Soviet-era science, translated into English

ON THE STRUCTURE AND REINFORCING ACTION OF COLLOIDAL SILICIC ACID AS A FILLER FOR SYNTHETIC RUBBER

1958

SovietRxiv

View the original and related papers at https://sovietrxiv.org/items/ru-195801.59753

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

Abstract

Full Text

PHYSICAL CHEMISTRY

B. DOGADKIN, K. PECHKOVSKAYA, and E. GOL' DMAN

ON THE STRUCTURE AND REINFORCING ACTION OF COLLOIDAL SILICIC ACID AS A FILLER FOR SYNTHETIC RUBBER

(Presented by Academician P. A. Rehbinder, 25 XII 1957)

Numerous studies have been devoted to the question of the interaction of rubber with a filler. Nevertheless, many essential aspects of this process still remain unclear. In particular, the influence of the structure of the filler and of the nature of its distribution on the reinforcing effect has been little studied.

It was shown (1) that active carbon blacks capable of reinforcing rubber form thixotropic structures in which, to one degree or another, contact is established between carbon-black particles (network structures). Non-reinforcing carbon blacks form systems in which there is a relatively uniform distribution of the carbon black in the form of primary or secondary particles in the rubber medium. Thus, there is a mutual relationship between the nature of the distribution of carbon black and the effect of reinforcement.

Table 1

Characteristics of filler samples	Tensile strength, kg/cm^2	Relative elongation, %	Residual elongation, %	Tear resistance, kg/cm
Active	115.7	527	34.6	43.3
Of medium activity	69.0	452	37.0	34.0
Inactive	39.4	300	16.0	27.0

The purpose of the present investigation was to study the nature of the distribution in sodium-butadiene rubber of colloidal silicic acid as a representative of a new class of reinforcing agents that have recently acquired great practical importance.

The choice of the object of study in this case was also determined by the fact that, from the same raw material and by the same method, varying only the conditions of the technological process, it is possible to obtain samples of colloidal silicic acid that differ substantially in reinforcing effect. Hence arises the possibility of

Figure 1 and Figure 2: graphs

Figure 1: Figure 1 and Figure 2: graphs

comparing active and inactive fillers that are considerably more closely related to one another than all previously studied samples of carbon blacks.

To carry out the investigation, a series of samples of colloidal silicic acid was prepared that possessed high, medium, and low reinforcing action in rubbers based on sodium-butadiene rubber (Table 1). The chemical composition of these samples was practically identical. They also differed only slightly in specific surface area, pH, and a number of adsorption characteristics (adsorption of toluene, stearic acid, rubber) (Table 2).

However, rubber compounds prepared on the basis of sodium-butadiene rubber and containing the samples studied proved to be substantially different both with respect to the structure of the compound and to the physicomechanical properties of the vulcanizates.

To study the structure of the compound, easy solubili-

···of colloidal silicic acid in a dilute solution of caustic soda, in contrast to rubber, which does not dissolve in it. By boiling the mixture with such a solution, we then measured the amount of filler that had passed into solution. It turned out that the more active the colloidal silicic acid, the faster and more completely it could be extracted from the mixture with rubber. By analogy with bentonite (^{2}) and carbon-black (^{3}) mixtures, it may be assumed that particles of the more active colloidal silicic acid possess the ability to form chain structures, whose presence allows the solvent to penetrate easily into the mixture, and the resulting silicate solution to be removed from it just as easily. In the absence of dissolution it is assumed that a more or less thick rubber interlayer between the isolated silicic-acid particles prevents diffusion of the solvent to the filler particles. It is important to note that, in terms of the degree of dissolution in an aqueous NaOH solution, the active and inactive samples are identical.

Table 2

Characteristics of filler samples	Specific surface, m^2/g	Adsorption of toluene, mmol/g	Adsorption of stearic acid, mmol/g	Adsorption of rubber, g/g	pH
Active	61.8	9.4	0.47	0.13	8.7
Of medium activity	–	8.8	–	–	8.4
Inactive	50.3	7.7	0.56	0.108	10.0

SovietRxiv

Fig. 1. Relationship between filling and the leachability coefficient of active and inactive silicic acid from three-component mixtures containing inactive (1) and active (2) silicic acid.

Fig. 2. Relationship between the leachability coefficient and the physicomechanical properties of vulcanizates. 1 —tensile strength, 2 —relative elongation, 3 —residual elongation, 4 —tear resistance.

To characterize the degree of structuring of the filler in the mixture, a "leachability coefficient" was used, characterizing the fraction of filler passing into the alkaline solution from its total content in the mixture.

Figure 1 shows the dependence of the leachability coefficient on the degree of filling for samples of colloidal silicic acid with the greatest reinforcing ability (active sample) and with the least reinforcing ability (inactive sample). As can be seen, active silicic acid is completely leached at such degrees of filling (about 35 volumes per 100 parts by weight of rubber) at which the inactive sample, under the same conditions, practically does not dissolve. This confirms the difference in the nature of the distribution of the two investigated silicic-acid samples in sodium-butadiene rubber.

It is interesting to note that, after removal of the active silicic acid by leaching, the remaining specimen of the raw rubber compound proves to be just as insoluble in an organic solvent as before leaching. The fact that the active specimen is leached out of the compound considerably more easily than the inactive one cannot be explained by the formation of different amounts of rubber–filler gel, since one would then have to assume that the active specimen binds rubber to a lesser extent than the inactive one, which contradicts existing ideas on the interaction of rubber with filler.

Table 3

Calcination temperature, °C	L. p. p., %	Leaching coefficient after 10 h, %	Tensile strength, kg/cm^2	Relative elongation, %	Permanent elongation, %	Tear resistance, kg/cm
–	–	100	111.5	448	30.8	39.3
400	10.5	91.0	115.6	626	54.0	50.9
600	12.4	12.5	52.8	494	17.0	17.7

It seems to us that the data obtained, as well as the results of earlier work (1, 4, 5), indicate that in the structure of the insoluble rubber–filler gel, alongside bonds between rubber and filler (6, 7), cross-links between the polymer molecules themselves are of substantial importance.

A study of the physicomechanical properties of vulcanizates containing the investigated specimens of colloidal silicic acid showed that the higher the coefficient of

SovietRxiv

Fig. 3. Dissolution kinetics of technical-grade silicic acid: 1—active, 2—inactive

Figure 2: Fig. 3. Dissolution kinetics of technical-grade silicic acid: 1—active, 2—inactive

leaching of the filler from a given system, the higher the strength characteristics of the vulcanizate. These data are shown in Fig. 2.

All the tested specimens may be divided, according to degree of activity, into three groups: a) inactive specimens, for which the leaching coefficient is less than 25%; b) specimens of medium activity, for which the leaching coefficient is 40–50%; and c) active specimens, for which the leaching coefficient reaches 70–100%. The considerable majority of the specimens investigated are arranged in the same order with respect to the physicomechanical indices of the corresponding vulcanizates.

A substantial decrease in the activity of a specimen of colloidal silicic acid can be achieved by heating it at a temperature of 600°. These results are shown in Table 3.

The comparatively low temperature at which the observed changes occur indicates a certain instability of the crystal lattice of silicic acid, probably associated with the conditions of precipitation. At 600°, recrystallization evidently occurs, as a result of which the elementary crystallites constituting its particle pass into another, more stable crystalline form; this transition is accompanied by a loss of the activity of the material as a rubber-reinforcing agent.

The unstable state of the crystal lattice of the active specimen should be reflected in a number of properties of the material, in particular in its behavior toward solvents. For this purpose we investigated the dissolution kinetics of technical-grade (active and inactive) and dialyzed (active and inactive) colloidal silicic acid in an aqueous solution of caustic soda at different temperatures.

As can be seen from Figs. 3 and 4, the technical-grade active specimen dissolves in 1% NaOH solution at all the temperatures investigated more slowly than the inactive one. Conversely, the active specimen purified by electrodialysis dissolves faster than the inactive specimen subjected to the same purification. Thus, impurities adsorbed on the surface of silicic acid retard, to a greater extent, the dissolution of the active modification than of the inactive one.

active. After removal of these impurities by electrodialysis, the dissolution of the active sample, as we had assumed, proceeds at a higher rate than the dissolution of the inactive one.

Fig. 3. Dissolution kinetics of technical-grade silicic acid:
1 —active, *2* —inactive

Fig. 4. Dissolution kinetics of dialyzed silicic acid:
1 —active, *2* —inactive

SovietRxiv

Fig. 4. Dissolution kinetics of dialyzed silicic acid: 1—active, 2—inactive

Figure 3: Fig. 4. Dissolution kinetics of dialyzed silicic acid: 1—active, 2—inactive

This difference in the dissolution rates of dialyzed products of identical chemical composition indicates a difference in the structure of the elementary cell, which is less stable in the case of the active sample. The latter may be associated with the presence of distortions or defects as a result of the capture of foreign atoms or ions during the precipitation of silicic acid from solutions.

Scientific Research Institute
of the Tire Industry

Received
12 XII 1957

REFERENCES CITED

1. B. Dogadkin, M. Feldshtein, *Kauchuk i rezina*, No. 12 (1939).
2. B. Dogadkin, K. Pechenkovskaya, L. Chernichkina, *Koll. zhurn.*, **8**, 1-2, 31 (1946).
3. B. Dogadkin, K. Pechenkovskaya, M. Dashevskii, *Koll. zhurn.*, **10**, 5, 357 (1958).
4. F. Menadue, *India-Rubb. J.*, **85**, 689 (1933).
5. F. Endter, *Kautschuk u. Gummi*, **5**, No. 2, 17 (1952).
6. S. Polinchak et al., *Rubb. Age*, **70**, 6, 754 (1952).
7. V. Garten, *Nature*, **173**, 997, No. 4412 (1954).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.