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Strain sensing in single carbon fiber epoxy composites by simultaneous in-situ Raman and piezoresistance measurements

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ABSTRACT

The change of electrical resistance in continuous single carbon fibers and single carbon fiber/epoxy model composites with applied strain has been investigated with a new method combining simultaneous *in-situ* Raman and electromechanical measurements. In all cases, a sudden increase to infinity of the relative electrical resistance corresponds to fiber fracture. The gage factors of the piezoresistance curves were determined. Reinforcement/matrix interface are compared for sized and unsized systems. It is shown that, in principle, it is possible to correlate the fiber strain and the variation of electrical fiber resistance as a function of the applied strain for a single fiber embedded in epoxy. This study indicates that carbon fibers embedded in epoxy matrix may serve as electrical strain sensors to detect both their own onset of damage and that of the composite under load, prior to specimen fracture.

1. Introduction

Carbon fibers [1] and carbon nanotubes (CNT) [2] used as reinforcement in various structural materials like polymers, cements and metals are electrically conductive and show drastic changes of their electrical resistance when there are strained. The piezoresistance properties of single carbon fibers under tensile loading have been shown previously by several authors to provide rich information about the mechanical behavior of the fibers [3–8]. In this case piezoresistance effects can be used for precise strain sensing of bare carbon fibers alone, or in bundles, as well as of carbon fibers embedded in a matrix of composites. Since the pioneering work of Conor and Owston [3], it is known that the change of electrical resistance of strained carbon fibers can be linked to the degree of misorientation of graphitic crystallites. However, there are relatively few studies devoted to the electromechanical properties of single fibers, mainly because the measurement technique requires an appropriate method to connect the fiber to the electrical measurement setup. From the early works of Owston [4], Berg et al. [5], and later from DeTeresa et al. [6], it is nevertheless established that the electrical properties of the fibers depend strongly on their macroscopic mechanical and microstructural properties such as elastic modulus and contact resistance between carbon fibers crystallites. For instance, DeTeresa et al. [6] showed that piezoresistance in low and high modulus carbon fibers increases quasi-linearly with tensile strain while it decreases with compressive strain. Sudden increase of resistance to infinity on compression was linked to the failure of the fiber. Since then, much effort has been made to ameliorate single fiber specimen handling for reliable electrical testing [7,8].

Based on this, subsequent electrical resistance measurements focused on multiple carbon fibers embedded in various matrix materials with the aim to monitor load transfer, failure and damage properties. Up to now, these investigations concern mainly carbon fiber bundles without epoxy [9,10], laminates [11–16], hybrid carbon/glass fiber composites [17], and carbon fiber polymer- and cement-matrix composites [18]. Still, the electromechanical studies of a single carbon fiber itself, embedded in an epoxy matrix, have only been conducted by a few numbers of investigators [19–23]. As a matter of fact, piezoresistance techniques applied to such specimen type should yield valuable information concerning the individual damage behavior of fiber in composite. Influences of residual stress [20,21], sizing and diameter of the embedded fiber [23], and

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epoxy curing [24–26] on electrical properties have been partially reported. Also, on more basic grounds, the most appropriate methods to avoid electrical contact artifacts in electrode fabrication of specimens were discussed to interpret experimental discrepancies concerning negative and positive piezoresistance [12,13].

Additionally, it has been widely demonstrated that *in-situ* techniques like Raman spectroscopy are very precise tools for determining mechanical and structural properties [27] such as fiber strain under tensile load or compression [28]. This method has been first applied to carbon fibers by Robinson et al. [29], and later successfully used by e.g. Huang et al. [30] and Paipetis et al. [31] to investigate the interfacial behavior and effect of fiber sizing in carbon fiber/epoxy model composites, respectively. Raman spectroscopy has been also used for characterizing other carbon-based materials like for instance CNTs or CNT-based composites [32–34], carbon fibers coated with CNTs [35], cellulose fibers coated with CNT networks [36], and to study strain induced effects in mechanically deposited single layer graphene [37].

The main idea sustaining the present work is to combine piezoresistivity and *in-situ* micro-Raman measurements for determining the relationship between the strain of a carbon fiber alone (which is an internal property) or embedded in an epoxy matrix and its relative electrical resistance. As a consequence, such a method can be used to investigate the interfacial properties between fiber and matrix, as well as for examining the damage of the embedded fiber under tension or compression in real time. Additionally, piezoresistance measurements afford a new low-cost method to replace conventional stress-strain technique for predicting the occurrence of damage in carbon fiber/epoxy composites under tensile loading in a non-destructive way.

To the authors' knowledge, it seems there has been no detailed study devoted so far to the simultaneous measurement of *internal* carbon fiber strain by micro-Raman spectroscopy and piezoresistance dependence under deformation. The main goal of the paper is to fill this gap by presenting an original study combining Raman spectroscopy and piezoresistance measurements of single carbon fiber epoxy composites under tensile load. Unsized and sized fibers have been used for the study to show that fiber damage and interfacial properties in composite systems can be efficiently probed by this non-destructive method. Consequently, the electromechanical behavior of the bare carbon fibers and composite materials investigated in this paper shows that piezoresistance measurements are a good approach for designing accurate strain sensors able to monitor *in-situ* and in *real time* their damage.

2. Experimental

2.1. Materials

For each specimen, a single carbon fiber (TohoTenax HM35, sized and unsized) of 6.7 μm in diameter was used as conductive material. This is a high modulus fiber with a tensile modulus of 345 GPa and a tensile strength of 3240 MPa. The ultimate elongation did not exceed 0.9% and the electrical resistivity was 10^{-3} Ω cm. TohoTenax HM35 fibers were supplied as untwisted 12,000-filament tows sized with an epoxy-compatible material. In order to achieve unsized configuration of HM35 fibers an isothermal heat-treatment at 600 °C for 2 h was carried out on the sized configuration. The specimen matrix was prepared with epoxy resin LM E20 and hardener LM H20 both provided by the LM Wind Power company. The choice of this epoxy system is motivated by its use in the manufactured products of the company. Curing treatment does not affect mechanical properties of the fiber while favoring reinforcement between matrix and fiber.

2.2. Preparation of specimens

Two types of specimen shown in Fig. 1 and Fig. S1a,e were prepared for electromechanical test. To measure the piezoresistance in a single carbon fiber, a specimen configuration based on a simple rectangular cardboard frame containing a rectangular hole with rounded corners was used (Fig. 1a). In this case the single carbon fiber was very firmly attached with LM Wind Power epoxy resin to the cardboard so that the fiber ran along the long axis of the hole without slipping from the glue under subsequent applied strain. Manual pretensioning was applied to each fiber before gluing. Conductive carbon paste cement was then brushed onto the cardboard frame to establish electrical contact between the copper wire and the fiber. The dogbone-shaped specimen specially designed for electromechanical tests of single carbon fiber/epoxy composites is shown in Fig. 1b. The specimens were manufactured by careful alignment and fixation of the single carbon fiber along the specimen cavity in a silicon mold. Additionally, a pair of copper wires was fixed on the silicon mold as well. Conductive cement was used to connect electrically the intersection point between the conductive carbon fiber and copper wires. Then the hardener was added to the epoxy resin, and stirred for several minutes. Prior to injecting the suitable amount of epoxy resin into the silicon mold with a syringe, the mixture was degassed under vacuum during 15 min. Afterwards the silicon mold was placed into a furnace, and the specimens were precured at 80 °C for 4 h and then postcured at 120 °C for 0.5 h.

2.3. Experimental procedure

2.3.1. Piezoresistance measurement methods

Electromechanical testing of single carbon fiber and single carbon fiber/epoxy matrix composite was carried out by recording the relative change of electrical resistance as function of elongation, i.e. piezoresistance. Before performing any tests on the specimens with non-embedded fibers the resistance in the individual sample with and without copper wires connected to the fibers by conductive carbon cement is measured using a multimeter. In the same way the resistance of the dog-bone samples is measured before and after curing. In that way the change in resistance caused by the contact resistance and curing process can be determined which was found to be negligible.

To measure piezoresistance in the single non-embedded carbon fiber, the assembly of fiber and test frame was placed in a home-made mechanical testing system with a constant cross head speed of 0.001 mm/min (see Fig. S1b). The grips of the strain rig were fixed to the cardboard frame without affecting the electrical contacts of the current leads. Prior to horizontal tension application, the cardboard frame was cut horizontally along the dashed lines as indicated in Fig. 1a. The applied strain ε_{appl} was determined from the total cross head displacement. In these tests the low cross head speed was used to ensure that the fiber did not fail instantly and the bridge output voltage and the cross head displacement was recorded once per second. For the non-embedded fiber the applied force was not measured since the applied force is too small for the sample with the load cells at hand.

For the dogbone-shaped specimens a home-made mechanical testing system with a constant cross head speed of 0.025 mm/min was used (Fig. S1f), and the applied load on the sample was measured using a 2 kN load cell. Once per second the cross head displacement, the bridge output voltage and the applied load was recorded. The clamps of straining rig were made from metal with machined pattern of specimen ends, and mounted in spherical bearings to ensure that no bending effects are applied to the specimen during tension. In turn the current leads were passed