

CERAMIZABLE SILICONE RUBBER-BASED COMPOSITES

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Abstract

The work reviews the state-of-the-art in the field of ceramizable silicone rubber-based composites used in cable industry. Phenomenon of ceramization is based on preventing volatiles of polymer thermal decomposition from evacuation by creation of ceramic layer in composite surface. Usually, the layer is composed of mineral filler particles, connected by fluxing agent. The ceramic barrier has to characterize itself by micro-porous structure:

- protecting copper wire inside the cable from heat transfer leading to melting, and
- exhibiting good mechanical strength, assuring integrity of electrical circuit.

Subject literature provides information on the application of Ca- or Al-based mineral fillers, combined with fluxing systems, to fill silicone rubber - silica compounds.

In this study various mineral fillers, together with boron oxide as a fluxing agent, have been tested. Acidic character of B₂O₃, inhibiting peroxide curing of silicone rubber, was compensated by admixing of MgO and its good dispersion in the composite matrix, was obtained by co-grinding of the minerals, enabling the decrease of their particle size. The best ceramic phase, created on fire, was found for composites filled with wollastonite or mica. They represent the lowest mass loss and the stable porosity of ceramic phase up to the highest temperatures tested.

Keywords: composites, silicone rubber, mineral fillers, ceramization

1. INTRODUCTION

Despite the significant progress in the area of engineering of materials, resources and systems of fire precautions and tools for firefighting, fires of flat buildings all the time threaten to the life of people and are the reason of substantial material losses [1]. This is why special security regulations have been imposed, referring especially to the objects of public utility, like shopping centers, sport halls, museums, cinemas and theatres, airports, underground and railway stations – in a word all places of large concentration of people, great material or cultural value. One of the obligatory regulations concerns the flame resistance of electrical cable insulation which should additionally assure integrity of electrical circuit under fire for not less than 90 minutes, making possible the safe evacuation of people and goods from buildings.

Neither silicone rubber, nor chlorosulphonated polyethylene, polyvinyl chloride or crosslinked polythene, used so far by cable industry, are able to meet the present requirements, due to their limited thermal stability and low mechanical strength at high temperature under fire. Solution to the problem seems to be the application of ceramizable rubber composites. Electrical insulation made of silicone rubber filled with a proper selection of mineral fillers and fluxing system, can create the integral, effective heat barrier under fire, protecting copper wire from melting, additionally assuring durability of cable construction.

2. CERAMIZATION

There are some reports on application of Ca-based (CaO, Ca(OH)₂, calcite – CaCO₃, wollastonite – CaSiO₃) or Al-based (Al₂O₃, Al(OH)₃, boehmite – AlOOH, mica, montmoryllonite) minerals as fillers for silicone rubber [2, 3]. In a combination with an adequate selection of fluxing agents (glass frits, zinc or ferric oxides, zinc borate etc.), shifting the melting of ceramic phase to lower temperatures, it results in the ceramization process taking place simultaneously to degradation of a polymer matrix (starting already from 350 °C), limiting the escape of its volatile products [4, 5]. Finally, on surface of the composite a porous but integral ceramic layer is created, which does not break into fragments when the material is directly exposed to the action of fire (even > 1000 °C – close to the melting temperature of copper) – Fig. 1 [6].

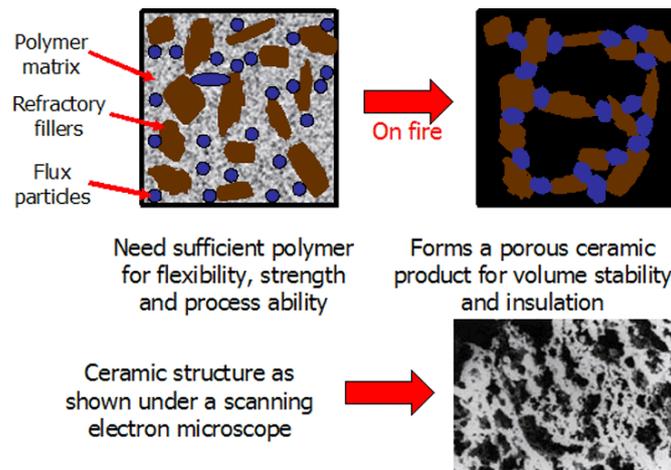


Fig. 1 Scheme illustrating ceramization process of polymer composites [6].

2.1 Influence of a solid phase on a ceramization process

Taking into account differences in the thermal degradation process of mineral fillers, used in the technology of ceramizable silicone composites, they can be divided into three groups:

- composites containing non-hydrated fillers (calcium oxide, calcite, wollastonite),
- composites containing fillers, releasing water at elevated temperatures (calcium or aluminium hydroxides, boehmite), and
- composites containing fillers of hydroxylic groups present on the surface (aluminium oxide, mica).

Mechanisms of thermal degradation of fillers based on calcium and aluminium are presented in Fig. 2 [7, 8]. Products of thermal decomposition of silicone rubber are silica and cyclosiloxanes. Below 600 °C calcium-based fillers do not influence thermal stability of a polymer matrix.

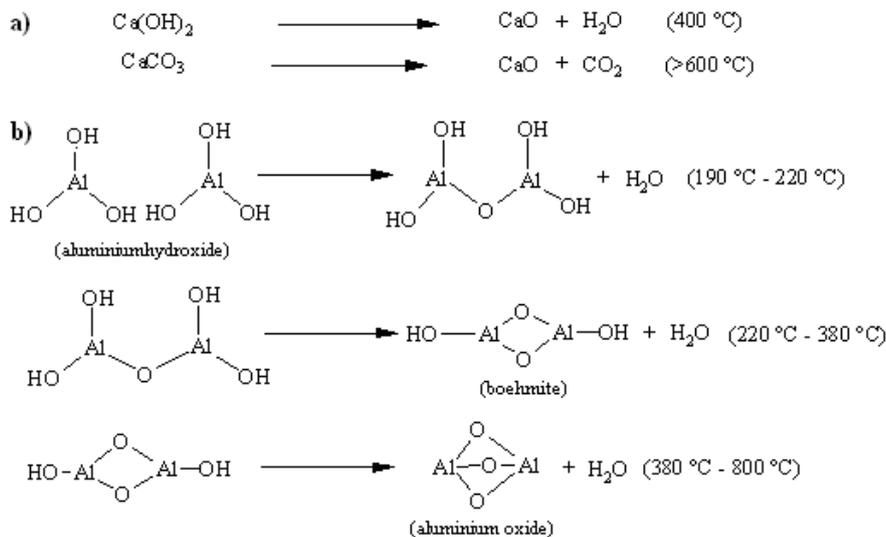


Fig. 2 Mechanisms of thermal degradation of fillers: a) based on Ca, b) based on Al [7,8].

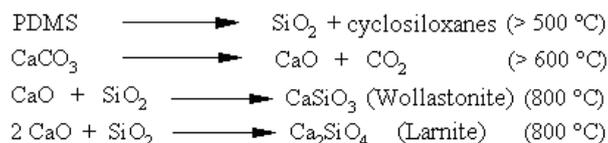


Fig. 3 Chemical reactions accompanying the degradation of silicone rubber composites filled with CaCO_3 [8].

However, when temperature increases, together with the degradation of CaCO_3 (about 680 °C), accompanied by the release of CaO, the chemical reaction between silica and calcium oxide takes place, resulting in the production of a crystalline

phase mainly composed of wollastonite, together with a small amount of larnite – Fig. 3 [8]. Contrary to the materials filled with CaCO_3 , composites containing $\text{Ca}(\text{OH})_2$ decompose in a one-step process, starting already below the temperature of silicone rubber degradation. Similarly to the composites filled with CaCO_3 , produced CaO reacts at elevated temperature with silica, leading to the creation of new crystalline phase. Due to higher amount of CaO , resulting from thermal degradation of a filler, the crystalline phase contains this time more larnite.

Thermal degradation of silicone rubber composites containing fillers based on aluminium proceeds via two steps. The first step generally takes place in the temperature range 240-440 °C (in the case of $\text{Al}(\text{OH})_3$, a decomposition with the release of water starts already at 190 °C). It can be explained by the sorption of rubber macromolecules onto filler particles during the preparation of rubber mix. Boehmite, produced at the first step of the thermal degradation of aluminium hydroxide, degrades at the second step (450-650 °C), simultaneously with a silicone rubber, to aluminium oxide, with the release of water. Contrary to Ca-based fillers, which react with the degradation products of a silicone rubber, leading to the creation of new ceramic phase in a co-crystallization process, this time only a barrier layer, protecting the bulk of material from a heat transfer, is produced. Its efficiency depends on a shape and dimensions of filler particles [9].

Mica and aluminium oxide do not degrade in the discussed range of temperature. In their case only some water is created, due the release of hydroxyl groups from the surface of filler particles. The presence of OH groups on the surface of Al_2O_3 particles manifests itself by a catalytic action on the thermal degradation of silicone rubber, which starts at the temperature even up to 100 °C lower in comparison to a rubber itself. However, the degradation of composites containing mica takes place in a significantly higher temperature (480 °C) than the temperature at which water starts to release from the surface of mica (300 °C). This situation can be explained by hydrogen bonding between OH groups and macromolecules of silicone rubber. Owing to a plate form of mica particles, a physical barrier is created on a composite surface, limiting emission of the volatile products of the thermal degradation of a silicone rubber [10].

2.2 Characteristic of a ceramic layer

Apart good heat insulation, prolonging the time to material ignition and the decrease of a heat release during fire, the micro-porous structure has to be strong enough to maintain the integrity of an electrical circuit. The structure changes with an increase of temperature [11, 12]. The smallest pores, of nanometer dimensions, disappear. The total degree of material porosity also decreases, what has been found to be dependent on the kind of filler applied – Fig. 4 [12].

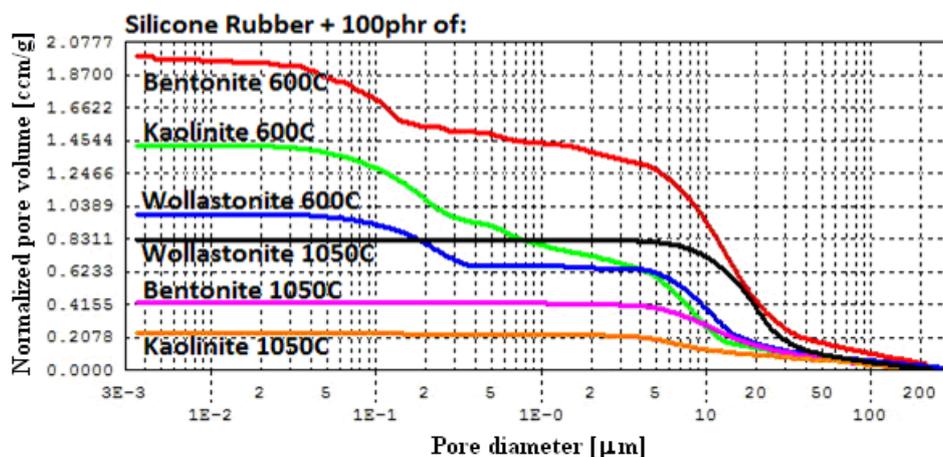


Fig. 4 The influence of a ceramization temperature on the distribution of pores size for the silicone composites filled with various kinds of ceramic phase [12].

The smallest changes to a porosity have been observed for the composites containing wollastonite, which additionally characterizes themselves by the smallest mass loss accompanied the increase of temperature. Created ceramic phase should exhibit limited thermal shrinkage, what allows to avoid problems concerning breaking or delamination of the surface layer from a polymer substrate. There are a lot of patent declarations on the composition of ceramizable silicone composites and the way of their [13-15].

3. RESULTS AND DISCUSSION

3.1 Silanization of filler particles

Silicone rubber filled with high amounts of mineral fillers exhibit moderate mechanical strength, far from the expectations of a cable industry. In order to improve mechanical properties of the composites, wollastonite and quartz, used as fillers of

the silicone composites studied, have been subjected to surface silanization with vinyl silane (VST) and methyl silane (TST), respectively – Fig. 5.

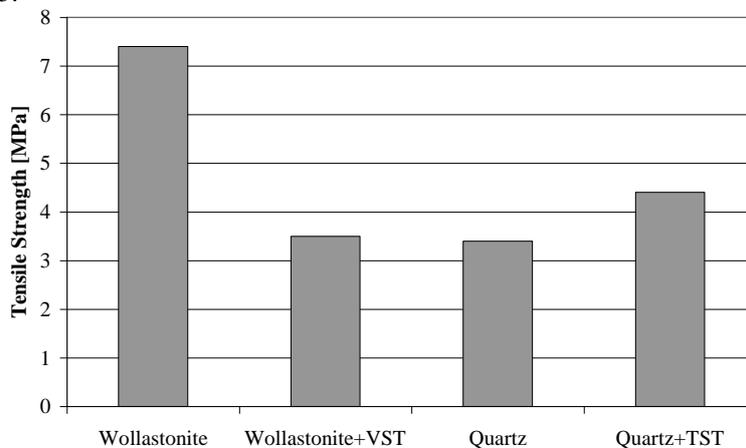


Fig. 5 Influence of fillers (wollastonite or quartz) silanization on tensile strength of the silicone composites.

Tensile strength of the composites filled with unmodified powders are similar, whereas the kind of applied silane decides mechanical properties of the materials. Vinyl groups, present on the surface of Wollastonite VST, apart improvement of polymer-filler interactions, is involved in crosslinking of the composite. In the case of methyl groups on Quartz TST only the stronger interphase interactions (possibility of chemical bonding between methyl groups of silicone rubber and silane) are responsible for improved mechanical properties of the composites. This time a filler-matrix compatibilization is not accompanied by a significant stiffening of the material.

Unfortunately, the silanization of fillers makes problems with creation of continuous ceramic layer on the surface of composites during fire. It can be subscribed to a decrease of the surface energy of powders subjected to silanization, adversely effecting their wettability by a fluxing agent – Fig. 6.

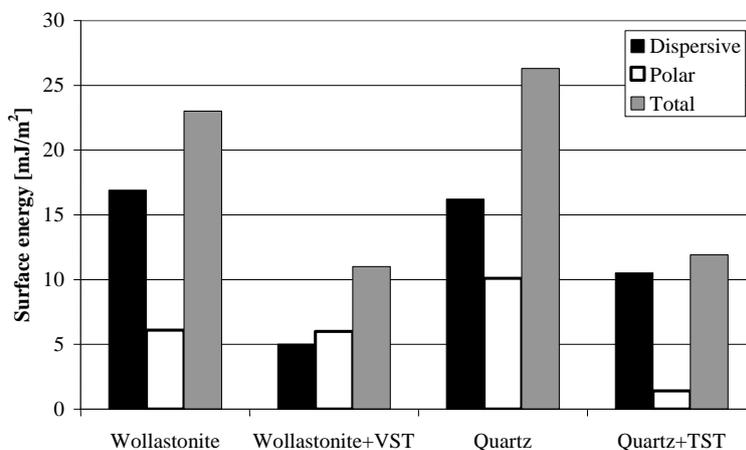


Fig. 6 Influence of silanization on the surface energy and its components for the ceramic powders studied.

To cope with a ceramization problem it has been decided to modify a fluxing agent, replacing the low melting temperature glass frit with B_2O_3 . Despite the dominant role of a flux in the ceramization process, some role is played undoubtedly by the characteristic of mineral fillers, apart the surface energy, shape and dimension distribution of their particles. The significant difference has been observed between morphologies of the ceramized layer obtained for the composites containing wollastonite and quartz. The needles of the former facilitate integrity of the ceramic shield, contrary to rectangular grains of quartz.

3.2 Ceramizable silicone composites containing B_2O_3

A fluxing agent should start melting at the temperature below the degradation of a silicone matrix takes place, preventing its volatile products from escaping. In order to assure such a behaviour two concepts have been tested and namely:

- the modification of a silicone rubber with a phenyl-silicone resin, increasing the thermal stability of a polymer matrix, and
 - application of a low melting temperature fluxing agent – B_2O_3 , enabling ceramization at lower temperatures.
 Already addition of 5 phr of phenyl silicone resin to silicone rubber significantly improves its thermal stability. It starts degrading at about $450\text{ }^\circ\text{C}$, what is quite close to the melting temperature of boron oxide (K-1). Due to the acidic character of B_2O_3 , inhibiting peroxide crosslinking, used commonly in silicone technology, the composition of mixes has to be modified by the addition of magnesium oxide (K-2), exhibiting a base character. In the composites studied this time an inactive quartz together with a wollastonite have been replaced by a system of an active pyrogenic silica and mica (Phlogopite), respectively. In order to lower the size of fillers particles and to improve dispersion of the components, all ceramic powders were co-milled prior to introduction to a polymer matrix (K-3). The applied changes make possible to obtain the composites of good mechanical properties, meeting the requirement of a cable industry ($TS > 5\text{ MPa}$) – Fig. 7.

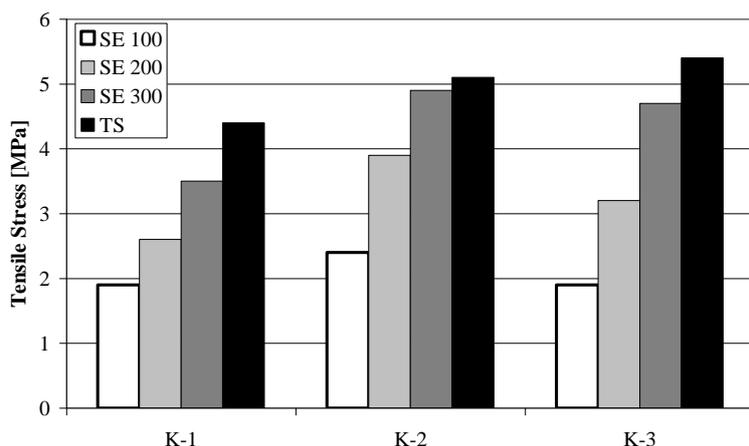


Fig. 7 Influence of the addition of MgO (K-2) and co-milling (K-3) of ceramic powders on mechanical properties of the silicone composites (K-1). SE 100, 200 and 300 - strains at 100%, 200% and 300% of a relative elongations.

Mechanical strength of the composites is accompanied by morphological changes to the materials after ceramization. Similarly to the commercial composites, their morphology is dominated by micro-pores – Fig. 8.

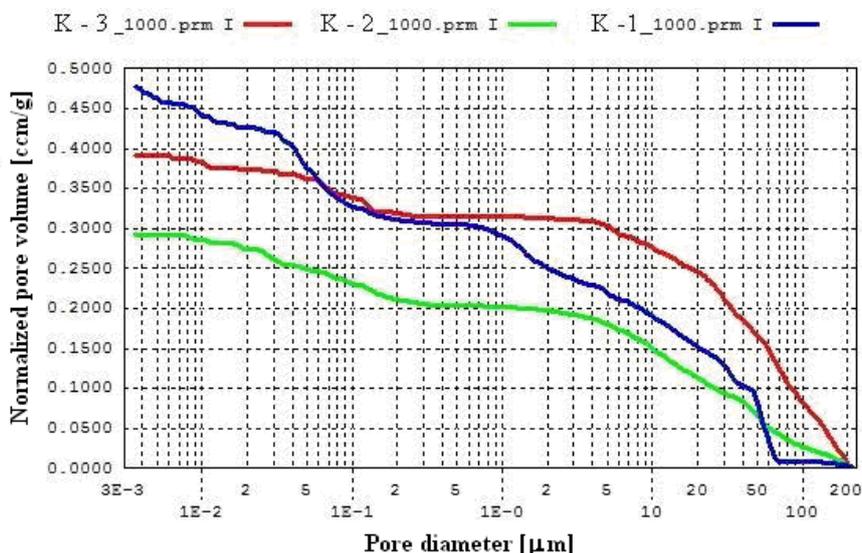


Fig. 8 The normalized pore volume vs. pore size for the composites studied at $1050\text{ }^\circ\text{C}$.

The porous structure of the all composites studied do not vary much from the structures of commercial composites after ceramization.

4. SUMMARY AND CONCLUSIONS

The ceramization of polymer composites opens new perspectives for fire protection of an electrical installation and other elements of building construction from the action of fire and high temperature (even up to $1000\text{ }^\circ\text{C}$). The paper presents the

state of the art together with the original experimental data on electrical cable insulations based on a silicone rubber. However, in the subject literature there are also some reports devoted to ceramization of other polymer materials of the potential importance for civil engineering, like PVC or ethylene-propylene copolymers. The significant improvement of flame resistance is the effect of a ceramic layer, produced by particles of mineral fillers combined by a melted fluxing agent, preventing volatile products of the thermal decomposition of polymer from accessing a fire zone. At higher temperatures, which can arise during fire, a partial decomposition of a solid phase can result in cocrystallization, leading to creation of new ceramic phase.

In comparison to conventional methods used to improve flame resistance of polymers, the ceramic layer created on their surface under fire characterizes itself by:

- micro-porous structure, insulating the bulk of a composite material from a heat transfer, additionally protecting the material behind a polymer coating, and
- maintaining good mechanical strength under fire.

It means that ceramizable polymer composites can be applied as shields and coatings, protecting from the distribution of fire and temperature, additionally assuring the integrity of electrical circuits or mechanical constructions. The experimental data presented point on differences in the morphology of ceramic layer created on the surface of composites containing various mineral fillers. The best properties have been obtained for the mixes of a silicone rubber with silica filled with wollastonite or mica. In this case, the mass loss of composites due to their exposition to the action of fire was the smallest and the porous ceramic structure created on their surface was able to withstand up to very high temperatures. Boron oxide has been applied as an effective fluxing agent in the ceramizable silicone composites studied. It has been also presented to what extent the surface modification of filler particles or a polymer matrix can improve mechanical properties of the composites in order to meet the requirements of a cable industry.

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