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Abstract

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ON THE INTERACTION OF SULFUR WITH RUBBER UNDER THE INFLUENCE OF γ-RADIATION

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In our earlier work (^{1}) it was shown that, under the action of γ-rays, sulfur is added to rubber; moreover, at temperatures above 80° an increase in the structuring effect is observed, while at temperatures below 80° the effect of formation of cross-links in natural rubber (NR) decreases. Sulfur enters into the composition of the polymer in the form of polysulfide groupings capable of isotopic exchange with elemental radioactive sulfur. Compared with a vulcanizate made from pure rubber, the static strength increases, but the heat resistance of the vulcanizate decreases.

Since the process of radiation vulcanization is regarded as proceeding through stages involving the interaction of free radicals, it seemed of interest to follow the reaction of sulfur with rubber by the method of electron paramagnetic resonance (EPR). The spectra were recorded on a spectrometer with high-frequency modulation in the 3 cm range over the temperature interval from $-140°$ to $+20°$. Irradiation was carried out with doses of 6-11 Mr at $+20°$ and at $-196°$.

It turned out that irradiation of NR and of its mixture with 2% sulfur at $+20°$ leads to the formation of radicals whose spectra are identical in both cases ($g = 2.003 \pm 0.003$, width about 15 oersteds), and whose concentration is $(1–2.5) \cdot 10^{14}$ mg^{-1}. These radicals are distinguished by great stability, being detected 30-45 days after irradiation at concentrations of $(0.05–0.1) \cdot 10^{14}$ mg^{-1}.

According to generally accepted ideas, it may be assumed that, upon irradiation of rubber, free radicals arise as a result of detachment of a hydrogen atom and rupture of the –C–C–bonds of the molecular chains of the rubber. Along with alkyl radicals, allylic-type radicals are formed, stabilized by the effect of conjugation of the free valence with the neighboring double bond. They apparently manifest themselves as long-lived polymer radicals.

In the case of irradiation at $-196°$, the spectrum of NR differs from the spectrum of its mixture with sulfur; each spectrum is a superposition of lines, indicating the presence of several types of radicals. The line width for NR is 28 oersteds, for the mixture with sulfur 30 oersteds; the g-factor of both spectra is 2.003 ± 0.003.

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

The initial concentration of radicals for pure rubber is $(4.9 \pm 0.7) \cdot 10^{15}$ mg^{-1}, and for the mixture with sulfur $(2.6 \pm 0.6) \cdot 10^{15}$ mg^{-1}. The inhibiting effect of sulfur may be attributed, by analogy with the action of benzene, to delocalization of the electron in the eight-membered ring of its molecules.

If samples irradiated at $-196°$ are warmed in air at room temperature for 1-1.5 min, the spectrum becomes exactly the same as the spectrum of long-lived radicals obtained by irradiating the same samples at $+20°$. It follows from this that, in the case of irradiation at $-196°$, radicals of different stability are formed, both

long-lived and short-lived. The lifetimes of the latter at room temperature are measured in seconds. Changes in the concentration of radicals and in the nature of the lines were investigated when the sample was warmed from $-196°$ to $+20°$ in vapors of boiling liquid nitrogen. This temperature interval was traversed stepwise, in increments of 6-7°. The temperature was raised to the specified point, the sample was kept at this temperature for a certain time (in different cases the holding time was 30 sec., 2 min., 5 min.), then the sample was again frozen to $-140°$, and at this temperature the spectrum was recorded.

Fig. 1. Relative change in the concentration of radicals upon warming of samples irradiated at $-196°$:
I –natural rubber; *II* –NR mixture with 2% S

Fig. 1 shows the decrease in the concentration of radicals as a result of increasing the temperature with a 5 min. holding time. As can be seen, when heated from -196 to $-120°$, no changes in the spectrum are observed. The interval of intense radical decay corresponds to the glass-transition region of rubber (temperature from -80 to $-50°$). This means that the reaction activity of the radicals sharply increases in the region of the jump in mobility of individual segments of the molecular chain. In the temperature region indicated above, substantial changes in the line shape also occur. Whereas upon warming irradiated NR it is possible to observe only the decay of the initial short-lived radicals (Fig. 2), in the case of the NR + S mixture, simultaneously with the decay of the initial short-lived radicals, the appearance of new short-lived radicals with a large g-factor is observed (Fig. 3).

Fig. 2. Change in the spectrum of NR irradiated at $-196°$ during stepwise warming; the warming temperatures are indicated

Fig. 3. Change in the spectrum of a mixture of rubber with 2% S, irradiated

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

at −196°, during stepwise warming; the warming temperatures are indicated

The picture obtained in the latter case may be interpreted in two ways: either, upon warming of the irradiated NR mixture with sulfur, at least two new different radicals are formed, or one radical with an anisotropic *g*-factor arises, containing an $-\mathrm{S}-\mathrm{S}-$ group analogous to the peroxide group $-\mathrm{O}-\mathrm{O}-$, established for the case of irradiation of Teflon in the presence of oxygen ([2]).

The concentration of the new radicals arising upon warming of the irradiated mixture of natural rubber with sulfur varies, depending on the warming temperature, along a curve with a maximum in the region of about −80°.

(Fig. 4). This means that, at the given temperature, the most favorable ratio is observed between the rates of formation of new radicals and their destruction, ensuring the greatest recorded concentration of radicals.

For the most clearly expressed additional line, characterizing the newly arising radicals, the *g*-factor is 2.027 ± 0.003. This value coincides with the value determined for sulfur radicals (3) contained in the melt at 200°. On the basis of the foregoing, it may be considered that the new radicals are formed as a result of the interaction of sulfur molecules S_8 with polymer radicals of rubber Ka·, formed under the action of γ-rays. Such an interaction does not occur below the glass-transition temperature. It is possible only at temperatures at which the molecular chains of rubber acquire the necessary mobility, and consists in the opening of the eight-membered sulfur ring:

Fig. 4. Dependence of the concentration of short-lived radicals on the thawing temperature of a mixture of NR with 2% S, irradiated at −196°

$$\mathrm{Ka}\cdot + S_8 \rightarrow \cdot\mathrm{Ka}S_8\cdot . \tag{1}$$

The polymer-sulfide radical $\mathrm{Ka}S_8\cdot$ may then decompose further with liberation of sulfur radicals

$$\mathrm{Ka}S_8\cdot \rightarrow \mathrm{Ka}S_{(8-x)}\cdot + S_x\cdot . \tag{2}$$

Thus, an important fact is observed: the formation of sulfur radicals as a result of the interaction of polymer radicals with sulfur molecules at low (negative) temperatures. Elemental sulfur under the action of γ-rays apparently does not form radicals, since in our experiments irradiation of crystalline sulfur leads only to the appearance of a weak signal, which may be attributed to lattice defects.

Radicals of the type Ka$S_{(8-x)}\cdot$ have a longer lifetime than polymer radicals Ka·, while radicals $S_x\cdot$ are more active. For this reason, the radical decay curve (Fig. 1) for the mixture NR + S covers a broader temperature region than the analogous curve for pure rubber. The interaction of polymer radicals with one another and with rubber molecules leads to spatial structuring of the rubber. The structuring effect appears in the temperature region in which, according to EPR data (Fig. 1), the most rapid disappearance of radicals occurs during the "thawing" of irradiated rubber.

Sulfur, during irradiation of rubber at low temperatures, reduces the structuring effect (1). This action of sulfur may be a consequence of the above-described phenomenon of inhibition by sulfur of the process of formation of polymer radicals.

The polymer radicals containing sulfur that are formed by reactions (1) and (2) may be stabilized through the formation of terminal ring groups, which also leads to a decrease in the effect of formation of cross-links. Sulfur biradicals $S_x\cdot$, apparently, take part in structuring events by interacting with double bonds of molecular chains. This interaction, however, may also lead to the formation of intramolecular ring structures, which do not increase the number of cross-links. As already noted, sulfur structures formed in the initial stages of irradiation (at a dose up to 10 Mr) are 70% capable of isotopic exchange with elemental sulfur labeled with S^{35}; further irradiation decreases the exchange capacity to 40% (at a dose of 50 Mr). Such a high degree of isotopic exchange indicates the presence in the vulcanizates studied—

in vulcanizates of polysulfide linear structures S_x, where $x > 1$. As we have shown earlier (1), the presence of these polysulfide structures substantially increases the static strength of radiation vulcanizates.

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Note: Figure translations are in progress. See original paper for figures.