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## CERAMIZABLE SILICONE RUBBER COMPOSITES. INFLUENCE OF TYPE OF MINERAL FILLER ON CERAMIZATION

The phenomenon of silicone rubber ceramization is based on preventing the release of volatile compounds resulting from the thermal decomposition of the polymer matrix through the creation of a ceramic coating on the composite surface. Usually, the coating is composed of mineral filler particles, combined with a fluxing agent. The ceramic barrier created is to protect the copper wire inside the cable from melting, which is additionally strong enough to maintain the mechanical integrity of the electrical circuit. The paper presents experimental data on the mechanical properties of silicone rubber composites, the morphology and strength of their ceramized layer and associated thermal characteristics and flammability of the materials. The results were analysed in terms of their material composition, type, size and surface modification of the mineral fillers. The composite with wollastonite exhibited the most stable structure and properties. Their porosity was the least dependent on the thermal conditions of ceramization, leaving a considerable amount of sub-micron pores up to the highest temperatures.

Keywords: silicone composites, ceramization, mechanical strength, thermal properties

### CERAMIZUJĄCE KOMPOZYTY Z KAUCZUKU SILIKONOWEGO. WPLYW RODZAJU NAPEŁNIACZY MINERALNYCH NA CERAMIZACJĘ

Zjawisko ceramizacji kauczuku silikonowego polega na przeciwdziałaniu uwalnianiu się lotnych związków powstających w wyniku termicznej dekompozycji matrycy polimerowej, poprzez utworzenie ceramicznej powłoki na powierzchni kompozytu. Najczęściej powstaje ona wskutek połączenia cząstek napelniaczy mineralnych za pomocą szklistego topnika. Tego typu ceramiczna bariera ma za zadanie zabezpieczyć miedzianą żyłę wewnątrz przewodu elektrycznego przed stopieniem, będąc jednocześnie na tyle wytrzymałą mechanicznie, aby zapewnić integralność obwodu elektrycznego. W niniejszej pracy zaprezentowano wyniki badań właściwości mechanicznych silikonowych kompozytów ceramizujących, badania morfologii i wytrzymałości powstającej fazy ceramicznej oraz związane z tym zjawiskiem: charakterystykę termiczną i palność badanych materiałów. Uzyskane wyniki badań analizowano z punktu widzenia składu materiału, rodzaju, rozmiaru oraz modyfikacji powierzchni napelniaczy mineralnych. Najbardziej stabilną strukturą i właściwościami odznaczały się kompozyty zawierające wollastonit. Ich porowatość była najmniej zależna od termicznych warunków ceramizacji, zachowując znaczną zawartość porów o rozmiarach submikronowych aż do najwyższych temperatur.

Słowa kluczowe: kompozyty silikonowe, ceramizacja, wytrzymałość mechaniczna, właściwości termiczne

## INTRODUCTION

Flame resistant coatings of electrical cables play a very important role from the point of view of electrical installation performance during a fire. Apart from the mandatory conditions: self-extinguishing, low heat of combustion, limited spread of fire and emission of toxic gases, the material for cable coverings should secure the integrity of electrical circuits at high temperatures. They give indispensable time for the evacuation of buildings or any means of public transportation on fire, supporting the functioning of the power supply

and steering of fire protection systems. In Europe there are two existing standards: EN 50200 and IEC 60331-31:2004, according to which electrical cables are classified from the point of view of their fire durability. The time of correct performance of an electrical cable, subjected to the action of fire at temperatures of  $830 \pm 870^\circ\text{C}$ , reflects its class of flame resistance, e.g. PH90 - 90 min.

The materials applied for the coverings of PH class electrical cables are silicone rubbers filled with silica,

mica (muscovite) and other components, able to form a relatively quickly compact and stiff protective coating, strong enough to maintain the integrity of an electrical circuit, even up to the melting temperature of the metal core [1]. Such materials became commercially available from the beginning of the present century (Corning Dow and Wacker Chemie). Since that time we have witnessed permanent progress in the field.

The paper discusses their influence on the ability of silicone rubber - silica composites, additionally containing wollastonite, muscovite, calcium and aluminium hydroxides or montmorillonite, to ceramize. The fillers differ according to their content, aspect ratio, dimensions and size distribution of particles. The performance of the composites during fire testing has been explained based on the results of their thermal analysis (TGA/DSC and microcalorimetry), as well as morphological studies (microporosimetry and SEM) and breaking strength analysis of the ceramized phase produced during fire or heat treatment.

## EXPERIMENTAL PROCEDURE

### Materials

Four commercial silicone rubber composites of various origin, designated as: F, S, W and N, used for the insulation of electrical cables were the subject of our studies. Detailed information on their composition remains confidential. Nevertheless, from our previous work [2] it follows, that the materials have a similar base made of silicone rubber filled with pyrogenic silica in the amount of ca. 50 phr. Another 50 phr of fillers, being admixed to the base, have been identified as the mineral phase, which differs significantly according to their composition and kind of components - Table 1.

TABLE 1. Mineral phase composition of studied composites  
TABELA 1. Skład fazy mineralnej badanych kompozytów

Silicone composite	Mineral phase composition [wt.%]						
	Wollastonite CaSiO <sub>3</sub>	Quartz SiO <sub>2</sub>	Kaoli- nite	ZnO	Mica (Musco- vite)	Gibb- syte Al(OH) <sub>3</sub>	Portlan- dite CaOH
F	-	-	-	35.5	64.5	-	-
S	-	96.5	3.5	-	-	-	-
W	-	-	-	-	-	96.7	3.3
N	52.0	40.2	7.8	-	-		

The composites studied were ceramized under various conditions:

- by firing in an open flame (measured temperature exceeded 1000°C) with 2 min soaking time, or
- by heating in a Linntherm (Germany) laboratory furnace, from room temperature up to 600, 800 and 1000°C with a heating rate of 20°C/min, followed by 20 min of soaking.

### Methods

Thermal analysis of the composites was performed by Differential Scanning Calorimetry/Thermogravimetry (DSC/TG) using a Netzsch STA449F3 Jupiter instrument (Germany), operated with a heating rate of 20°C/min. The heat releasing rate of the composites was determined by Pyrolysis Combustion Flow Calorimetry (PCFC) with a Fire Testing Technology microcalorimeter (USA), according to the ASTM D7309-2007 standard. The microstructure of the composites subjected to ceramization was analyzed by Scanning Electron Microscopy (SEM) with an FEI & Oxford Instruments Nova Nano SEM 200 apparatus (The Netherlands). Prior to the observations, the sample cross-sections were carbon coated to avoid charging. The pore size distribution of the ceramized composites was determined with a Quantachrome Poremaster 60 mercury porosimeter (USA). The shrinkage parameters of the composites due to heat treatment:  $W_h$  - height shrinkage and  $W_r$  - radial shrinkage, were calculated from changes in the dimensions of cylindrical specimens of radius  $r_0 = 16$  mm and of height  $h_0 = 14$  mm:

$$W_h = \frac{h_1}{h_0} \cdot 100; \quad W_r = \frac{r_1}{r_0} \cdot 100$$

where:  $h_0, r_0$  - dimensions of virgin sample;  $h_1, r_1$  - dimensions of heat treated samples.

The same heat treated specimens were subjected to compression tests using a Zwick Roell Z2.5 instrument (Germany). The mechanical strength of the ceramized composites was each time calculated as an average value of 5 determinations.

## RESULTS AND DISCUSSION

It has been proved that after pyrolysis at high temperatures, some mineral additives are able to form a ceramizable residue in a silicone rubber composite [2]. This residue, due to the reaction between the inorganic fillers and silica issued from the decomposed polymer matrix, forms an eutectic liquid phase at the edges of the fillers, able to penetrate into the matrix region [3]. The extent of the eutectic formation was shown to be influenced by factors such as particle size and the chemical composition of the fillers.

The residue of the fired silicone rubber or silica filled elastomer exhibits a form of white powder. There is no evidence of the solidification of silica particles, even after heating at 1100°C. However, the addition of mica (ca. 20 phr) results in an eutectic reaction (starting already at 900°C) between the mica particles and the silica matrix, producing a liquid phase around their surface, which facilitates binding. At lower firing temperatures (600°C) the problem of binding between the product of pyrolysis (silica) and filler comes back, resulting in the formation of a fragile surface shield.

The problem can be overcome by the addition of certain inorganic materials to the silicone rubber-mica

composite, e.g. glass frits, zinc oxide, ferric oxide and zinc borate, facilitating the formation of a strong ceramic, required by electrical cable application, at lower temperatures. Hamdani et al [4, 5] reported on the application of Ca-based (CaO, Ca(OH)<sub>2</sub>, calcite - CaCO<sub>3</sub>, wollastonite - CaSiO<sub>3</sub>) or Al-based (Al<sub>2</sub>O<sub>3</sub>, Al(OH)<sub>3</sub>, boehmite - AlOOH, mica, montmoryllonite) refractory fillers for silicone rubber. In combination with an adequate selection of flux agents, 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. The integral ceramic layer being created on its surface prevents the volatile products of silicone rubber decomposition [6, 7] from escaping, which makes it porous - Figure 1 [8].

The incorporation of mineral fillers to the silicon rubber matrix changes the thermal properties of the composites - Figure 2.

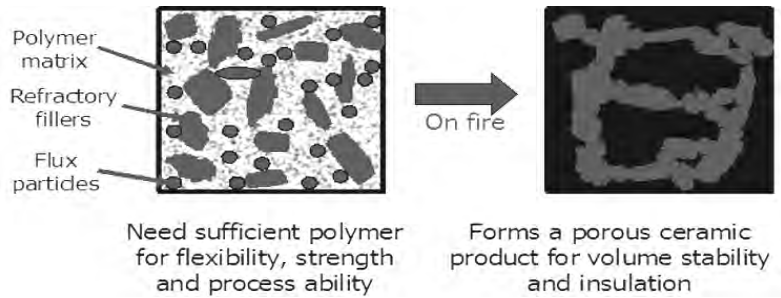
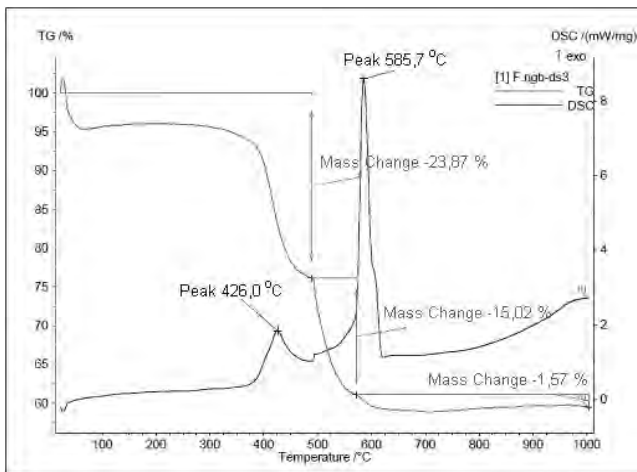


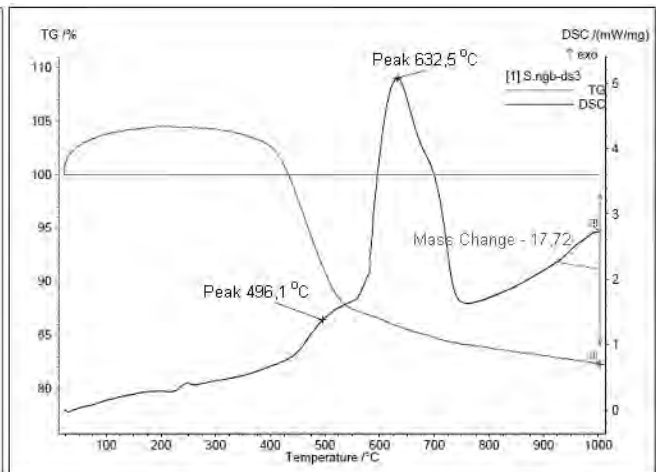
Fig. 1. Scheme illustrating ceramization process of polymer composites [8]

Rys. 1. Schemat ilustrujący proces ceramizacji kompozytu polimerowego [8]

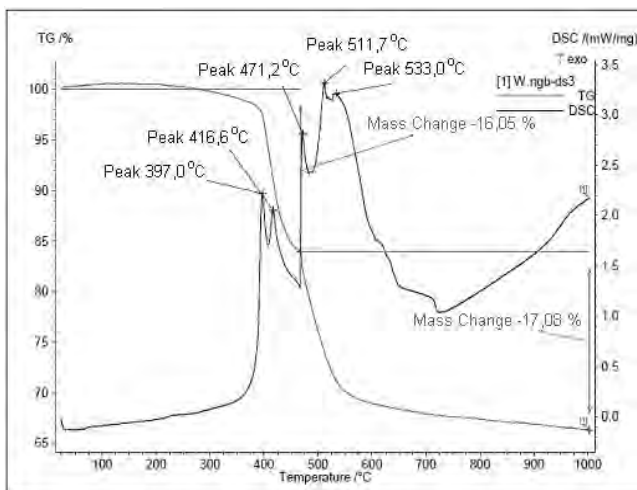
A) composite F



B) composite S



C) composite W



D) composite N

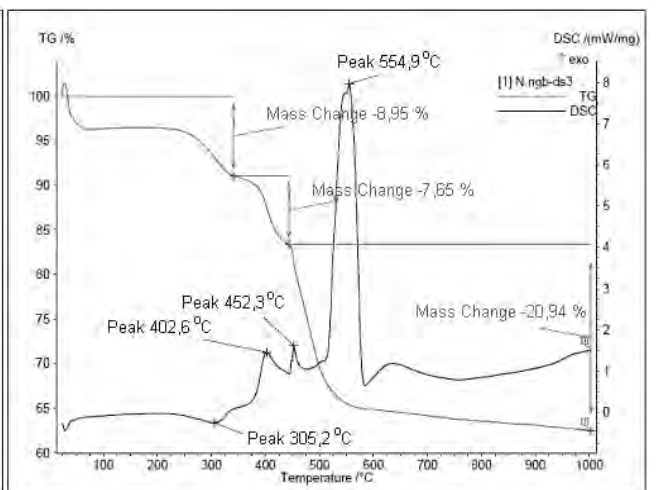


Fig. 2. Results of DSC/TG analysis of studied composites

Rys. 2. Wyniki analizy DCS/TG badanych kompozytów

The main weight loss is associated with the polymer phase of the composites. From the results of TG analysis (green curve) it follows, that the studied composites exhibit a different temperature range of thermal decomposition of silicone rubber. It means that the polymer phase disappears from the system with varying efficiency, depending on the composition of its mineral phase. The process is practically already finished at ca. 600°C for composite N, materials F and W need another 20–30°C to be completed, whereas composite S requires a temperature even exceeding 800°C. Above 800°C, the effects associated with weight loss are practically not observed. It depends on the flux composition required for each of the composites, which has to start melting before the degradation of the silicone matrix is completed. This fact determines the temperature range in which the ceramization process of the composites can take place effectively. Exothermic effects connected with elastomer degradation are difficult to separate. This is a result of the presence of the large amount of ceramic phases. Their structural changes are covered by the strong effects coming from the decomposition of the mineral part decomposition. Nevertheless, composites F and W are characterized by a very narrow melting peak (blue curve), contrary to the broad peaks present in the DSC spectra of the other materials studied. It can be associated with the thicker polymer-filler interphase present in composites N and S. The two regions of maxima visible in the former indicates two kinds of interphase, e.g. originating from two kinds of fillers being applied, whereas the highest melting temperature of the latter can be the result of the strongest polymer-filler interactions. The admixing of mineral fillers to the silicone base decreases the heat release rate (HRR) of the composites - Figure 3. The lower the HRR index, the higher the flame resistance of the material. Apart from the HRR value, also its maximum temperature and time to its appearance are important. The former indicates the best conditions for combustion of the material, whereas the latter classifies the studied composites according to the flame susceptibility of the materials.

The highest effect is observed for composite S, which represents the lowest heat release values. Despite

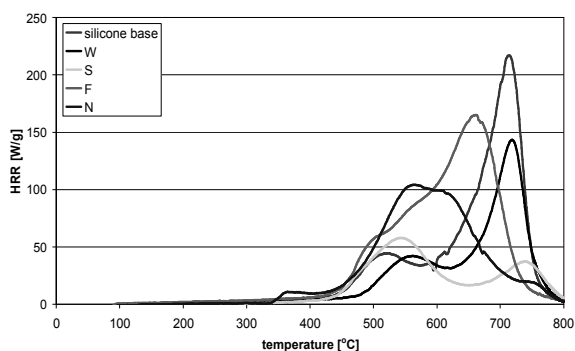
the fact that the maximum of the HRR curve for the material appears in the shortest time, another maximum in the longest time is present as well. Material N combusts at a similar time but more vigorously. Composite F seems to be the worst material, regarding flame resistance. It releases the highest heat in a comparatively short time.

SEM analysis of composites subjected to ceramization makes it possible to reveal the influence of heat treatment conditions on the structure of the materials - Figure 4.

Microscopic analysis of the samples ceramized in a laboratory furnace at 800°C (see left column pictures in Fig. 4) demonstrates significant differences among the studied composites. Material N contains the highest amount of pores, contrary to other composites, for which pores are more difficult to be identified. Detailed information on the pore size distribution of the studied composites is presented in Figure 5.

The porosity of composites N and to a small extent S, contrary to the other materials studied, is represented by two populations of pores: sub-micro and micro ones. The porosity of the composites depends on the ceramization conditions (see right column pictures in Fig. 4). The smallest pores, of sub-micrometer dimensions, disappear when the materials have been fired directly in a flame. The total degree of material porosity also decreases, which has been found to be dependent on the kind of mineral fillers applied [2, 9]. The smallest changes to porosity have been observed for the composites containing wollastonite (N), which additionally are characterized by the smallest mass loss accompanied by an increase in temperature and heating rate [10]. The created ceramic phase should exhibit limited thermal shrinkage, which avoids problems concerning the breaking or delamination of the surface layer from the polymer substrate [11]. Apart from good heat insulation, prolonging the time to material ignition and the decrease in heat release during fire, the micro-porous structure has to be strong enough to maintain the integrity of an electrical circuit. The comparison between the composites studied is given in Table 2.

A) temperature evolution



B) time evolution

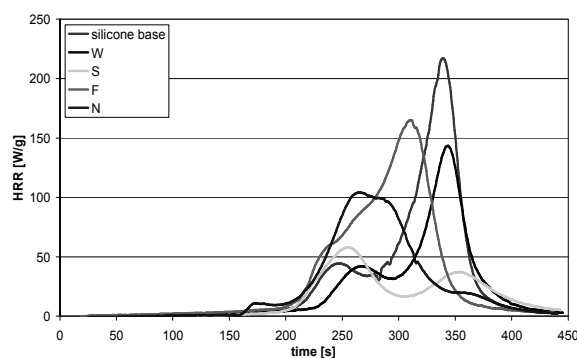


Fig. 3. Heat release rate (HRR) of studied composites

Rys. 3. Szybkość wydzielania ciepła (HRR) badanych kompozytów w funkcji temperatury (A) i czasu (B)

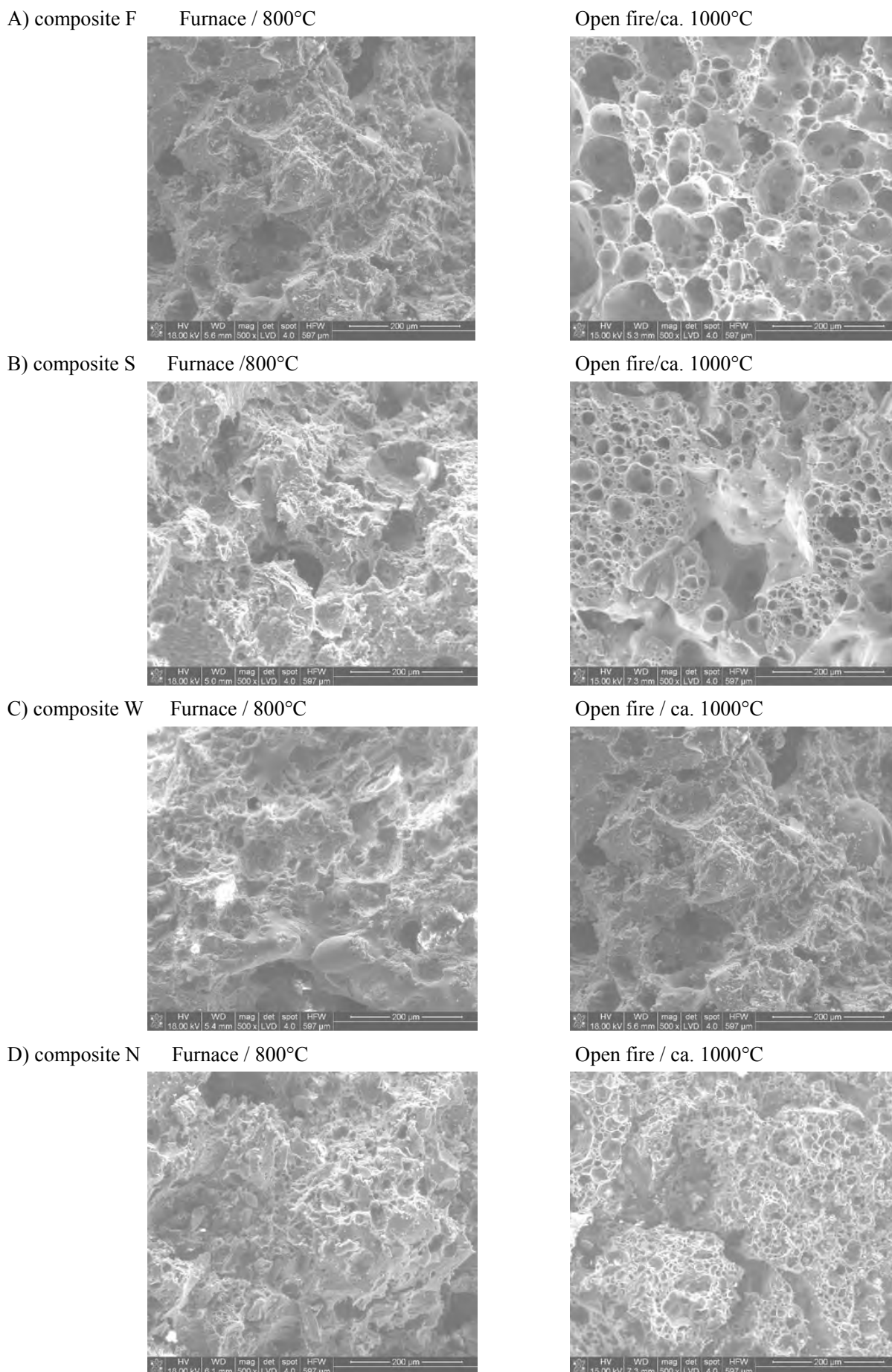
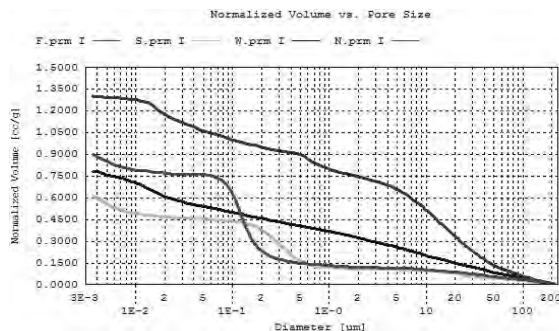


Fig. 4. SEM images of studied composites after ceramization: furnace heated at 800°C (left), fired in open flame (right)

Rys. 4. Zdjęcia SEM badanych kompozytów po ceramizacji: próbki ogrzewane w piecu w 800°C (lewe), spalane w płomieniu (prawe)

A) cumulative analysis



B) aggregative analysis

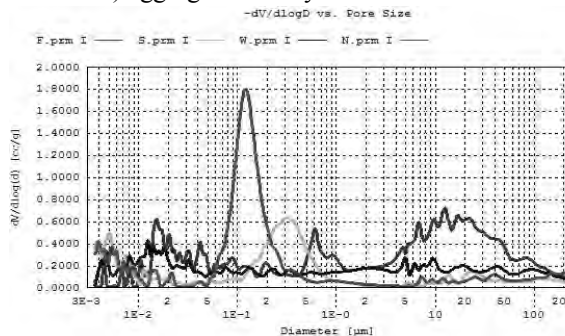


Fig. 5. Pore size distribution for studied composites after ceramization at 800°C

Rys. 5. Dystrybucja wielkości porów badanych kompozytów po ceramizacji w piecu w 800°C: krzywe kumulacyjne (A) i agregacyjne (B)

TABLE 2. Strength and shrinkage parameters of studied composites after ceramization

TABELA 2. Wytrzymałość i skurcz badanych kompozytów po ceramizacji

Parameters Composite	Furnance / 800°C			Open fire / ca. 1000°C		
	$W_h$ [%]	$W_r$ [%]	Force at break [N]	$W_h$ [%]	$W_r$ [%]	Force at break [N]
F	78.93	111.84	7.8	83.62	104.23	32.3
S	91.19	112.35	1480	96.94	103.36	188.0
W	86.55	107.51	16.3	97.73	110.23	54.4
N	97.21	108.30	86.0	79.64	92.08	130.0

The thermal conditions of ceramization strongly influence the shrinkage and mechanical strength of the studied composites. Generally, the higher the shrinkage of the material, the lower the strength of the ceramized composite. Composite N is the only one which shrinks significantly when subjected to direct fire.

CONCLUSIONS

The strength of the ceramized composites depends on the kind of minerals and composition of the mineral phase admixed to the silicone rubber-silica base. The performed investigations allowed us to evaluate the differences in structure of the ceramic phase being formed. The composites containing muscovite and wollastonite have relatively high porosity, contrary to the materials with quartz and calcined kaoline as well as aluminium hydroxide, exhibiting a low porosity level.

The most important for the ceramization process is degradation of the polymer base, taking place usually in the temperature range from 600–800°C, when mineral components do not interact strongly with each other. In a composite for which the decomposition of silicone rubber can be shifted to a higher temperature, the ceramized phase created exhibits a sub-micron porous structure of the highest durability. The conducted experiments also revealed differences in the ceramization effects associated with the thermal conditions of the process. Ceramization performed in an open flame at ca. 1000°C led to ceramic structures distinctly different in porosity and pore size distribution in comparison to the materials gradually heated in a furnace up to 800°C. Generally, firing of the composites in an open

flame produces materials of low porosity, without small pores. As a result of the process carried out at a lower temperature in a furnace, a highly porous ceramic phase of a very wide pore size distribution range is created.

It was established that the composite with wollastonite (N) showed the most stable structure and properties. Its porosity was the least dependent on the thermal conditions of ceramization, leaving a considerable amount of sub-micron pores up to the highest temperatures. It should be profitable from the application point of view, because of the potential increase in fracture resistance of the ceramized composite and a decrease in its thermal conductivity. The conclusions listed above could be helpful in designing an optimal microstructure of silicone composites dedicated for fire resistant applications, e.g. in the cable industry.

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