

Optimisation of the Ceramic Phase for Ceramizable Silicone Rubber Based Composites – microstructural aspect

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Keywords: composites, ceramization

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

Introduction

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 make the main part of electrical circuits, responsible for 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 durability under flame, maintaining circuit integrity and energy supply during fire, indispensable to secure time for evacuation or emergency landing. Integrity of electrical cables can be obtained by application of covering insulation made of polymer composites ceramizing at high temperature arising during fire [1]. The paper presents results of investigation on optimization of ceramic phase using different composition of the mineral part of composites. As the main crystalline component bentonite, kaolinite or wollastonite were used. The influence of these phases on silicone matrix was recognised in previous works [2,3]. Investigation of composite transformations (polymer degradation and material ceramization) during heating up to 1050°C showed the influence of a type of crystalline phase on the composite microstructure after ceramization at the whole interesting temperature range (600 – 1050°C) [4].

Experimental

Materials used for investigation were silicone rubber-basing composites. They were composed of silicon rubber containing silanized Silbond binder (45 phr; *phr* – *parts per hundred of rubber*) and the mixture of glassy phase (in SiO₂- Na₂O-CaO-MgO-Al₂O₃ 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). 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.

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

Results and Discussion

Figures 1 – 3 show results of XRD diffraction analyses of investigated composites containing 100phr proportion of ceramic compound. The content of crystalline phases recognized in investigated materials after ceramization is given in the left upper corner of each figure.

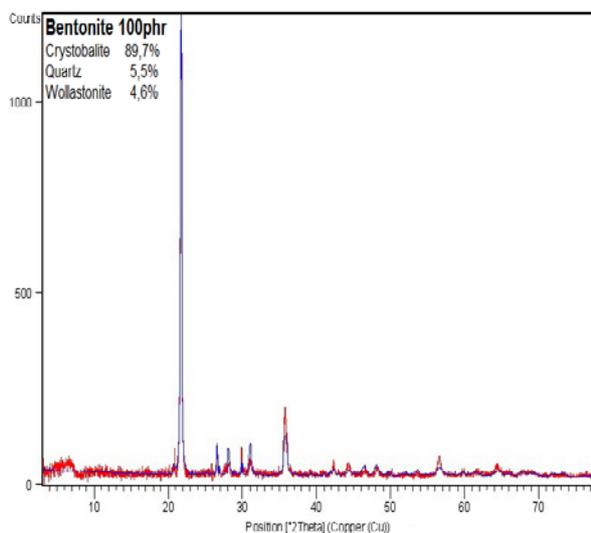


Fig. 1. XRD diffraction pattern of crystalline phases formed during ceramization of bentonite containing sample.

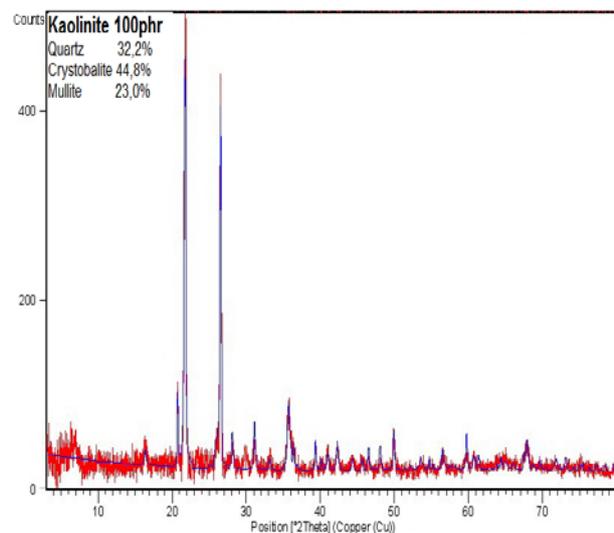


Fig. 2. XRD diffraction pattern of crystalline phases formed during ceramization of kaolinite containing sample.

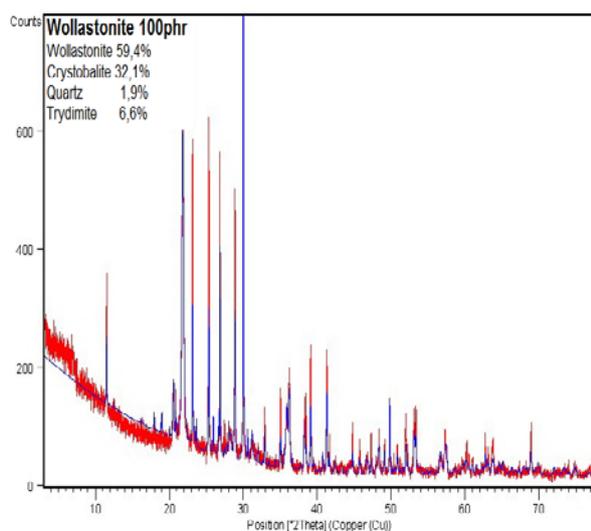


Fig. 3. XRD diffraction pattern of crystalline phases formed during ceramization of wollastonite containing sample.

During heat treatment of each type of composite a big amount of silica is 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 ceramized composite porosity, especially .

The description of pore size distribution of materials subjected to high temperature (“ceramized“) were collected in Figures 4 - 8. Figure 4 compares pore size distribution for composites containing 100 phr of “ceramic mixture”. After firing at 600°C porosity of each composite is rather high - the highest in bentonite containing material, the lowest in wollastonite containing one. Firing at 1050°C decreased porosity in all materials (Fig. 5), but this effect was observed for bentonite and kaolinite containing materials mainly. Composite with wollastonite showed relatively stable porosity, however the structure of porosity was changed, the smallest pores were eliminated.

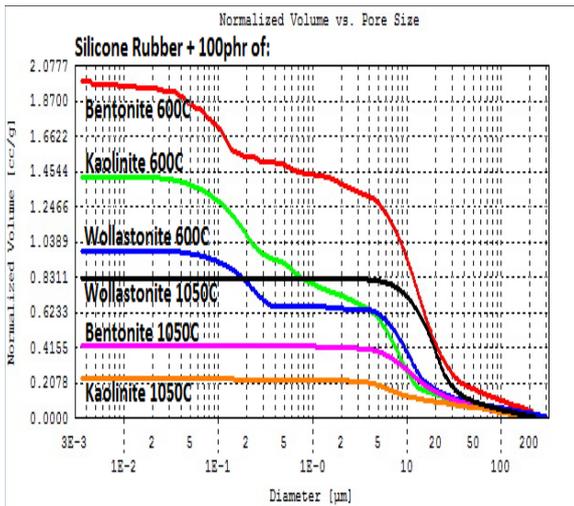


Fig. 4. Cumulative curves of pore size distribution for composites containing 100phr of crystalline phase ceramized at 600 and 1050°C

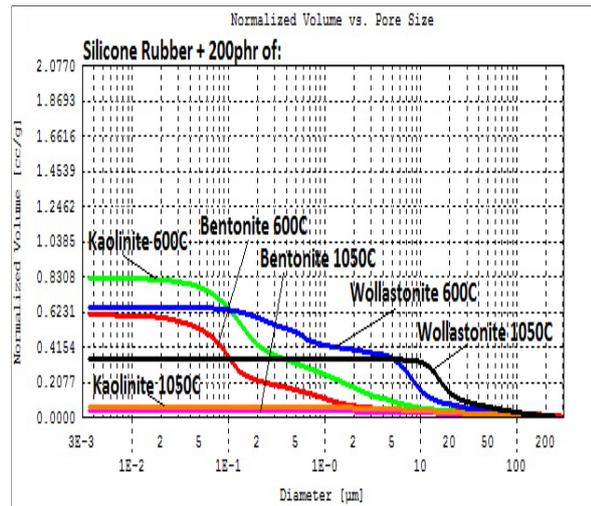


Fig. 5. Cumulative curves of pore size distribution for composites containing 200phr of crystalline phase ceramized at 600 and 1050°C

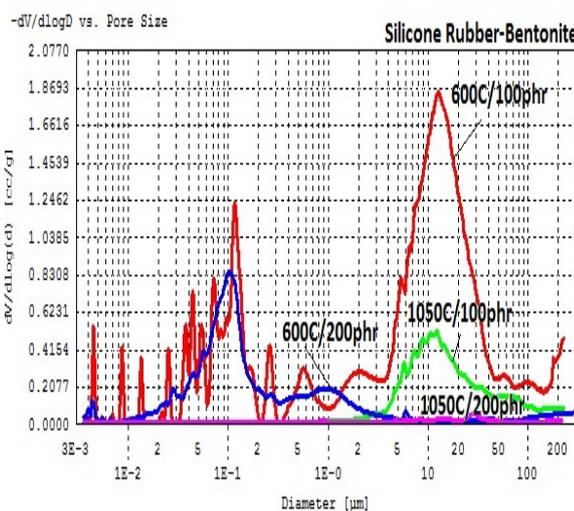


Fig. 6. Differential curves of pore size distribution for composites containing 100phr and 200phr of bentonite ceramized at 600 and 1050°C.

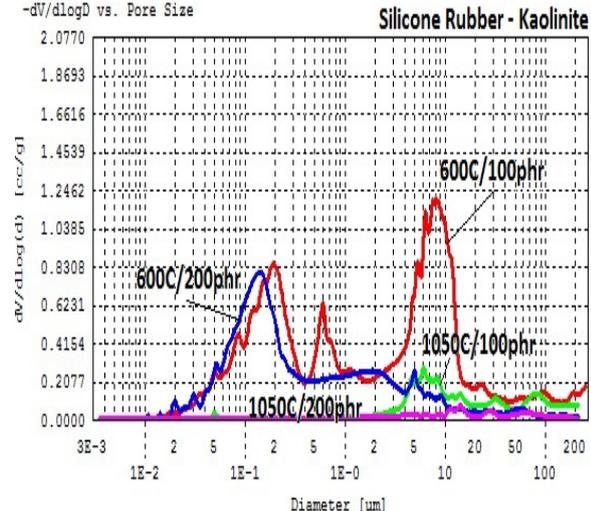


Fig. 7. Differential curves of pore size distribution for composites containing 100phr and 200phr of kaolinite ceramized at 600 and 1050°C.

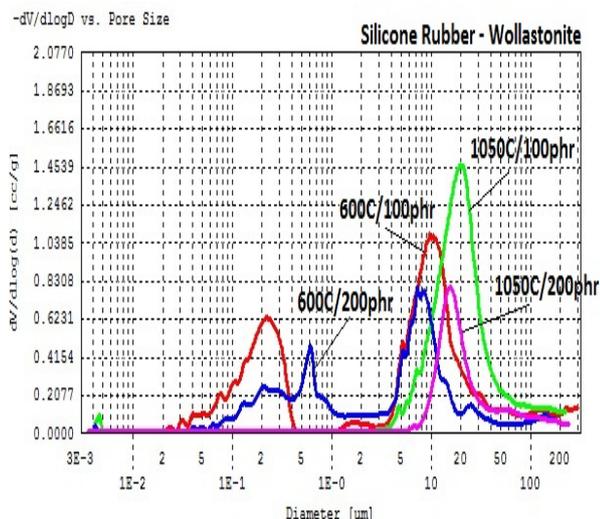


Fig. 8. Differential curves of pore size distribution for composites containing 100phr and 200phr of wollastonite ceramized at 600 and 1050°C.

Figures 6 – 8 illustrate the differential pore size distributions of ceramized composites. These plots distinctly indicates the modal values of pore size. Decomposition of bentonite (100phr) lead to relatively big pores (~15 µm). The higher amount of bentonite (200phr) gives mainly glassy phase with minimal porosity. The similar behaviour show materials with kaolinite additive. In composites containing wollastonite porous microstructure is preserved even after firing at high temperature for both types of composition – 100phr and 200phr.

Summary

Performed investigations allowed us to describe the differences in microstructure of silicone rubber-basing composites containing the additive of different crystalline phase.

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

Composites containing wollastonite additive lead to the microstructure which changed relatively slow 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 potential increase of fracture resistance of ceramized composite and should decrease its thermal conductivity.

Acknowledgments

Authors are greatly indebt to Dr. M.M. Bućko from Technology of Ceramics and Refractories Department of AGH for his XRD analyses.

We would also to express our thanks to M.Sc. R. Lach for assistance in porosimetry measurements.

The work was financially supported by the European Union within a framework of National Coherence Strategy under Innovative Economy Operating Programme; grant no. POIG.01.03.01-00-067/08.

References

- [1] Processable silicone composite materials having high temperature resistance. US Patent 5552466 (03.08.1996)
- [2] S. Hamdani, C. Longuet, D. Perrin, J.-M. Lopez-Cuesta, F. Ganachaud, *Polymer Degradation and Stability* **94** (2009) 465-495
- [3] K. Hayashida, S. Tsuge, H. Othani, *Polymer* **44** (2003) 5611-5616
- [4] Z. Pędzich, D. Bieliński, *Kompozyty/Composites* **10** [3] (2010) 249-254