

Tailoring the multiphase composite materials' electrical properties

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The paper aims to present the electrical properties of multiphase (particle-particle combinations) polymeric composite materials and the influencing factors on their electrical behaviour. The samples were manufactured using a self-developed manufacturing technology, from different combinations of iron and graphite particles embedded (different volume fractions) into a poly-vinyl acetate (PVAc) matrix known for its insulating character. The electrical properties (e.g. resistivity, resistance or conductivity) and their variation with electrical current were retrieved using a LCR meter, followed by the use of an impedance analyzer in case of the measurements done on samples subjected to an external stress state, for different values of external forces applied using a LS 100 Plus device in compressive state, on 5 samples for each category considered. The experimental data are subjected to statistical analysis, and graphical representation of retrieved values will aid to quantify the influencing factors on the electrical behaviour of the multiphase composites considered.

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1. Introduction

The composite materials exhibiting electromagnetic properties have different applications in electronics, these materials being known as “electronic composites”. Electro-conductive polymeric composites are often employed as heating elements, temperature or force/pressure dependent sensors, self-limiting electrical heaters, switching devices or antistatic materials for electromagnetic interference shielding of electronic devices, etc.

The lack of intensive studies with respect of material characterization in order to retrieve their electrical properties leaves enough spaces to be covered especially due to the large number of possible combinations among the matrix and fillers. Some studies have been already reported, like the ones focusing on the influence of the matrix material [1,5,7,8], others on the conductive fillers influence [3] and the mechanisms that are responsible for the conduction process within the composite structure [2], [5-9].

Electrical conduction in polymers have been extensively studied in order to understand the nature of charge transport in these materials. Polyvinyl acetate (PVAc) is a good insulating material with low conductivity and hence is of importance in microelectronic industry. It's electrical conductivity depends on the thermally generated carriers and also on the addition of suitable dopants. Generally, the problem of the electrical conduction in composite materials, especially in multiphase ones, is a difficult one because the electrical conduction in such heterogeneous systems can lie

anywhere between the conductivities of the components depending both on the fillers volume fraction and the morphology of the medium.

The herein paper will not attempt to present the percolation theories or the electrical conduction mechanism adapted to characterize the multi-phase composite structures manufactured using a self-developed technology. It's beyond the subject of this paper, the authors being more interested on the influencing factors on the effective electrical conductivity properties. The experimental data were correlated with some theoretical prediction based on analytical models available in technical literature. With respect to the last ones, these range from approximate methods and rigorous bounding techniques to numerical methods. Among these techniques the Effective Medium Theory (EMT) is considered as the most powerful approach to be used in the effective properties estimation of composite materials and in this category the oldest one is the Maxwell-Garnett mixing rule whose formalism resemble with the inferior limit proposed by Hashin-Shtrikman and used herein in one of the homogenization step.

The experimentally studies carried out by the authors represent the consequence of the extensive studies on different composite material structures, ranging from long or short, uniform or random distributed fibre reinforced composites or metal/non-metal two-phase particle reinforced polymeric composites with the aim of mechanical, electrical, thermal properties retrieving [3,4]. To approach the multi-phase composite materials from the same perspective was just a natural trend in this attempt of

novel materials development to aid various structural applications.

2. Experimental design

2.1 Materials

The experimental research was carried out on 5 different cylindrical samples for each class (3 different classes) of multi-phase composites, for which we used as:

- matrix – commercially available polyvinyl acetat resins (out of another 4 tested).
- particles – conductive phase is made of technical pure Fe having an average particle sizes of 100 μm mixed with graphite particles with an average particle size of 1 μm , embedded into different volume fraction in such way that the overall particle volume fraction of both inclusions were kept constant (70%).

2.2 Manufacturing technology

The specimens were manufactured using a self-developed manufacturing technology based on compression and use of an external thermal source (controlled temperature oven) to aid the matrix polymerisation process. The samples had the same geometrical values (with minor differences) 20x6 mm (diameter x specimen length) and will be taken into account in the resistivity estimation.

2.3 Measurements

Measurements were performed via the four-terminal method using an LCR meter (Hewlett-Packard Co.) and before the measurements the surfaces were covered with a narrow silver coating. The equivalent resistance of the composite samples depends upon the electrical current passing through them and in these cases a NCC (Negative Current Coefficient) type was retrieved. The electrical conductivity for each sample was calculated using the following well-known expression:

$$\sigma = \frac{1}{\rho} = \frac{h \pi I}{\pi h U} \quad (1)$$

where ρ is the resistivity of the filler, h is the thickness of the sample, I is the electrical current and U is the voltage through the sample.

2.4 Statistical analysis

Was carried out to retrieve the effective electrical conductivity of each class of combinations and were pure basic statistics methods.

3. Theoretical models

A two-step homogenization scheme is applied in order to retrieve the effective electrical conductivity of the multiphase composite samples considered herein. As it is

acknowledged in the case of effective elastic modulus prediction in case of multiphase composites a stepping methodology used to retrieve this property do not lead to the same results with those predicted using an overall methodology such is the generalized average volume method [7].

The first step will lead to the so called *equivalent matrix* as a consequence of homogenization between the first types of fillers embedded into the polymeric matrix (graphite particles) while the second step will lead to the effective conductivity of the multiphase composite structures.

Among the theoretical methods are those proposed by Pal [6], derived from the classical Maxwell expression in which different differential forms were considered. The expressions of these models are as following:

$$\left(\frac{\sigma_{mf}}{\sigma_m}\right)^{1/2} \left(\frac{\sigma_p - \sigma_m}{\sigma_p - \sigma_f}\right) = \exp(\alpha V_p^m) \quad (2)$$

for the first model, called herein *model 1* and

$$\left(\frac{\sigma_{mf}}{\sigma_m}\right)^{1/2} \left(\frac{\sigma_p - \sigma_m}{\sigma_p - \sigma_f}\right) = \left(1 - \frac{V_p}{V_p^{max}}\right)^{-\alpha V_p^{max}} \quad (3)$$

respectively, called herein *model 2*, V_p^m being the maximum packaging volume fraction (0.673, from [5]) and α is a correction factor to account for the deviations from the assumptions made by Maxwell in the derivation of its expression.

All electrical conductivities lies between some limits, know as the superior and inferior bounds. The most well known bounds are the Wiener bounds corresponding to the series and parallel connexion of phases, the dispersive and the continuous. Other bounds, more rigourous than the classical Wiener bounds are those proposed by the Hashin and Shtrikman, like:

$$\sigma_c^{mf} = \sigma_{mf}(1 - V_p) + \sigma_p V_p - \frac{(1 - V_p)V_p(\sigma_p - \sigma_{mf})^2}{\sigma_{mf}V_p + \sigma_p(1 - V_p) + \sigma_{mf}} \quad (4)$$

for the inferior limit and

$$\sigma_c^{sup} = \sigma_{mf}(1 - V_p) + \sigma_p V_p + \frac{(1 - V_p)V_p(\sigma_p - \sigma_{mf})^2}{\sigma_{mf}V_p + \sigma_p(1 - V_p) + \sigma_p} \quad (5)$$

for the superior limit, respectively.

The theoretical model developed by Milton is far more complex and represents the inferior limits of the effective electrical conductivities in case of particle reinforced composite materials. The expression is assigned to the theoretical models of so called “3 points limits”, and can be applied upon any type of 3D combinations having $\sigma_p \gg \sigma_m$:

$$\frac{\sigma_p f}{\sigma_{ms}} = \frac{1 + (1 + 2V_p) \left(\frac{\sigma_p - \sigma_{ms}}{\sigma_p + 2\sigma_{ms}} \right) - 2 \left[(1 - V_p) f - V_p \right] \left(\frac{\sigma_p - \sigma_{ms}}{\sigma_p + 2\sigma_{ms}} \right)}{1 + (1 - V_p) \left(\frac{\sigma_p - \sigma_{ms}}{\sigma_p + 2\sigma_{ms}} \right) - [2(1 - V_p) f + V_p] \left(\frac{\sigma_p - \sigma_{ms}}{\sigma_p + 2\sigma_{ms}} \right)} \quad (6)$$

where f represents a parameter that takes into account the composites' microstructure, with values ranging between 0 and 1. These limits are considered in the second homogenization step, in which σ_{ms} is the electrical conductivity of the equivalent matrix from the first homogenization step, σ_p being the electrical conductivity of the disperse phase in the second homogenization step and V_p the particle volume fraction.

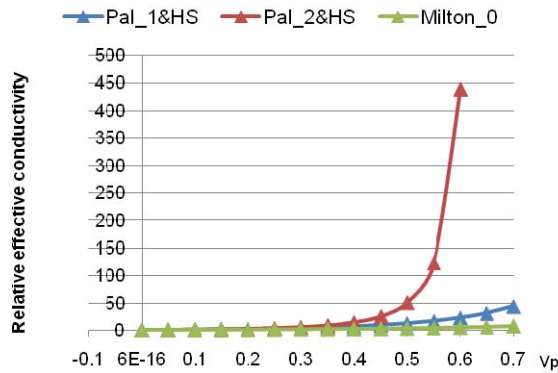


Fig. 1 Relative effective electrical conductivity variation with the filler volume fraction in case of an iron-graphite multiphase polymeric composite material

In fig. 1 is being presented the normalized effective electrical conductivity variation in case of the graphite and iron reinforced polymeric multiphase composite materials for which the first step homogenization scheme was applied for the graphite-polymeric matrix combination leading to an equivalent matrix, whereas the second step was applied for the iron particles and the matrix material from the previous homogenization step.

4. Results and discussions

In Fig. 2 is being shown one of the micrographic structure for a multiphase composite sample manufactured corresponding to a combination of 40% graphite powder and 30% iron particles embedded into a PVAc matrix. As it can be seen from the picture the conductive paths differ due to the manufacturing process, being the reason for different zone measures of the resistivity in case of composite samples.

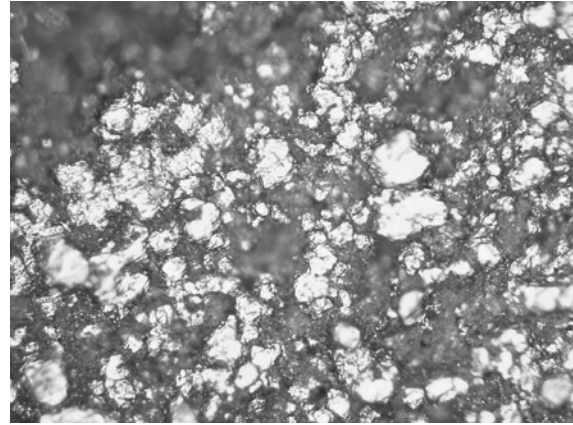


Fig. 2 SEM micrograph of a multiphase composite structure

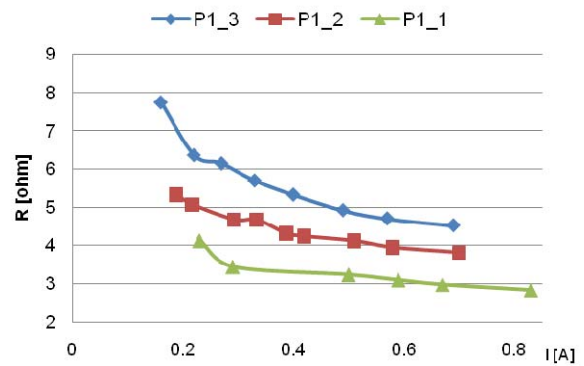


Fig. 3. $R(I)$ dependence for multi-phase composite materials containing 40 % Fe, 30% graphite and PVAc matrix.

In fig. 3 is being show the variation of electrical resistance with respect to the applied current intensity for 3 similar samples of conductive polymer matrix investigated, containing 40 % Fe and 30 % graphite. As can be seen, the variation follows an exponential that may further explained by the phenomenon that takes place within the structure and which are characteristics to the class of extrinsic semi-conductive materials, actually explained as a Joule-Lentz effect.

It is generally acknowledged that the electrical conductivity of the particle reinforced polymeric composites is primarily a result of contact between particles. The percolation theory explains the conduction mechanism and the fact that particle volume fraction and electrical conductivity do not follow a linear relationship. In turn, it increases abruptly at a certain particle volume fraction known as a percolation threshold. This threshold corresponds to the particle volume fraction at which the particles begin to touch among them sufficiently to form somewhat continuous electrical conduction paths within the composite structure [1], [5].

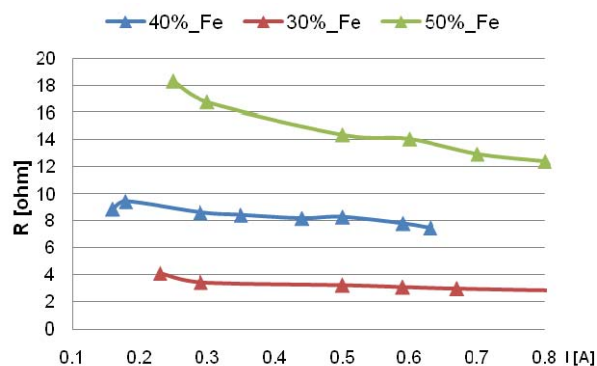


Fig. 4. $R(I)$ dependence for multiphase composite materials containing different volume fraction of the conductive fillers (different volume fraction - 30 to 50 % Fe)

In Fig. 4 is being shown the variation of the electrical resistance for different composite samples containing different filler volume fractions summing up a 70% dispersing phase content. From figures 3 and 4 it can be seen that the resistance dependence with intensity of the electrical current vary from sample to sample, for each individual category and among the 3 different classes, becoming higher with the increase of the Fe particle content (actually decrease of the graphite content).

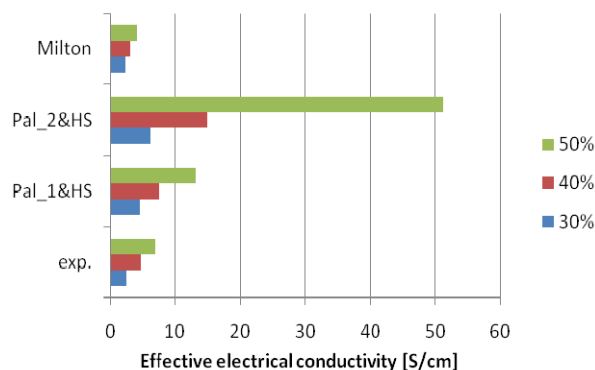


Fig. 5. Theoretical-experimental comparison of effective electrical conductivity for multiphase composite materials containing different volume fraction of the conductive fillers (different volume fraction - 30 to 50 % Fe)

In Fig. 5 is being represented the theoretical and experimental mean values vs. particle volume fraction of the multiphase composite samples revealing the fact that the experimental values are closer to the values obtained using the Pal – model 1 and Hashin-Shtrikman lower limit homogenization scheme. As it can be seen, the values may become closer to the ones predictable using the Pal – model 1 and Milton homogenization scheme but for another value of the f factor. The latter can be identified by several trials or a numerical method applied upon the associated expression.

4. Conclusions

The electrical characteristics of multiphase conductive polymeric composites was investigated with the aim of sizing their effective electrical conductivity. A master curve for electrical resistance vs applied intensity variation in case of different fillers volume fraction was obtained, illustrating the effect of particles distribution as well as their material combination.

All of the theoretical models predicting the electrical conductivities of the composite materials are idealized ones and fails to encompass the particle interaction or particle dimensions, the only correction being done on the values of the empirical factors which in some extent accounts for these microstructure related parameters.

Future work aims effective conductive evaluation of the manufactured multiphase composites for a smaller diameter of Fe particles (average 50 μm) and the variation of the former property with an external applied load and with temperature variation.

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