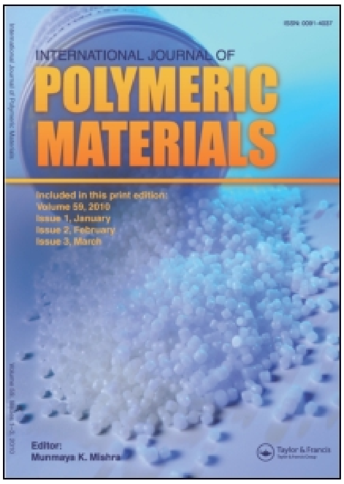

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The Effect of Technological Factors on Electric Conductivity of Filled Silicon Elastomers

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There is effect of some technological factors (kind and content of fillers, olygomer additions, vulcanization method) on the technical characteristics of filled silicon rubbers on the polydimethylvinylsiloxan (SKTN) base investigate. It is established that these factors essentially influence the microstructure of composites and connected with its conductive network. It has been shown that the higher indexes belongs composites which are produced by the method of filling polymerization and especially with using alteration by various siliconorganic components of thermally splitted graphite. The density of vulcanization network is estimated by the application of sol-analysis method, while NMR method is applied for a estimation of macromolecules in the composites and sensitivity of materials to external deformation.

Silicon elastomers have many unique properties due to chemical binds Si—O and Si—C.[1] These elastomers have high elastic state at temperatures $-90 \div 300°C$, high insulation properties, resist to influence of crown discharges. The silicon elastomers—the best insulators with specific volume conductivity about 10^{-15} $(\text{Okm}\cdot\text{m})^{-1}$, but after the introduction of some types of carbon black, graphite and metallic powders they become a conductor with conductivity like semiconductors.[2] The conductivity of these materials depends on fillers content and some technological conditions. The filled with carbon black silicon elastomers after vulcanization acquire good mechanical properties. A choice of fillers they must pay attention to surface structure and the sizes of powder particles. A good result is achieved at utilization of fine-grained carbon materials, which size is some micrometers with specific surface about $10^3\ \text{m}^2\cdot\text{g}^{-1}$.

During the last ten years we carry out investigations by technology and physical and chemical properties of conductive silicon rubbers, filled by another low-molecular elastomers and carbon black.

The conductive rubbers we have obtained on the base of polydimethylmethilvinilsiloxan SKTV (molecular weight 500000). In some composition we have introduced the silicon low-molecular (olygomer) substances (molecular weight 25000).

The obtain of materials we carried out mainly by peroxid vulcanization[3] and by utilization cure agent diethylaminomethilthreeetoxysilan ADE-3.[1] Sometimes the rubbers we obtained by method of polymerization filling.[4]

The vulcanization of SKTV with cure agent ADE-2 we carried out at room temperature by the following reaction:

$$3H\text{—}(O\text{—}Si(CH_3)_2\text{—})_n\text{—}(O\text{—}Si(CH_3)(CH{=}CH_2)\text{—})_m\text{—}OH$$

$$+\ (C_2H_5)_2NCH_2Si(OC_2H_5)_3 \rightarrow (C_2H_5)_2NCH_2Si\text{—}X_3 + 3C_2H_5OH$$

where

$$X = (O\text{—}Si(CH_3)_2\text{—})_n\text{—}(O\text{—}Si(CH_3)(CH{=}CH_2)\text{—})_m\text{—}OH$$

We carried out the vulcanization by analogical reaction using initiator

$$(C_4HgO)_3Ti\text{—}O\text{—}Ti(C_4HgO)_3{:}6H\text{—}X$$

$$+\ (C_4HgO)_3Ti\text{—}O\text{—}Ti(C_4HgO)_3X_3Ti\text{—}O\text{—}TiX_3 + 6C_4HgOH.$$

where

$$X = (\text{—}O\text{—}Si(CH_3)_2\text{—})_n\text{—}(\text{—}O\text{—}Si(CH{=}CH_2)_m\text{—}OH$$

Production technology of filled conductive rubbers (CFSR) with use of diethilaminomethilthreeetoxysilon (ADE-3) includes the following stages:

1. Preparing of rubber mixture;
2. Rolling at 15–25°C about 10–15 min;
3. Production of rubber plates with thickness of 1–3 mm and drying at room temperature and during 24 hours;
4. The thermical treatment of rubbers mixture at regime: 100°C during 2 hours, 150°C-4 h and 200°C-6 h.

Similar technology was used for production of CFSR by polymerization filling method. But in this case some polymerized on the chemical modified carbon black powder cycled siliconic monomers were used, as a start product. This method includes the following manipulation: in the retort with three throat, with a stirring rod and ventile for the regulation of argon current definite carbon black and metallic K with definite proportion were placed. After the intermixing at 100°C during 2 h with subsequent cooling till room temperature we have added some organcyclosiloxan and one of three dry monomer 1,3,5,7-tetramethil-1,3,5,7-tetramethilcyclotetrasiloxan, 1,3,5-three-methil-1,3,5, three fenilcyclothreesiloxan and hexamethilcyclothreesiloxan. The obtained mixture was intensively mixed at temperatures in a range of 70 ÷ 110°C during 2–6 hours. The time intervals and temperatures were due to the type of monomer. The composition had been treated by water or 0.1% water solution of acetic acid. The cure agent was introduced to this material and then it was subjected to the same procedures, as at low temperature vulcanization by use of ADE-3.

Some experiments were carried out by polymerization filling method, in which carbon black was placed by thermal splitted graphite (TSG).[5]

The production of CFSE by peroxid vulcanization method had been carried out by well-known standard.[3]

During the receipt of conductive rubber there was established a number of dependences between electrical specific volume resistance ρ_v and some technological factors, namely, ρ_v of rubber mixtures essentially depends on treatment time at rolling on type and content of filler as well as on content of related silicon olygomers.

It has been showed experimentally, that at low temperature vulcanization with the application of ADE-3 agent, ρ_v of rubber mixtures at first was increased and then during some time this increase was retarded. During more prolonged rolling of ρ_v mixture it is again increased.[6] The character of ρ_v dependence on rolling time may be explained in the following way.

There are some complicated physical and chemical processes taking place in rubber mixture among which the macromolecule crosslinking and destruction processes are basic. The vulcanization process taking place at this time, promotes the formation of the vulcanization network and subsequently the increase of internal tension in the rubber mixture. Therefore the probability of mechanical destruction of space crosslinking molecular structures growth with the increase of rolling time.

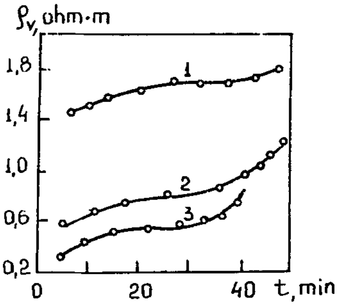

FIGURE 1 Relative ρ_v – T(T – rolling time) for rubber mixture based on SKTN and carbon black P267 at 40(1), 50(2) and 60 mass.part (3) content. Cure agent ADE-3.

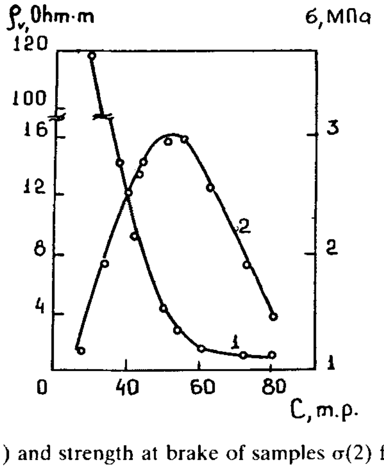

FIGURE 2 Dependence ρ_v(1) and strength at brake of samples σ(2) for CFSR on filler content.

TABLE I

Technical parameters of rubbers, obtained by different methods

Production method	Content of carbon black	Specific volume resistance Ohm.sm	Percolation threshold mass. part	Average divergence of aver. significance for film surface Im^2, %	Physico-mechanical		
					Tensile strength MPa	Relatively lengthening at tensile %	Residual lengthening at tensile %
Vulcanization by ADE-3	20	10^6		120	0.8	101	4.0
	30	26.10^4		98	1.7	246	5.5
	40	$1.1.10^3$	20	75	2.1	292	5.7
	50	245		45	3.0	360	7.9
	60	65		32	2.3	250	4.3
Peroxid vulcanization	40	$4.5.10^4$		360	3.3	386	16.0
	50	636	25	216	4.1	272	11.5
	60	118		92	4.2	266	8.8
polymerization filling	10†	1.32		0.9	2.1	150	0
	20†	0.13		0.6	2.6	230	0
	20	140	4	10.2	2.7	210	4.2
	30	12.5		1.4	6.1	315	4.9
	40	5.6		1.1	3.8	190	5.0
	50	0.9		0.8	2.3	150	3.6
	60	0.8		0.8	2.3	155	3.2

† In this case TSG was used as a filler.

This process leads to the increase of macroscopical defects in the matrix of rubber mixture. Apparently, these processes introduce corrections in the distribution of conductive filler particles. For example, because of the increase of a number of broken contacts between carbon black particles ρ_v of rubber mixture is increased. It should be noted that this process has been accelerated at the increase of filler contents (Figure 1).

The dependence of ρ_v of CFSR on filler content is in a good agreement with well known dependence for all conductive polymer composition (Figure 2). The choice of optimal carbon black concentration in the composition, as a rule, is limited by mechanical strength of material. Here the optimum corresponds to filler content, which provides the strength maximum (Figure 2).

With the purpose to reveal the role of the method of the influence on the properties of CFSR we have investigated the rubbers, which were synthesized with the application of vulcanizator ADE-3 by polymerization filling and peroxid vulcanization.

According to the data of Table I, the conditions of vulcanization essentially influences the conductive rubbers properties. Thus, ρ_v rubbers, consisting 40 mas.parts of carbon black, received by the application of ADE-3, is low by one order than ρ_v for analogous rubber, received by the application of peroxid vulcanization, but is higher about two orders than for rubbers received by polymerization filling. At comparatively high filling this difference becomes stronger. For example, ρ_v for the rubbers with 60 mass.part of filler produced by peroxid vulcanization and polymerization filling methods differs more than by 2 orders. Essentially the difference takes place for the significance of homogenity and the threshold of percolation (this is a minimal consistence of filler, which is corresponding to the insulator-conductor transition). Threshold of percolation for the rubbers consisting of TSG (0,7 mass.part of filler) is essentially lower than for another rubbers.

Vulcanization method has an effect on some mechanical properties of rubbers too. The rubbers which were produced by peroxid vulcanization consisting of 50 and 60 mass.p. and by polymerization filling consisting of 30 mass.p. of filler have high strength properties. The last materials have no residual extension.

The elucidation of reasons of these differences between properties of filled rubbers needs the application of some methods of structural analysis. It is known that the considerable influence on the physical properties of filled rubbers has on the one hand the structure of vulcanization set, namely, its density[7] and the on the other hand—interaction between the components of the composite.[8] With this purpose the structure parameters of vulcanization network were measured by the method of zoll-analyse.[9] According to the concentration and molecular mass of zoll-fraction S all main parameters of vulcanization network were calculated, in particular, the density of set N_c. Simultaneously the mobility of elastomeric segments had been investigated by the application of NMR method using the significance of the spin-lattice relaxation time T_1 and spin-spin relaxation time T_2 analyzing the slump of free induction in the semilogarifmic coordinates by the method of the least squares (the spectrometer of the firm "Minispec-Brucker" was used in this work by the application of pulse consistence 180°–90° by Meibaum-Hill). In this case the fact was taken into the account that the mobility of elastomeric chains adsorbed by carbon black particles is strongly limited at the distance of 5 Å.[7] Introduction between phases has been estimated by the definition of sensitivity of resistance to small deformations. In this case it was supposed that material sensitivity to deformation is increased at the enlargement of content of crosslinkage elastomer, involving the conductive phase of composite into the deformation.[10] The data on zol-analyse, NMR and tensil sensitivity for some composition were obtained. Experiments were carried out in order to determine the influence of vulcanization network of low molecular appendix on macromolecular mobility and density with the application of polymer-olygomer composites. Polydimethilsiloxan SKTN was used as a olygomer (mol.mass 28.000). The data of measurement are shown in Table II. These data allow us to make following conclusions:

1. The use of ADE-3 as a cure agent leads to decrease of zol-fraction with the increase of filler contents at simultaneous crosslinkage bind density increase (vulcanization network), what confirms well-known conclusion about linear-proportional dependence of degree of filler introduction—elastomer on specific contents surface.[8] Comparatively small output of zol-fraction and/or relative high density of vulcanization network in the rubbers obtained by peroxid vulcanization, due to arising of crosslinks at higher degree, because of contents of vinil groups, which take part in the crosslinkage at peroxid vulcanization in the elastomer macromolecules on the content of silanol group, which takes place to the linkage at vulcanization by cure agent ADE-3. The equality of significances of zol-fraction and vulcanization density for rubbers obtained by polymerization filling methods and peroxid vulcanization may be accounted for by the fact, that although the vulcanization of polymerization filled elastomer proceed also by the use of ADE-3, but in this case increase of S and N_c due to the intensification of introduction of elastomer-filler because of increasing integral surface of filler at increase of degree of filler dispersion at produced semiproduct result on polymerization of monomers at filler particle presence.
2. Times of relaxation T_1 and T_2 are in accordance with macromolecular segments mobility. Their values are in accordance with a regularity: with the increase of vulcanization network density with corresponding decrease of

TABLE II

Technical parameters of CFSR based on SKTN and carbon black

Production method	Filler content, mass.p	S, %	Ncx10^{16} bundle/ sm^3	T_1 ms	T_2 ms	Tensil sensitivity K
Vulcanization by ADE-3	40	5.6	4.5	35.0	45	7
	50	4.9	7.0	312	45	7.5
	60					
Filling at polymerization	50 + 10 SKTN	7.5	5.5	447	67	8.5
	50 + 20 SKTN	4.2	5.5	380	55	10.0
	50 + 3 SKTN	5.0	4.5	400	60	7.5
	40	2.2	10	300	15	11.1
Peroxide vulcanization	50	3.1	9.2	305	16	11.5

mobility of macromolecules, T_1 and T_2 are decreased too. On the other hand, increase rubber density leads to increase of sensitivity of the material to mechanical deformations (high value of sensitivity to tensil K corresponds to rubbers with high density of vulcanization network).

3. By introducing to the rubber mixture of olygomer polydimethilsaloxan of SKTN type the filler dispersion becomes easy in the matrix. But the olygomer without vinil group should decrease Nc, and, consequently, increase a part of soft component of elastomeric matrix. Probably, there is a critical olygomer concentration, at which the effect from increase of average surface of interaction of polymer-filler will prevail over the processes, leading to decrease of Nc. This composition may be reinforced at the generation of penetrative networks of low and high molecular olygomers. This statement practically is reflected in small extremal dependence of all measured parameters on olygomer contents.

SUMMARY

There is effect of some technological factors (type and content of fillers, olygomer additions, vulcanization method) on the technical characteristics of filled silicon rubbers on the polydimethilvinilsiloxan SKTN base investigate. It is established that these factors essentially influence the microstructure of composites and connected with it the conductive network. It has been shown, that the highest indexes have composites which are produced by the method of filling polymerization and especially while using of modificated by various silicoorganic components of thermical splitted graphite. By the application of sol-analyse method the density of vulvanization network is estimated and by NMR method—mobility of macromolecules in the composites and accordingly the sensitivity of materials to external deformation.

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