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The role of irreversible and reversible phenomena in the piezoresistive behavior of graphene epoxy nanocomposites applied to structural health monitoring

Leonel M. Chiacchiarelli [a], Marco Rallini [a], Marco Monti [a,b], Debora Puglia [a], Jose M. Kenny [a,c], L. Torre [a,*]

[a] University of Perugia, Civil and Environmental Engineering Department, UdR INSTM, Strada di Pentima 4, 05100 Terni, Italy
[b] ECNP – European Centre for Nanostructured Polymers, Strada Comunale Savonesa 9, 15057 Rivalta Scrivia (AL), Italy
[c] Institute of Polymer Science and Technology, CSIC, Juan de la Cierva 3, 28006 Madrid, Spain

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ABSTRACT

The use of graphene for the development of a strain and damage sensor was evaluated and modeled. To achieve this, a graphene epoxy reactive mixture was used as a conductive coating which was cured onto a carbon fiber reinforced composite. This methodology proved to be very effective where substantial changes in piezoresistivity (up to 400%) were found as a function of strain (up to 2%). This contributed to a very high linear gauge factor ($56.7^{\pm 0.69}$). The role of reversible and irreversible phenomena in the sensor piezoresistivity was modeled using the concepts of tunneling currents and conduction paths. In order to predict the response at higher deformation, an irreversible component was introduced to account for the substantial increase of piezoresistivity. A model which incorporated both components was able to predict the piezoresistivity up to high deformation.

1. Introduction

In the last decades, fiber reinforced polymers (FRPs) are being increasingly used as materials for structural applications in aerospace, naval and automotive fields. Their high specific strength and stiffness, in combination with a superior corrosion performance with respect to metallic materials are the main drivers of this paradigmatic change. Since the mechanical performance of composite materials may be severely altered when damage takes place, the serious interest in the use of FRP in structural applications has led to the necessity of the development of innovative ways to monitor the status of the structure in which the FRP is utilized.

Among traditional non destructive inspection techniques used to evaluate the structural integrity, those that exploit electrical properties of the materials are known to be effective to detect damage or to measure strain [1,2]. These techniques have already been applied by exploiting the bulk electrical properties of carbon fiber reinforced composites [3,4]. However, the insulating polymer matrix complicated the electrical measurements by a substantial decrease and modification of conductivity. Moreover, the random character of the in-plane and out-of-plane fiber contacts in the composite strongly affected the electrical measurement reproducibility. Consequently, the effectiveness of this approach can be at least partially questioned.

As widely reported in literature [5–17], the use of conductive nanoparticles such as carbon black, carbon nanotubes and carbon nanofibers can significantly enhance the electrical conductivity of the insulating polymer matrix in which they are embedded. In addition, in most cases, the concentration to which this effect was pronounced (percolation threshold) was found to be very low. For example, Kim et al. [7] found that with a 3 wt.% of graphene nanoparticles, the conductivity increase was low enough so as to measure piezoresistivity phenomena.

Graphene is a single layer of sp^2-bonded carbon atoms that can be thought of as an individual atomic plane extracted from graphite [18,19]. Recent studies have demonstrated that few stacked graphene layers, which essentially represent partially exfoliated graphite, can be applied successfully as fillers for polymeric matrices [20–25]. This filler is commonly referred to as graphene nanoplatelets (GNPs). In recent years, due to the outstanding mechanical properties of graphene, its application to reinforce polymer matrices has become of essential importance in polymer science [26]. Simultaneously, the electrical properties of the graphene based nanocomposites have also been studied [7,26], where the remarkable electronic properties of graphene represent the main driving force of these developments. In fact, it has been hypothesized that the velocity of electrons in graphene is in the order of 10^6 m/s [19]. Liang et al. [22] studied the electromagnetic interference (EMI) shielding of graphene/epoxy composites,

* Corresponding author.
E-mail address: torrel@unipg.it (L. Torre).

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showing that these systems had a low electrical percolation threshold and a good shielding efficiency. Enhanced electrical conductivity for exfoliated graphite based composites was also found by Biswas et al. [23].

As far as the piezoresistive behavior of nanoparticle-based composites is concerned, most publications have focused on the use of carbon nanotubes as a filler [27–30]. A recent review by Alamusi [6] elucidates which are the main variables that control the piezoresistive behavior of those nanocomposites. For the case of graphene, only recent publications have dealt with aspects of the piezoresistive behavior [7,31]. Kim et al. [7] studied the piezoresistive behavior of graphene–epoxy nanocomposites with concentrations of 3 wt.%. In addition, the sensor had a gauge factor of 11.4 and its behavior was considered reversible up to strain of 10^{-3}. Eswaraiah [31] has developed a piezoresistive sensor based on graphene nanofiller and a polyvinylidene fluoride matrix. They found that the sensing capabilities were improved when the filler concentration was around 2 wt.%. Therefore, the study of the piezoresistive behavior of graphene based composites is very limited. In addition, the piezoresistive behavior at higher strains (up to 10^{-2}) has not been reported.

In this work, starting from the optimized graphene-epoxy nanocomposite already developed by our group [32], the piezoresistive behavior of an epoxy–graphene nanocomposite was studied with particular emphasis on its application as a strain sensor in a carbon fiber reinforced composite subjected to bending loads. For this reason, the liquid reactive mixture was used as a conductive coating that can be easily poured and cured onto the surface of the composite for strain and damage sensing purposes. Subsequently, the electrical resistance as a function of composite deformation was studied, focusing on the reversible behavior after several bending cycles. Finally, the electrical resistance was modeled using a phenomenological model, taking into account the irreversibility of piezoresistivity at higher deformation.

2. Materials and methods

An Epikote 862 diglycidyl ether of bisphenol F (DGEBF) epoxy resin, kindly supplied by Hexion, was used as a matrix. Diethyltoluenediamine (DETDA), supplied by Lonza, was used as curing agent (26.4 phr). Graphene nanoplatelets (GNPs) were supplied by Cheap Tube Inc. (Grade 2). According to the manufacturer, the GNPs had a surface area of 100 m^2/g, an average thickness of around 10 nm and an average diameter of 25 μm. They were used as supplied by the manufacturer. A GNP concentration of 2 wt.% was chosen according to previous results of the authors [32]. The scheme of the preparation of the graphene-based composite reactive mixture is depicted in Fig. 1. In the first step, GNPs were added to chloroform (Sigma Aldrich, ACS grade) at a concentration of 2 mg/ml. The colloidal suspension was then sonicated with a Vibracell® VC750 tip sonicator for 1 h at an amplitude of 30% (225 W). Then, the epoxy monomer was added and the mixture was further sonicated for 1 h at identical conditions. Afterwards, in order to fully remove the solvent, the solution was heated on a hot plate (Infrared spectroscopy was used to corroborate solvent evaporation). Finally, the hardener was added and the system was magnetically stirred for 5 min. This reactive mixture was then used to create a coating (50 × 6 mm^2 area) onto the carbon fiber/epoxy composite (CFRC) specimens. As depicted in Fig. 2, a metal mask (thickness 0.6 mm) and the aluminum electrodes were previously prepared and placed on top the CFRC specimens. To avoid an electrical short-circuit, a thin layer of acrylic paint was also applied (yellow area in the figure). Finally, the coated specimens were cured at 130 °C for 5 h. DSC tests were performed on the cured system in order to check if any residual heat of reaction was present. The complete absence of any exothermal peak after the Tg, which was measured around 130 °C, confirmed the full cure of the system.

A carbon fiber/epoxy composite was used as a reference structural material in which the sensing performance of the graphene-based sensor was evaluated. The composite was a $[0/90]_{2S}$ cross-ply laminate manufactured through the vacuum infusion technique. From this laminate (2 mm thickness), the rectangular specimens necessary for this study were cut (80 × 10 mm).

A Keithley electrometer, model 6517B, was used to measure the electrical resistance. The instrument electrodes were attached at the end of the aluminum conductive strips (Fig. 2) and a continuous voltage of 100 V was applied while the fiber reinforced specimen was subjected to a flexural load in a three-point bending test configuration (LLOYD Instruments LR30 K mechanical testing machine). The flexural test geometry and parameters followed the guidelines of the ASTM D 790 standard. Even though the results presented in the following sections are associated to one specimen, all the deductions performed in this work were based from the analysis of at least five testing specimens. Finally, it is worth to

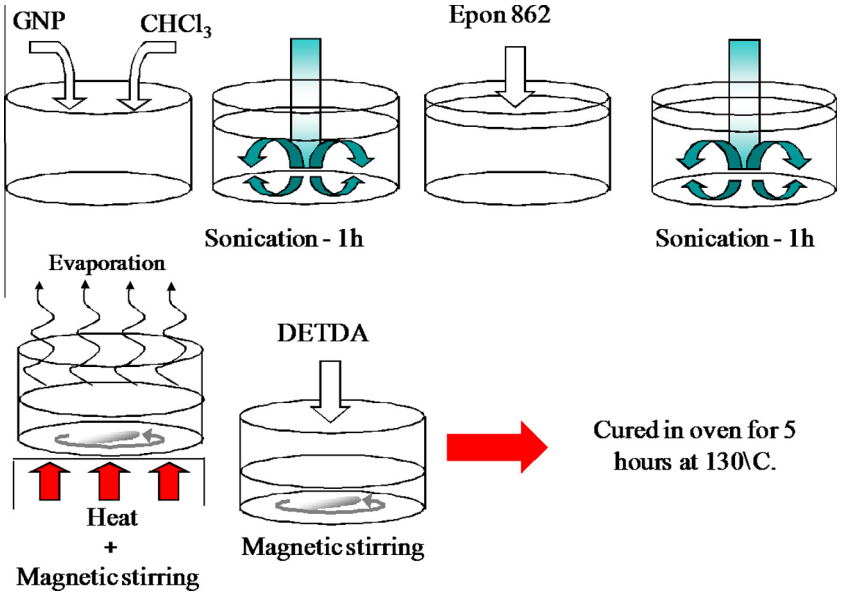

Fig. 1. Scheme of the preparation of the graphene-epoxy composite reactive mixture.