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Physical Chemistry

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1957

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Abstract

Full Text

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ON THE CHANGE IN THE DEGREE OF SULFIDITY OF SULFUR STRUCTURES IN VULCANIZATES UNDER LIGHT EXPOSURE

(Presented by Academician P. A. Rebinder, November 22, 1956)

In work ([1]) we showed that sulfur vulcanizates of sodium-butadiene rubber–polysulfide* and thiuram**, differing from one another in the character of their cross-links, possess different light resistance. The polysulfide vulcanizate is the more light-resistant. The action of ultraviolet light on it is accompanied by the decomposition of sulfur bonds and the formation of free sulfur, which, in contrast to elemental sulfur, does not participate in the processes of photovulcanization, i.e., is "inactive." The nature of this inactive sulfur and how the degree of sulfidity of the sulfur structures in the above-mentioned vulcanizates changes under light exposure had not been established. Therefore it was impossible to answer unambiguously the very important question of why the polysulfide vulcanizate has greater light resistance than the thiuram vulcanizate. The present work is devoted to the study of this question.

Investigation of the type of sulfur bonds in vulcanizates is of substantial importance; however, the literature contains no reliable methods for their determination. Elucidating the character of the bonds in vulcanizates by chemical methods encounters great difficulties because of the impossibility of separating sulfur structures of different degrees of sulfidity, as well as identical sulfur structures bound to the polymer in different ways.

Thus, for example, with the aid of sodium sulfite ([2]) and methyl iodide ([3]) one can determine only the relative sulfur content in the form of polysulfides. It must be noted, however, that the results of analysis with Na_2SO_3 are affected in a complex manner by the degree of sulfidity and the nature of the radicals R_1 and R_2 in a grouping of the type R_1–S –R_2. Since the character of this influence has not been established, the results of the corresponding analysis cannot be interpreted accurately, which can sometimes lead to erroneous conclusions. It is possible that for this reason the indicated method did not succeed in detecting polysulfide structures in the thiuram vulcanizate ([4]).

Likewise, the method of exchange reactions using radioactive sulfur ([5]) and the thermomechanical method ([6]), based on studying the relaxation of stress in a vulcanizate at various temperatures, also do not make it possible to determine reliably the degree of sulfidity of sulfur structures in vulcanizates. Spectral

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methods have not been applied specifically to the solution of this problem. Work ([7]) concerns the investigation of infrared–

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* Composition of the polysulfide vulcanizate: rubber 100 parts by weight, stearic acid 2 parts by weight, zinc oxide 5 parts by weight, sulfur 6 parts by weight, diphenylguanidine 1 part by weight. Vulcanization was carried out at 143° for 20 min.

** Composition of the thiuram vulcanizate: rubber 100 parts by weight, stearic acid 2 parts by weight, zinc oxide 5 parts by weight, tetramethylthiuram disulfide 3 parts by weight. Vulcanization was carried out at 143° for 90 min.

absorption spectra of sulfur vulcanizate NR. A weak absorption band at 600 cm^{-1} was found, which the authors of this work attributed to the stretching vibration of C–S bonds; no di- and polysulfide bonds were detected by them. Later ([8,9]), the infrared spectra of aliphatic sulfides and polysulfides were studied in detail. It was established that the stretching vibrations of C–S bonds (maximum 600-700 cm^{-1}) ([8]) and S–S bonds (maximum 430-490 cm^{-1}) ([9]) have weak absorption bands in the infrared region.

Taking into account, moreover, that the concentration of sulfur bonds in soft vulcanizates is small and lies at the threshold of sensitivity of the infrared method, we could not apply this method for our investigations. At present, UV spectroscopy apparently possesses greater sensitivity to differences in sulfur structures. It was shown in ([10]) that the maximum for n-hexadecyl sulfide corresponds to 2250, for n-hexadecyl disulfide to 2480-2520, for n-hexadecyl trisulfide to 2500-2600, for n-hexadecyl tetrasulfide to 2900-3000, and for hexasulfide and for S_8 in solution in alcohol and hexane to 3200 Å and higher. Comparing the data obtained in this work with the data of works ([11,12]), it may be concluded that the absorption bands of various types of sulfur structures are quite intense, are characteristic of the given type of structures, and depend little on the nature of the remaining part of the molecule. As the degree of sulfidity increases, the absorption maximum shifts into the long-wavelength region of the spectrum.

In view of the above, it seemed advisable to us to use UV spectroscopy to study the change in the degree of sulfidity of the sulfur structures of polysulfide and thiuram vulcanizates under the action of UV light.

The investigation was carried out with vulcanizates whose composition was given above. These vulcanizates were studied in the form of films 10 μ thick, from which free sulfur, vulcanization accelerators, and products of their decomposition had first been removed by extraction with a mixture of methanol and acetone for 100 h in a nitrogen atmosphere. The vulcanizate films were irradiated with filtered light from a PRK-2 mercury-quartz lamp with $\lambda > 2900$ Å from a distance of 25 cm. The absorption spectra were recorded on a universal ZMR-2 monochromator in the region 2200-7000 Å. A quartz prism was used as the dispersing system for the UV region, and a glass prism for the visible region.

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Fig. 1. Absorption spectrum of a polysulfide vulcanizate in the ultraviolet and visible regions: 1 –purified rubber, 2 –extracted vulcanizate before irradiation, 3 –extracted vulcanizate after 6 h of irradiation.

Figure 1: Fig. 1. Absorption spectrum of a polysulfide vulcanizate in the ultraviolet and visible regions: 1 –purified rubber, 2 –extracted vulcanizate before irradiation, 3 –extracted vulcanizate after 6 h of irradiation.

The experimental procedure was as follows: first, spectra were recorded of films of polysulfide and thiuram vulcanizates purified by extraction from free ingredients; then these films were subjected to irradiation for 6 h; after irradiation they were again extracted for 100 h, and then their spectra were again recorded. In all cases, in order to eliminate errors introduced by the experiment itself, the spectra were recorded on one and the same film. The reproducibility between parallel experiments was satisfactory—the discrepancy did not exceed 1%. To determine the degree of sulfidity of the free sulfur formed during the decomposition of sulfur bonds of the polysulfide vulcanizate under irradiation, its spectrum was recorded in alcoholic solution; for comparison, the spectrum of elemental sulfur in alcoholic solution was recorded.

The experimental results are presented in Figs. 1-3.

As follows from the data of Fig. 1, an increase in absorption intensity is observed in the interval 2200-5400 Å for the polysulfide vulcanizate (2) in comparison with pure rubber (1). This is explained by the presence in the polysulfide vulcanizate of sulfur structures of various degrees of sulfidity. The observed maximum in the region 2300-2500 Å (2) is characteristic of monosulfides and disulfides. The maximum at 3250 Å is characteristic of hexasulfides. Absorption in the longer-wavelength region ($>$ 3400 Å) indicates that sulfides of still higher order are present in the vulcanizate. Irradiation of the polysulfide vulcanizate is accompanied by

with a decrease in the absorption intensity (Figs. 1, 3). This decrease is associated with the decomposition of polysulfide bonds, with sulfides of higher order being less light-stable.

In Fig. 2, for the thiuram vulcanizate, the absorption maximum in the region of 2500-2600 Å (2) corresponds to the presence of disulfides and trisulfides in the vulcanizate. The absorption maximum in the region of 2800-2900 Å (2) indicates the presence of tetrasulfides. The decrease in absorption in the long-wavelength region indicates that the content of sulfides of higher order is insignificant. Irradiation of the thiuram vulcanizate is accompanied by the decomposition of polysulfide bonds, predominantly hexasulfides and sulfides of higher order (the 3200-4000 Å region).

Fig. 1. Absorption spectrum of a polysulfide vulcanizate in the ultraviolet and visible regions: 1 –purified rubber, 2 –extracted vulcanizate before irradiation, 3 –extracted vulcanizate after 6 h of irradiation.

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Fig. 2. Absorption spectrum of a thiuram vulcanizate in the ultraviolet and visible regions: 1 –purified rubber, 2 –extracted vulcanizate before irradiation, 3 –extracted vulcanizate after 6 h of irradiation.

Figure 2: Fig. 2. Absorption spectrum of a thiuram vulcanizate in the ultraviolet and visible regions: 1 –purified rubber, 2 –extracted vulcanizate before irradiation, 3 –extracted vulcanizate after 6 h of irradiation.

Fig. 3. UV absorption spectrum

Figure 3: Fig. 3. UV absorption spectrum

Comparison of Figs. 1 and 2 shows that, in the ultraviolet and visible regions, the thiuram vulcanizate exhibits more intense absorption than the polysulfide vulcanizate, although the thiuram vulcanizate contains four times less combined sulfur than the polysulfide one. This can apparently be explained by the different distribution of combined sulfur among sulfur structures. It is known (10-12) that the intensity of the absorption bands of sulfur structures differs: the maxima for hexasulfide (3200 Å, $\log \varepsilon 4.0$), tetrasulfide (2900-3000 Å, $\log \varepsilon 3.39$), trisulfide (2500-2600 Å, $\log \varepsilon 3.22$), disulfide (2480-2520 Å, $\log \varepsilon 2.63$), and sulfide (2250 Å, $\log \varepsilon 2.2$). The observed intense absorption band at 3250 Å in the polysulfide vulcanizate indicates a relatively higher content of hexasulfide in it; the minimum in the region of 2900-3000 Å indicates an insignificant amount of tetrasulfide; the decrease in the region of wavelengths 2480, 2500, and 2600 Å indicates that the relative content of di- and trisulfides is small. A different picture is observed for the thiuram vulcanizate: it apparently contains a larger amount of mono-, di-, tri-, and tetrasulfides; sulfides of higher order in this vulcanizate are evidently few.

Fig. 2. Absorption spectrum of a thiuram vulcanizate in the ultraviolet and visible regions: 1 –purified rubber, 2 –extracted vulcanizate before irradiation, 3 –extracted vulcanizate after 6 h of irradiation.

It follows from Fig. 3 that the absorption region of inactive sulfur lies in the interval 2200-3200 Å, whereas for elemental sulfur this region is much broader—from 2200 to 4000 Å. This indicates that the sulfur structures that form inactive sulfur have a lower degree of sulfidity than those that form elemental sulfur. Since the vulcanizates we studied were irradiated with UV light with $\lambda > 2900$ Å, in this region only limited activation of inactive sulfur occurred, as a result of which it did not bring about photovulcanization; elemental sulfur in this region was sufficiently activated, and therefore it promoted the photovulcanization of rubber.

Fig. 3. UV absorption spectrum: **1**—elemental sulfur (S_8) in alcohol; **2**—inactive sulfur (formed during the decomposition of sulfur bonds of a polysulfide vulcanizate under irradiation) in alcohol.

Consideration of the experimental material leads to the conclusion that the

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higher light resistance of a polysulfide vulcanizate, compared with a thiuram vulcanizate, is explained by the difference in absorption in the UV region by the corresponding sulfur structures of these vulcanizates.

The authors express their gratitude for assistance in carrying out the experimental part of the study to Prof. V. M. Tatevskii, V. M. Gryaznov, and V. D. Yagodovskii.

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Received
22 XI 1956

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