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Effect of carbon black nanoparticle intrinsic properties on the self-monitoring performance of glass fibre reinforced composite rods

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ABSTRACT

Self-monitoring composite rods, made of an internal conductive core surrounded by an external structural skin, were manufactured and tested. Both parts were made of glass fibre-epoxy. Electrical conductivity was achieved in the inner core by incorporating as an alternative high surface area or low surface area carbon black in the resin. Self-monitoring performance was assessed by simultaneous mechanical and electrical resistance measurements. The aim was to correlate the electrical resistance variation to stress. Only one type of material showed appropriate self-monitoring properties, since increase of electrical resistance was recorded at increasing loading (both monothonic and cyclic tensile loading), while electrical resistance recovery at high loads was found in the other case. Calorimetric analysis, rheological measurements and SEM observations were carried out to explain this result. Filler dispersion seems to be the key feature affecting the self-monitoring properties. Only high surface area nanoparticles can ensure self-monitoring reliability.

1. Introduction

In past years, self-monitoring polymer composite materials were proposed as innovative monitoring systems, that can provide contemporarily structural and sensing properties [1–3]. Such materials gained particular interest in the field of civil engineering applications, where the use of polymer composite reinforcing rods has become more and more attractive, in order to overcome corrosion problems, typical of steel reinforcements. Usual polymers employed in these applications are epoxy, vinylester-epoxy, polyester, etc. [4]. Polymer composite rods generally present linear elastic failures, i.e. a lack of ductility, which can lead to sudden fractures [5]. Therefore these reinforcements are usually applied together with health-monitoring systems, to prevent catastrophic failures. Both traditional (such as strain gauges, piezoelectrics [6]) and innovative monitoring systems (fibre optics, etc. [7,8]), usually make use of sensors that, placed either inside or outside the concrete structure, are invasive, complicated, expensive and, in the case of external sensor, do not allow continuous monitoring throughout structure service life. To overcome such drawbacks, an alternative monitoring method has been proposed more recently, which makes use of self-monitoring materials, providing both the structural and sensing functions [9–11]. Such materials are usually realized with polymer composites, since they offer intrinsic versatility (i.e. possibility to include different phases within the matrix), ease of fabrication and low costs, which are attractive features for mass production, as in the case of civil engineering. The working principle of self-monitoring materials is based on the correlation between the change of electrical resistance of a conductive phase and the stress/strain occurring to the material [12,13]. In the case of polymeric composites, usually the conductive phase is carbon either in the form of long fibres (CFRP) [14–16] or particles (CPRP) [17–19] or, more recently nanotubes [20,21]. In the first case, when dealing with unidirectional CFRP rods, carbon fibres can operate both as reinforcement and sensitive part and, therefore, are particularly applied in civil engineering applications, where they are usually used in combination with glass fibres to form hybrid composites (CF-GFRP), that can allow to reach some pseudo-ductility [22,23]. From the monitoring point of view, this solution present low sensitivity at low strains (unless prestressing is provided [12]) and generally low maximum electrical resistance variation (about 10%) until fracture. Therefore the authors in [24] suggested to employ such system as non-continuous health monitoring, and to tailor the composite composition (i.e. glass/carbon fibre ratio) to use this material as a "guard sensor", generating an alarm warning at specific stress. Good self-monitoring results were, instead, obtained in CFRP laminates to monitor cracking and delamination at interlaminar interface [25]. The use of carbon particle as conductive phase, instead, has been more recently proposed and showed good self-monitoring potentialities. Okuhara et al. [26] reported that, differently from CFRP, the

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introduction of micrometer carbon flakes in the resin allows to achieve more sensitivity, in particular at low strain, and to perform continuous monitoring. This system presents an interesting "memory" function, in the sense that a residual electrical resistance can be found after cyclic loading, that can be somehow correlated to the maximum stress applied to the material. Moreover, Okuhara et al. [27] and Indada et al. [9] observed that carbon particle type and geometrical shape play a significant role in the self-monitoring behaviour. They showed that the use of graphite carbon flakes is particularly suitable for high sensitivity samples, while the use of spherical carbon black particles increase the material capability to memorize maximum applied load. The self-monitoring efficiency of carbon nanoparticles within polymer matrix encouraged and stimulated the research in the more innovative and promising field of carbon nanotube (CNT) loaded polymers [28–31], whose penetration in industrial manufacturing is not shortly expected due to difficulty in CNT manipulation and processing. CNT loaded polymers in the form of film have shown [30,31] to be very promising as strain sensing, but have to be used as external sensors, while good self-monitoring has been achieved in [28] in monitoring delamination of cross-ply laminates with CNT dispersed in the resin. More recently a very interesting work [32] compared the self-monitoring performance of CB-epoxy and MWCNT-epoxy composites and evidenced that self-monitoring in CNT samples shows a distinct dependency of the electrical resistivity on mechanical load, that was attributed to the peculiar nanofiller fibre-like structure.

The different self-monitoring behaviour of CFRP and CPRP systems is related to their different conditions of electrical conductivity, which, in turn, are linked to the material microstructure. In the case of aligned long carbon fibres, the system can be assimilated to a bunch of conductive wires. The electrical current flows either in fibres direction and in transverse direction by means of bridge contacts between neighbouring fibres. This occurrence explains the low sensitivity of such system since, even when some carbon fibres are broken and the longitudinal current flow is obstructed, electrical conductivity is still insured by means of bridge contacts among broken fibres, that allow current flow in transverse direction [1]. In the case of carbon particles, instead, the electrical model is that of a number of conductors randomly dispersed in an insulating matrix. The theory for such systems reports that conductivity is achieved when a percolation pattern is formed [33,34], i.e. a sufficient numbers of contacts between conductive particles is present to insure current flow. In this conditions, the system quickly changes from being insulator to being conductive. When such system undergoes increasing strain, separation between conductive particles occurs, resulting in higher electrical resistance. Sensitivity is enhanced since the conductive particles gradually separate under strain, with a consequent continuous enhancement of resistivity. Moreover, beyond matrix yielding and after loading, a permanent separation between particles occurs, which generates the "memory effect". In this latter system, the conductivity and, hence the self-monitoring performance, depends on a variety of factors usually related to the peculiar matrix/filler intrinsic properties, such as filler content, intrinsic conductivity, surface area and geometrical shape [35,36]. Some of these features affect conductivity since they interact with particle dispersion and formation of aggregates, particularly important when dealing with nanofillers. In fact, when carbon nanoparticles (CnP) are mixed to an insulating polymer matrix different mesostructures can appear, depending on the filler intrinsic properties. In particular, it is well known [37] that carbon nanoparticles with high surface area and Oil Absorption Number (OAN) present the so-called "high structure", i.e. highly branched aggregates, which leads to the formation of the conductive network at lower carbon content (low percolation threshold).

In this research two types of hybrid self-monitoring composite rods, made of an internal conductive core surrounded by an external structural part, were manufactured and fully characterized. Both the internal core and the external part were made of glass fibre-epoxy, nevertheless, electrical conductivity was achieved in the inner core by incorporating carbon nanoparticles within the resin. In particular, the manufactured self-monitoring composite materials contain, as an alternative, two types of carbon black nanoparticles with different surface areas, OAN and particle size. The aim was to correlate the composite self-monitoring performance to the conductive filler properties, by characterizing the filler interaction with the epoxy matrix. Tensile tests were carried out, on both kind of samples, together with electrical resistance measurements, to assess the self-monitoring performance, while their microstructure was observed by field emission scanning electron microscope (FE-SEM). DSC and rheological measurements were performed in order to correlate the measured self-monitoring performance to the material microstructure of both systems. Prior to self-monitoring testing, percolation behaviour of both systems was assessed to find conductivity threshold.

2. Materials and methods

The manufactured composite materials consisted of an internal electrically conductive core surrounded by an insulating sheath (Fig. 1).

Both parts are made of unidirectional glass fibres (Cofitech, Caselle, Italy, 475W, 2400 tex) in epoxy resin (pure epoxy resin with isofordiammine cycloalifatic hardener, SP system, Gurit, Newport, UK). The manufacturing process is hand-pultrusion. A two-step process was employed: first a glass fibre bundle was pulled through the epoxy resin previously loaded with carbon particles to gain the necessary electrical conductivity, further three additional glass fibres were pultruted around the central conductive core to obtain the insulating sheath and to insure good mechanical properties. Cure reaction was carried out at 60 °C for 3 h. Table 1 reports the main characteristics of the realized samples. In final specimens the internal conductive core was made longer than the external sheath to provide electrical contacts, that were applied at specimen ends using a highly conductive silver paint (Electrolube), to allow electric resistance variation measurements (digital multimiter Keithley DMM 2700). The electrical resistance of both wires and contacts between wires and specimens surface is included in the two-points measurement scheme adopted. Nevertheless, preliminary electrical resistance measurements carried out with both two-points and four-points methods showed a difference in specimen resistance evaluation of around 1 Ω that, being far lower than the specimens electrical resistance (Table 4), can be considered negligible [31,38]. Specimens ends were provided of external metallic cylindrical tabs for tensile testing (Fig. 1a). In Fig. 1d a particular showing sample gripping in tensile test *jig*, with the electrical contact above the metallic cylinder not affected by any gripping pressure. The CnP/resin mixture was prepared by adding the particles to the resin and mechanically stirring at 600 rpm for 1 h. Successively the hardener was added to the mixture (38 phr) that was kept under mechanically stirring for further 5 min and sent to the pultrusion process. Two types of carbon nanoparticles (Printex XE 2b Evonik-Degussa, Essen, Germany and Super P, Timcal Ltd., Bodio, Switzerland) were used as an alternative to prepare the electrically conductive element: both are spherical carbon black powders with particle average diameters of respectively 30 and 40 nm, but different surface areas. Table 2 reports the main characteristics of the chosen CnP.

Percolation was assessed by measuring electrical resistivity of samples with different carbon contents (Keithley DMM 2700)