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Hybrid carbon fibre–carbon nanotube composite interfaces

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ABSTRACT

Both low and high modulus carbon fibres are coated with carboxylated single wall carbon nanotubes (SWNTs). It is shown that it is then possible to follow, for the first time, the local deformation of low modulus carbon fibres and composite interfaces using Raman spectroscopy. By deforming coated single carbon fibre filaments in tension, and following the shift in the position of a band located at ~2660 cm^{-1} (2D band) it is possible to calibrate the local stress state of a fibre embedded in an epoxy resin. To follow the interface between the fibres and the epoxy resin, a thin film model composite is used. Point-to-point variation of stress along a single fibre, both inside and outside the resin, is recorded and stress transfer models are used to determine the interfacial shear stress (ISS). Values of the ISS (~20 MPa) are obtained for the thin film model composites for untreated high modulus fibres. A beneficial interfacial effect of the presence of SWNTs on the surface of the high modulus carbon fibre samples is demonstrated resulting in an increase in the maximum ISS (>30 MPa) compared to uncoated samples. Similarly coated low modulus fibres exhibit a very high ISS (>50 MPa). These increases are attributed to an enhanced contact between the resin and the fibres due to an increased surface area as a result of the nanotubes and additional bonding caused due to the presence of carboxylate groups.

1. Introduction

There has been an increase in interest in carbon fibres in recent times due to their widening use in the aerospace, automotive, sports equipment and wind/tidal energy sectors. A range of carbon fibres are currently commercially available with mechanical properties ranging from low to high modulus and strength. Critical to their performance in a composite material is the interface between the fibre and the resin.

A number of groups have attempted to graft carbon nanotubes to the surface of carbon fibres [1–4] with the aim of improving the interface with a resin material. Of particular note, the interface between carbon fibres and a polymer matrix material has been recently reported to be enhanced by using carbon nanotubes (CNT) [5]. Interfacial shear stresses were recorded using single fibre fragmentation in a PMMA matrix and found to increase from 12.5 MPa for an as received fibre to 15.8 MPa for a CNT grafted fibre. The formation of hierarchical composites using carbon nanotubes to enhance composite interfaces has recently been reviewed [6].

Raman spectroscopy has been widely used to follow the deformation micromechanics of both carbon fibres [7–9] and composites [10,11]. In order to do this the position of the 2D band, located at ~2660 cm^{-1}, is followed as a function of tensile (or compressive) deformation on a single carbon fibre filament. The slope of a linear regression to these data is then used as a calibration of the local stress state in a model composite, allowing point-to-point mapping to take place [10,11]. In lower modulus carbon fibres the 2D band is typically absent, and so stress mapping and interfacial analysis is more difficult. Carbon nanotubes have been coated onto fibres from which Raman spectroscopic analysis of local stress states is not possible e.g. glass [12–14]. Here the nanotubes can be directly deposited onto the fibre, or incorporated into a silane coating.

In the present work we use the approach of coating the surface of both high and low modulus carbon fibres with SWNTs. It is shown for the first time that point-to-point stress mapping of a low modulus carbon fibre can be obtained from within a model composite geometry. The positive effect of the presence of SWNTs at the interface is demonstrated, giving a means for improving the properties of composites reinforced with low modulus carbon fibres.

2. Experimental methods

2.1. Materials

Two commercial grades of carbon fibre were used for this study; namely a high modulus carbon fibre (M46 J) provided by

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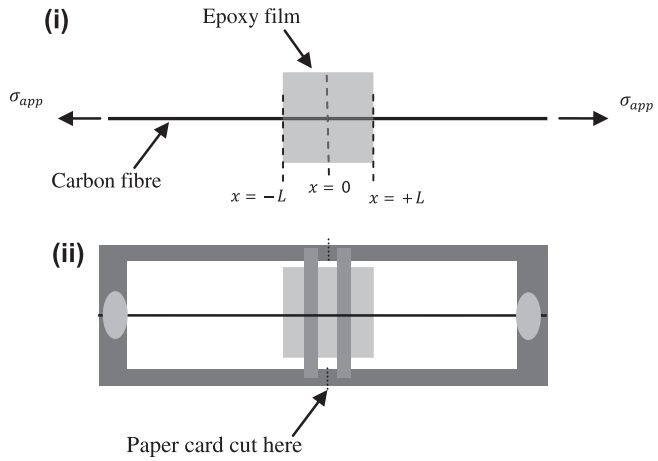

Fig. 1. Schematics of (i) a single carbon fibre-epoxy film model composite indicating the applied fibre stress (σ_{app}), the length along the interface (x) from $-L$ to $+L$ and (ii) the testing card used to deform the model composite sample.

Toray and a low modulus fibre (Tenax-J) by Toho-Tenax. Each fibre was used as-received and had no pre-treatment of its surface. Carboxylic acid treated single walled carbon nanotubes (SWNTs) were provided by Sigma Aldrich (Sigma Aldrich, Dorset, UK). The technical data sheet for these SWNTs states that they have diameters in the range 1.3–1.5 nm, lengths in the range 500–1500 nm and that they contain <15 wt.% metals. The epoxy resin used as a matrix material for the model composites was provided by Vantico, Polymer Specialties, UK. The formulation is a two part curing system of a resin (LY5052) containing 34–42% butanediol diglycidyl ether and 60–70% epoxy phenol-novolac resin and a hardener (HY5052) comprised 35% isophorone diamine, 50–60% 2,2-dimethyl-4,4-methylenebis (or cyclohexylamine) and 1–5% 2,4,6-tris (or dimethylaminomethyl) phenol. The silane coupling agent used in this study was 3-aminopropyl-triethoxysilane which is supplied by Avocado Research Chemicals, UK. A release agent named Ambersil Formula 10 was used, which is a dry film, non-silicone mould release agent and was provided by Ambersil House, UK.

2.2. Model composite preparation

Single carbon fibre filaments were removed from a bundle using tweezers and placed over the window of a cardboard testing frame. Each end of the fibre was glued to the cardboard using an Araldite™ epoxy resin and allowed to cure. To coat the single fibres with SWNTs a 0.1% by weight dispersion of nanotubes in ethanol was sonicated for 2 h. A 1.5 vol.% silane solution was also prepared, stirred and hydrolysed. These two solutions were mixed in a 1:1 ratio and stirred magnetically for 30 min. After that the fibre card samples were soaked in this mixture for 20 min, and then removed and heated at a temperature of 120 °C for 2 h. These samples then just had one single silane layer containing SWNTs, without the presence of an epoxy layer. Samples were then further coated with a thin layer of epoxy resin by placing them in the epoxy/hardener mixture for 5 min, followed by hot curing.

A thin-film epoxy resin-fibre system was prepared as a model composite to determine the properties of the interface. To prepare these samples, a small glass coverslip was placed below the fibre in the middle of a testing card window, supported by two cardboard strips to prevent them from applying load to the fibre before testing or rotating during mechanical deformation (see Fig. 1). After that a small droplet of epoxy resin was applied to the surface of the glass slide and another glass slide was placed on top of the first one, sandwiching the fibre between the two. Adjustments were also made to the position of the slides so that they were in line with each other as much as possible to overcome edge effects. This approach has been previously reported by Mottershead and Eichhorn [15]. These model composites were placed with a room with a controlled environment (temperature of 23 °C and 50% humidity) for 7 days to make sure they were fully cured.

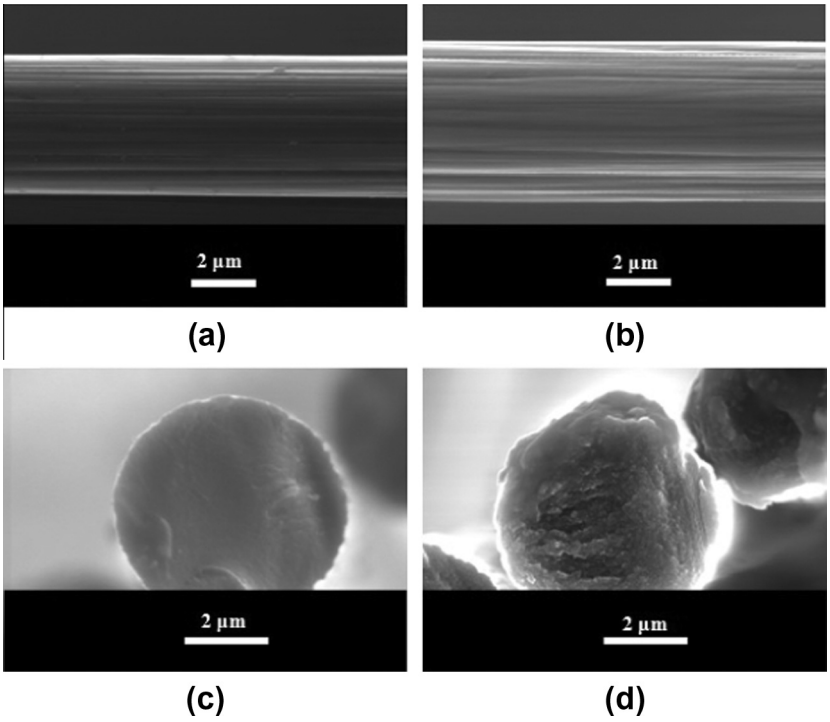

Fig. 2. Typical Scanning Electron Microscope (SEM) images of carbon fibres; (a) high modulus and (b) low modulus filaments along a free fibre length; (c) high modulus and (d) low modulus cross-sections.