Polish Society of
Composite Materials
Polskie Towarzystwo
Materiałów Kompozytowych

12: 4 (2012) 251-255

COMPOSITES
THEORY AND
PRACTICE

Zbigniew Pędzich[1], Alicja Bukańska[1], Dariusz M. Bieliński[2,3], Rafał Anyszka[2], Jan Dul[3], Grzegorz Parys[3]

[1] AGH - University of Science & Technology, Advanced Ceramics Department, al. Mickiewicza 30, 30-059 Krakow, Poland
[2] Lodz University of Technology, Institute of Polymer & Dye Technology, ul. Stefanowskiego 12/16, 90-924 Lodz, Poland
[3] Division of Elastomers & Rubber Technology, Institute IMPiB, ul. Harcerska 30, 05-820 Piastów, Poland
**Corresponding author. E-mail: pedzich@agh.edu.pl*

Received (Otrzymano) 22.10.2012

MICROSTRUCTURE EVOLUTION OF SILICONE RUBBER-BASED COMPOSITES DURING CERAMIZATION IN DIFFERENT CONDITIONS

The work describes the microstructural changes occurring during the ceramization of silicone rubber-based composites in different conditions. Ceramization is a phenomenon which assures the compactness of polymer-based composites in the case of its thermal degradation caused by open fire or exposure to high temperatures. Polymer-based materials used as wire coatings contain a certain amount of mineral additives. Their type, volume, and grain size distribution are decisive for shaping the microstructure of a ceramized body. Moreover, the ceramization conditions can strongly influence its final microstructure. The total porosity, open porosity, pore size distribution and ceramized body compactness evolve with changes to the degradation temperature of the composites at which they have been studied.

Keywords: silicone composites, ceramization, microstructure

EWOLUCJA MIKROSTRUKTURY KOMPOZYTÓW SILIKONOWYCH PODCZAS CERAMIZACJI W RÓŻNYCH WARUNKACH

W niniejszej pracy opisano zmiany mikrostrukturalne kompozytów silikonowych poddanych ceramizacji w różnych warunkach. Ceramizacja jest procesem zapewniającym zwartość kompozytów polimerowych w przypadku termicznej degradacji materiałów, spowodowanej ogniem bądź poddaniem ich na działanie wysokiej temperatury. Polimerowe materiały przeznaczone na osłony przewodów elektrycznych zawierają określoną ilość napełniaczy mineralnych. Ich rodzaj, udział objętościowy oraz wielkość cząstek decydują o mikrostrukturze warstwy ceramicznej. Co więcej, o strukturze kompozytów po ceramizacji w znacznej mierze decydują również warunki, w jakich prowadzono proces ceramizacji. Całkowita objętość porów, objętość porów otwartych, dystrybucja wielkości porów oraz zwartość struktury zmienia się wraz ze zmianą temperatury degradacji, w jakiej badano kompozyty.

Słowa kluczowe: kompozyty silikonowe, ceramizacja, mikrostruktura

INTRODUCTION

Strict law regulations concerning fire hazards in special function structures, like schools and other buildings serving educational purposes, trade and recreation centers, supermarkets, hospitals, sport halls, airports, multistorey buildings, cinemas, theatres, museums, art galleries, railways and metro stations, briefly speaking, all those places, where a great number of people are usually present or goods of significant cultural and/or material value, have nowadays been established in many countries. According to the existing regulations, the functioning of monitoring systems, fire signalization and power supply installations have to be guaranteed for 90 min.

Metal rods in the protective covering make 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. The flame resistance of electrical cable covering insulation is very important for the integrity of the whole electrical circuit. Materials used nowadays, based on silicone rubber or PVC are incombustible, but the problem concerns their mechanical durability under flame, to maintain circuit integrity and energy supply during fire, indispensable to secure time for an evacuation or emergency landing. The integrity of electrical cables can be obtained by applying a covering insulation made of polymer composites ceramizing at a high temperature arising during a fire. Using different crystalline phase additives, it is possible to assure the proper course of composite degradation and its transformation during the ceramization process.

There are some reports on the application of Ca-based (CaO, $Ca(OH)_2$, calcite - $CaCO_3$, wollastonite

- $CaSiO_3$) or Al-based (Al_2O_3, $Al(OH)_3$, boehmite - AlOOH, mica, montmoryllonite) minerals as fillers for silicone rubber [1-3]. In combination with an adequate selection of fluxing agents (glass frites, zinc or ferric oxides, zinc borate etc.), shifting the melting of the ceramic phase to lower temperatures, results in the ceramization process taking place simultaneously to the degradation of the polymer matrix (starting already from 350°C), limiting the escape of its volatile products [4, 5]. Finally, on the 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 melting temperature of copper).

Many particular solutions to this problem have also been patented [6-11]. The paper presents the results of investigations on the optimization of the ceramic phase using a stabilized composition of the mineral part of composites and changing the fluxing agent.

EXPERIMENTAL PROCEDURE

The materials used for the investigations were silicone rubber-based composites. The composite mixes were prepared using a Brabender (Germany) Plasticorder internal micro-mixer, operating with a rotor speed of 20 rpm during incorporation of the components and 60 rpm during their homogenization (10 min). They were composed of a mixture of silicone rubber compounds, filled with a silica, playing the role of the polymer matrix in which minerals: mica, titanium oxide and glassy phases of different compositions, playing the role of the fluxing agent, were incorporated in fixed amounts. The crosslinking agent - dichlorobenzoyl peroxide, was added to the mixtures on a David Bridge (UK) two-roller external mixer at 40°C. The composition of the studied silicone mixes is given in Table 1, together with identification of the applied fluxing agents.

Ceramization tests were performed using three different algorithms of furnace temperature increase. The first method of heating was a relatively slow temperature increase from 20°C up to 1000°C with a 300°C/h heating rate and 20 minutes of soaking time at maximum temperature.

TABLE 1. **Composition of studied silicone mixes**
TABELA 1. **Skład badanych kompozycji silikonowych**

No	Component	Content [phr]
1	Silicone mix, Polsil 60 (50 phr of silica)	70
2	Silicone mix, Polsil 40 (22 phr of silica)	30
3	Fluxing agent*	10
4	Mica (Phlogopite)	15
5	TiO_2	5
6	2,4 - dichlorobenzoyl peroxide	2.5

* Fluxing agents (frits) used for investigations: - FR2050 (commercial grade, Reimbold & Strick, Germany); - RC-9 (synthetized at Institute of Ceramic and Building Materials, Warsaw, Poland, based on their own patents); - Z-01 (synthetized ibid., according to our instructions)

The second method of firing was rapid placement of the fired samples in a furnace heated up to 1000°C. The soaking time was also 20 minutes.

The third method of firing was similar to the second one, however, the maximum temperature was 800°C. The ceramized samples were subjected to compression tests using a Zwick & Roell Z2.5 instrument (Germany). The maximum force required to destroy a composite sample was detected. The mechanical strength of the ceramized materials was calculated as the average value of 5 determinations.

The pore size distribution of the ceramized bodies was measured by mercury porosimetry using a Quantachrome Poremaster 60 (USA) device. The microstructures of the ceramized samples were examined by scanning electron microscopy using a Nova Nano SEM 200 FEI (UK) apparatus.

RESULTS AND DISCUSSION

The macroscopic images of the ceramized samples after the strength test were collected in Figure 1. These images illustrate the differences in morphology of samples fired in different conditions.

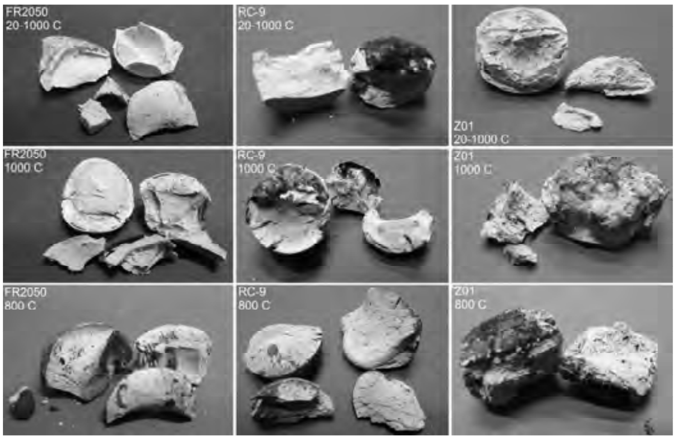

Fig. 1. Images of investigated composites ceramized in different conditions after strength tests

Rys. 1. Zdjęcia badanych kompozytów, sceramizowanych w różnych warunkach, po testach wytrzymałościowych

Figures 2-4 illustrate the ceramized samples morphology in the micrometric scale. There were general similarities in the microstructures of composites containing different frits ceramized under similar conditions. The samples fired slowly up to 1000°C showed a compact microstructure. All the ceramic components, even large mica grains (flakes), were tight joined with the glassy phase produced during ceramization.

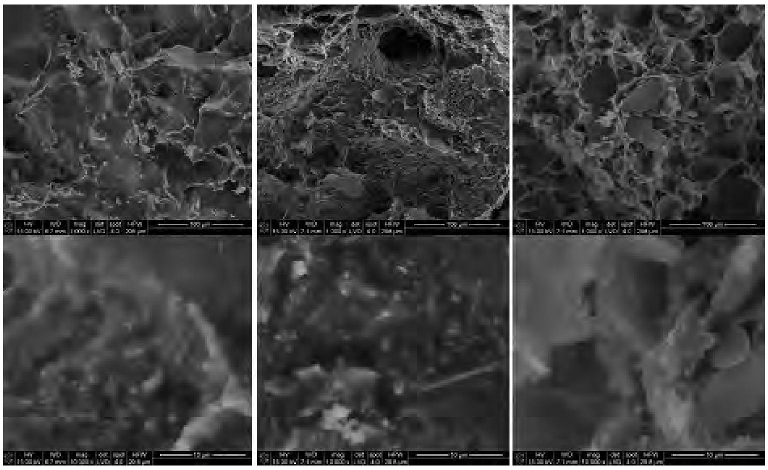
Slow firing 20-1000°C Rapid firing at 1000°C Rapid firing at 800°C

Fig. 2. SEM images of composite composite FR2050 frit, ceramized in different conditions

Rys. 2. Zdjęcia SEM kompozytu zawierającego frytę FR2050, sceramizowanego w różnych warunkach

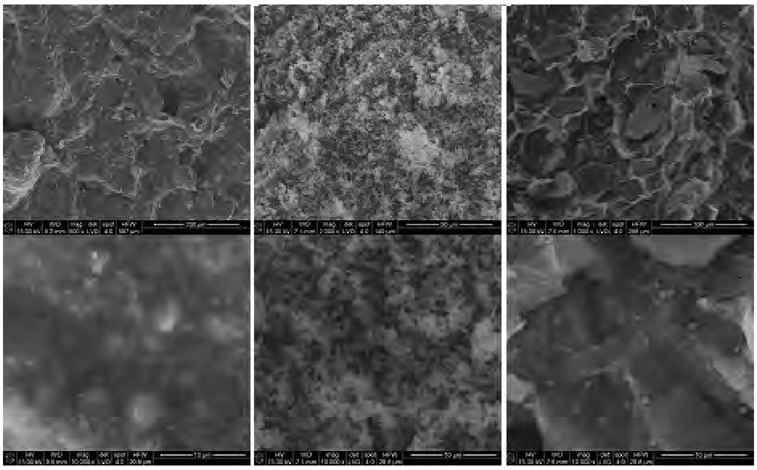
Slow firing 20-1000°C Rapid firing at 1000°C Rapid firing at 800°C

Fig. 3. SEM images of composite containing RC-9 frit, ceramized in different conditions

Rys. 3. Zdjęcia SEM kompozytu zawierającego frytę RC-9, sceramizowanego w różnych warunkach

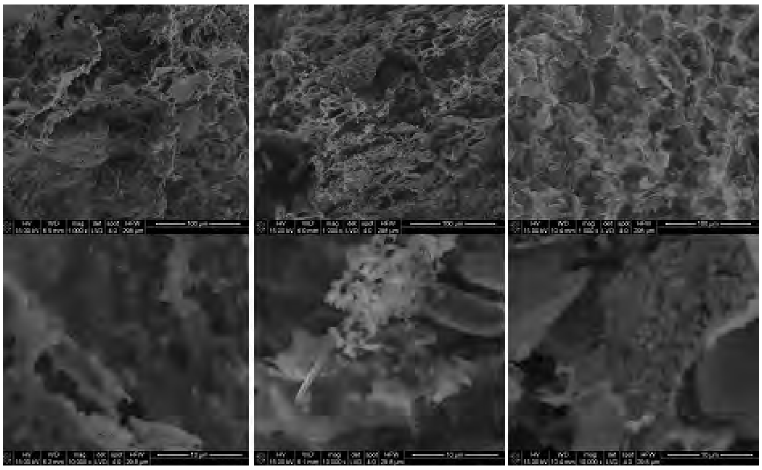
Slow firing 20-1000°C Rapid firing at 1000°C Rapid firing at 800°C

Fig. 4. SEM images of composite containing Z01 frit, ceramized in different conditions

Rys. 4. Zdjęcia SEM kompozytu zawierającego frytę Z01, sceramizowanego w różnych warunkach

The microstructures of samples fired in a rapid way were much more porous. In the samples heated at 1000°C, there was a significant amount of nanometric silica produced during polymer degradation. Fine particles of silica were especially present in the sample containing RC-9 frit. This free silica on the ceramized sample surface could be bound with the rest of the material during successive heating, but in the case of a real fire, the external conditions could make it impossible. Such a structure is weaker than the compact structure achieved during slow heating. All the samples heated at 800°C have a loose microstructure with distinct mica flakes protruding from the glassy phase. Particles of nanometric silica were also present. The results of the strength tests describe the state of compactness of the ceramized bodies. In fact, all the investigated samples have the same mineral composition. The only difference is the type of fluxing agent. Table 2 collects the results of measurements of the maximum force noticed during the compression test. The analysis of this data showed that each tested frit influenced the ceramized composite compactness in a different way. After fast firing at 800°C, the composite containing Z01 frit showed the maximum strength. Its strength was about three times higher than the composite containing FR2050 frit. The increase in temperature of the fast firing up to 1000°C did not change the strength of the composites containing FR2050 and RC-9 frites. The material containing Z01 frit showed a significant strength loss ~50%.

TABLE 2. **Compression strength of ceramized silicone composites**

TABELA 2. **Wytrzymałość na ściskanie sceramizowanych kompozytów silikonowych**

No	Sample	Average maximum force during compression test [N]		
		800°C	1000°C	20÷1000°C
1	FR2050	20 ±5	23 ±6	64 ±8
2	RC-9	48 ±4	48 ±5	431 ±60
3	Z01	67 ±7	26 ±4	76 ±8

± - denotes standard deviation

Slow firing in the temperature range of 20÷1000°C led to the strongest ceramized bodies for each investigated composition. The difference was in the scale of strength improvement. The material containing FR2050 frit after slow firing was about 250% stronger than the fast fired one. The composite with the RC-9 frit addition showed almost a one order of magnitude strength increase after applying the slow firing procedure. The using of Z01 frit led to a composite material which showed a compactness decrease when the fast firing temperature increased. It could not be beneficial for the strength of a fast ceramized body. The porosimetric data collected in Figure 5 shows a correlation between the strength and porosity of ceramized bodies. Generally, samples fired rapidly at 800°C have the biggest pore volume. The smallest pore volume was detected in the samples slowly fired up to 1000°C.

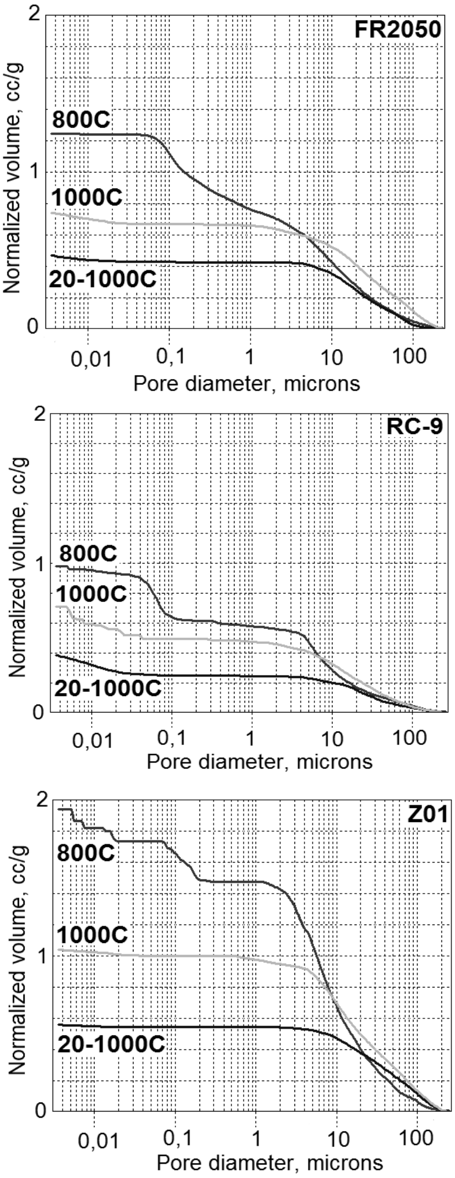

Fig. 5. Pore size distribution plots of ceramized samples investigated in presented work. Type of fluxing agent is indicated in right top corners of plots. Description of plots indicate ceramization conditions

Rys. 5. Dystrybucja rozmiaru porów próbek po ceramizacji, prezentowanych w niniejszej pracy. Rodzaje topników zostały podane w prawym górnym rogu. Opisy krzywych odnoszą się do warunków ceramizacji

It is worth noting that rapid firing at 800°C gave samples with a distinct fraction of small pores (~ 0,1 micron and less). It suggests that at this temperature, all the used fluxing agents did not assure proper wettability of the mineral components of the fired material. The microstructures of the ceramized bodies have a relatively big pore volume and their size distributions were rather wide. The higher firing temperature (1000°C) causes small pores to close and the pore size distributions were narrow. It was probably an effect of the better wettability of the fluxing agents. They effectively join the mineral particles of the composites. Anyway, the most compact microstructures were created when the ceramization proceeded relatively slowly.

CONCLUSIONS

Polymer based composite materials dedicated for electrical cable coverings must show their ability to ceramize in an emergency situation when a fire happens. In practice, it is not possible to predict the fire conditions, i.e. the rate of temperature increase, the maximum temperature, etc. A good cable covering should have properties as stable as possible. Polymer matrix degradation takes place at temperatures up to 700°C [12]. At higher temperatures, the ceramic components and products of polymer degradation are responsible for the material properties. These properties should be stable or should change in a predictable way.

The performed studies confirmed that the type of used fluxing agent strongly influenced the compactness of silicone based composites after ceramization. These studies allowed us to compare the effectiveness of various fluxing agents, which can be applied as composite components. Depending on the used frit, the composites showed different microstructures and mechanical properties after ceramization. The mentioned properties could distinctly change with the ceramization condition changes. The final microstructure and strength did not depend only on the maximum temperature. Furthermore, the firing kinetics are very important for the ceramized body properties.

Acknowledgements

The authors are greatly indebted to M.Sc. B. Trybalska from the Technology of Ceramics and Refractories Department of AGH University for her assistance during SEM analyses.

The work was financially supported by the European Union in the frame of the Regional Development Fund, Project POIG.01.03.01-00-067/08-03.

REFERENCES

[1] Hamdani S., Longuet C., Lopez-Cuesta J.-M., Ganachaud F., Polym. Deg. Stabil. 2010, 5, 1911-1919.

[2] Hamdani S., Longuet C., Perrin D., Lopez-Cuesta J.-M., Ganachaud F., Polym. Deg. Stabil. 2009, 94, 465-495.

[3] Hayashida K., Tsuge S., Othani H., Polymer 2003, 44, 5611-5616.

[4] Principal types of particulated fillers: particulate-filled polymer composites, eds. M. Hancock, R. Rothon, 2nd ed., RAPRA Technology Ltd., UK 1995, 85-88.

[5] Hermansson A., Hjertberg T., Sultan B-A., Fire Mater. 2003, 27, 51-70.

[6] Alexander G., Rigopoulos N., Marney D., WO Patent 2010/097705 A1, 2010.

[7] European Patent 0 708 455 A1, 1996.

[8] Beckley D.A., Stites J., US Patent 5552466, 1996.

[9] Ariagno D., Barruel P., Viale A., European Patent 0 467 800, 1992.

[10] Branlard P., George C., Leuci C., European Patent 1 238 007, 2003.

[11] Flammwidrige Zusammensetzung zur Herstellung von elektrischen Kabeln mit isolations- und/oder Funktionserhalt, EP 0 708 455 A1, 24.04.1996.

[12] Pedzich Z., Bielinski D.M., Mikrostruktura kompozytów silikonowych po ceramizacji, Kompozyty (Composites) 2010, 10(3), 249-254.