Ceramic-forming silicone compounds

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In view of the increase in energy use by industrial plant and home appliances, in the manufacture of cables, sealants, protective coatings, junctions, etc., there is an urgent need to create non-flammable and also ceramic-forming electrical insulation materials.

Organosilicon polymers are promising materials for this purpose, which is due to their high thermal stability in the environment and to the formation of considerable inorganic residue in the form of silica during thermo-oxidative processes. By comparison with many other polymers, polyorganosiloxanes exhibit a low combustion rate, without forming burning drops, and a low level of emissions in the form of non-toxic gases. However, in “pure” polyorganosiloxane, the residues, after their combustion, comprise a powder that is capable of being structured into a ceramic material.

Therefore, research in the field of the development of ceramic-forming insulation materials based on liquid and high-molecular-weight siloxane rubbers and Vulcanisates cured by a radical, addition, or polycondensation mechanism is of significant interest.

In the production of silicone ceramic-forming material, the need arises to add fillers and additives promoting the formation of a solid material.

There are a number of patents in which formulations and technologies for the manufacture of ceramic-forming silicone materials have been proposed. Thus, for the manufacture of fire-resistant cables, it is proposed that up to 50 parts calcium carbonate per 100 parts silicone polymer be introduced into the composite, in which these components amount to over 92% of the material [1].

For the formation of a ceramic coating by combustion, 15-75 parts ceramic-forming fillers are introduced into the silicone rubber: magnesium and calcium silicates and alkaline aluminosilicates (mica) combined with aluminium, magnesium, calcium, zirconium, zinc, iron, tin, and barium oxides [2], 8-40 parts inorganic phosphate, and 5-30 parts mixture of mica and low-melting glass, which form a liquid phase at 800°C [3].

In Mansouri and Burford [4], for the production of strong ceramic Elastosil R401/80S (Wacker) and NPC80 (Dow Corning), up to 20% mica GA100, as ceramic-forming filler, is introduced into silicone rubbers vulcanised by dicumyl peroxide. In the heat treatment of vulcanised specimens of the rubber mixes indicated above at a temperature of 1050°C in air, ceramic material is formed. Investigation of this material by electron microscopy has shown that a highly porous ceramic system is formed.

The authors attribute this to the formation at high temperatures of pore-forming gaseous products during the depolymerisation and oxidation of the siloxane polymer. The yield of ceramic material for NPC80 and for Elastosil R401/80S amounted to 62 and 52% respectively. Investigation of the structure of the initial vulcanisate and the ceramic system formed enabled the authors to propose the following scheme of its formation. At the start, in the initial rubber mix specimen, at temperatures of up to 800°C, no interaction between the mica particles is observed. Then, at temperatures of 800-900°C, in a specimen containing partially melted mica particles, their interaction with the rest of the fillers begins to occur. And finally, at a temperature above 900°C, bonds are formed between the inorganic melt and the mica particles, with the formation of a three-dimensional ceramic structure.

The aim of this work is to select fillers and catalytic additives for silicon rubber composites of polycondensation vulcanisation that will promote
the formation of ceramic-like materials during their combustion. The following materials were investigated:

1. Pentaelast-710 (P-710) organosilicon compound, grade A. A two-component material consisting of a base which, mixed with a catalyst, is cured at room temperature for 24 h [5].

2. Catalyst Pental-18P (K-18P) – a crosslinking agent for cold-curing polycondensation silicone compounds. The base is a solution of dibutyl tin dicarboxylate in ortho silicic acid esters [6].

3. Rubber SKTN-B – a liquid silicone rubber with terminal hydroxyl groups.

The fillers used were calcium metasilicate CaSiO₃, in the form of micronised wollastonite, aluminium hydroxide Al(OH)₃, micronised magnesium oxide (MgO), micronised high-purity kaolin (Al₂O₃·2SiO₂·2H₂O), and micronised natural calcium carbonate (CaCO₃) in the form of whiting. Metalloorganosiloxanes of the formula M[O₂C₅H₇]₄, where R = H(Me₂SiO)ₙSiMe₂H, \( n = 1, 2 \), and M = Sm, Fe, Ce, obtained by hydroxylation of metal acetylacetonates with \( \text{SiO}_2 \cdot \text{H}_2 \cdot \text{O} \), were used as catalytic additives.

MOC catalysts for ceramic formation were used by direct introduction into the rubber mix, and cerium compounds were used in the form of a 10% paste in divinylsiloxane rubber DVK-5. Preparation was carried out by mixing the catalyst and DVK-5 with subsequent grinding for 1 h on a bead mill. As a result, a homogeneous paste not containing any inclusions was obtained.

A sample of compound P-710 or rubber SKTN-B was weighed in a ceramic dish, and, during thorough mixing on a three-roll colour mill, calculated amounts of all the ingredients of the composite (with the exception of the crosslinking agent) were added.

For the tests, round sheets of 100 mm diameter and 2 mm thickness were manufactured. To this end, a calculated amount of catalyst K-18P was introduced into a compound containing the necessary components, and, after thorough but rapid mixing, it was placed in a fluoroplastic mould, vacuum treated to remove any air bubbles, and, after closure of the fluoroplastic lid, squeezed in a press at a pressure of 1013 kPa. Vulcanisation was carried out at room temperature for 3 days. As a result, a sheet of 2 mm thickness and 12 cm diameter was obtained, from which dumb-bell testpieces were cut out using a cutting tool according to GOST 270, and from which specimens were cut for assessment of ceramic formation.

Physicomechanical tests of the vulcanisates were conducted according to GOST 270-75 and GOST 262-93 on an RM-50 tensile testing machine with mechanical clamps.

After determination of the physicomechanical properties, ceramic formation tests were carried out. Ceramifiability was assessed in the following way. Four weighed specimens of rubber measuring 20 x 35 x 2 mm were placed in a muffle furnace and held in air at 850°C for 15 min. The obtained specimens of ceramic residue were tested for strength by determining the force necessary to cause complete failure of the specimen by pressing it with a metal rod with a ball (5 mm diameter) on its end.

To obtain ceramic-forming compounds, an investigation was made of the effect of different fillers (calcium carbonate, wollastonite, magnesium oxide, aluminium hydroxide, kaolin) and catalytic additives (iron and samarium metalloorganosilicon complexes (MOC-Fe + MOC-5m), and also compounds of cerium (Cat.Ce)), which should promote ceramic formation. Standard compound P-710 (as the cheapest and most readily available, with satisfactory physicochemical and dielectric properties) based on liquid hydroxyl-containing silicone rubber SKTN-A and cured by catalyst K-18P by a polycondensation mechanism was chosen as the base. The content of ceramic-forming filler was varied from 20 to 40 wt% in terms of the P-710.

It was established that, in the presence of different fillers, different amounts of vulcanisation catalyst are required. To select the necessary amount of K-18P, testpieces were manufactured, for which the time of absence of residual tackiness of the material was determined. Composites for which the vulcanisation time was ~30 min were chosen as the base. The consumption of catalyst K-18P was 3.5–5%.

Composites based on compound P-710 and containing 20–40% ceramic-forming fillers are viscous, low-flow pastes.

The composition of the composites, the physicomechanical properties of the vulcanisates, and the yield and strength of the ceramic are presented in Table 1.

Figure 1a shows specimen 1 after ceramification at 850°C. From Figure 1a it can be seen that, during heat treatment of a rubber specimen containing none of the fillers or catalytic additives mentioned above, no ceramic is formed. The yield of inorganic residue is slightly lower than the content of inorganic components in the composite (Table 1, specimen 1). This makes it possible to conclude that, at high temperature, the silicone polymer is depolymerised and escapes in the form of dimethylcyclosiloxane \([\text{Me}_2\text{SiO}]_n\), taking with it part of the inorganic components. As a result, a powdery inorganic ash is formed. An investigation was made of the properties of compounds containing 20% ceramic-forming fillers \([\text{CaSiO}_3, \text{Al(OH)}_3, \text{or MgO}]\) in the presence of 1 wt% catalytic additive in the form of an iron and samarium metalloorganosilicon complex (MOC-3-Fe +
MOC-3-Sm). For vulcanisates of all composites, successive reduction in elongation at break to 210, 120, and 95% is observed, in accordance with the listed order of fillers. The strength properties of the vulcanisates increase in the presence of CaSiO₃ and decrease with Al(OH)₃ and with MgO. The yield of inorganic residue after holding of specimens for 10 min at 800°C amounted to 39.7, 37.8, and 39.2% respectively, which is slightly lower than or practically coincides with the content of inorganic fillers (40%) (Table 1, specimens 2 to 4).

From Figures 1b to d and from Table 1 it can be seen that, during ceramification at 850°C of rubber specimens based on compound P-710 and containing CaSiO₃, a baked inorganic residue (ceramic) is formed, retaining its shape, with a strength of 0.6 N. In the presence of Al(OH)₃, the baked inorganic residue readily disintegrates, from which it can be concluded that no ceramic is formed.

When MgO is introduced into the composite, a very weakly ceramicised residue is formed, with a strength of 0.2 N.

Composites based on compound P-710 and containing 20 and 40% kaolin and 0.5, 1.0, and 1.5% Cat.Ce were obtained. For the vulcanisates of the obtained composites, considerable reductions in

<table>
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<th>Specimen number</th>
<th>Amount of K-18P (%)</th>
<th>Content of catalytic additive (%) (paste)</th>
<th>Amount of ceramic-forming filler (parts)</th>
<th>Strength (kPa)</th>
<th>Elongation at break (%)</th>
<th>Yield of ceramic (%)</th>
<th>Content of inorganic filler (%)</th>
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</table>

Figure 1. Inorganic residue of compound P-710A (a), P-710A + 20% CaSiO₃ + 1% MOC(Fe + Sm) (b), P-710A + 20% Al(OH)₃ + 1% MOC(Fe + Sm) (c), and P-710A + 20% MgO + 1% MOC(Fe + Sm) (d) after holding of the specimen for 15 min at 850°C.
the elongation at break and in the tensile strength are observed by comparison with the initial P-710 (Table 1). The physicomechanical properties of the vulcanisates decrease successively with increase in the content of ceramic formation catalyst. With increase in the content of Cat.Ce from 0.5 to 1.5%, the elongation at break decreases, while the tensile strength increases.

Figure 2 shows inorganic residues for composites filled with kaolin (specimens 5 to 7) after ceramification. During the heat treatment of these specimens, an inorganic residue is formed in the form of ceramic plates. For specimen 8, a ceramic-like material is not formed. For all specimens, the yield of inorganic residue exceeds the content of inorganic components, which indicates the partial participation of polydimethylsiloxane combustion products in ceramic formation processes. The maximum strength of the ceramic amounts to 0.4 N for specimen 6.

An investigation of the properties of vulcanisates based on compound P-710 and containing 20 and 40% whiting and 0.5, 1.0, and 1.5% Cat.Ce (Table 1, specimens 9 to 12) showed that considerable reductions in elongation at break and tensile strength are observed (Table 1).

The physicomechanical properties of the vulcanisates decrease successively with increase in the content of ceramic formation catalyst. With increase in the content of Cat.Ce there is a reduction in the elongation at break and tensile strength.

Figure 3 shows inorganic residues for composites filled with calcium carbonates after ceramification. From the presented figures it can be seen that, as a result of heat treatment of specimens 9 to 12 at 850°C, in all cases ceramic plates are formed, for which the yield and strength characteristics were determined. It was found that the yield of inorganic residue, calculated with allowance for the decomposition of the calcium carbonate or its interaction with SiO₂, was higher than the calculated yield, which points to the partial participation of polydimethylsiloxane combustion products in ceramic formation processes:

\[
\begin{align*}
\text{CaCO}_3 & \rightarrow \text{CaO} + \text{CO}_2 \\
\text{CaCO}_3 + \text{SiO}_2 & \rightarrow \text{CaSiO}_3 + \text{CO}_2
\end{align*}
\]

From Table 1 it can be seen that, from specimen 9, a ceramic with a low strength of 0.2 N is formed. The strength of the ceramic from specimens 10 to 12 increases 3–3.5-fold and amounts to 0.6–0.7 N.

An investigation of the properties of vulcanisates based on compound P-710 and containing 20 and 40% wollastonite and 0.5, 1.0, and 1.5% Cat.Ce (Table 1, specimens 13 to 16) showed that there is a considerable reduction in the elongation at break and tensile strength by comparison with the initial P-710.
The physicomechanical properties of the vulcanisates decrease successively with increase in the content of ceramic formation catalyst. With increase in the content of Cat.Ce from 0.5 to 1.5% there is a reduction in the elongation at break and tensile strength.

Figure 4 shows inorganic residues for wollastonite-filled composites after ceramification. From the presented data it can be seen that, as a result of the heat treatment of specimens 13 to 16 at 850°C, ceramic plates are formed, for which the yield and strength characteristics were determined. For all specimens, the yield of inorganic residue exceeds the content of inorganic components, which points to the partial participation of polydimethylsiloxane combustion products in ceramic formation processes. The maximum strength of the ceramic amounts to 0.9 N for specimen 15.

As a result of the conducted research it was established that compound P-710A, vulcanised by a polycondensation mechanism, forms no ceramic. Kaolin, whiting, and wollastonite are promising additives for the production of ceramic-forming composites based on standard compounds vulcanised by a polycondensation mechanism.

The greatest effect of ceramic formation is observed in a composite based on P-710 and containing 40% wollastonite and 1.0% Cat.Ce, for which the yield of ceramic amounts to 54.3% and the strength to 0.9 N.

Comparison of experimental data on the yields of inorganic residue with data on the content of inorganic components makes it possible to conclude that, at high temperature, the main part of the polydimethylsiloxanes escapes in the form of polydimethylcyclosiloxanes, which burn up in the gas phase to form SiO2 smoke and take no part in ceramic formation.

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