\text{CH}_3-\text{C}-$), 1.2–1.89 m (6H, $-\text{CH}_2\text{CH}_2-\text{C}-$, $-\text{CH}_2-$),

2.47d (2H, $\text{C}-\text{CH}_2$), 2.63 q (4H, $-\text{CH}_2-\text{S}-$

CH_2-), 3.41–3.72 m (5H, $\text{CH}_2-\text{O}-\text{CH}_2-$,

2 $\triangle_{\text{CH}}$). An absence of duplicate at 2.86 ppm

belonging to $-\text{CH}-$ proton in fragment $\begin{array}{c} \text{S}-\text{CH} \\ | \\ \text{CH}_3 \end{array}$,

and also an appearance of only one peak belonging to OTDO in GLC (Figure) shows that as a result of reaction only OTDO was prepared.

Chromatogram of OTDO (column $l_k = 3\text{m}$; 10% apiezone on zeolite 545; $t = 200^\circ\text{C}$; $J_{\text{det.}} = 100\text{ mA}$, gas-bearer rate (helium) – 37 ml/min).

Results and discussion

With the aim of elucidation of dependence of the physico-mechanical parameters values on nature and composition of 2-(2-oxa-6-thia-decyl)oxirane there has been carried out the vulcanization of rubber mixture containing above-mentioned oxiranyl sulphide and without it. In the literature [1] the physico-mechanical parameters of rubber prepared from rubber mixture of the similar composition, but with the participation of GMCPC have been taken (Table 2).

Table 2. Physico-mechanical parameters of rubbers prepared by vulcanization of rubber mixture of butyl rubber

Parameters	Known rubbers		Rubbers having OTDO in the composition (samples)		
	rubber, not containing OTDO and GMCPC	rubber, containing GMCPC	example 1	example 2	example 3
Vulcanization time, min	40	20	40	40	40
Modulus at 300% elongation, MPa	8.0	8.1	8.4	8.2	7.8
Modulus at 400% elongation, MPa	11.5	10.8	11.2	11.0	9.3
Breaking resistance, kgs/cm ²	22.0	24.0	23.5	26.2	22.5
Specific elongation, %	600	650	700	730	760
Residual elongation, %	36	28	32	36	50
Hardness on TM-2	64	58	56	58	54
Rebound elasticity, % at 20 ⁰ C	8.0	9.0	10.0	10.0	11.5
Endurance at multiple stretching (500 cycle/min), min ⁻¹	67.5	114.13	120.39	196.5	142.43
Mooney viscosity at 120 ⁰ C	–	–	51	48	45
Time to beginning of prevulcanization at 120 ⁰ C, min	–	–	23.5	20.0	18.2

In passing from one experiment to another one a quantity of oxiranyl sulphide was changed as shown in Table 1, and a quantity of the remaining ingredients was kept mainly constant. The carrying out the investigations in this style creates a possibility to reveal the causes of changes of the obtained results.

It is seen from Table 2 that the rubbers forming from mixtures of ingredients containing OTDO have higher endurance in multiple stretching (EMS) than the rubbers not containing OTDO in the composition. In addition, the rubber containing GMCPC shows also the higher EMS value than the rubber of butyl rubber not containing OTDO. This index is also differed in rubbers containing OTDO and GMCPC in ingredient mixture. In the first case (example 1) its value is higher than in the second case (example 2). It is also seen that with increase of a quantity of OTDO from 1 to 3 m.p., in the mixture EMS value of rubber increases from 120.39 to 196.5 cycles/min. Further increase of a quantity of OTDO up to 8 m.p., leads to a decrease of EMS to 142.43. These results can be explained by the fact that, as shown in [8], during vulcanization, owing to availability of epoxide compound in the rubber mixture, due to interaction of epoxide ring with labile rubber atoms, its structuring can be activated and, consequently – increase of its some physico-mechanical properties, including EMS.

If one agree with this assumption, the rubber prepared from mixture of ingredients containing GMCPC, having in molecules such

groups, as oxirane, carboxyl and ether helping increase of EMS by structuring during its preparation by vulcanization should have EMS value higher than the rubber containing OTDO, having only oxirane and ether group in the molecule, helping structuring, in the composition of ingredient mixture. However, the results of experiments showed the reverse result and, consequently, this assumption cannot be accepted.

The obtained data can be explained, taking into account the fact that in addition of above-mentioned one, the finding factor of sulphide group C–S–C in the composition of OTDO influences on the vulcanization process. Due to this, it better dissolves the sulphur (incoming in composition of ingredients of a mixture) than GMCPC. Especially, it has been shown in work [9] that some compounds, dissolving such sulphur, convert the vulcanization mixtures to homogeneous ones.

Under this condition, at rubber vulcanization, the particles of the ingredients are permitted to interact with each other to an even greater degree, than in the absence of OTDO in the composition of ingredients. Finally, it is prepared the rubber having higher EMS values than the rubbers not having OTDO in the composition of ingredients or containing GMCPC.

The above-mentioned decrease of EMS value in increase of a quantity of OTDO in the ingredient mixture to 8 m.p., can be explained by increase of softness of the rubber and consequently, by decrease of its physico-mechanical properties, including EMS.

Conclusions

1. It has been shown that at vulcanization of butyl rubber in the presence of OTDO the prepared rubber has a higher endurance value in multiple stretching in comparison with rubbers prepared in the presence of GMCPC and without participation of OTDO and GMCPC.
2. It has been revealed that the vulcanization of butyl rubber in the presence of OTDO leads to a preparation of rubber having a great endurance value in multiple stretching than the rubber prepared in the presence of GMCPC.
3. It has been detected that at vulcanization of butyl rubber having OTDO in the ingredient mixture with increase of a quantity of OTDO in the mixture from 1 to 3 m.p. EMS value of the rubber is increased from 120.39 to 196.5 min⁻¹. The further increase of a quantity of OTDO to 8 m.p., leads to a decrease of this index to 142.43 min⁻¹.
4. It has been established that at synthesis of OTDO by interaction of ECH with 4-thia-1-octanol (addition product of butyl mercaptane to 2-propen-1-ol) instead of the expected mixture of isomers of OTDO and OTMNO it is prepared an individual OTDO.

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2-(2-OKSA-6-TİADESİL)OKSİRAN İŞTİRAKİ İLƏ BUTİLKAUÇUKUN VULKANLAŞDIRILMASI

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Tərkibində sadə efir, tioefir qrupları olan 2(2-oksa-6-tiadesil)oksiran iştirakı ilə butilkauçukun vulkanlaşdırılması həyata keçirilmişdir. Alınan rezinin fiziki-mexaniki kəmiyyətlərinin qiymətləri təyin edilmişdir. Göstərilmişdir ki, həmin məhsulun dəfələrlə dartılmaya qarşı davamlılığı kauçukun özündən alınan rezinin davamlılığına nisbətən çox yüksəkdir.

Açar sözləri: vulkanlaşma, butilkauçuk, ingredient, 2-(2-oksa-6-tiadesil)oksiran, epixlorhidrin.

ВУЛКАНИЗАЦИЯ БУТИЛОВОГО КАУЧУКА В ПРИСУТСТВИИ 2-(2-ОКСА-6-ТИАДЕЦИЛ)ОКСИРАНА

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Исследована вулканизация резиновой смеси бутилкаучука, содержащего в составе эфир- или тиоэфирсодержащий оксиран, и определены физико-механические свойства полученного вулканизата. Выявлено, что его выносливость при многократном растяжении выше, чем у вулканизата, полученного из резиновой смеси бутилкаучука, не содержащего вышеуказанный оксиран.

Ключевые слова: вулканизация, бутилкаучук, ингредиент, 2-(2-окса-6-тиадецил)оксиран, эпихлоргидрин.