

# MECHANICAL PROPERTIES OF SILICONE-BASED COMPOSITES DESTINED FOR WIRE COVERS

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## Abstract

The work collects results of investigation on the mechanical properties of silicone rubber-based composites dedicated for the cable industry. Such materials are the composites containing various mineral fillers, like silica, mica, titanium oxide and glassy phases of different compositions, playing a role of a fluxing agent.

The presence of mentioned above ceramic phases could assure the proper behaviour of a composite material subjected to high temperature or flame. At such conditions the composites studied produce a micro-porous but stiff and coherent layer, composed of the mineral filler particles, bounded by a low melting temperature glass phase. The ceramized layer plays a role of a heat insulator for a copper wire inside, additionally preventing electrical circuit from a short-circuit phenomenon. Incorporation of a distinct amount of ceramic phases influences processing and exploitation properties of the silicone composites. In the study presented, the influence of a kind of fluxing agent on mechanical strength of the materials before and after ceramization was investigated. The results were discussed from the point of view of the ceramized phase morphology, studied by SEM and porosimetry.

**Keywords:** composites, silicone rubber, mineral fillers, ceramization

## 1. 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 centres, 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 [1-4]. The paper presents results of investigations on the influence of different composition of the glassy phase part of materials on their mechanical strength and ability to ceramization. As the main mineral components, apart the fluxing agents studied, silica, mica and TiO<sub>2</sub> were applied. Investigation of the ceramic phase morphology, prosity and mechanical properties was carried out for the samples ceramized at various temperatures and with different heating rates.

## 2. EXPERIMENTAL

Materials used for investigation were silicone rubber-based composites. Composite mixes were prepared using a Brabender Plasticorder internal micro-mixer (Germany), operating with rotors 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 a polymer matrix in which minerals: mica, titanium oxide and glassy phases of different compositions, playing the role of a fluxing agent, were incorporated at a fixed amount. The crosslinking agent - dichlorobenzoyl peroxide, was added to the mixes on a David Bridge two-roller external mixer (UK) at 40°C. The composition of the silicone mixes studied is given in Tab. 1, together with a short description on the fluxing agents applied.

Tab. 1 Composition of the silicone mixes studied

No	Components	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 <sub>2</sub>	5
6	2,4 – dichlorobenzoyl peroxide	2.5

\* Fluxing agents tested:

FR – 2035, FR – 2040, FR – 2050, FR – 2055, FR – 2060, FR – 2065 (commercial grade, Reimbold & Strick, Germany)  
 BTS – 16, BOT, RC – 9 (synthesized at the Industrial Institute for Ceramic and ... Materials, based on their own patents)  
 Z – 01, Z – 02, Z – 03 (synthesized *ibid.*, according to our instructions)

Mechanical properties of the composites were determined with a Zwick 1435 instrument (Germany), according to ISO 37. Dumbell specimens were used. Cylindrical composite samples of ca.  $r_0 = 16$  mm of radius and  $h_0 = 14$  mm high, were heat treated at 800 and 1000°C during 20 min. in air and their appearance after the test documented photographically, together with measurements of changes to the dimensions. The following relative parameters were proposed to compare the influence of high temperature on the composites studied:

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

where:

$h_0, r_0$  – dimensions of virgin sample

$h_1, r_1$  – dimensions of heat treated samples

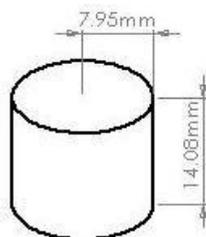


Fig. 1 Dimensions of samples used for the heat treatment experiments.

These 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 an average value of 5 probes.

Additionally, the composite samples were also heated with various speed: 20-1000°C for 20 min., 1000°C for 10 min. and 800°C for 5 min., and fired - using a controlled temperature of 1050°C (the temperature closed to the melting temperature of copper). Microstructure of ceramized samples was examined by a Nova Nano SEM 200 microscope (FEI, UK). Pore size distribution analysis was carried out on heat treated samples using a Poremaster 60 (Quantachrome, USA) mercury porosimeter.

### 3. RESULTS AND DISCUSSION

#### 3.1 Mechanical properties of the composites

Mechanical properties of the silicone composites tested are presented in Tab. 2. The materials meet the requirements of the cable industry ( $TS > 5$  MPa and  $E_b > 300$  %).

Tab. 2 Mechanical properties of the silicone composites studied

No	Sample	SE <sub>100</sub> [MPa]	SE <sub>200</sub> [MPa]	SE <sub>300</sub> [MPa]	TS [MPa]	E <sub>b</sub> [%]
1	FR 2035	2.50	3.51	4.81	5.59	356
2	FR 2040	2.44	3.51	4.93	5.97	369
3	FR 2050	2.42	3.42	4.66	5.75	376
4	FR 2055	2.29	3.34	4.70	5.91	380
5	FR 2060	2.40	3.50	4.89	5.42	342
6	FR 2065	2.51	3.62	5.10	6.49	380
7	BOT	2.76	3.84	5.20	5.09	288
8	BTS 16	2.65	3.89	5.30	5.99	354
9	RC 9	2.69	3.73	5.10	6.49	391
10	Z 01 A	2.48	3.42	4.57	5.17	373
11	Z 02 C	2.59	3.58	4.79	5.87	390
12	Z 03 B	2.45	3.56	4.94	6.58	408

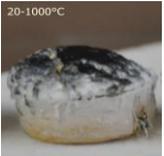
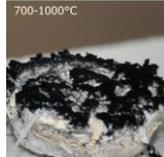
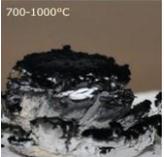
Apart a BOT sample, all the composites studied exhibit values for the relative elongation at break far above  $E_b = 300\%$ . In some cases (Z 03 B, RC 9, Z 02 C)  $E_b$  is even close to 400 %, what is advantageous taking into account processing, but seems to be a little bit too high from the application point of view.

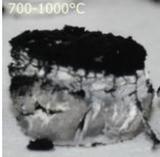
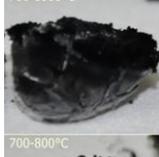
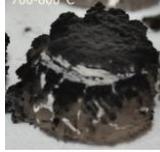
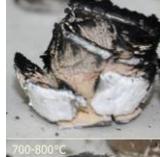
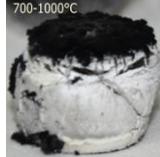
Composites RC 9 and FR 2065 are the strongest among the materials studied  $TS = 6,49$  MPa, whereas the weakest is again BOT of  $TS = 5.09$  MPa.

### 3.2 Behaviour of the composites on fire

The data obtained points on the significant relationship between the experimental conditions and the behaviour of the composites during ceramization. Samples heated slowly from room temperature up to  $1000^\circ\text{C}$  seem to represent the highest integrity, whereas when the composites are heated faster the samples crack readily, losing shape, and additionally their surface becomes covered by a black powder, which is the most probably SiC. Pictures of the composite samples after thermal heating realized at various conditions, together with relative changes to their dimension parameters:  $W_r$  and  $W_h$ , are presented in Tab. 3.

Tab. 3 The effect of thermal heating on ceramization and dimensions of the silicone composites studied

Sample	Parameters	Sample	Parameters	Sample	Parameters
Z-01 „A”	$W_h = 69.7\%$ $W_r = 119.0\%$	Z-02 „C”	$W_h = 68.3\%$ $W_r = 107.6\%$	Z-03 „B”	$W_h = 64.8\%$ $W_r = 117.1\%$
					
	$W_h = 74.2\%$ $W_r = 130.4\%$		$W_h = 85.7\%$ $W_r = 118.5\%$		$W_h = 88.4\%$ $W_r = 123.8\%$
	$W_h = 86.1\%$ $W_r = 120.0\%$		$W_h = 90.3\%$ $W_r = 133.0\%$		$W_h = 95.1\%$ $W_r = 136.9\%$

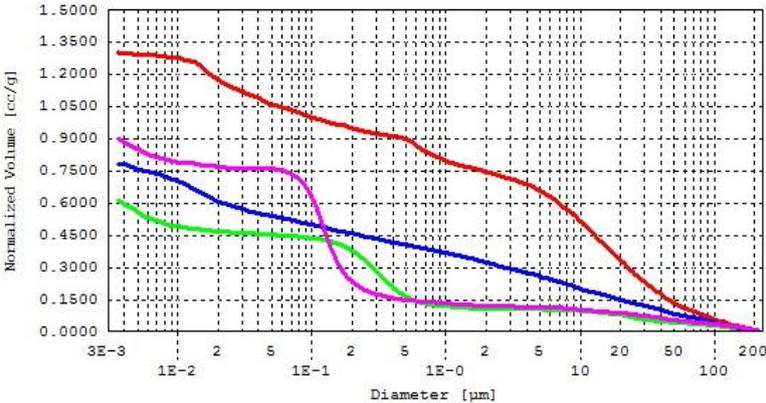
<p><b>BST-16</b></p>  <p>20-1000°C</p>  <p>700-1000°C</p>  <p>700-800°C</p>	<p><math>W_h = 83.7 \%</math> <math>W_r = 99.3 \%</math></p> <p><math>W_h = 86.7 \%</math> <math>W_r = 114.2 \%</math></p> <p><math>W_h = 81.5 \%</math> <math>W_r = 108.5 \%</math></p>	<p><b>BOT</b></p>  <p>20-1000°C</p>  <p>700-1000°C</p>  <p>700-800°C</p>	<p><math>W_h = 71.2 \%</math> <math>W_r = 98.6 \%</math></p> <p><math>W_h = 78.8 \%</math> <math>W_r = 129.4 \%</math></p> <p><math>W_h = 89.0 \%</math> <math>W_r = 124.1 \%</math></p>	<p><b>RC-9</b></p>  <p>20-1000°C</p>  <p>700-1000°C</p>  <p>700-800°C</p>	<p><math>W_h = 67.4 \%</math> <math>W_r = 94.5 \%</math></p> <p><math>W_h = 84.3 \%</math> <math>W_r = 113.6 \%</math></p> <p><math>W_h = 88.8 \%</math> <math>W_r = 119.5 \%</math></p>
<p><b>FR-2055</b></p>  <p>20-1000°C</p>  <p>700-1000°C</p>  <p>700-800°C</p>	<p><math>W_h = 73.8 \%</math> <math>W_r = 95.6 \%</math></p> <p><math>W_h = 90.5 \%</math> <math>W_r = 147.3 \%</math></p> <p><math>W_h = 95.5 \%</math> <math>W_r = 132.2 \%</math></p>	<p><b>FR-2060</b></p>  <p>20-1000°C</p>  <p>700-1000°C</p>  <p>700-800°C</p>	<p><math>W_h = 75.2 \%</math> <math>W_r = 109.4 \%</math></p> <p><math>W_h = 72.7 \%</math> <math>W_r = 117.2 \%</math></p> <p><math>W_h = 92.1 \%</math> <math>W_r = 136.6 \%</math></p>	<p><b>FR-2065</b></p>  <p>20-1000°C</p>  <p>700-1000°C</p>  <p>700-800°C</p>	<p><math>W_h = 94.0 \%</math> <math>W_r = 121.3 \%</math></p> <p><math>W_h = 132.5 \%</math> <math>W_r = 126.0 \%</math></p> <p><math>W_h = 103.3 \%</math> <math>W_r = 121.1 \%</math></p>
<p><b>FR-2035</b></p>  <p>20-1000°C</p>  <p>700-1000°C</p>  <p>700-800°C</p>	<p><math>W_h = 80.0 \%</math> <math>W_r = 93.4 \%</math></p> <p><math>W_h = 73.1 \%</math> <math>W_r = 111.4 \%</math></p> <p><math>W_h = 121.0 \%</math> <math>W_r = 91.7 \%</math></p>	<p><b>Fr-2040</b></p>  <p>20-1000°C</p>  <p>700-1000°C</p>  <p>700-800°C</p>	<p><math>W_h = 66.5 \%</math> <math>W_r = 94.0 \%</math></p> <p><math>W_h = 85.6 \%</math> <math>W_r = 113.5 \%</math></p> <p><math>W_h = 88.8 \%</math> <math>W_r = 138.9 \%</math></p>	<p><b>FR-2050</b></p>  <p>20-1000°C</p>  <p>700-1000°C</p>  <p>700-800°C</p>	<p><math>W_h = 67.4 \%</math> <math>W_r = 104.8 \%</math></p> <p><math>W_h = 80.3 \%</math> <math>W_r = 124.0 \%</math></p> <p><math>W_h = 80.3 \%</math> <math>W_r = 124.0 \%</math></p>

All of the materials studied increase in volume due to the heat treatments applied. It can be explained by a micro-porous structure of the ceramic being produced and it is an advantageous phenomenon for two reasons. First of all, porous structure improves heat insulation, preventing melting of a copper wire inside the cable. Secondly, owing to the absence of shrinkage, cracking of wire covers and resulting short-cut phenomenon can be avoided.

### 3.3 Morphology of the ceramized layer

Mechanical strength of the composites is accompanied by morphological changes to the materials after ceramization. The porous structure of the all composites studied do not vary much from the structures of commercial composites after ceramization [5]. Similarly to the commercial composites, their morphology is dominated by micro-pores – Fig. 2.

A) cumulative analysis



B) derivative analysis

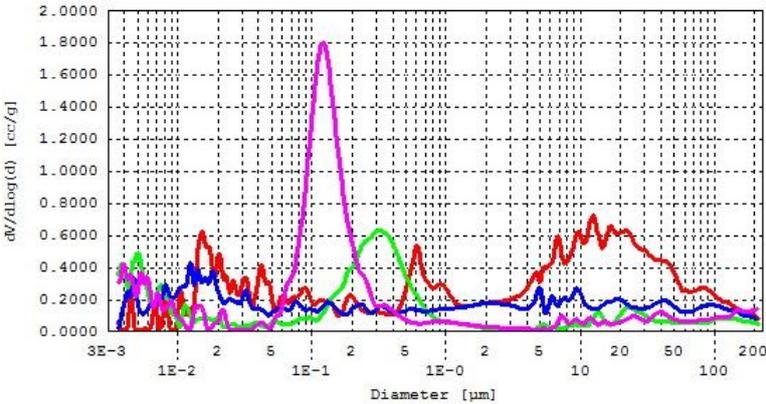


Fig. 2 The normalized pore analysis for the commercial composites, subjected to the ceramization at 1050 °C.

The structure of the ceramized composite samples is reflected by SEM images, representing porous but continuous morphology – Fig. 3 [6].

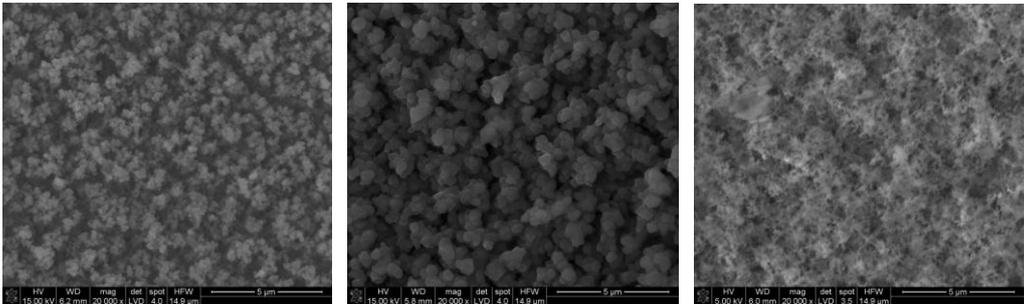


Fig. 3 Examples of the surface morphology (SEM) of commercial silicone composites fired at 1050 °C.

### 3.4 Mechanical properties of the ceramized samples

Compression strength of the ceramized samples depends on the conditions of their heat treatment. Generally, longer treatment at higher temperature makes the materials stronger. Compression strength of the ceramized composite samples studied is compared in Tab. 4.

Tab. 4 Compression strength of the ceramized silicone composites

No	Sample	The average maximum force [N]		
		800°C	1000°C	20-1000°C
1	FR 2035	-	107.0	75.0
2	FR 2040	30.1	104.0	210.0
3	FR 2050	19.5	23.2	63.7
4	FR 2055	-	16.3	190.0
5	FR 2060	11.9	81.5	80.3
6	FR 2065	-	48.9	42.9
7	BOT	22.9	22.9	118.0
8	BTS 16	193.0	18.4	426.0
9	RC 9	48.4	47.6	431.0
10	Z 01 A	67.4	25.9	75.8
11	Z 02 C	14.9	40.8	58.0
12	Z 03 B	12.7	13.8	85.6

The most of the glass phases studied, apart FR 2035, FR 2055 and FR 2065, showed to be promising in terms of the potential application as a fluxing component for ceramizable silicone composites. The exemptions resulted in composites which were not able to produce a ceramic phase of acceptable strength at 800°C.

## 4. SUMMARY AND CONCLUSIONS

The performed studies allowed us to compare the effectiveness of various fluxing agents, which can be applied as a components of ceramizable silicone composites. Despite satisfactory contribution to mechanical properties of the composites, they result in different structure of a ceramic phase being produced during their heat treatment (especially at lower temperatures), which finally results in its poor/or lack of strength. Experiments carried out with various heating rates demonstrated that this factor should be also considered by the technologists designing the ceramizable composites. Thermal conditions existing during flame firing of the materials may result in completely different behaviour in comparison to the composites e.g. heated gradually to the same temperature in an oven.

## References

- [1] Processable silicone composite materials having high temperature resistance. US Patent 5552466, 03.08.1996.
- [2] D. Ariagno, P. Barruel, A. Viale, 1992, "Heat-vulcanisable organopolysiloxanes, intended for coating of electrical cables", European Patent 0,467,800.
- [3] P. Branlard, C. George, C. Leuci, 2003, "Polyorganosiloxane compositions vulcanisable by hot process useful in particular for making electric wires or cables", European Patent 1,238,007.
- [4] A fire performance material and cable including the material, WO Patent 2010/097705 A1, 02.09.2010.
- [5] Z. Pedzich, D.M. Bielinski, 2010, "Microstructure of silicone composites after ceramization", Composites, 10, pp. 249-254.
- [6] D.M. Bielinski, 2010, "Ceramizable silicone rubber composites", Int. Rubber Conf., Sao Paulo, Brazil, 15-17.06.010.

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