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INFLUENCE OF CRYSTALLINE ADDITIVES TO SILICONE RUBBER BASED COMPOSITES ON THEIR MICROSTRUCTURE AFTER CERAMIZATION PROCESS

The paper presents the results of investigations on the composition of mineral components used for ceramizable silicone rubber-based composites. By using different crystalline phase additives, it is possible to assure the proper course of composite degradation and its transformation during the ceramization process. Three crystalline components were tested as an additive to silicone rubber - bentonite, kaolinite and wollastonite. They were added simultaneously with the glassy phase. These compounds during firing evolved (decomposed) and introduced into the ceramized material a polycrystalline structure, responsible for its properties. The characteristic of the ceramized composite body created during heating was investigated by mercury porosimetry. The porosity evolution was described in the range of 600÷1050°C.

Keywords: composites, ceramization

WPŁYW DODATKÓW KRYSZTALICZNYCH W KOMPOZYTACH NA OSNOWIE SILIKONOWEJ NA ICH MIKROSTRUKTURĘ PO CERAMIZACJI

Praca prezentuje wyniki badań nad składem mieszanki mineralnej stosowanej w kompozytach na osnowie silikonowej, ulegających w czasie degradacji wysokotemperaturowej zjawisku ceramizacji. Stosując dodatek różnych faz krystalicznych, możliwe jest zapewnienie takiego przebiegu procesu degradacji kompozytu i jego ceramizację. Badano wpływ trzech faz krystalicznych jako dodatków do gumy silikonowej - bentonitu, kaolinitu i wollastonitu. Były one dodawane równolegle z fazą szklistą. W czasie spalania kompozytu składniki te ewoluowały (przemiany polimorficzne, rozkład) i budowały w ceramizującym kompozycie polikrystaliczną mikrostrukturę odpowiedzialną za jego właściwości. Charakterystykę mikrostrukturalną powstających w czasie spalania sceramizowanych tworzyw określano za pomocą porozymetrii rtęciowej. Opisano ewolucję porowatości powstającej w zakresie temperature degradacji 600÷1050°C.

Słowa kluczowe: kompozyty, ceramizacja

INTRODUCTION

The flame resistance of electrical cable covering insulation is very important from the safety point of view of people using means of transport, visiting shopping centers, sport halls, theatres or cinemas. Metal rods in protective covering comprise the main part of electrical circuits, responsible for the distribution of electricity in cars and planes, providing power supply for elevators or fire-fighting systems. Material used nowadays, based on silicone rubber or PVC is incombustible, but the problem concerns its mechanical resistance to flames, maintaining circuit integrity and energy supply during a fire, indispensable to securing time for evacuation or an emergency landing. The integrity of electrical cables can be obtained by applying a cover-

ing insulation made of polymer composites ceramizing at high temperatures arising during a fire [1]. The paper presents the results of investigations on the optimization of a ceramic phase using different compositions of the mineral part of the composites. As the main crystalline component, bentonite, kaolinite or wollastonite were used. The influence of these phases on a silicone matrix was recognised in previous works [2- 4]. The investigation of composite transformations (polymer degradation and material ceramization) during heating up to 1050°C showed the influence of the type of crystalline phase on the composite microstructure after ceramization in the whole investigated temperature range (600÷1050°C) [5].

EXPERIMENT

The materials used for the investigation were silicone rubber-based composites. They were composed of silicon rubber containing a silanized Silbond binder (45 phr; *phr* - *parts per hundred of rubber*) and a mixture of the glassy phase (in $\text{SiO}_2\text{-Na}_2\text{O-CaO-MgO-Al}_2\text{O}_3$ system), borax and as the crystalline component one of three different crystalline phases - bentonite (Bentox, Certech, Poland), kaolinite (KOC, Poland) or wollastonite (OF60, Otavi Minerals GmbH, Germany) (100 or 200 phr). The glassy phase, borax and the crystalline component ratio was (3:2:7).

Additives necessary for the proper crosslinking of the silicone base were also added.

The vulcanized composites were examined by DSC/TG (Differential Scanning Calorimetry/ Thermogravimetry) up to 1050°C (Netzsch STA449F3 Jupiter).

XRD diffraction patterns were collected using Panalytical X'Pert Pro equipment. The samples were also fired for 1 hour in air using controlled temperatures of 600 and 1050°C in air. The microstructure of the ceramized samples was investigated using the mercury porosimetry method (Poremaster 60 Quantachrome).

RESULTS AND DISCUSSION

Figures 1 and 2 shows that despite the kind of crystalline phase and its content, the process of degradation of silicone proceeded in a comparable range of temperatures in each composite type. The DSC analyses of the degradation in composites containing the lower amount of "ceramic mixture" (glass-borax-crystalline component) - 100 phr, showed many steps of this process, which could be distinctly separated. The typical behaviour is commonly known [2, 3]. The exothermic effect connected with structural changes in the ceramic part of the composite are difficult to separate. The DSC image of silicone degradation in the composites containing the higher amount of "ceramic mixture" (200 phr) was different. The exothermic effects connected with elastomer degradation are difficult to separate. This is a result of the presence of a large amount of ceramic phases. Their structural changes were covered by the strong effects coming from the mineral part decomposition.

The thermogravimetric measurements (Figs. 3 and 4) showed that there were essential differences in weight losses for the composites containing 100 phr of a "ceramic mixture". The difference between the composite containing wollastonite and the one containing bentonite was about 8%. The weight loss for the kaolinite containing composite was on an intermediate level.

The composites containing 200 phr of a "ceramic mixture" showed lower weight losses. Generally, this effect must be ascribed to the elastomer/ceramic ratio. During composite decomposition, the main weight loss

is connected with elastomer degradation. Anyway, it is worth noting that these weight losses were much more uniform for all the composites (the difference did not exceed 2%) than observed with the lower "ceramic mixture" content.

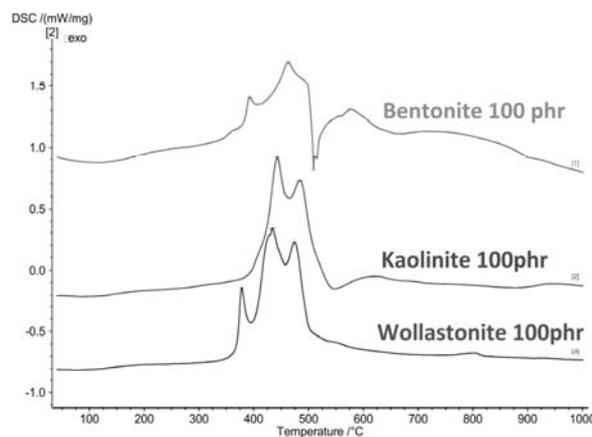


Fig. 1. DSC curves of composites containing 100 phr crystalline phase

Rys. 1. Krzywe DSC dla kompozytów zawierających 100 phr dodatku faz krystalicznych

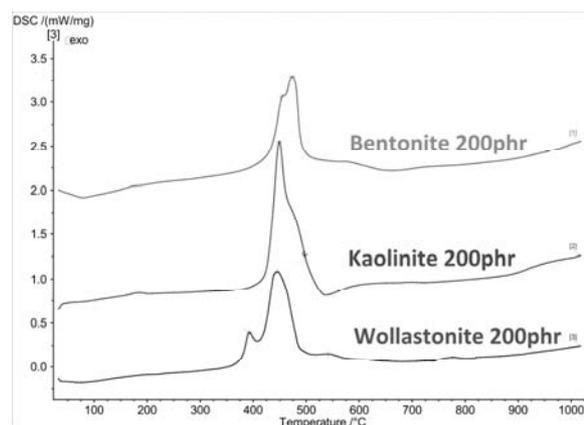


Fig. 2. DSC curves of composites containing 200 phr crystalline phase

Rys. 2. Krzywe DSC dla kompozytów zawierających 200 phr dodatku faz krystalicznych

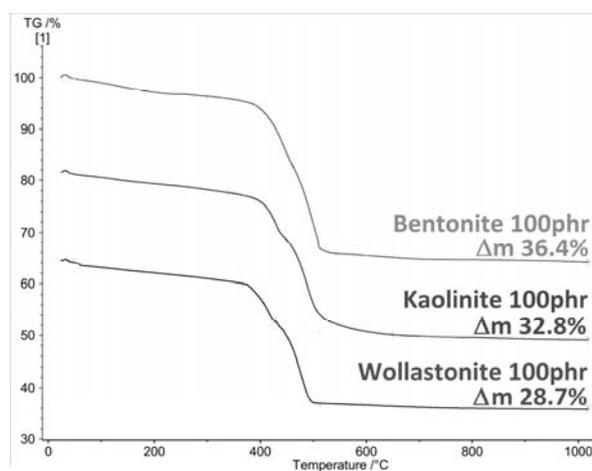


Fig. 3. TG curves of composites containing 100 phr main ceramic phase

Rys. 3. Krzywe TG dla kompozytów zawierających 100 phr dodatku faz krystalicznych

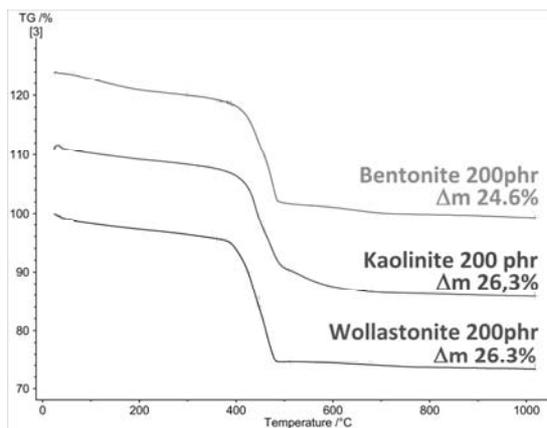


Fig. 4. TG curves of composites containing 200 phr main ceramic phase
Rys. 4. Krzywe TG dla kompozytów zawierających 100 phr dodatku faz krystalicznych

Figures 5-7 show the results of XRD diffraction analyses of the investigated composites containing a 100 phr proportion of ceramic compound. The content of crystalline phases recognized in the investigated materials after ceramization is given in the left upper corner of each figure.

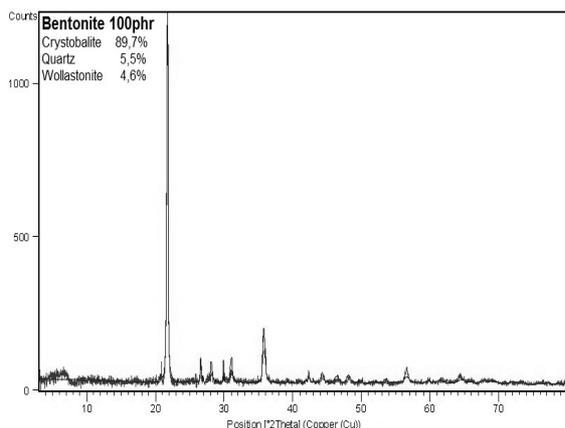


Fig. 5. XRD diffraction pattern of crystalline phases formed during ceramization of bentonite containing sample
Rys. 5. Obraz dyfrakcyjny XRD faz krystalicznych powstających w trakcie ceramizacji próbek zawierających bentonit

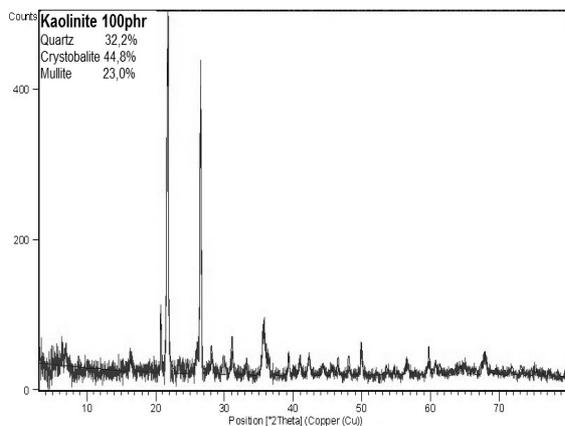


Fig. 6. XRD diffraction pattern of crystalline phases formed during ceramization of kaolinite containing sample
Rys. 6. Obraz dyfrakcyjny XRD faz krystalicznych powstających w trakcie ceramizacji próbek zawierających kaolinit

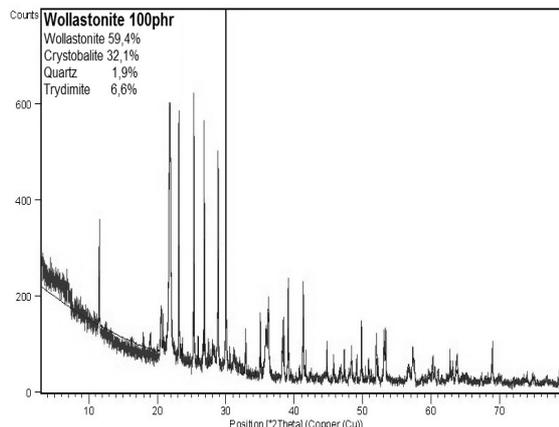


Fig. 7. XRD diffraction pattern of crystalline phases formed during ceramization of wollastonite containing sample
Rys. 7. Obraz dyfrakcyjny XRD faz krystalicznych powstających w trakcie ceramizacji próbek zawierających wollastonit

During the heat treatment of each type of composite, large amounts of silica are released and created as the result of silicone rubber decomposition. Each investigated composite has its own crystalline compound - bentonite, kaolinite or wollastonite. These compounds during firing evolved (decomposed) and introduced into each ceramized material its individual polycrystalline microstructure. This microstructure influences the ceramized composite porosity, especially.

The description of the pore size distribution of the materials subjected to high temperatures (“ceramized”) are collected in Figures 8-12. Figure 8 compares the pore size distribution for the composites containing 100 phr of a “ceramic mixture”. After firing at 600°C, the porosity of each composite is rather high - the highest in the bentonite containing material, the lowest in the wollastonite containing one.

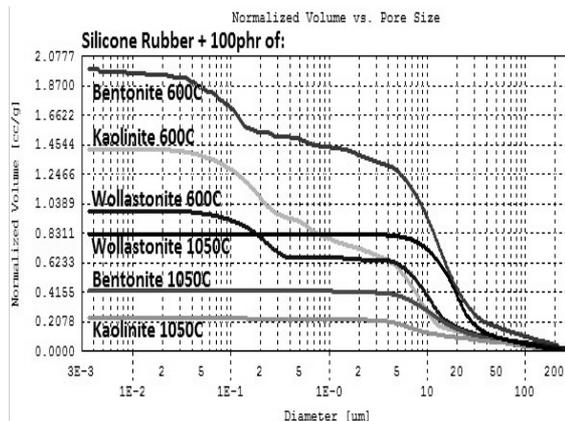


Fig. 8. Cumulative curves of pore size distribution for composites containing 100 phr of crystalline phase ceramized at 600 and 1050°C
Rys. 8. Krzywe kumulacyjne rozkładu wielkości porów w kompozytach zawierających 100 phr faz krystalicznych sceramizowanych w 600 i 1050°C

Firing at 1050°C decreased the porosity in all the materials (Fig. 9), but this effect was observed for the bentonite and kaolinite containing materials mainly.

The composite with wollastonite showed relatively stable porosity, however, the structure of the porosity changed - the smallest pores were eliminated.

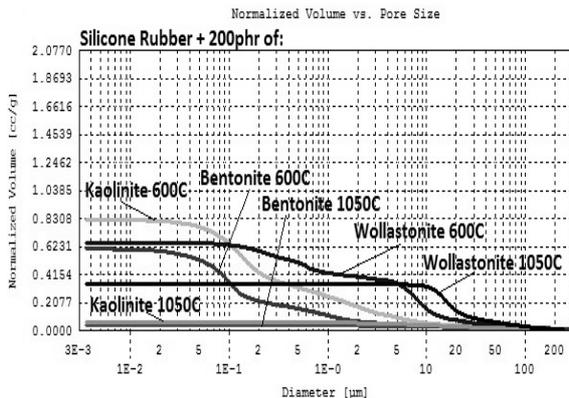


Fig. 9. Cumulative curves of pore size distribution for composites containing 200 phr of crystalline phase ceramized at 600 and 1050°C

Rys. 9. Krzywe kumulacyjne rozkładu wielkości porów w kompozytach zawierających 200 phr faz krystalicznych sceramizowanych w 600 i 1050°C

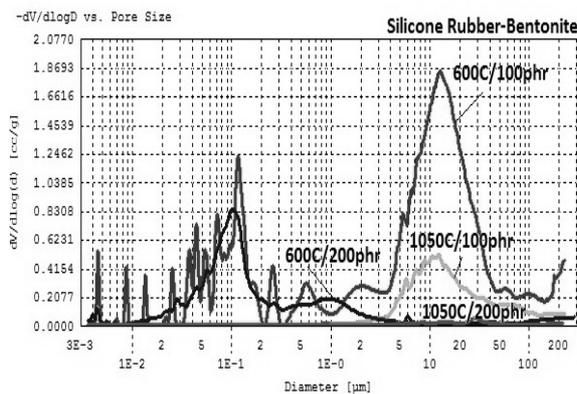


Fig. 10. Differential curves of pore size distribution for composites containing 100 and 200 phr of bentonite ceramized at 600 and 1050°C

Rys. 10. Krzywe różniczkowe rozkładu wielkości porów w kompozytach zawierających 100 i 200 phr bentonitu sceramizowanych w 600 i 1050°C

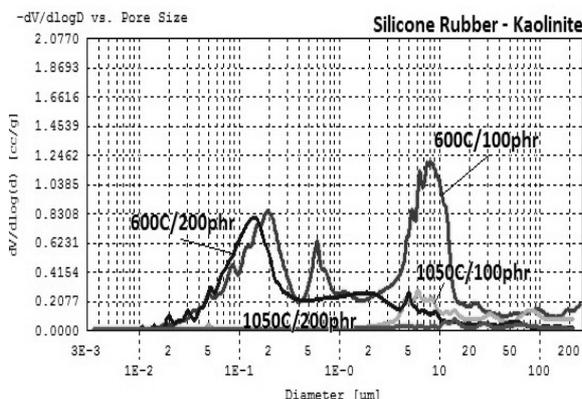


Fig. 11. Differential curves of pore size distribution for composites containing 100 and 200 phr of kaolinite ceramized at 600 and 1050°C

Rys. 11. Krzywe różniczkowe rozkładu wielkości porów w kompozytach zawierających 100 i 200 phr kaolinitu sceramizowanych w 600 i 1050°C

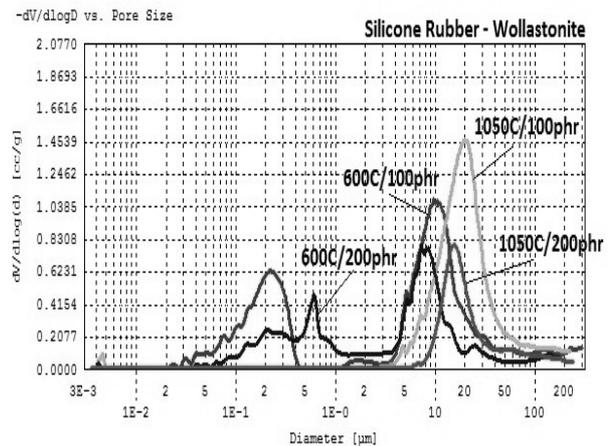


Fig. 12. Differential curves of pore size distribution for composites containing 100 and 200 phr of wollastonite ceramized at 600 and 1050°C

Rys. 12. Krzywe różniczkowe rozkładu wielkości porów w kompozytach zawierających 100 i 200 phr wollastonitu sceramizowanych w 600 i 1050°C

Figures 10-12 illustrate the differential pore size distributions of the ceramized composites. These plots distinctly indicate the modal values of pore size. The decomposition of bentonite (100phr) leads to relatively big pores (~15 µm). The higher amount of bentonite (200 phr) gives mainly a glassy phase with minimal porosity. Similar behaviour is shown by materials with the kaolinite additive. In composites containing wollastonite, a porous microstructure is preserved even after firing at high temperatures for both the types of composition - 100 and 200 phr.

SUMMARY

The performed investigations allowed us to describe the differences in microstructure of silicone rubber-based composites containing an additive of a different crystalline phase.

It was established that the composites with bentonite and kaolinite additives during ceramization finally create an almost non-porous microstructure.

The composites containing the wollastonite additive lead to a microstructure which changed relatively slowly with firing temperature and crystalline phase content. A distinct amount of porosity is present up to the highest temperatures of firing. It should be profitable because of the potential increase of fracture resistance of this ceramized composite and should decrease its thermal conductivity.

Acknowledgments

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