ON THE INTERACTION OF CARBON BLACK WITH SULFUR IN THE PROCESS OF RUBBER VULCANIZATION

1957

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

G. A. BLOKH and A. G. YAROSHEVICH

ON THE INTERACTION OF CARBON BLACK WITH SULFUR IN THE PROCESS OF RUBBER VULCANIZATION

(Presented by Academician P. A. Rehbinder, 3 IV 1957)

Until recently, the mechanism by which carbon black reinforces rubber was explained from a physical point of view. According to the work of P. A. Rehbinder and his co-workers ([1]), the measure of the mutual bonding between filler and rubber is taken to be the decrease in the free energy of the system upon wetting 1 cm^2 of the surface of filler particles with rubber. Rubber adsorptively bound to the surface of carbon-black particles and forming around them a stretched film of high strength ([2]) is "bound," or film, rubber. On the surface of fillers, when adsorptively bound rubber is present, according to Kobeko ([3]) a phenomenon resembling the "crystallization" of rubber occurs, which leads to an increase in the intermolecular interaction of the rubber chains and to strengthening of the rubber. According to Kusov ([4]), at the optimum filling of rubber with carbon black, the rubber mixture is a continuous mass—a molecular spatial network, at the nodes of which the carbon-black particles are located.

Recent studies of the structure and composition of carbon blacks ([5-7]) make it possible to interpret the mechanism of rubber reinforcement by carbon blacks also from chemical standpoints. It has been established ([6]) that the structure of carbon black contains oxygen-containing active groups: —OOH, OH, COOH, C=O. The presence of C=C bonds is noted, the latter being especially characteristic of the structure of furnace blacks obtained in an atmosphere poor in oxygen. The possibility that carbon black participates in the chemical reactions of vulcanization is also indicated by the unsaturated character of carbon blacks that add bromine. It is noted ([8]) that the reactivity of carbon blacks, determined by the content of oxygen groups (for example, quinone groups) on the surface of its particles, changes greatly under the influence of heat treatment. Complete removal of these groups by calcining carbon black at 800° makes the carbon black chemically inert, and mixtures of rubber with such carbon black do not change upon heating. It has been established ([9]) that paraquinone dioxime, paranitrosodiphenylamine, hexachlorocyclopentadiene, and others are promoters of the reaction of rubber with carbon black, causing the formation of radicals of rubber molecules, which react with the active centers of the surface of carbon-black particles with the formation of valence bonds. It seems highly probable that, in the vulcanization process, a chemical interaction of carbon blacks with

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

accelerator-vulcanizing substances takes place. In our earlier published works ([10], [11]), some experimental data are presented showing that interaction of carbon black with sulfur is indeed observed in the process of rubber vulcanization. The method of radioactive isotopes opens broad possibilities for studying this problem, which is important for rubber technology.

In the present communication, kinetic data are given on the interaction of carbon blacks (gas black, lampblack) with sulfur and accelerators. The investigation of this question was carried out by studying: (a) the interaction of radioactive sulfur with carbon black under the temperature conditions of vulcanization, (b) the adsorption of rubber molecules from a benzene solution by the surface of carbon-black particles subjected-

···in mixtures with sulfur and accelerators after various heat treatments; (c) the influence of preliminary heating of the carbon black–sulfur–accelerator mixture on the physicomechanical properties of rubbers based on various synthetic rubbers.

Experimental Part

Kinetics of the binding of radioactive sulfur with gas black and lamp black. We investigated a carbon black-sulfur mixture in which the contents of carbon black and sulfur S^{35} were in the ratio $100 : 3$. Three series of experiments were carried out.

Fig. 1. Kinetics of extraction of radiosulfur as a function of the heating time of the carbon black-sulfur mixture at 150°: **A**–gas black, **B**–lamp black.

I series. Accurate weighed portions of carbon black (gas black, lamp black) were uniformly mixed with an accurate weighed portion of radioactive sulfur and subsequently heated for 1, 3, 5, 8, and 10 hours at 145°.

II series. Accurate weighed portions of radioactive sulfur, before mixing with carbon black, were heated at 145° for 1-10 hours, after which they were mixed with the carbon black.

III series. Accurate weighed portions of carbon black and radioactive sulfur were mixed and were not subjected to heating.

Fig. 2. Kinetics of sulfur binding with carbon black: **1**–gas black and sulfur heated together at 150°; **2**–sulfur heated at 150° and mixed with gas black; **3**

–lamp black and sulfur heated together at 150°; **4**–sulfur heated at 150° and mixed with lamp black; **5**–gas black and sulfur without heating.

Subsequently, from each series, weighed portions of carbon black mixed with sulfur were taken to determine the initial radioactivity. After this, the above-mentioned mixtures of carbon black with sulfur S^{35}, subjected to various heat treatments, were exposed to continuous cold extraction with benzene for 600 hours in order to remove free radiosulfur. At strictly defined extraction intervals, carbon black samples were taken and re-examined for residual radioactivity. The arrangement of experiments in series II and III made it possible to elucidate the quantitative aspect of the adsorption binding of sulfur with carbon black. Comparison of the residual radioactivity of series I experiments with the radioactivity of series II and III made it possible to establish the actual picture of the chemical binding of sulfur with carbon black. The kinetic data on the binding of sulfur with gas black and lamp black are given···

are given below. Analysis of the curves in Figs. 1 and 2 makes it possible to establish with complete clarity that, in the process of heating carbon black with sulfur, chemical interaction takes place between them. Even after 600 hours' extraction of the sulfur with benzene, it was not possible to remove all the sulfur from its mixture with carbon black. Gas black is chemically bound with sulfur to a considerably greater degree than lampblack. Our data, obtained with the aid of radioactive sulfur, are in close agreement with the data of Studebaker (ˆ12), who indicates that when 1 part sulfur was heated with 9 parts carbon black for 18 hours at 150°, 0.64% sulfur became chemically bound with the carbon black.

Adsorption of rubber molecules by carbon black-sulfur complexes. It seemed of interest to determine to what extent preliminary heating of carbon black alone and of carbon black in a mixture with accelerator-vulcanizing substances, placed in a benzene solution of rubber, would change the adsorption of rubber molecules by the surface of carbon black particles. Adsorption of rubber molecules by carbon black will lead to a change in the viscosity of the rubber solution, which may serve as an indication of a change in the adsorption activity of the carbon black with respect to rubber in connection with the interaction of the carbon black with the accelerator-vulcanizing group and the formation on the surface of the carbon-black particles of new carbon black–sulfur complexes. In setting up the experiments we somewhat modified the procedure developed by Yurzhenko (ˆ13). Into flasks containing 60 ml of a 0.1% solution of divinyl-styrene rubber were placed: a) 2-g portions of carbon black subjected to heating at 145°; b) 2-g portions of carbon black in a mixture with 0.1 g sulfur, subjected to heating at 145°; c) 2-g portions of carbon black in a mixture with 0.1 g sulfur and 0.03 g mercaptobenzothiazole, subjected to heating at 145° for from 1 to 3 hours. The relative viscosity of the initial 0.1% solution of SKS-30 rubber was determined beforehand. Depending on the time for which the carbon blacks and carbon black–sulfur mixtures remain in the rubber solution, adsorption of rubber molecules from the solution occurs on the surface of the carbon-black

Fig. 3. Kinetics of the change in viscosity of an SKS-30 solution in benzene as a function of the composition of the adsorbent and the nature of its treatment: 1 —carbon black—sulfur—captax, 2 —carbon black—sulfur, 3 —carbon black; a — heating at 150° for 3 hours, b —without heating.

Figure 3: Fig. 3. Kinetics of the change in viscosity of an SKS-30 solution in benzene as a function of the composition of the adsorbent and the nature of its treatment: 1 —carbon black—sulfur—captax, 2 —carbon black—sulfur, 3 —carbon black; a —heating at 150° for 3 hours, b —without heating.

Figure 4

Figure 4: Figure 4

particles, which entails a change in the viscosity of the solution. Separation of the carbon black from the rubber solution was achieved by centrifugation. The kinetic data are shown in Fig. 3.

From the curves it is evident that heat treatment of carbon black at 145° for from 1 to 3 hours increases the adsorption of rubber molecules by the surface of the carbon-black particles, which is manifested in a change in the viscosity of the rubber solution. The picture changes in the case of adsorption of rubber molecules by carbon black-sulfur complexes. In the case of preliminary heating of carbon black with sulfur and accelerator for 3 hours, the adsorption of rubber molecules on the surface of the carbon-black particles decreases, which leads to an exceedingly small change in the relative viscosity of the rubber solution. This is explained, apparently, by the formation of new carbon black-sulfur compounds or polysulfide compounds formed on the surface of the carbon blacks as a result of the interaction of the carbon black with the accelerator-vulcanizing group, which leads to a decrease in the adsorption of rubber molecules on the surface of the carbon-black particles.

Fig. 3. Kinetics of the change in viscosity of an SKS-30 solution in benzene as a function of the composition of the adsorbent and the nature of its treatment: *1* —carbon black—sulfur—captax, *2* —carbon black—sulfur, *3* —carbon black; *a* — heating at 150° for 3 hours, *b* —without heating.

The effect of preliminary heating of carbon black with accelerative-vulcanizing substances on the tensile strength of rubbers. Various mixtures based on natural and synthetic rubbers were investigated; they were prepared in such a way that mixtures of carbon black with sulfur and accelerators, previously subjected to heat treatment at 100 and 150° for various lengths of time, were introduced into the formulations of the mixtures on the rolls. It was established (10, 11) that preliminary heating of carbon black with sulfur and accelerators promotes an increase in the strength of rubbers. This is of fundamental importance for restructuring the technological process of preparing rubber compounds (see Fig. 4).

Fig. 4. Effect of preliminary heating of carbon black–sulfur–accelerators on the tensile strength of rubber based on SKB: 1 –carbon black–sulfur–captax–DPG, 2 –carbon black–sulfur–captax, 3 –carbon black–sulfur–thiuram; *a* – heating at 130° for 120 min., *b* –without heating

We believe that the reactions of interaction between vulcanizing and accelerating substances, with the formation of intermediate polysulfide compounds, take place on the enormous surface of carbon-black particles. The active modifications of sulfur that arise are bound not only adsorptively but also chemically to the active oxygen-hydrogen centers of the carbon-microcrystalline structure of carbon black and to the molecular structure of the film-like, stretched, oriented surface of the rubber particles. The structural node that arises in this process is formed not only by rubber and sulfur, but also by carbon black, which is chemically bound both to the rubber and to the sulfur.

Dnepropetrovsk Chemical-Technological
Institute named after F. E. Dzerzhinsky

Received
12 VII 1956

CITED LITERATURE

1. P. A. Rehbinder, B. V. Margaritov, *Kauchuk i rezina*, **4** (1938); P. A. Rehbinder, G. A. Ab, S. Ya. Veiler, *DAN*, **33**, 444 (1941); A. S. Kolbanovskaya, P. A. Rehbinder, O. I. Luk' yanova, *Koll. zhurn.*, **12**, No. 3, 208 (1950).

2. A. A. Trapeznikov, *DAN*, **22**, No. 2 (1939).

3. P. P. Kobeko, *Amorphous Substances*, Publishing House of the Academy of Sciences of the USSR, 1952.

4. A. B. Kusov, *Kauchuk i rezina*, **9** (1940).

5. V. V. Keltsev, P. A. Tesen, *Carbon Black*, Moscow, 1952.

6. A. M. Gessler, *Rub. Age*, **1**, 2 (1953); **4**, 561 (1954).

7. J. Landre, *Rev. Gen. Caoutchouc*, **30**, 9, 647 (1953).

8. C. Barton, *Rub. Chem. Techn.*, **28**, 1 (1955).

9. K. Doak, *Canad. J. Techn.*, **33**, 1 (1955).

10. G. A. Blokh, Session of the Academy of Sciences of the Ukrainian SSR on the Peaceful Use of Atomic Energy, Publishing House of the Academy

of Sciences of the Ukrainian SSR, 1956.

11. G. A. Blokh, *Khim. prom.*, **2**, 14 (1956).

12. M. L. Studebaker, *Rub. Age*, **77**, 1 (1955).

13. A. I. Yurzhenko, I. I. Maleev, *DAN*, **103**, 6 (1955).

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