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Abstract

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On the Structure of the Network of Vulcanizates of Carboxyl-Containing Polymers

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At the present time it is well known that the principal physicomechanical properties of rubbers depend substantially on the molecular structure of the starting polymer. At the same time, it is beyond doubt that an equally important factor determining these properties is the structure of the vulcanization network—its density, regularity, the strength of the vulcanization bonds, etc.

Of particular interest from the standpoint of studying the structure of the vulcanization network are rubbers obtained on the basis of caoutchoucs whose macromolecules contain small amounts of functional groups, for example, carboxyl groups ([1]).

Vulcanization of such carboxyl-containing polymers with metal oxides leads to the formation of highly elastic rubbers with unusually high strength in unfilled mixtures at a high value of the modulus of elasticity, characterized, however, by considerable flow ([2]). The latter, however, is readily eliminated by introducing ordinary vulcanizing agents (thiuram and others) into the mixture.

Thus, differing extremely little from ordinary synthetic caoutchoucs in the molecular structure of the starting polymer, vulcanizates of carboxyl-containing caoutchoucs possess specific physicomechanical properties, evidently connected with the peculiarities of the structure of their vulcanization network.

We studied the structure of the vulcanization network of polymers of the indicated type by the method of determining the equilibrium swelling of vulcanizates in organic solvents. The use of this method is based on the statistical theory of three-dimensional polymers of Flory—Rehner ([3]), which relates the magnitude of the equilibrium swelling Q to the average value of the molecular weight of the chain segment enclosed between neighboring nodes of the network.

According to this theory,

$$M_c = -\frac{\rho V_1 v_2^{1/3}}{\mu v_2^2 + v_2 + \ln(1 - v_2)}, \tag{1}$$

where μ is a thermodynamic constant characterizing the interaction in the given

polymer–solvent system, v_2 is the volume fraction of polymer at equilibrium swelling, equal to $v_2 = \frac{1}{Q+1}$ (Q is the volume of solvent absorbed by unit volume of polymer), V_1 is the molar volume of the solvent, and ρ is the density of the polymer. (The value M_c, evidently, is inversely proportional to the number of cross-links in the vulcanizate.)

The method used by us in the presence of two types of vulcanization bonds—chemical bonds formed by thiuram, and "salt" bonds, formed—

carboxyl groups of the polymer with metal oxides—made it possible not only to determine separately the number of vulcanization junctions of both types, but also to draw definite conclusions concerning the nature of the "salt" bonds.

For this purpose, for each specimen the value of the equilibrium swelling in pure benzene and in benzene with a small (~1%) addition of glacial acetic acid was measured. The addition of acetic acid destroyed the "salt" bonds, as was proved by the complete solubility, in this case, of all specimens vulcanized only with metal oxides.

Table 1

Network density of vulcanizates obtained in the presence of various metal oxides (vulcanization for 240 min at 143°)

No.	Oxide	Amount of oxide, %	$M_c \cdot 10^{-3}$, total	$M_c \cdot 10^{-3}$, thiuram	$M_c \cdot 10^{-3}$, "salt"	Amount of thiuram reacted, % of that introduced	Amount of bound carboxyl groups, %
Hardness of initial rubber 425 g, methacrylic acid content 1.5%	Hardness of initial rubber 425 g, methacrylic acid content 1.5%	Hardness of initial rubber 425 g, methacrylic acid content 1.5%	Hardness of initial rubber 425 g, methacrylic acid content 1.5%	Hardness of initial rubber 425 g, methacrylic acid content 1.5%	Hardness of initial rubber 425 g, methacrylic acid content 1.5%	Hardness of initial rubber 425 g, methacrylic acid content 1.5%	Hardness of initial rubber 425 g, methacrylic acid content 1.5%
1	MgO	3	13.6	42	20	14.5	29.0
2	MgO	5	14.7	41	22	14.5	25.0
3	CaO	3	26.0	43	65	14.0	9.0
4	CaO	5	20.0	38	42	15.5	14.0

No.	Oxide	Amount of oxide, %	$M_c \cdot 10^{-3}$, total	$M_c \cdot 10^{-3}$, thiuram	$M_c \cdot 10^{-3}$, "salt"	Amount of thiuram reacted, % of that introduced	Amount of bound carboxyl groups, %
5	ZnO	10	15.3	21	53	28.0	11.0
Hardness of rubber 1825 g, methacrylic acid content 1.5%	Hardness of rubber 1825 g, methacrylic acid content 1.5%	Hardness of rubber 1825 g, methacrylic acid content 1.5%	Hardness of rubber 1825 g, methacrylic acid content 1.5%	Hardness of rubber 1825 g, methacrylic acid content 1.5%	Hardness of rubber 1825 g, methacrylic acid content 1.5%	Hardness of rubber 1825 g, methacrylic acid content 1.5%	Hardness of rubber 1825 g, methacrylic acid content 1.5%
6	MgO	3	9.6	25	16	24.5	37.0
7	MgO	5	10.0	25	18	24.0	33.0
8	CaO	3	16.5	21	75	28.0	8.0
9	CaO	5	13.0	21	35	28.0	17.0
10	ZnO	10	10.2	14	40	43.5	15.0
Hardness of rubber 900 g, methacrylic acid content 0.75%	Hardness of rubber 900 g, methacrylic acid content 0.75%	Hardness of rubber 900 g, methacrylic acid content 0.75%	Hardness of rubber 900 g, methacrylic acid content 0.75%	Hardness of rubber 900 g, methacrylic acid content 0.75%	Hardness of rubber 900 g, methacrylic acid content 0.75%	Hardness of rubber 900 g, methacrylic acid content 0.75%	Hardness of rubber 900 g, methacrylic acid content 0.75%
11	MgO	3	16.5	23	60	26.0	20.0
12	MgO	5	16.5	22	65	27.0	18.0
13	CaO	3	19.0	24	107	25.0	10.0
14	CaO	5	16.0	21	38	29.0	18.0

Thus, whereas the value of the equilibrium swelling in the pure solvent corresponds to the total number of vulcanization bonds (n), the value Q in the solvent with an addition of acetic acid characterizes the density only of the "thiuram" network (n_T), and, consequently, the number of "salt" junctions is equal to the difference $n - n_T$.

By the indicated method, the structure of a series of vulcanizates of divinyl-

Fig. 1

Figure 1: Fig. 1

styrene carboxyl-containing rubbers (with a methacrylic acid content of 0.75 and 1.5%), vulcanized in the presence of 2% thiuram and various amounts of oxides of Mg, Ca, and Zn, was investigated.

It was established that the density and structure of the network depend substantially on the nature of the oxide. Thus, the amount of "salt" bonds is greatest for vulcanizates obtained in the presence of MgO, and smallest with ZnO; moreover, only 8 to 40% of the carboxyl groups contained in the polymer take part in the reaction forming vulcanization bonds* (see Table 1).

* It should be noted that, in vulcanization with Mg and Ca oxides, 1% Zn oxide was additionally introduced into the mixture, promoting the reaction of formation of "thiuram" bonds. This circumstance does not introduce any significant error into the calculation, owing to the comparatively small activity of ZnO, noted above, in the formation of "salt" bonds ($M_c \simeq 50000$ at 10% ZnO).

The specific form of the swelling curves is noteworthy. Whereas for samples obtained in the presence of Zn oxide (see Fig. 1) the swelling curves reach saturation (as for most ordinary vulcanizates) after approximately 5 hours, for the magnesium and calcium samples to reach equilibrium in benzene (see Fig. 2) no less than a day is required; moreover, after a period of rapid swelling, a prolonged (about 15 h) approximately linear increase in the weight of the samples is observed. This phenomenon was not observed when the same samples were swollen in benzene with the addition of acetic acid.

Fig. 1. Swelling curves of samples vulcanized in the presence of 2% thiuram and 10% ZnO. 1 —in benzene, 2 —in benzene with the addition of acetic acid

The indicated circumstance made it possible to suppose that, in the case of samples vulcanized in the presence of MgO and CaO, there occurs a gradual decrease in the number of transverse "salt" bonds, which are broken in the course of swelling.

In the presence of such bonds, the values of M_c calculated from the limiting swelling values correspond to a state of dynamic equilibrium between bonds being broken and newly forming bonds, which should change when the swelling temperature is changed*. Thus, the supposition expressed above could be tested by studying the temperature dependence of swelling. The corresponding data are given in Fig. 3, from which it follows that, when the swelling temperature is raised to 65°, the value of M_c of the magnesium sample increases noticeably. Consequently, carboxyl-containing polymers vulcanized with the aid of magnesium oxide are undoubtedly characterized by the presence of the aforementioned weak bonds. Calculation of the bond energy E, carried out for these vulcanizates according to the Arrhenius equation, gives values of 1000–2000 cal/mole,

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

i.e., values on the order of intermolecular forces.

Fig. 2. Swelling curves of samples vulcanized in the presence of 2% thiuram and 5% MgO. 1 —in benzene, 2 —in benzene with the addition of acetic acid

Fig. 3. Temperature dependence of swelling in benzene of a sample vulcanized in the presence of 10% MgO

It is characteristic that a further increase in the temperature of the solvent—swelling in chlorobenzene and xylene at 125-130°—leads to complete dissolution of the above-mentioned vulcanizates, which under ordinary conditions possess high physicomechanical properties. It should be noted that the given values of E correspond to the energy of bonds in a stressed swollen network, weakened by forces of interaction with the solvent and by the stress of the network. The latter can be approximately estimated by differentiating the expression for the elastic component of the entropy of swelling.

* An increase in the swelling temperature in the case of a stable vulcanization network should lead to a certain decrease in the swelling limit, caused by a decrease in the molar volume in accordance with equation (1). The value μ, for μ close to 0.3, depends little on temperature.

The calculation leads to values on the order of 10^{-6} dyn per bond, or $5 \cdot 10^6$ dyn/cm^2 at $Q \approx 10$, i.e., values an order of magnitude smaller than the strength of bonds due to dispersion forces.

It follows from the above that the vulcanization of carboxyl-containing polymers by metal oxides is evidently, in practice, not associated with the formation of normal chemical bonds corresponding to the structure of the neutral magnesium, calcium, and zinc salts of high-molecular-weight acids.

More probable is the hypothesis first advanced by V. A. Kargin that the emergence of a "salt" network occurs through the formation of compounds of the basic-salt type, which, owing to their poor solubility in the polymer, either form crystalline agglomerates or remain bound to the large oxide particles distributed in the polymer.

In this case, the strength of the vulcanization bonds should depend on the solubility of these salts in the polymer, namely, it should decrease as solubility increases.

Taking as compounds modeling the high-molecular-weight-salt—polymer system

the oleates of magnesium, calcium, and zinc and, accordingly, isooctane, we established that the solubility of the indicated salts decreases substantially in the series Mg > Ca > Zn (from 10.8 to 0.7 wt. %). This fact confirms the point of view presented here concerning the nature of the crosslinks formed during vulcanization of carboxyl-containing polymers by metal oxides, which apparently play the role of a kind of "active filler."

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REFERENCES

1. B. A. Dolgoplosk, E. I. Tinyakova et al., *Kauchuk i rezina*, No. 3, 11 (1957).
2. B. A. Dolgoplosk, V. N. Reikh et al., *Kauchuk i rezina*, No. 6, 1 (1957).
3. P. I. Flory, J. Rehner, *J. Chem. Phys.* **11**, 512, 521 (1943).

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