EFFECTIVE ELECTRICAL CONDUCTIVITY ESTIMATION FOR A NOVEL MULTI-PHASE COMPOSITE MATERIAL

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Abstract: The paper aims to present a novel configuration of a mixed conductive particles embedded into a non-conductive polymeric matrix, that we call a multi-phase composite material, developed to exhibit predictable electrical conductivities. Graphite and iron particles, having different volume fractions, were blend together into a PVAc matrix with the aim of sizing the influencing factors on sample’s measured electrical conductivities. The retrieved values were plotted against some theoretical models from literature.

Key-Words: multi-phase, particle, composite, effective, electrical, conductivity, percolation

1 Introduction

The composite materials exhibiting electromagnetic properties have different applications in electronics, these materials being known as “electronic composites”. Electronic composites, whose properties can be controlled by thermal or electromagnetic means, play an important role in micro- and nano-electromechanical systems (MEMS/NEMS) such as sensors, actuators, filters and switches.

Some of them can be designed to exhibit shielding effects due to biological safety reasons as a natural consequence of the ever-growing applications of advances electrical and electronic devices.

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], [6], others on the conductive fillers influence [3] and the mechanisms that are responsible for the conduction process within the composite structure [2], [6].

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.

The herein paper will not attempt to present the percolation theories or the electrical conduction mechanism adapted to this multi-phase composite structure. It’s beyond the subject of this paper, the authors being more interested on the influencing factors on the electrical conductivity property.

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 acetate 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.). 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.

2.4 Statistical analysis
Was carried out to retrieve the effective electrical conductivity of each class of combinations and were pure base statistics methods.

3 Theoretical models
Technical literature provides several outstanding reviews of mixing laws and effective media theories for electro-composites, a “brand name” for the electrical conductive composite materials. In the dilute limit, all such equations are reduced to Maxwell’s equation:

\[ \frac{\sigma_c}{\sigma_m} = 1 + \frac{3(r-1)}{r+2} V_p \]  

(1)

where \( \sigma_c \) is the effective electrical conductivity of the composite material, \( \sigma_m \) is the conductivity of the matrix phase, \( r \) is the ratio of particle conductivity (\( \sigma_p \)) to that of the matrix, \( V_p \) is the volume fraction of particles (the higher-order terms are being neglected). The previous notations and symbols have the same meaning for all the following derived theoretical models.

The other models extend calculations beyond the dilute range. For example, the Maxwell-Wagner equation (also known as the Maxwell-Garnett equation or Wiener’s rule based on the well-known Clausius-Mossoti equation, is given by:

\[ \frac{\sigma_c}{\sigma_m} = \frac{2(r-1)\sigma_p + (r+2)\sigma_m}{(r+2)-(r-1)\sigma_p} \]  

(2)

This model is formally equivalent to the Hashin-Shtrikman lower bound (conductive particles) and upper bound (insulating particles) and sometimes is referred to as the Maxwell-Wagner-Hashin-Shtrikman equation(s).

Bruggeman’s asymmetric medium theory for conducting spheres is given by:

\[ \frac{\sigma_c}{\sigma_m} = (1 - V_p)^{-3} \]  

(3)

whereas for insulating spheres the Bruggeman’s asymmetric equation is:

\[ \frac{\sigma_c}{\sigma_m} = (1 - V_p)^{3/2} \]  

(4)

Another theoretical model was developed by Meredith and Tobias who extended Fricke’s treatment of ellipsoidal particles, within a Clausius-Mossotti framework, by mixing half of the spheres at a given volume fraction, calculating the composite conductivity, and using this as the matrix for a new composite made with the addition of the other half of the spheres. The resulting equations are:

\[ \frac{\sigma_c}{\sigma_m} = \frac{(1+V_p)(2+V_p)}{(1-V_p)(2-V_p)} \]  

(5)

for conducting spheres and

\[ \frac{\sigma_c}{\sigma_m} = \frac{8(2-V_p)(1-V_p)}{(4+V_p)(4+V_p)} \]  

(6)

for insulating spheres, 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 \( \sigma_p > \sigma_m \):

\[ \frac{\sigma_c}{\sigma_m} = \frac{1+(1+2V_p)\frac{\sigma_p-\sigma_m}{\sigma_p+2\sigma_m}-2(V_m f - V_p)\left(\frac{\sigma_p-\sigma_m}{\sigma_p+2\sigma_m}\right)^2}{1+V_m\left(\frac{\sigma_p-\sigma_m}{\sigma_p+2\sigma_m}\right)-(2V_m f + V_p)\left(\frac{\sigma_p-\sigma_m}{\sigma_p+2\sigma_m}\right)^2} \]  

(7)
where \( f \) represents a parameter that takes into account the composites’ microstructure, with values ranging between 0 and 1.

Another recently developed theoretical model was developed by \( \text{Pal} \) [8], namely:

\[
\frac{\sigma_c}{\sigma_m} = \left(1 - \frac{V_p^m}{V_p}ight)^{-3\alpha V_p^m}
\]  

(8)

for conductive inclusions embedded in non-conducting matrix, \( V_p^m \) being the maximum packaging volume fraction and \( \alpha \) is a correction factor to account for the deviations from the assumptions made by Maxwell in the derivation of its expression (see (1)).

In figure 2 the same property but using the model developed by Pal, for conductive and non-conductive particles. 

In here we have to mention the fact that were not presented the variations from the other previous theoretical models due to the fact that are simplified ones and give large values from the experimental data.

### 4 Results and discussions

In figure 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 [1,6].
Fig. 4 R(I) dependence for multi-phase composite materials containing different volume fraction of the conductive fillers (30 to 50 % Fe)

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 Comparison between experimental and theoretical models values of effective electrical conductivity in case of multi-phase composites

In figure 5 is being plotted the experimental and the theoretical values (Pal and Milton, for a 0.5 correction factor) in case of the different volume fractions of the conductive fillers considered for the multi-phase investigated composite materials. The experimental values are closer to the ones of the Pal theoretical model. For the variation according to the Milton’s theoretical model was used a homogenization concept, meaning the fact that the relative effective value was computed in two-step: the first for graphite and the matrix, leading to a so called effective matrix, the second for the Fe particles and the effective matrix.

5 Conclusions
The electrical characteristics of multi-phase 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 the matrix materials.

Future work aims effective conductive evaluation of the manufactured multi-phase 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.

References:

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