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Thermo-structural analysis and electrical conductivity behavior of epoxy/metals composites

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ABSTRACT

This paper reports on the elaboration and characterization of epoxy resin filled with metallic particles powder (aluminum, tin and zinc) composites. The scanning electron microscopy (SEM) pictures, density measurements and x-ray diffraction analysis (DRX) showed a homogeneous phase of obtained composites. The differential scanning calorimetry revealed a good adherence at matrix-filler interfaces, confirming the SEM observations. The measured glass transition temperatures depend on composites fillers' nature. Afterwards, the electrical conductivity of composites versus their fillers' contents has been investigated. The obtained results depict a nonlinear behavior, indicating an insulator to conductor phase transition at a conduction threshold; with high contrast of ten decades. Hence, the elaborated materials give a possibility to obtain dielectric or electrically conducting phases, which can to be interesting in the choice of desired applications. Finally, the obtained results have been successfully simulated on the basis of different percolation models approach combined with structural characterization inferences.

1. Introduction

Significant research of electrically conducting composite materials of polymers filled with conductive particles has undergone a considerable growth during the last decades [1].

Indeed, the low density of these composites got various advantages over other conductive materials, including ease of processing, flexibility, ability to absorb mechanical shock, corrosion resistance, electrical conductivity control [2] and ultra high dielectric constant obtaining at different frequencies [3–5]. These properties are used in different technological applications in a variety of areas such as conductive adhesives, cold seals, electromagnetic/radio frequency interference (EMI/RFI) shielding for electronic devices (computer and cellular housings for example), self regulating heaters, photo thermal optical recording, direction finding antennas, chemical sensors, static charges dissipating materials, energy storage (capacitor devices), flame retardancy, organic electronic components: organic light emitting diodes (OLEDs), photovoltaic solar cells (OPVs), shape memory devices, biomedical and many more [1,6–13].

It is widely known that polymeric materials are typically insulators. However, their use as conductive polymer composites is obtained by filling an insulating polymer having good mechanical properties with highly conductive particles, such as metal powders [14,15] or carbon black [16]. It has been showed that the electrical conductivity of composite increases nonlinearly with increasing filler content in a relatively uniform insulating medium of randomly distributed conductive particles [15]. These materials reveal a critical conduction threshold at which the conductivity increases by several orders of magnitude from insulating to conducting phase [15–18]. Moreover, it has been shown that the conduction threshold depends also on the nature of the matrix and the characteristics of the fillers (nature, size, morphology, etc.) [15,17].

This phenomenon has been interpreted on the basis of percolation theory [6,15,19,20]. Different percolation models have been proposed for describing the behavior of electrical conductivity against filler concentration [21,22]. The classical statistical models [19–22] are mostly used to relate the electrical conductivity of composite to the existence of clusters of connected particles, giving rise to the so-called infinite conducting cluster, above the conduction threshold. These statistical models are simple and do not suppose interactions between

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matrix and filler media. They give good values of percolation thresholds compared to that obtained experimentally and a universal power exponent around 2. However, in some experimental cases, important discrepancies are observed. The obtained exponent is very different from 2 [23]. In order to understand this discrepancy, other models have been proposed. These models consist to take in consideration the characteristic of matrix, fillers or possible interactions between matrix and fillers. One of these models is due to Mamunya et al. [24,25], which consists to introduce polymer matrix-filler interface interactions effect on the conductivity vs. filler concentration in the basic equation. Thus, this model allows values of critical exponent different from 2. The deviation of exponent value from 2, should be due to the interaction contribution. Elsewhere, a General Effective Media (GEM) model was developed by McLachlan et al. [26,27], combining the effective media and percolation theories. The use of this model requires continuous insulator-conductor phase transition with moderate contrast.

Elsewhere, epoxy resin is used in many industries owing to its excellent mechanical, chemical and electrical properties [1,2,6,28]. It is mostly used as matrix in conducting polymer composites [1,15,16,29]. Thus, the aim of our research is to develop safe and economical epoxy resin composites with superior structural, thermal and electrical properties. In order to do that, the conductive fillers (Al, Sn and Zn) were mixed in an epoxy matrix. They can be useful either electrically conductive or as dielectric materials [1–5,29,30]. The observed electrical behavior will be simulated and discussed in above cited models frame.

2. Materials and methods

The used matrix is a bisphenol-A epoxy F resin (Araldite) with a hardener (HY956/Ciba-Geigy). The measured density of polyepoxy obtained is d≈1.14 (g cm^{-3}) at 22 °C. The fillers were the commercial powders of aluminum (Al), tin (Sn) and zinc (Zn), delivered by Panreac (Castellar del Vallès, Spain). The characteristics of these constituents are listed in Table 1.

All series of composites have been prepared by employing the same procedure, as described elsewhere [28]. Adequate quantity of metallic powder was introduced in the resin fluid and dispersed manually in order to obtain the homogeneity. The formed viscous suspension was flowed in Teflon mold casts and placed during one hour on the rotating rollers in an oven maintained at 100 °C. The mixture has been rotated during the polymerization process, in order to prevent the sedimentation of the particles whose density is larger than that of polymeric ones. The homogeneity of the composite samples has been checked by means of conductivity and density measurements on different parts of the same sample.

The experimental density of the composites was measured in accordance with ASTM D 792-91 norm; using the same method, as exposed elsewhere [31].

Scanning electron microscope Philips XL30 with an accelerating voltage up to 30 kV and fully computer-controlled and equipped with an X-micro-analyzer detector (EDX) was used to analyze the morphology of the metallic particles and their dispersion inside the composite samples.

Table 1
Characteristics of the epoxy resin used in this study: density (d), resistivity (ρ) and viscosity (η) at 25 °C, and properties of filler particles, purity, mean size (φ) and density (d).

Epoxy F	d (g /cm^3)	ρ (Ω cm)	η (mPa s)
	1.14	$1.34*10^{14}$	9000–10000
Filler particles	**Purity (%)**	**Φ (μm)**	**d(g/cm^3)**
Al	98	30–70	2.7
Zn	96	5–25	7.14
Sn	99	5–25	7.30

Philips (X'Pert PRO) powder diffractometer with Cu Kα X-ray was used to investigate the amorphous nature of glass matrix and filler effects in composites. We recorded continuous spectra between 2θ=3° and 90° with the same step for all the samples of 2θ=0.067°.

Thermal behaviors were determined by DSC measurements using TA Q100 instrument equipped with a cooling system. The base line was calibrated by scanning the temperature domain with an aluminum empty pan. The temperature and the enthalpy were calibrated using indium as a standard. All the experiments were carried out with 10 mg of polymer composites under gas nitrogen flow of 50 ml/min and heat rate of 20 °C/min.

The electrical measurements were made by usual technique of two electrodes method as used elsewhere [17], taking average of five data points on each sample. Sample thickness was measured at five locations and averaged using a micrometer Schmidt Technology model J50, with an accuracy of 0.01 mm. The contact resistance is decreased by coating the sample surfaces with silver paint and dried during 24 h. The volume electrical resistances higher than 10^3 Ω were measured using a programmable megohmeter Quadtech model 1865. The lower resistances than 10^3 Ω were determined using a digital multimeter Leader model 856. A constant voltage of 100 V was applied to the samples and after one minute its resistance was measured, using a test cycle of 20 s charge, 20 s dwell, 20 s measure, and 20 s discharge. Before starting a new measurement, the electrodes were short-circuited for 5 min to remove any effect of the previous electrification.

3. Results and discussion

3.1. Morphology

Scanning Electron Microscopy (SEM) studies have been undertaken to analyze the morphology and the dispersion of metallic filler inside the polymeric matrix. The obtained images with EDX analysis using the same magnification (200x) for pure epoxy matrix, loaded with 26.6 vol % of aluminum, 34.7 vol% of zinc and 25.7 vol% of tin, are represented in Fig. 1. Although the micrograph of the matrix shows some holes of porosity, the material might be considered as quite homogenous. It is also evident from the composite micrographs that the repartition of metallic fillers is fully random and as it can be seen that all composites exhibit the same and almost homogeneous morphology. It is clearly revealed from these pictures and EDX analysis that the composites are essentially formed with two components, matrix and incorporate fillers. The white- grey and the black continuous area, observed in the cross section, is metallic clusters and epoxy matrix, respectively. Moreover, these composites have a texture reflecting the presence of small void and pores inside the polymer matrix as well as metallic clusters of varying sizes, with some more rounded than others, showing two components, metallic and polymeric one. This means that the studied composites could be considered as binary system.

3.2. Density and porosity

Fig. 2 depicts the dependence of measured densities of epoxy/metal composites on the filler volume fractions. There is a linear increase in density when increasing metallic contents. This linear behavior is corroborated by the scanning electron microscopy observations and EDX analysis, showing that the composites are binary system, constituted of the polymer matrix and the incorporated fillers. Hence, the overall theoretical density $\mathbf{d_t}$ of the composite can be calculated by using the following relation [15]:

$$d_t = (1 - \phi)d_m + \phi d_f \quad (1)$$

where, m and f stand for matrix and filler, ϕ is the volume fraction of filler.

The comparison between the theoretical and the experimental data of the studied composites is illustrated in Fig. 2a. The measured