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Comparing single-walled carbon nanotubes and samarium oxide as strain sensors for model glass-fibre/epoxy composites

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ABSTRACT

The study of the interfacial stress transfer for glass fibres in polymer composites through the fragmentation test requires certain assumptions, such as a constant interfacial shear stress. In order to map the local interfacial properties of a composite, both Raman spectroscopy and luminescence spectroscopy have been independently used. Unlike other polymer fibre composites, the local strain state of a glass fibre cannot be obtained using Raman spectroscopy, since only very broad and weak peaks are obtainable. This study shows that when single-walled carbon nanotubes (SWNTs) are added to the silane sizing as a strain sensor, it becomes possible to map the local fibre strain in glass fibres using Raman spectroscopy. Moreover, if this model glass fibre contains a small amount of Sm_2O_3, as one of the components, luminescence spectroscopy can be simultaneously used to confirm this local fibre strain. A combined micromechanical properties study of stress transfer at the fibre–matrix interface using luminescence spectroscopy, together with Raman spectroscopy, is therefore reported. The local strain behaviour of both Sm^{3+} doped glass and SWNTs in the silane coating are shown to be consistent with a shear-lag model. This indicates that Sm^{3+} dopants and SWNTs are excellent sensors for the local deformation of glass fibre composites.

1. Introduction

Glass fibre reinforced plastic (GFRP) composites are widely used because they have high mechanical strength, good chemical resistance, good thermal properties and low cure shrinkage. The properties of these composites combined with their low cost has led to their use in a number of critical applications such as in civil aircraft, wind turbines, aerospace structures and piping systems for offshore environments [1]. One crucial factor in controlling the properties of composites is the fibre–matrix interface. Modification of the interface using silane treatment to improve the bonding between the fibre and the matrix is often applied [2]. Many methods have been used to characterize the stress transfer from the matrix to the reinforcing phase, and the properties of the interface, to understand the behaviour of composite materials. The micromechanical tests employed include the pull-out test [3] and the fragmentation test [4]. In the case of brittle fibres, with a matrix like an epoxy resin, the fragmentation test is usually preferred. Recently the Raman scattering technique has been implemented to analyse the micromechanics a variety of fibres and composite systems [5,6]. This approach is only suitable, if a well-defined Raman spectrum is obtained from the reinforcement, and if the matrix is transparent to the laser.

Glass fibres, however, do not have well-defined Raman spectra. In order to overcome this, a Raman active material has been previously incorporated at the fibre–matrix interface to follow the fibre deformation and micromechanical behaviour. The first successful approach using this technique was carried out by Young et al. [7,8]. In this case, a diacetylene–urethane co-polymer coating was used as a strain sensor on the fibres to map the strain distribution along the fibre during a fragmentation test. In effect this generated two interfaces; one between the matrix and the co-polymer and another between the co-polymer and the fibre.

Single-walled carbon nanotubes (SWNTs) have a unique Raman spectrum [9] with intense, well-defined resonances which consist of four main bands; radial breathing modes (RBMs) in the range 100–400 cm^{-1}, a defect induced mode at 1300–1500 cm^{-1} (D-band), a tangential mode at 1500–1600 cm^{-1} (G-band), and an overtone of the D-band at 2500–2700 cm^{-1} (G′-band). It has been found that the G′-band shifts significantly from its original position during deformation; to a lower wavenumber position when the SWNTs are under tension, and to higher wavenumber position when the SWNTs are under compression [10–12]. Deformation of SWNTs can therefore be followed by monitoring changes in the Raman G′-band position. SWNTs distributed within an epoxy matrix have been previously employed to map the stress along glass fibres [10,11]. A recent study on the application of a sizing containing SWNTs onto the surfaces of glass fibres to follow their local deformation in polypropylene composites has also been reported by

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Wagner and coworkers [13]. A similar approach, but with an epoxy resin, has also been recently reported by Sureeyatanapas and Young [12].

Changes in the fluorescence spectrum of Cr^{3+} doped sapphire and Ruby (Cr^{3+} doped Al_2O_3) have been used to follow fibre deformation under compression or pressure [14,15]. This approach has also been used to follow local stress in a single alumina fibre [16] during fragmentation. Moreover, a similar technique has been applied to an Er^{3+} doped glass fibre to determine residual stresses [17]. A recent study by Hejda et al. [18] on the use of samarium fluoride (SmF_3) doping to follow the stress state in a glass fibre has also been reported; Sm^{3+} also has a unique luminescence spectrum with bands that shift with stress.

In this study we report the use of an alternative to the fluoride, namely Sm_2O_3, as a dopant in glass fibres. Although the use of SWNTs as a strain sensor on glass fibres in epoxy resin matrix composites has been previously reported [12], this has not been combined with a doped glass fibre. It was suspected, from a previous study, that SWNTs interfere with the interfacial stress transfer process [12], and so there is a need to verify if this is the case. By comparing the local strain measurements using SWNTs with another technique, it also serves to validate the approach.

Therefore, in this study, both the local strain from Sm^{3+} doped glass fibres and SWNT doped sizing on the surface of the fibres are simultaneously compared and tested. The main purpose was to determine the accuracy of using SWNTs as a strain sensor at the fibre–matrix interface to study the interfacial stress transfer. Both approaches could provide facile methods for the local sensing of fibre–matrix mechanical properties and failure in glass fibre reinforced plastics (GFRP).

2. Experimental

2.1. Materials

Glass was first synthesized by mixing a composition of 55.6% SiO_2, 11.6% Al_2O_3, 18.7% CaO, 0.6% Na_2O, 2.6% MgO, 9.9% B_2O_3, and 0.8% Sm_2O_3 together in a platinum crucible which was then transferred to a furnace. The composition was then melted at a temperature of 1500 °C for 3.5 h. Glass rods were then drawn from the melt using an iron wire [18]. After that the rods were stretched under a gas flame to produce fibres with diameters in the range 40–60 μm. The Sm^{3+} ions were present in a sufficient amount for their luminescence spectrum to be detected, whilst not adversely affecting mechanical properties [19]. Single-walled nanotubes (SWNTs) (Thomas Swan Ltd., UK) produced by electric arc-discharge were functionalized using carboxylic acid (Sigma–Aldrich Co., Ltd., UK). The epoxy resin matrix was a mixture of Araldite resin LY5052 (butan-1,4 diol diglycidyl ether resin) and Aradur hardener HY5052 (isophorone diamine) (Vantico, Polymer Specialties, UK). The mixing ratio was 100 parts of LY5052 to 38 parts of HY5052. The silane coupling agent used was a 3-aminopropyl-triethoxysilane (Avocado Research Chemicals, UK).

2.2. Composite specimen preparation

Samarium oxide (Sm_2O_3) was included in the glass composition, while the SWNTs were distributed along the fibre surface. Firstly, 0.1% SWNTs were sonicated in ethanol solution for 2 h before 1.5% by weight of an amino-silane coupling agent was added. The glass fibres were then sized in the mixture solution for 10–15 min before drying. The fibres were then coated with ethanol/epoxy mixture and hot-cured at 120 °C for 2 h. A full description of the preparation procedure used to coat the glass fibres with SWNTs is described in a previous publication [12].

The fibres were then prepared for mechanical testing. For single fibre deformation, a filament with a 50 mm gauge length was mounted onto a card window. This paper window was subsequently cut on either side, leaving a free fibre to be deformed in tension. For the fragmentation test, a 20 mm long sized fibre was embedded in the epoxy matrix, formed to a dumbbell shape within a mould, and then cured at room temperature for 7 days before the experiment. Room temperature curing of the resin system was used in order to minimize shrinkage. A strain gauge was attached to the surface of the sample in order to record the surface strain in proximity to the fibre during deformation.

2.3. Single fibre mechanical properties characterization

Forty individual fibres of 50 mm gauge length were tested by deforming in axial tension using an Instron 1121 mechanical testing machine. The machine was set up with a 10 N load cell, and fibres were deformed using a cross-head speed of 8.3×10^{-6} m s^{-1} under controlled temperature (23 ± 1 °C) and humidity (50 ± 5%) conditions. Stress–strain curves were then plotted to determine Young's modulus of the fibres.

Scanning electron microscopy (JEOL 6300 SEM) was used to characterize the SWNT/sizing on the glass fibre surface, and to determine the diameter of the fibres. A gold coating was applied for 10 s to create a conductive thin layer. The SEM was operated at 5 kV to minimize damage to the fibres.

2.4. Spectroscopic methods for local strain determination

Raman spectroscopy was used to characterize the SWNTs in the silane coating and luminescence spectroscopy for the doped glass fibres. It was possible to do this simultaneously, using the same instrumentation. Raman spectra were collected using a Renishaw system 1000 spectrometer, equipped with an Olympus BH-2 microscope. A ×50 long working distance objective lens was used, which focussed the laser to a 1–2 μm spot. A HeNe laser was used for the examination of the SWNTs in the sizing on the glass fibre surface. The laser beam was focused on the fibre surface, where SWNTs could be visibly observed. The resonance Raman spectra from the SWNTs were recorded using a 15 s exposure time, with two accumulations (repeated scans were added together to improve the signal-to-noise ratio). In order to reduce heating effects in the SWNTs, 10% of the maximum power of the laser was used.

Luminescence spectroscopy was used to characterize the Sm^{3+} doped glass fibres. As already mentioned, luminescence spectra were recorded using the same Renishaw system 1000 spectrometer, but operating using an absolute wavenumber scale. An argon ion laser was used to excite Sm^{3+} luminescence. The laser beam was focused in the middle of fibre in order to do this. Luminescence spectra were recorded using a 10 s exposure time and three accumulations, with 10% of maximum laser power.

3. Results and discussion

3.1. Fibre characterization

The glass fibres were found to have mean Young's modulus of 75.0 ± 3.8 GPa which is about the same value as commercial E-glass fibres [20]. Therefore, the addition of a Sm_2O_3 doping did not appear to significantly affect the mechanical properties of the glass fibres.

Fig. 1 shows SEM images comparing glass fibres before and after the application of SWNTs/silane sizing, without the epoxy resin coating. It can be clearly seen that the roughness of the surface increased due to aggregated SWNTs on the fibre surface after the siz-