Influence of Boron Oxide on Ceramization of Silicone-basing Composites

Zbigniew Pędzich[1], Dariusz M. Bieliński[2, 3], Rafał Anyszka[2],
Magdalena Zarzecka-Napierała[1]

Affiliation 1:
Advanced Ceramic Department
AGH – University of Science and Technology
Kraków, Poland

Affiliation 2:
Institute of Polymer and Dye Technology
Technical University of Łódź
Łódź, Poland

Affiliation 3:
Institute for Engineering of Polymer Materials and Dyes,
Piastów, Poland

E-mail: pedzich@agh.edu.pl

Abstract

The paper presents results of investigation on composition of some mineral components used for ceramizable silicone rubber-basing composites.

The paper reports results of investigation on the influence of boron oxide presence in ceramic filler composition. This component is added as the agent controlling the composite transformation when silicone degradation is advanced and creation of continuous ceramic microstructure begin.

The process of silicone matrix degradation during heating up to 1050°C were examined by DSC/TG technique. Microstructural characteristic of ceramized composite bodies created during heating was investigated by mercury porosimetry. The porosity evolution was described in the range of 600 – 1050°C. The strength of ceramized bodies was estimated by compressing test of composite balls heat-treated in the range of 450 – 1000°C. Images of composite microstructures after ceramization was observed using SEM equipment.

Keywords: Silicone rubber, composites, boron oxide

Introduction

Composites with silicone rubber matrix are widely are used for coating of electrical wires working under fire hazard.

Very important property of silicone rubber – ceramic filler composite materials is a possibility of its degradation process during firing in controlled way. Silicone matrix burns at temperatures not exceeded 600°C [1], therefore composite integrity must be assured by its ceramic components from low temperatures.

Additionally, at higher temperatures of firing ceramic shell formed around the wire core must shows good and stable mechanical properties up to temperatures close to the melting temperature of copper.

Using different crystalline phase additives it is possible to assure the proper course of the composite degradation and its transformation during ceramization process[2-4].

Presented work describe results of investigations on the influence of boron oxide and boron containing glass on microstructure and mechanical properties of silicone-basing composites bodies after their ceramization.

Experimental

Composite mixtures prepared for investigations were composed of silicone rubber MV-1,00 (Silikony Polskie, Nowa Sarzyna, Poland), DCP - dicumyl peroxide (Sigma–Aldrich), boron oxide B_2O_3 (Sigma–Aldrich, additiionally milled), calcined kaolin (Polestar 200R, Imerys, France), glass in $CaO-B_2O_3-SiO_2$ system prepared in Department of Glass of AGH University.

Samples for investigations were prepared using Brabender micromixer. During incorporation of components into silicone rubber rolls rotated with speed of 20 rpm. Homogenization process were performed with rotation speed of 60 rpm during 10 minutes.

Table 1 informs about composition of samples used in investigations. Numbers in table are weight parts of each component.

Table 1. Composition of investigated samples.

Sample	1-1	1-2	2-1	2-2
Silicone Rubber	100	100	100	100
Calcined Kaolin	160	140	140	120
$CaO-B_2O_3-SiO_2$ glass	20	40	20	40
B_2O_3	20	20	40	40
DCP	0.6	0.6	0.6	0.6

The ratio of silicone rubber and all ceramic components was stable for each composite in

amount to 200 phr (*phr - parts per hundred of rubber*). Proportions between kaolin, glass and B_2O_3 were changed.

Determination of silicone rubber thermal degradation process were carried out utilizing DSC/TG (*Differential Scanning Calorymetry / Thermogravimetry*) method. The Netzsch STA449F3 Jupiter eqipment was used.

Composite samples in for of 20 mm in diameter balls were heat-treated at different temperatures (450, 550, 650, 700, 800 and 1000°C) in air atmosphere for 20 minutes. These samples were subjected to compresion tests using Zwick-Roell Z2.5 equipment. The maximum force before destroying of each composite sample was detected.

Pore size distribution measurements were carried out on samples heat-treated at 650 and 1000°C using Quantachrome Poremaster 60 mercury porosimeter.

Microstructures of samples were analyzed using SEM/EDS methods. The FEI & Oxford Instruments Nova Nano SEM 200 apparatus was utylized.

Results and Discussion

Figure 1 illustrates the process of thermal decomposition of silicone rubber used as composite matrix in presented investigations. This is a typical image of such process. Decomposition of silicone rubber starts about 300°C, the most intensive mass loose is observed at 484°C. The end of intensive mass loose could be ascribed to about 600°C. Total amount of mass loose is 53% of starting mass.

The most intensive exothermic effect is observed at 584°C. It is connected with creation of silica phase in nanograins form[5].
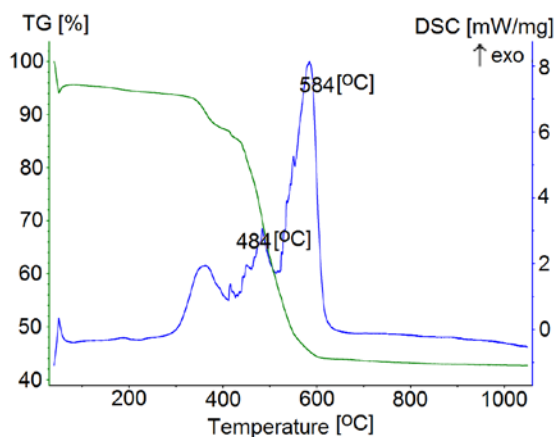

Fig. 1 The DSC/TG curves for silicone rubber.

Figure 2 shows a typical run of compaction force vs. strain curve. Such dependence was used to evaluation of ceramized composite balls strength.

The progress of composite degradation process could be observed in Figure 3 showing the dependence between maximum compaction force noticed during compression tests and heat-treatment temperature. This force could describe the compressive strength of the samples. Generally, samples containing lower content of boron oxide (1-1 and 2-1) show lower strength. The range of the maximum force changes for mentioned samples is between 5 – 50 N. Samples with higher boron oxide content (1-2 and 2-2) change their strength in much wider range (30 – 240 N).
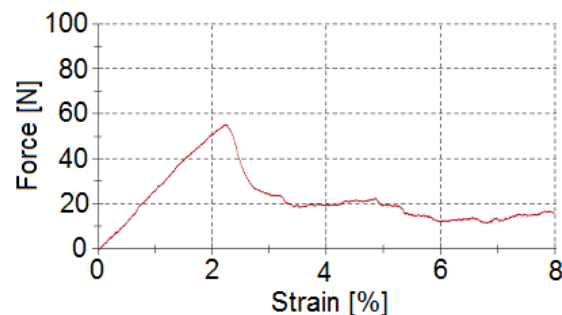

Fig. 2 A typical run of the compaction force vs. strain curve during compaction tests. This particular plot concerns 1-2 composite sample heat treated at 550°C.
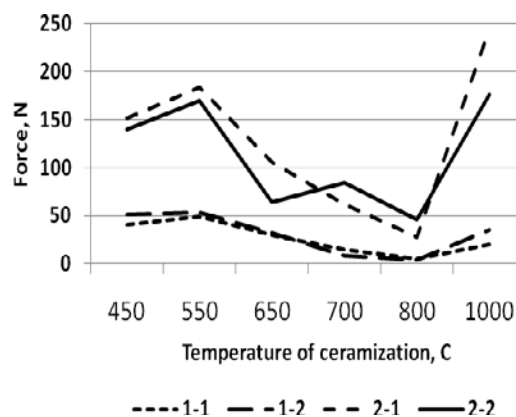

Fig. 3 The maximum pressing force vs. heat-treatment temperature for investigated composites.

Such results suggest that composite matrix degradation is the main factor influenced the ceramized body strength. In all composite bodies ceramized up to 800°C a distinct tendency to strength decrease was observed. It means that up to this temperature connection between ceramic parts of composites and silica produced during rubber decomposition is not strong. Glass in $CaO-B_2O_3-SiO_2$ system with melting point ~780°C could not assure proper wettability of ceramic components. Strength of samples heat-treated at 1000°C were increased. This increase observed in the case of low boron oxide content samples (1-1 and 2-1) was not significant. In samples containing higher amount of boron oxide (1-2 and 2-2) strength increase was very distinct.
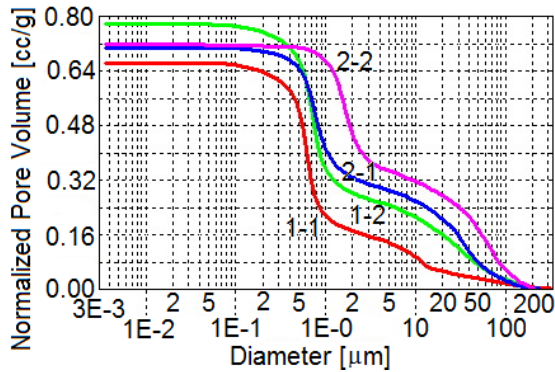
Fig. 4 The normalized pore volume (V) vs. pore size for investigated composites heat-treated at 650°C.
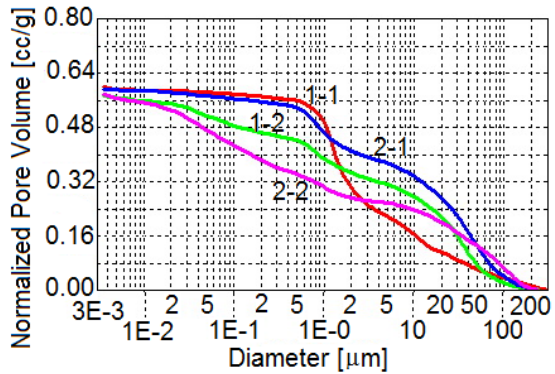

Fig. 5 The normalized pore volume (V) vs. pore size for investigated composites heat-treated at 1000°C.
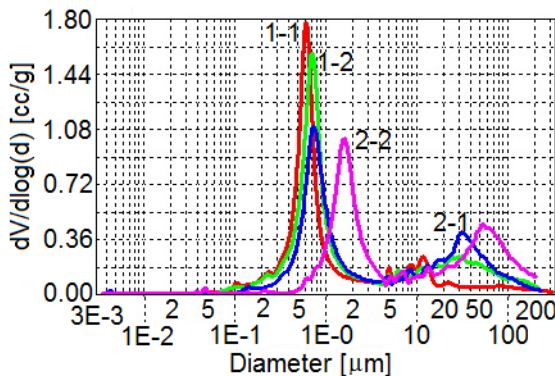

Fig. 6 The normalized differential curve dV/log(d) vs. pore size for investigated composites heat-treated at 650°C (d – pore diameter).
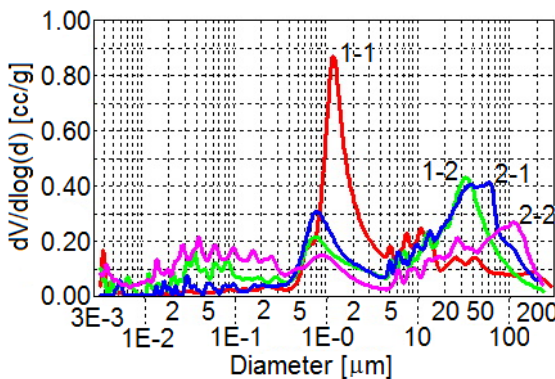

Fig. 7 The normalized differential curve dV/log(d) vs. pore size for investigated composites heat-treated at 1000°C (d – pore diameter).

Analyzes of porosity created during ceramization process are collected in Figures 4 - 7. Cumulative curves of samples ceramized at 650°C (Fig. 4) are similar. Slightly bigger pore volume was detected for samples containing higher boron oxide content. After ceramization at 1000°C, the total pore volumes for each sample were practically the same (Fig. 5). Samples differ in pore size distribution. In samples containing high amount of boron oxide small pores ($\sim 10^{-2}$ μm) have appeared and the pore range dominating in samples ceramized at 650°C (~ 1 μm) was moved to bigger pores ($\sim 20 - 100$ μm) in samples ceramized at 1000°C. The most stable with ceramization temperatures changes pore size distribution was noticed for 1-1 sample.

SEM observations confirms that in 1-1 sample the process of "joining" ceramic phase grains is limited. Figures 8 and 9 illustrate changes in microstructure between 650°C and 1000°C ceramization temperature.
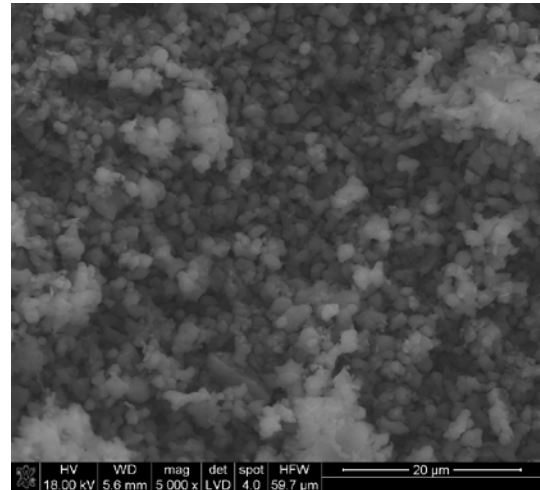

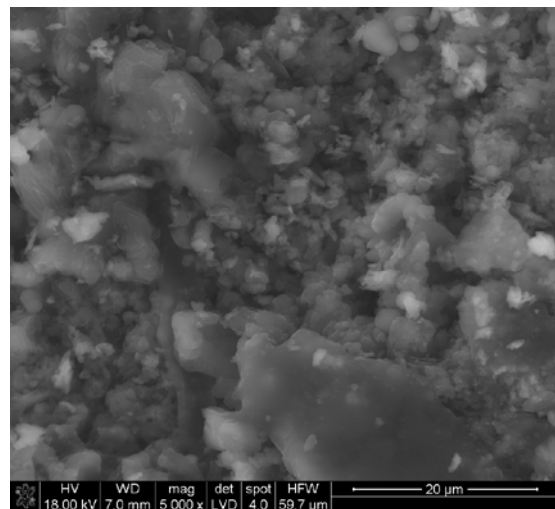**Fig. 8** A typical SEM image of 1-1 sample ceramized at 650°C.

Fig. 9 A typical SEM image of 1-1 sample ceramized at 1000°C.

After ceramization at 650°C the glassy phase is present in the form of isolated grains (Fig. 8). Even after firing at 1000°C glass joins individual grains in limited areas (Fig. 9).

Contrary to above described microstructures, in sample 2-2 continuous glassy phase is present from low temperatures (Fig. 10). After ceramization at the highest applied temperature glassy phase dominates in the microstructure. However, relatively high porosity composed of large pores is preserved in this material (see Fig. 7). This phenomenon not decrease the ceramized body strength what is very important for its application.
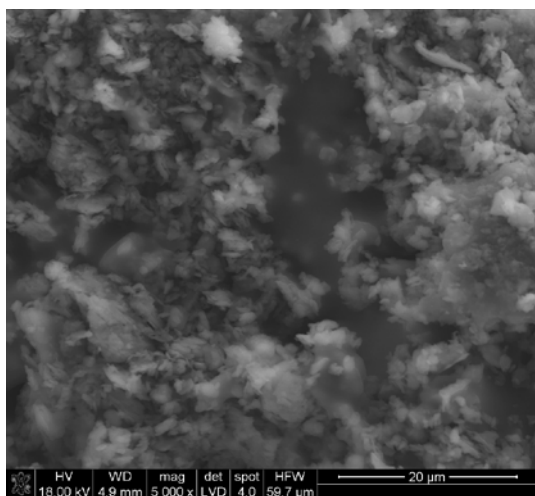

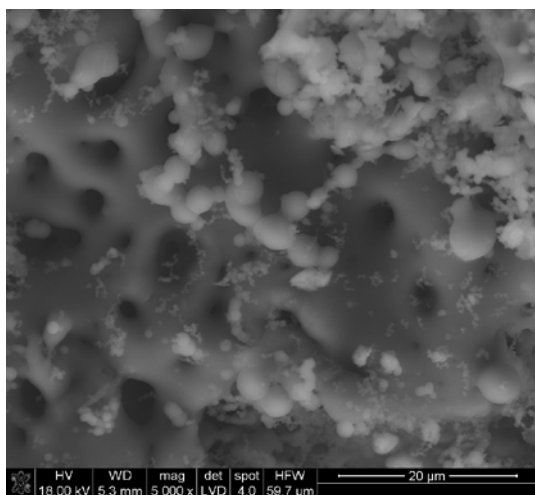**Fig. 10** A typical SEM image of 2-2 sample ceramized at 650°C.

Fig. 11 A typical SEM image of 2-2 sample ceramized at 1000°C.

Conclusions

Performed investigations allowed us to describe the differences in microstructure and mechanical strength of silicone rubber-basing composites containing calcined kaolin, glass in $CaO-B_2O_3-SiO_2$

system and boron oxide after ceramization at different temperatures.

It was establish that relatively strong ceramized bodies were form in samples with high content of boron oxide, the amount of glassy phase was not decisive. Relatively big pores present in microstructure after ceramization at higest temperatures did not decrease its strength.

In samples with low boron oxide content ceramized bodies showed low strength, because of weak connection between ceramic grains present in the material.

Conducted investigations showed that is possible to achieve, after ceramization of silicone-basing composite at a wide range of temperatures, the microstructure relatively porous and strong.

Acknowledgement

References

1. P.R. Dvornic, *Thermal stability of polysiloxanes: silicone–containing polymers*, in R.G. Jones, W. Ando, J. Chojnowski (eds), Kluwer Academic Publisher, Dordrecht, the Netherlands (2000) 185-212.

2. S. Hamdani, C. Longuet, D. Perrin, J.-M. Lopez-Cuesta, F. Ganachaud, Flame retardancy of silicone-based materials, *Polymer Degradation and Stability* **94** (2009), 465-495.

3. S. Hamdani, C. Longuet, J.-M. Lopez-Cuesta, F. Ganachaud, Calcium and aluminium-based fillers as flame-retardant additives in silicone matrices. I. Blend preparation and thermal properties, *Polymer Degradation and Stability* **95** (2010), 1911-1919.

4. K. Hayashida., S. Tsuge., H. Othani., Flame retardant mechanism of polydimethylsiloxane material containing compound studied by analytical pyrolysis techniques and alkaline hydrolysis gas chromatography, *Polymer* **44** (2003), 5611-5616.

5. G. Camino, S. Lomakin, M. Lazzari, Polydimethylsiloxane thermal degradation. Part 1. Kinetic aspects,. *Polymer* **42** [6] (2001), 2395-2402.