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Carbon/ceramic composites designed for electrical application

A. M. BONDAR, I. IORDACHE*
National Institute for Research and Development in Electrical Engineering ICPE – Advanced Research, Bucharest, Romania

Carbon-ceramic composites were composed of one or more different solid constituents (conductive and insulators) together with a pore phase. The resulting electrical conductivity of the body depends on the amounts and arrangement of each phase present, including the pores, as well as their individual conductivity. These composites were designed to display a combination of characteristics from components acting as microelectrical networks, microresistors (carbon) and microcapacitors (insulators) randomly dispersed in space. To understand the correlation between material microstructure and electrical properties, a basic ideal model is required. Resistance-capacitance values can be used in the form of equivalent circuits. This allows the active physical and/or chemical processes to be represented as RC elements. These can be logically constructed to represent the whole system. Different microstructure features of a composite material contain different charge conduction and susceptibility processes which produce different impedance contributions on a typical Cole-Cole - plot and can be modeled by equivalent electrical circuits. The structural texture was investigated by SEM and the electrical behavior was investigated by impedance analyzer. A key result for ceramic matrix composites is the approximately exponential increase in resistivity above the percolation limit enabling the materials to rapidly and effectively absorb the energy associated with current surges in electrical equipment and thus they are very attractive electrical volume resistor materials. EMI shielding was investigated by exposing composite samples to high frequency electromagnetic fields (1 – 17) GHz. The composites tested show an attenuation between 31 – 42 dB.

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Keywords: Carbon/ceramic composite, Electrical conductivity

1. Introduction

The research envisaged aimed to develop the design process for the production of carbon-ceramic composite materials for electrical engineering applications. These carbon-ceramic composites can be considered to be designed materials, because the parts can be tailored to have the electrical properties in the direction and location that are necessary by strategically placing the micro-structural constituents. The requirements for the EVR and EWA materials are the following: the electrical resistivity, 50×10^5 - 5×10^3 $\mu\Omega$m and the attenuation, for (1 - 20) GHz, min. 20 dB.

In this research work it is investigated a spectrum of carbon-ceramic composites, ranging from discrete ceramic phases dispersed in a carbon matrix to discrete carbon phases dispersed in a ceramic matrix. The research is focused on the relationship between material properties, part design, part performance and part cost.

In a previous research it was explained [1] that the carbon matrix composites display electrical resistivity values in the appropriate range due to the conducting nature of the binder phase. Thus, the research has bee focused to develop an insulating ceramic phase. The carbon-ceramic composites developed in this stage are ceramic-matrix composites with dielectric components (kaolin and Al_2O_3) and a glassy bond derived from sodium silicate. Sodium silicate is used as a binder since it is cheap and offers an easy processing route having no requirement for difficult sintering operations. Natural graphite is used to provide the conductive phase. These composites were designed to display a combination of characteristics from components acting as microelectrical networks, microresistors (carbon) and microcapacitors (insulators) randomly dispersed in space. The research also concerns composite materials over/under the percolation threshold.

2. Experimental

The raw materials used in this study are presented in Table 1.

Table 1. The raw materials used.

Graphite	Alumina	Kaolin	Sodium silicate
< 63 μm	< 80 μm	< 250 μm	Water solution with a density of 2g/cm^3

A wide range of compositions have been investigated topica, to identify percolation thresholds and identify suitable compositions for exploitation in the specific applications. Within this range certain trends have been investigated, e.g. the effect of varying type of ceramic, whilst maintaining the graphite composition the same and similarly, investigating the effect of graphite content.

The filler materials (graphite, alumina, kaolin) were homogenised in a double-cone mixer for 30 min. at low speed. The mixed powders were homogenised with sodium silicate as binder and then dried in air, one day. After that, the composite granules were crushed and sorted to a granulation of 630 μm. The carbon/ceramic composite samples were obtained by forming the powder in a metal die to a pressure ~ 60 - 80 MPa.

The green samples were dried 24 h to a constant temperature of about 55±5 ^{o}C and then the composites were fired by a heat treatment at ~ 900 ^{o}C. The technology described before was used to make composites with different content of conductive part (graphite) and dielectric part (kaolin, alumina) with a constant mass ratio of sodium silicate binder to the ceramic parts. Then the relationships between the intimate structure and the electrical properties were investigated.

Impedance Spectroscopy [2] was used to characterise the composite pellets in the range of 10^{-3}-10^{7} Hz at 25 ^{o}C. This technique is a powerful non-destructive tool, providing useful information on the individual electrical properties of each microstructural feature and of the whole system.

Table 2. Range of compositions employed for designing ceramic-matrix composites, for electrical applications.

Raw materials	*Wt. %*										
	High resistivity 10^{12}-10^{10} μΩm		Medium resistivity $10^6 – 10^3$ μΩm								
	1					2	3	4	5	6	7
	11					21	31	41	51	61	71
Kaolin	85					75	65	55	45	35	25
Graphite	10					20	30	40	50	60	70
Al_2O_3	5					5	5	5	5	5	5
	12					22	32	42	52	62	72
Kaolin	80					70	60	50	40	30	20
Graphite	10					20	30	40	50	60	70
Al_2O_3	10					10	10	10	10	10	10
	13					23	33	43	53	63	73
Kaolin	75					65	55	45	35	25	15
Graphite	10					20	30	40	50	60	70
Al_2O_3	15					15	15	15	15	15	15
	14					24	34	44	54	64	74
Kaolin	70					60	50	40	30	20	10
Graphite	10					20	30	40	50	60	70
Al_2O_3	20					20	20	20	20	20	20
	15					25	35	45	55	65	75
Kaolin	65					55	45	35	25	15	5
Graphite	10					20	30	40	50	60	70
Al_2O_3	25					25	25	25	25	25	25
	16					26	36	46	56	66	
Kaolin	60					50	40	30	20	10	
Graphite	10					20	30	40	50	60	
Al_2O_3	30					30	30	30	30	30	
	17					27	37	47	57	67	
Kaolin	55					45	35	25	15	5	
Graphite	10					20	30	40	50	60	
Al_2O_3	35					35	35	35	35	35	
	18	18-2	18-4	18-6	18-8	28	38	48	58		
Kaolin	50	48	46	44	42	40	30	20	10		
Graphite	10	12	14	16	18	20	30	40	50		
Al_2O_3	40	40	40	40	40	40	40	40	40		
	19					29	39	49	59		
Kaolin	45					35	25	15	5		
Graphite	10					20	30	40	50		
Al_2O_3	45					45	45	45	45		

The electrical properties of a material are unique and can be revealed by utilising the frequency dependence of its constituent components. In addition, the study of frequency related phenomena as a function of the applied voltage or temperature is often essential in the performance testing of materials. In many systems the impedance varies as the frequency of the applied voltage changes, in a way that provides a valuable insight into its physical and chemical properties.

The electrical measurements were carried out at ~25 ^{o}C using a Solartron FRA 1260 Impedance Analyser. This applied a small a.c. voltage to the device under test (DUT) and the response was measured in terms of phase difference between the applied voltage and the response signal.

3. Results and discussion

The electrical characterisation has been carried out in two stages: the influence of the dielectric parts in the first stage and in the second stage the influence of the conductive part.

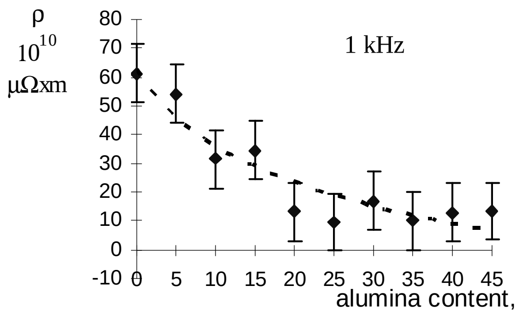


Fig. 1. The influence of alumina/kaolin ratio on electrical resistivity at fixed graphite content, 10%.

First the effect of varying the alumina/kaolin ratio was investigated, keeping the graphite content constant at 10%. This is the set of samples depicted in the first column in Table 2. The results, in Fig. 1, show that the electrical resistivity decreases slowly as the alumina content is increased up to 40 wt.%, from 60×10^{10} μΩm to 10×10^{10} μΩm without percolation. This very high resistivity shows that the materials with this graphite content lie below the percolation threshold for graphite and also the resistivity values are much higher than the target figures given before.

The effect of varying the graphite/dielectric ratio with alumina/kaolin ratio kept constant is shown in Fig. 2. The alumina content was 5% (i.e. the set of samples shown in the top row in Table 2, P11-0.11, P21-0.25, P31-0.43, P41-0.67, P51-1 and P61-1.5). It can be seen that there is drastic fall in resistivity from 47×10^{10} μΩm to 28.5×10^{6} μΩm between the graphite/dielectric ratios 0.11 and 0.25, indicating that the percolation threshold is placed somewhere in this range. These two compositions correspond to (P11 5% alumina, 85% kaolin, 10% graphite) and (P21 5%alumina, 80%kaolin, 20% graphite), respectively. It can be seen that compared to an increase in resistivity only up to a maximum of 10^3 μΩm using the carbon matrix, the ceramic matrix materials can be configured to allow the manipulation of the electrical resistivity over a range exceeds by far the values required as targets for the EVR application.

Different microstructural features of a composite material contain different charge conduction and susceptibility processes which produce different impedance contributions on a typical Cole-Cole- plot and can be modelled by equivalent electrical circuits. Typical responses range from: high frequency (10 MHz) grain bulk (Z_{gi}) contributions, mid frequency (100 kHz) grain boundary (Z_{gb}) contributions and low frequency (<10 Hz) electrode interface (Z_e) effects.

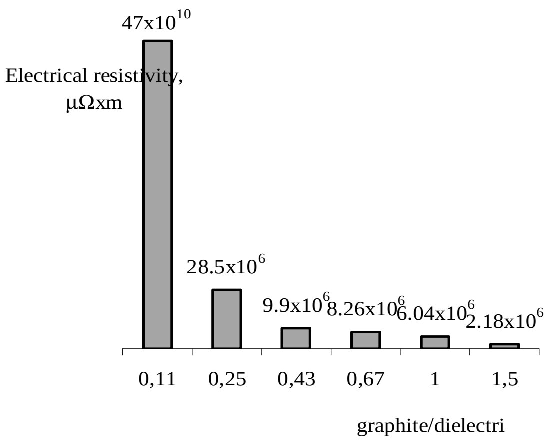


Fig. 2. The evolution of electrical resistivity as a function of conductive/dielectric phase ratio.

Impedance (Z) responses are significantly influenced by the ambient temperature and relative humidity. The Electrical Modulus (M) plots can reveal information otherwise not seen in other representations due to its different weighting on the impedance data. Similarly, the Complex Permittivity (ε) is best used to represent IS data when investigating dielectric losses. IS results for dielectric pellets, e.g. P18, show at least seven contributions.

To understand the correlation between the material microstructure and the electrical properties, a basic ideal model is required. Resistance-capacitance values can be used in the form of equivalent circuits. This allows the active physical and/or chemical processes to be represented as RC elements. These can be logically constructed to represent the whole system, Fig. 3.

The analogous equation to Ohm's law for ac is: $Z=V_0/I_0$, where V_0 and I_0 are the voltage and current waveform amplitudes and Z is defined as the impedance, the ac equivalent of resistance. Unless the sample behaves as a perfect resistor, there will be a phase difference (θ) between the applied voltage and the resulting current flow. In general, both the magnitude and the phase shift are frequency dependent. Impedance is a vector quantity which can be defined as a complex number, whose magnitude and direction can be expressed by real, Z' and imaginary, Z", components: $Z^* = Z' - jZ''$. For a representation of the system in Fig. 3, there is a Z^*_T, a total impedance of the circuit which includes all contributions. Finally, $Z^*_T = Z'_T + jZ''_T$, where: $Z'_T = R_T/(1 + (\omega R_T C_T)^2)$, and $Z''_T = R_T \cdot[(\omega R_T C_T)/(1+(\omega R_T C_T)^2)]$.

The most common method of representing the IS data is in the form of Z^*_T plots, Cole-Cole diagrams – semi-circles in the plane of (Z'_T ; Z''_T), Figs. 4 and 5 [3].

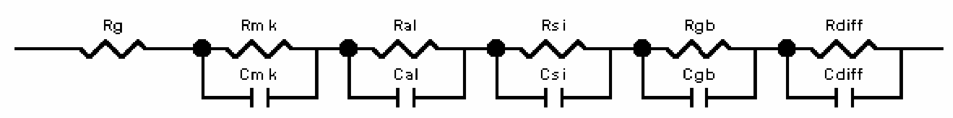


Fig. 3. P18 structure model using RC elements. Graphite contribution (R_g); Metakaolin contribution (R_{mk},C_{mk}); Alumina contribution (R_{al},C_{al}); Disolved silicate in kaolin (R_{si}, C_{si}); Grain boundary contributions (R_{gb}, C_{gb}); Diffusion mechanism (R_{diff}, C_{diff}); Electrode contact.

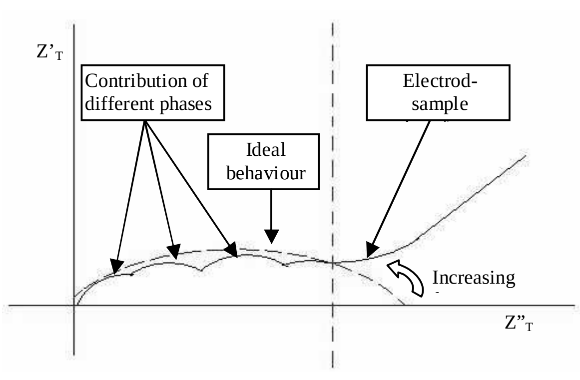


Fig. 4. Cole-Cole plot for a theoretical composite system.

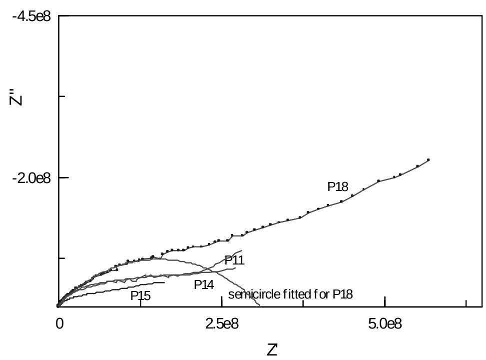
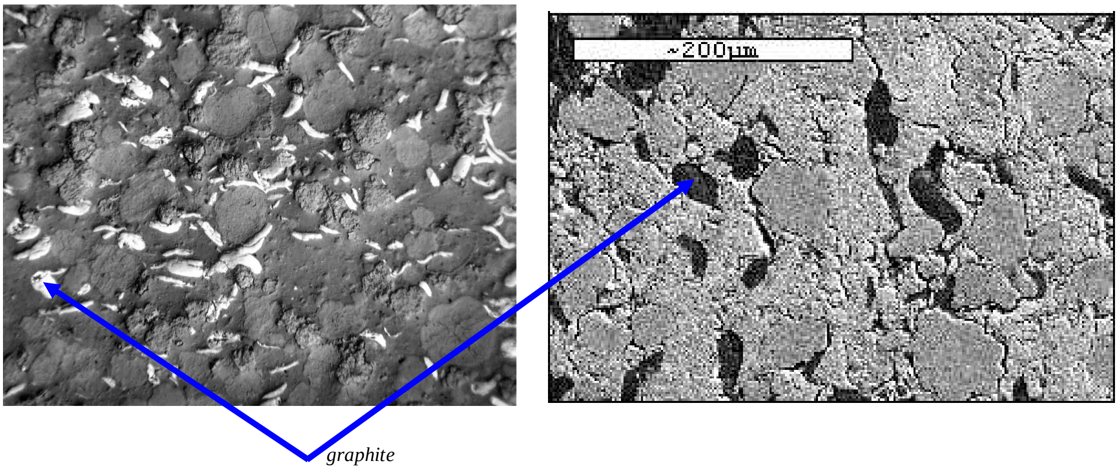


Fig. 5. Cole - Cole plot for the samples with constant graphite content (10%) and various the ratio of kaolin/alumina (P11 85/15, P14 70/20, P15 65/25, P18 50/40).

The theoretical representation for an ideal dielectric is a perfect single semicircle. In our case the IS figure represents all the contributions by a composed figure of overlapping semicircles.

It is important that this composed figure should resemble as closely as possible a single semicircle, which means that the whole composite will act and behave as a single entity.

This can be verified by comparing the values of the resistance and the capacitance given by a semicircle approximating to the data, with real measured values of the resistance and capacitance at a given frecuency.



a b

Fig. 6. Structure investigation of the sample P18: a) Optical Microscopy, mag. 20 times; b) SEM.

From all of the samples with 10%wt. Graphite, sample P18 shows this behaviour most clearly, Fig. 5, and this gives confidence that further modifications of the structure and composition into a region beyond the percolation threshold could yield materials with the required functional properties.

These composites have been modelled as equivalent parts of an electrical circuit comprising different capacitors and resistors which are associated with different phases of the composites.

In Fig. 5, conductive phases would give points located at the origin, because, unlike dielectrics they do not give any response. This group of composites has been modelled as dielectric networks with conductive inclusions. The optical and SEM micrographs shown in Fig. 6 sustain this model, the conductive graphite flakes are shown to be discontinuously dispersed within the dielectric ceramic matrix.

Fig. 7 shows the frequency response of the capacitance and resistance for three materials from this series at constant graphite content for the approximation that the composites comprise RC parallel circuits. All of the samples have the same general behaviour as the frequency is increased, the capacity falls and the resistance increases. The electrical resistance of the P18 (graphite 10 wt %, kaolin/Al_2O_3 50/40) sample shows the sharpest decrease, falling to a very small value (conductive behaviour) as the frequency is increased. This is a very desirable effect which allows the rapid absorption of energy due to a switching from a loss mechanisms due to relaxation towards a mechanism of purely resistive dissipation. This effect is critical to the proposed applications of these materials as electrical volume resistors for electrical circuit protection.

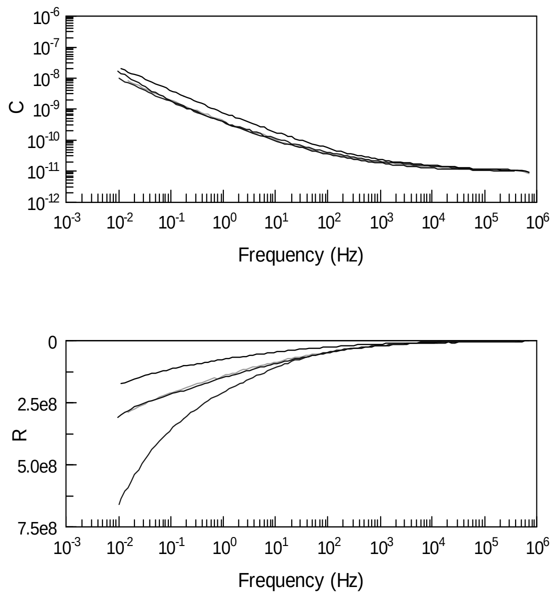


Fig. 7. Comparative frequency response in the range 10^{-2} – 10^{6} Hz of the composite pellets at room temperature (~25°C), in the approximation of composites representation as RC parallel circuits. C= Capacity and R = Resistance.

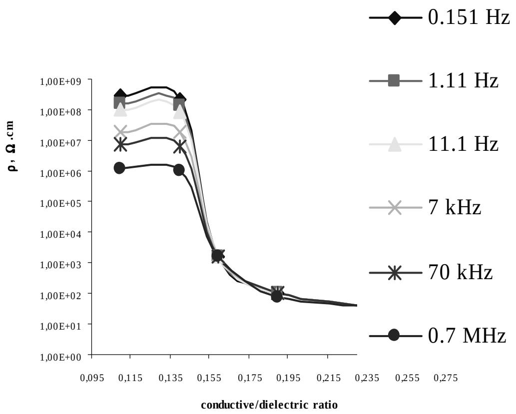


Fig. 8. Deeply investigation of the the electrical resistivity behaviour through percolation threshold (samples with 40% alumina).

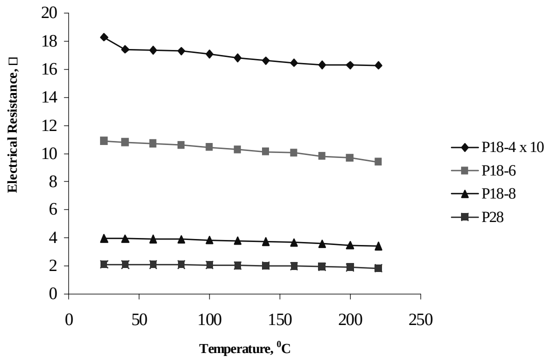


Fig. 10. DC electrical resistance for P18-4, P18-6, P18-8 and P28.

The percolation threshold has been established by varying the graphite content between 10 – 20 wt. % and the behaviour evaluated in the frequency range 10^{-2} – 10^{6} Hz by the IS technique [4]. It can be seen in Fig. 8 that at a ratio of conductive/dielectric phase of 0.135 the composites exhibit a dielectric feature, while for a ratio of 0.155 it is semiconducting. Thus, the percolation threshold lies between P18-1 (kaolin 48%, graphite 12%, alumina 40%) and P18-2 (kaolin 46%, graphite 14%, alumina 40%). The percolation of the conductive phase, as can be observed in Fig. 13, leads to continuous pathways for the electrical conduction causing the dramatic decrease in electrical resistivity.

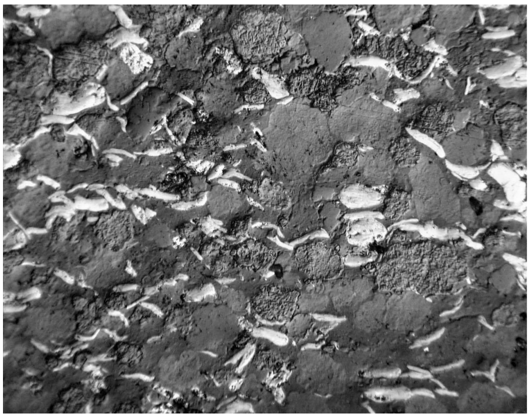


Fig. 9. Optical Microscopy, P28, ×20.

DC measurements for these composites in the temperature range of 25-220 °C show a small and negative temperature coefficient of variation of the electrical resistance similar to the behaviour of thermistors (Fig. 10). Based on these results the composition areas in which composites can be designed for specific applications can be identified as shown in Table 2.

4. Functional characterisation

From the medium resitivity region of the map presented in Table 2, sample P24 (kaolin 60%, graphite 20%, alumina 20%) was selected for functional tests relevant for the electrical power application. An arrangement as depicted in the Fig. 11 was used, with Rs consisting of a stack of three resistors. An increasing current was applied, up to 80 A, the upper limit of stable operation. At currents above 100 A the resistors tended to breakdown via electrical discharge. Corresponding electrical resistance and voltage drop over the stack were read at the different stages, as can be seen in Fig. 12.

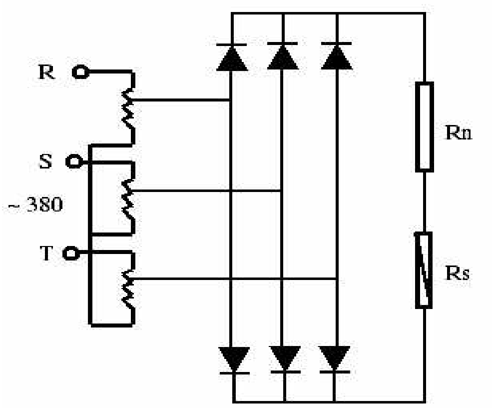


Fig. 11. Electrical diagram for measuring a three stack resistor Rn, using a bridge.

The measurements have proved that the composite resistors are powerful devices in the protection of the surge voltage which may arise in high power electrical supply lines. The behaviour of the resistors have also showed that they are capable of absorbing energy up to 7 kW, corresponding to the stable functioning limit of 80 A.

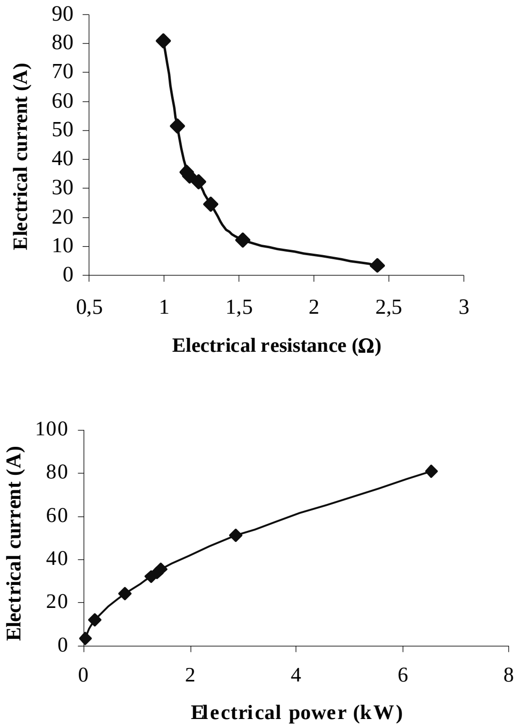


Fig. 12. Electrical characteristics for a stack of three resistors. Each resistor has the same size: diameter is 80 mm and thickness 10 mm.

Fig. 13 demonstrates that the AC resistance is relatively constant with temperature, which is desirable in this application. This capacity to absorb energy is relevant for at least two electrical engineering applications: protection of feed-back currents in high power electrical sources and protection of electrical generators with rotating diodes for currents $I_{n\ ex.}$= 25 – 40 A.

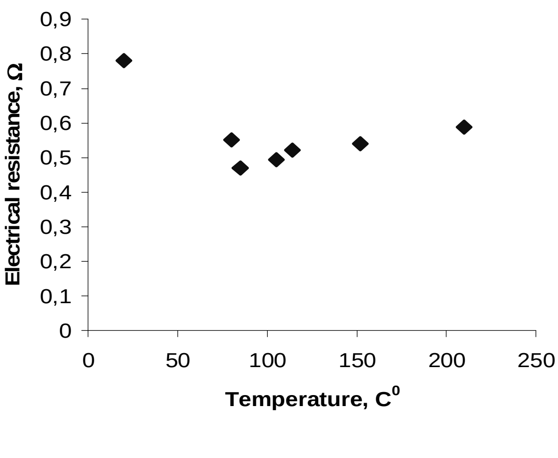


Fig. 13. AC Electrical resistance vs. temperature for sample P24.

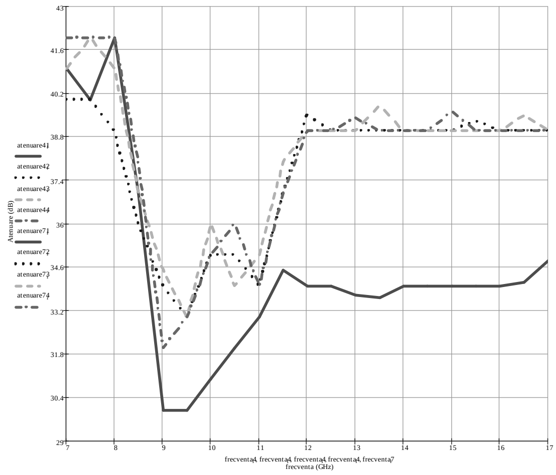


Fig. 14. Attenuation plotted vs frequency.

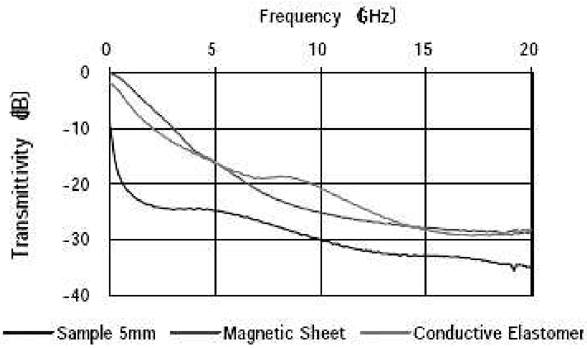


Fig. 15. Comparative attenuation for carbon/ceramic composite, magnetic sheet and conductive elastomer.

EMI shielding was investigated by the exposing composite samples to high frequency electromagnetic fields (1 – 17) GHz, using a Measurement Receiver CARNEL Labs, NM67A. The results are plotted as absorption in dB *vs* frecuency (Fig. 14). Generally, an EM shielding material should display attenuation limit of 20 dB. As can be observed from Fig. 14, the composites tested show an attenuation between 31 – 42 dB in the range of (1 – 17) GHz. They are thus potentially useful as EWA materials. Transmitted attenuation was evaluated using an HP 8720D NETWORK ANALYZER and sample P64 (conductive/dielectric ratio of 1.5) φ7 mm×φ3 mm×t5 mm. Transmitted attenuation reflects the electromagnetic wave shielding performance of the sample. The test result presented in Fig. 15 shows, that the sample has –20 to –30 dB transmitted attenuation. The result, Fig. 15, showed also that the material has a better performance than magnetic sheets (1 mm) and electrically conductive rubbers (2 mm) which are widely used and indeed are more expensive.

5. Conclusions

The carbon-ceramic composites developed in this section are ceramic-matrix composites having dielectric components (kaolin and Al2O3) with inclusion of a conducting phase (natural graphite). The research developed concerns also composites materials above and below the percolation threshold. The electrical characterisation has been developed in two stages: the influence of the dielectric parts in the first stage and in the second stage the influence of the conductive part. It has been shown that the electrical resistivity decreases slowly over the alumina range up to 40 % wt. from 60×10^{10} μΩm to 10×10^{10} μΩm without percolation. This representation corresponds to a texture of dielectric networks with conductive inclusions, which is confirmed by optical microscopy and SEM investigations. In the second stage, the evolution of electrical resistivity has been the investigated for the samples with the smallest alumina content (5 % wt) and the dependence between electrical resistivity and the ratio graphite/dielectric has been established. The percolation threshold has been placed somewhere between the ratio 0.11 and 0.25, where the electrical resistivity falls drastically from 47×10^{10} μΩm (P11 5% alumina, 85% kaolin, 10% graphite) to 28.5×10^{6} μΩm (P21 5% alumina, 80% kaolin, 20% graphite). DC measurements for these composites in the temperature range of 25-220 ^{o}C showed a small and negative temperature coefficient of variation of the electrical resistance. A key result is the approximately exponential increase in resistivity with increasing current for compositions above the percolation limit enabling the materials to rapidly and effectively absorb the energy associated with current surges in electrical equipment and thus they are very attractive EVR materials. Based on these results it is established with accuracy the composition areas in which can be designed composites for specific applications, both EVR and EWA.

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*Corresponding author: iordache.icpeca@gmail.com