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SWNT composite coatings as a strain sensor on glass fibres in model epoxy composites

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ABSTRACT

The preparation of a model glass-fibre/epoxy composite with single-walled carbon nanotubes (SWNTs) incorporated as a strain sensor on the fibre surface is described. A micromechanical study of stress transfer at the fibre–matrix interface followed using Raman spectroscopy properties is reported. The SWNTs were distributed along the fibre surface either by dispersing them in an amino-silane coupling agent or coating with an epoxy resin solution containing the SWNTs. The point-by-point mapping of the fibre strain in single fibre fragmentation tests has been undertaken for the first time using SWNTs on the fibres and the interfacial shear stress distribution along the fibre length was determined using the embedded SWNTs. The behaviour was found to be consistent with the classical shear-lag model. The effects of SWNT type and preparation procedure on the sensitivity of the technique were evaluated and optimized from single fibre deformation tests.

1. Introduction

Glass fibre–epoxy composites are important because glass fibres have high mechanical strength, good chemical resistance and compatibility with the epoxy matrix and the resins have good mechanical and thermal properties, excellent chemical resistance and low cure shrinkage. The properties of these composites combined with their low cost lead to their use in a number of critical applications such as in civil aircraft, jet engines, wind turbines, space structures and piping systems for offshore environments [1]. The strength of the fibre–matrix interface is a crucial factor controlling the properties of a composite. The modification of the interface to strengthen the bonding of glass fibres to matrices by chemically changing the surface using silane treatments has therefore been introduced [2,3]. The study and characterization of the properties of this interface therefore are necessary in order to understand the behaviour of the composites before use.

The micromechanics of fibre-reinforced composites have been analysed non-destructively using Raman scattering [4–10]. This can only normally be undertaken if a well-defined Raman spectrum is obtained from the fibre and if the matrix is essentially transparent to the laser beam. Glass fibres do not give strong Raman scattering but the interface between glass fibres and an epoxy matrix has been studied successfully by incorporating a Raman active coating or sizing onto the glass fibre to follow fibre deformation. Young and Stanford et al. [4,10] undertook the first successful micromechanical study of a glass-fibre/epoxy composite system using Raman spectroscopy to follow interfacial stress transfer. A diacetylene–urethane copolymer was coated on the fibres as a strain sensor to allow mapping of the strain distribution along the fibres during fragmentation tests. More recently, Barber et al. [11] successfully applied a sizing containing SWNTs onto the surfaces of glass fibre to follow the deformation of glass fibres in polypropylene composites. However, point-to-point strain mapping along the fibres using SWNT coatings on the fibres as a sensor to follow micromechanical deformation has not been undertaken before.

Carbon nanotubes, discovered in 1991 [12], have been studied extensively over the past 15 years [7,13,14]. This is because their high aspect ratio nanostructure has good electrical and thermal conductivities, very high mechanical strength and a high specific surface area. SWNTs give strong, very well-defined resonance Raman spectra and the Raman scattering process in SWNTs has been analysed by many researchers [4,11,15–17]. The SWNT Raman spectrum consists of 4 main bands; the radial breathing modes (RBM), a defect induced mode (D-band), the tangential mode (G-band), and the overtone of D-band (G′-band). It has been found that the G′-band shifts significantly from its original position during deformation. It shifts to lower wave number when SWNTs are under tension and to higher wave number when SWNTs are under compression [7–9,18]. Deformation of SWNTs can therefore be followed by monitoring the changes of position of the G′-band in the Raman spectrum. The deformation of SWNTs in polymers has been investigated and it has been shown that SWNTs can be used successfully as an electrical sensor [19], a pressure sensor [18,20], a

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chemical sensor [21], a corrosion sensor [22], and a strain sensor [11,15,16,22–24].

In this paper, the possibility of using SWNTs to monitor deformation at the glass-fibre/epoxy interface in model composites using Raman spectroscopy to map the strain point-by-point along the fibre has been investigated for the first time. This has involved developing a methodology of obtaining a good distribution of SWNTs along a glass fibre surface to enable a strong Raman signal to be obtained from the surface. The aim was then to study the micromechanical behaviour of interfaces in glass-fibre/epoxy composites using the SWNTs as a strain sensor. The SWNTs were incorporated on the glass fibre surfaces in either a coating or sizing on the fibre surface. Single fibre deformation was then undertaken to compare the different coating methods in terms of the distribution of SWNTs deposited along the fibres and the shift rate of G′-band with strain. The single fibre fragmentation test was then employed to study interfacial micromechanics of the glass-fibre/epoxy system and evaluate the efficiency of SWNTs as a fibre strain sensor in a composite.

2. Experimental

2.1. Materials

Two types of carbon nanotubes were used in this study. The first type supplied by the CNI Company, Houston, USA was produced using the "HiPCO" process (high-pressure gas-phase decomposition of CO) [25]. SWNTs from this process contain less graphitic deposits and amorphous carbon compared to other processes. The other type, purchased from Sigma–Aldrich Co., Ltd., UK, was carboxylic acid functionalized SWNTs synthesised using the electric arc discharge technique. Their average diameter was 1 nm and their length several microns [26]. The SWNTs used were kept at a minimum concentration to avoid any modification of the mechanical properties of the fibre–matrix interface due to their presence.

The glass fibres were produced manually from glass rods obtained from SGL (Scientific Glass Laboratories Ltd., UK). The epoxy resin matrix was a mixture of Araldite resin LY5052 (a low-viscosity epoxy resin) and Aradur hardener HY5052 (a mixture of polyamines) supplied by Vantico, Polymer Specialties, UK. The mixing ratio was 100 parts of LY5052 to 38 parts of HY5052. After cure, the resin had a Young's modulus of about 3 GPa and a shear yield stress of approximately 43 MPa [27]. The silane coupling agent used was an amino-silane, 3-aminopropyl-triehtoxysilane, supplied by Avocado Research Chemicals, UK.

2.2. Sample preparation

The glass fibres were produced by manually stretching hot glass rods. The glass rods were firstly heated in a hot flame until they started to soften. They were then quickly hot stretched to produce small diameter fibres that were cooled down before being broken into 10–15 cm lengths. The glass fibres were then cleaned in iso-propanol for 15 min then dried at 100 °C for 1 h to remove any organic contaminants. The amino-silane was used as a size on the glass fibre surfaces to enhance the adhesion between the fibres and epoxy using the following methods.

2.2.1. SWNT coating

A 1.5% by volume silane solution was prepared, stirred and hydrolyzed for 15 min. The glass fibres were then soaked and stirred in the silane solution for 15 min to ensure thorough silane coverage on the fibre surface. Condensation of the amino-silane on the fibre surface was carried out by heating the fibres in the oven at 120 °C for 2 h. At the same time, a 0.1% by weight dispersion of SWNTs in ethanol was sonicated for 2 h before mixing with the epoxy resin in ratio of 1:1 and stirred magnetically for another hour before adding the hardener. The fibres were then coated with the SWNTs/ethanol/epoxy resin mixture.

2.2.2. SWNT sizing

The second method involved mixing the SWNTs into the silane sizing solution by sonicating the SWNTs in an ethanol suspension for 2 h before adding the silane coupling agent. The method described above for the silane hydrolysis and condensation was then repeated. After the fibres had been sized, some were coated with the ethanol/epoxy resin mixture. Ethanol was mixed with epoxy resin to facilitate the coating process by reducing the viscosity of the resin.

Finally, the epoxy coatings of all of the samples were either cold-cured at room temperature for 7 days or hot-cured at 120 °C for 2 h. A summary diagram of the coated fibre preparation methods and the schematic structure of the finished samples is shown in Fig. 1. In the case of commercial glass fibres with smaller diameters than the glass fibre used in this case, however, the sizing and coating procedure may have to be modified.

2.3. Fibre characterization

To determine the mechanical properties of the glass fibres, 30 samples were tested in tension using an Instron 1121 mechanical testing machine with a 10 N load cell. Single fibres of 50 mm gauge

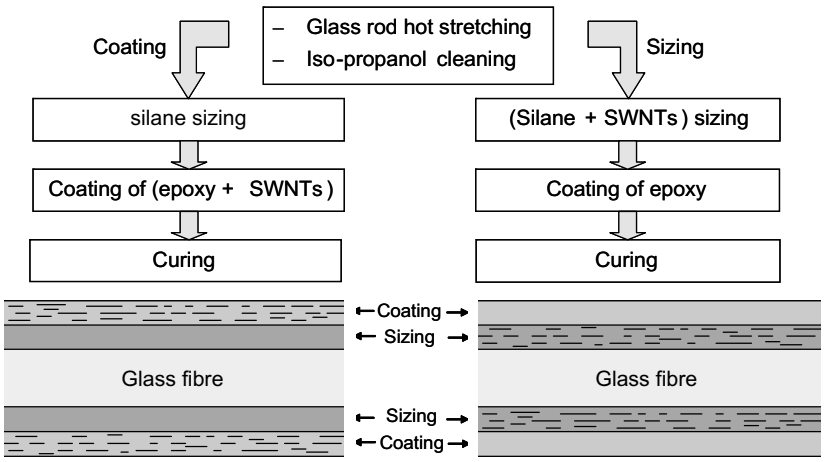

Fig. 1. Fibre preparation methods and schematic of finished samples (not to scale).