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Abstract

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On the Nature and Strength of Cross-Links in Radiation Vulcanizates of Polysiloxane Rubbers

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In studying the radiation vulcanization of polydimethylsiloxane rubber (SKT), we, together with other authors, showed the possibility of obtaining rubbers with increased heat resistance ([1]). Later we established that still more heat-resistant vulcanizates can be obtained by radiation vulcanization of polymethylvinylsiloxane rubber (SKTV), containing about 0.1% vinyl groups ([2]). At the same time it was found that the heat resistance of radiation vulcanizates of polysiloxane rubbers can be substantially increased by preliminary introduction into rubber mixtures containing various types of "white carbon black" (silicon dioxide) of additives of metal compounds of variable valence. As follows from the data given in Table 1, the vulcanizates mentioned above substantially surpass ordinary peroxide vulcanizates in heat resistance.

Table 1

Physico-mechanical indices of γ-vulcanizates of SKT and SKTV rubbers after aging at high temperatures

Aging conditions	SKT, specimen No. 1 Dose 14.5 Mr*a*	SKT, specimen No. 1 Dose 14.5 Mr*b*	SKT, specimen No. 1 Dose 14.5 Mr*c*	SKTV, specimen No. 1 Dose 7.4-10.2 Mr*a*	SKTV, specimen No. 1 Dose 7.4-10.2 Mr*b*	SKTV, specimen No. 1 Dose 7.4-10.2 Mr*c*	SKTV, specimen No. 2 Dose 7.4-10.2 Mr*a*	SKTV, specimen No. 2 Dose 7.4-10.2 Mr*b*	SKTV, specimen No. 2 Dose 7.4-10.2 Mr*c*
Initial	41	195	0	51	340	8	44	550	5
300° 10 days	35	160	0	42	320	2	38	360	7
300° 30 days	38	80	2	29	210	0	36	150	8
300° 40 days	26	75	4	–	–	–	37	110	6

Aging conditions	SKT, specimen No. 1 Dose 14.5 Mr*a*	SKT, specimen No. 1 Dose 14.5 Mr*b*	SKT, specimen No. 1 Dose 14.5 Mr*c*	SKTV, specimen No. 1 Dose 7.4–10.2 Mr*a*	SKTV, specimen No. 1 Dose 7.4–10.2 Mr*b*	SKTV, specimen No. 1 Dose 7.4–10.2 Mr*c*	SKTV, specimen No. 2 Dose 7.4–10.2 Mr*a*	SKTV, specimen No. 2 Dose 7.4–10.2 Mr*b*	SKTV, specimen No. 2 Dose 7.4–10.2 Mr*c*
330° 3 days	39	135	2	47	340	0	35	270	12
330° 8 days	31	50	2	36	130	7	–	–	–
330° 10 days	–	–	–	30	70	26	–	–	–
350° 8 h	26	100	2	25	200	14	–	–	–
350° 12 h	22	50	0	25	80	4	27	195	15
350° 24 h	–	–	–	–	–	–	29	110	0
370° 1–1.5 h	17	160	2	20	175	18	–	–	–
370° 2.5 h	–	–	–	16	100	12	15	260	24
380° 0.5 h	–	–	–	15	110	12	–	–	–
380° 1 h	–	–	–	26	50	3	11	60	0

Note. In Tables 1, 2, and 3: *a*–tensile strength in kg/cm^2, *b*–relative elongation in percent, *c*–residual elongation in percent.

This difference in heat resistance is so great that it naturally cannot be explained only by the presence of catalyst residues in the rubbers during peroxide vulcanization, but is connected with the structural features of the vulcanization network of radiation vulcanizates.

At present, apparently, it should be regarded as established that, in contrast to

peroxide vulcanizates of polydimethylsiloxanes, for which the presence mainly of cross-links is characteristic ···

$$> \mathrm{Si} - \mathrm{CH_2} - \mathrm{Si} < \quad \text{and} \quad > \mathrm{Si} - \mathrm{Si} <,$$

the principal type of crosslinks in radiation vulcanizates is

$$> \mathrm{Si} - \mathrm{CH_2} - \mathrm{CH_2} - \mathrm{Si} <,$$

formed through recombination of free radicals

$$> \mathrm{Si} - \mathrm{CH_2}\cdot.$$

This difference contributes to an increase in the heat resistance of radiation vulcanizates both because of the greater strength of the C–C bond in comparison with Si–C and Si–Si (62.8, 57.6, and 42.5 kcal, respectively), and because of the possibility that, in rubbers at high temperatures, a certain number of double bonds are formed according to the reaction:

$$> \mathrm{Si} - \mathrm{CH_2} - \mathrm{CH_2} - \mathrm{Si} < \leftrightarrow > \mathrm{Si} - \mathrm{CH} = \mathrm{CH} - \mathrm{Si} <,$$

which does not lead to rupture of the crosslink and prevents destruction of radiation vulcanizates at high temperatures.

During vulcanization of SKTV rubber under the action of radiation, the formation of a certain number of bonds

$$> \mathrm{Si} - \mathrm{CH_2} - \mathrm{CH_2} - \mathrm{CH_2} - \mathrm{Si} <$$

is possible, according to the reaction:

$$> \mathrm{Si}{-}\mathrm{CH} = \mathrm{CH_2} + \cdot\mathrm{CH_2}{-}\mathrm{Si} < \rightarrow > \mathrm{Si}{-}\dot{\mathrm{C}}\mathrm{H}{-}\mathrm{CH_2}{-}\mathrm{CH_2}{-}\mathrm{Si} < \xrightarrow{+\mathrm{H}\cdot} > \mathrm{Si}{-}\mathrm{CH_2}{-}\mathrm{CH_2}{-}\mathrm{CH_2}{-}\mathrm{Si} < .$$

Therefore, for the indicated vulcanizates, formation of a double bond according to the scheme given above is more probable than, apparently, and accounts for the greater heat resistance of radiation vulcanizates of SKTV.

It is interesting to note that the presence in peroxide vulcanizates of SKTV of a known amount of bonds

$$> \mathrm{Si} - \mathrm{CH_2} - \mathrm{CH_2} - \mathrm{Si} < \quad \text{and} \quad > \mathrm{Si} - \mathrm{CH_2} - \mathrm{CH_2} - \mathrm{CH_2} - \mathrm{Si} <$$

accounts for their higher heat resistance in comparison with the corresponding vulcanizates of SKT rubber.

Under certain conditions, the radiation-chemical method can achieve the production of vulcanizates possessing a more regular structure of the vulcanization network than peroxide vulcanizates. This, in particular, explains the possibility noted above of obtaining highly heat-resistant vulcanizates based on polysiloxanes: the introduction of additions of compounds of metals of variable valence, which can serve as centers of secondary electron radiation, promotes the formation of vulcanizate networks with a smaller number of defects and, correspondingly, the production of more highly heat-resistant rubbers. Therefore the radiation vulcanizates of polysiloxanes obtained by us also possess higher temperature resistance (see Table 2).

Table 2

Strength properties of γ- and peroxide vulcanizates of SKT at various temperatures

Specimen	At 150°: a	At 150°: b	At 150°: c	At 200°: a	At 200°: b	At 200°: c
Standard peroxide	12	195	0	10	140	0
No. 1	26	165	0	18	130	0
No. 3	41	215	0	23	200	0
No. 4	48	130	0	—	—	—

The data of the present investigation show the possibility of obtaining especially highly heat-resistant vulcanizates based on polysiloxane rubbers and make it possible to conclude that the actual strength of the Si—C bond in such vulcanizates is considerably higher than should be expected on the basis of the bond-dissociation energy data for this bond (57.6 kcal).

This circumstance is evidently connected with the high intermolecular interaction both within the polymer itself and between the polymer and the filler, which increases substantially as a result of exposure to radiation.

It was natural to assume the possibility of further increasing the actual bond strength in the vulcanization network of polysiloxanes and, accordingly, the heat resistance by introducing into the rubber compounds substances that promote the formation of new strong crosslinks, or "grafted" chains, which increase intermolecular interaction. Indeed, the introduction of halogenated polymers into rubber compounds leads to a further increase in the heat resistance of polysiloxanes. The corresponding data are given in Table 3.

Table 3

Resistance to thermal aging of γ-vulcanizates of SKTV rubber containing "white carbon black" and additions of a halogenated polymer at 330°
(irradiation in vacuum, dose 5.6 Mr)

Halogenated polymer	Initial	Initial	Initial	Thermal aging, 6 days	Thermal aging, 6 days	Thermal aging, 6 days	Thermal aging, 10 days	Thermal aging, 10 days	Thermal aging, 10 days	Thermal aging, 12 days	Thermal aging, 12 days	Thermal aging, 12 days
	a	b	c	a	b	c	a	b	c	a	b	c
20	40	190	2	41	170	2	36	160	2	—	—	—
35	68	180	4	67	130	6	54	130	5	67	65	4

Similar results were obtained when radiation vulcanization was carried out in vacuum, i.e., under conditions preventing the formation of weak crosslinks involving oxygen of the type

$$-\underset{|}{C}-O-O-\underset{|}{C}-$$

The results presented thus made it possible to determine the nature of the influence of the character of the crosslinks, their true strength, and the regularity of the structure of the vulcanization network on the heat resistance of vulcanizates based on polysiloxane rubbers.

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