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The tensile fatigue behaviour of a silica nanoparticle-modified glass fibre reinforced epoxy composite

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ABSTRACT

An anhydride-cured thermosetting epoxy polymer was modified by incorporating 10 wt.% of well-dispersed silica nanoparticles. The stress-controlled tensile fatigue behaviour at a stress ratio of $R = 0.1$ was investigated for bulk specimens of the neat and the nanoparticle-modified epoxy. The addition of the silica nanoparticles increased the fatigue life by about three to four times. The neat and the nanoparticle-modified epoxy resins were used to fabricate glass fibre reinforced plastic (GFRP) composite laminates by resin infusion under flexible tooling (RIFT) technique. Tensile fatigue tests were performed on these composites, during which the matrix cracking and stiffness degradation was monitored. The fatigue life of the GFRP composite was increased by about three to four times due to the silica nanoparticles. Suppressed matrix cracking and reduced crack propagation rate in the nanoparticle-modified matrix were observed to contribute towards the enhanced fatigue life of the GFRP composite employing silica nanoparticle-modified epoxy matrix.

1. Introduction

Fibre reinforced plastic (FRP) composites are widely used in ship hull, airframe and wind turbine structural applications due to their high specific strength and stiffness. The components in such structures invariably experience various types of constant and variable-amplitude fatigue loads in service. Safe operation of these structures for the designed lifetime requires that composite materials, in addition to their good static mechanical properties, need to have high fracture toughness and good fatigue-resistance.

The majority of engineering composite materials consist of a thermosetting epoxy matrix reinforced by continuous glass or carbon fibres. The epoxy, when polymerised, is an amorphous and highly cross-linked material. This cross-linked microstructure results in many useful properties such as a high modulus and failure strength, low creep, etc. However, it also leads to an undesirable property whereby the polymer is relatively brittle and has a poor resistance to crack initiation and growth which may affect the overall fatigue and fracture performance of FRP composite.

One of the ways to enhance the mechanical properties of FRPs is to improve the properties of the epoxy matrix by incorporating second phase fillers into the resin. Polymeric nanocomposites, where at least one of the dimensions of the filler material is less than 100 nm, have shown significant improvements in mechanical properties, e.g. [1,2]. Various types of particulate, fibrous and layered nano fillers have been employed in composites [3–13].

The beneficial effect of silica nanoparticles on the fracture toughness of epoxies and FRPs has been widely reported [3–10]. However, detailed studies on the fatigue behaviour of particle toughened nanocomposites are limited, e.g. [14]. Hence, the main aim of this investigation was to study the stress-controlled constant-amplitude tensile fatigue behaviour of a glass fibre reinforced plastic (GFRP) composite with a silica nanoparticle-modified epoxy matrix. Emphasis was placed on understanding the micro-mechanisms of the fatigue damage processes.

2. Experimental

2.1. Materials and processing

The materials were based upon a single-component hot-cured epoxy formulation. The epoxy resin was a standard diglycidyl ether of bisphenol A (DGEBA) with an epoxide equivalent weight (EEW) of 185 g/eq, 'LY556' supplied by Huntsman, Duxford, UK. The silica (SiO_2) nanoparticles were obtained as a colloidal silica sol with a concentration of 40 wt.% in DGEBA epoxy resin (EEW = 295 g/eq) as 'Nanopox F400' from Nanoresins, Geesthacht, Germany. The curing agent was an accelerated methylhexahydrophthalic acid anhydride, 'Albidur HE 600' (EEW = 170 g/eq) also from Nanoresins. The

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E-glass fibre cloth was a non-crimp-fabric with two layers of fibres arranged in a ±45° pattern with an areal weight of 450 g/m^2 from SP Systems, Newport, UK.

The DGEBA epoxy resin was weighed and degassed at 50 °C and −1 atm. The required quantity of silica nanoparticle-modified epoxy resin to give 10 wt.% of silica in the final formulation was also weighed and degassed. These were mixed together, a stoichiometric amount of curing agent was added, and the mixture was stirred and degassed. Typically, to prepare 500 ml (589 g) of 10 wt.% silica nanoparticle-modified resin, about 150 g of Nanopox, 184 g of LY556 and 255 g of HE600 was used. The resin mixture was then used to prepare both bulk epoxy sheets and GFRP composites.

To manufacture the bulk epoxy sheets, the resin mixture was poured into release-coated steel moulds. The filled moulds were placed in a circulating air oven. The temperature was ramped to 100 °C at 1 °C/min, and the epoxy was cured for 2 h. The temperature was then ramped to 150 °C at 1 °C/min and the plate was post-cured for 10 h. An atomic force microscope (AFM) image of the silica nanoparticle-modified epoxy polymer, obtained as described in [4], is shown in Fig. 1. The silica particles are about 20 nm in diameter and are evenly distributed in the epoxy.

The GFRP composite laminates were manufactured by resin infusion under flexible tooling (RIFT) [15] technique. E-glass fibre non-crimp fabric pieces of about 330 mm^2, were cut and laid up in a quasi-isotropic sequence $[(+45/-45/0/90)_s]_2$ with a fluid distribution mesh. The resin mixture was infused into the glass-cloth lay-up at 50 °C and −1 atm. Once the infusion was complete, the laminate was cured using the same cure cycle as the bulk plates, maintaining the vacuum throughout the curing process. The resulting GFRP composite laminates (with neat and silica nanoparticle-modified epoxy matrix) were about 2.5–2.7 mm thick, and had a fibre volume fraction of about 57%.

2.2. Tensile properties

The tensile properties of the bulk epoxies and GFRP composites were determined according to the ASTM D638 [16] and ASTM D3039 [17] test standard specifications respectively. Schematic drawings of the test specimens are shown in Fig. 2. The tensile tests were performed using a 100 kN computer-controlled screw-driven test machine with a constant crosshead speed of 1 mm/min. The average tensile properties, determined from five tests on each material, are shown in Table 1.

As observed in earlier investigations [4,5], the addition of silica nanoparticles increased the tensile strength and modulus of both the bulk epoxy and the GFRP composite. The ultimate tensile strength (UTS) increased by about 19% and 5%, whereas the modulus increased by about 17% and 7% in the bulk epoxy and GFRP composite respectively. Although the increases due to the addition of the nanoparticles are significant for the bulk epoxy, they are not so significant for the GFRP as the composite properties are fibre-dominated.

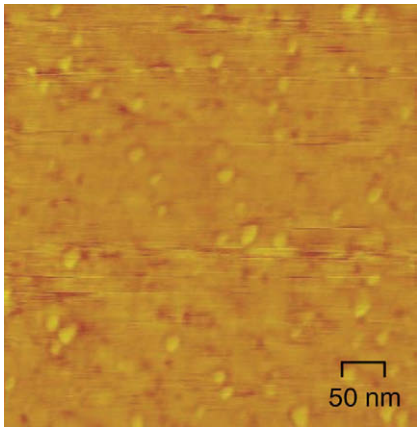

Fig. 1. Tapping-mode atomic force micrograph of 10 wt.% silica nanoparticle-modified bulk epoxy polymer.

2.3. Fatigue Testing

The fatigue test specimens, as shown in Fig. 2, were prepared from the bulk epoxy sheet and GFRP composite laminate. The sharp edges of the bulk epoxy test specimens were slightly rounded off with emery paper before testing, to avoid any stress concentration effect. The fatigue tests were performed as per the ASTM D3479 M test standard [18], using a 25 kN computer-controlled servo-hydraulic test machine. The tests were conducted at a stress ratio, $R = \sigma_{min}/\sigma_{max} = 0.1$ with a sinusoidal waveform at a frequency, $\nu = 1$–3 Hz. The test frequency was kept below 3 Hz to prevent thermal effects which lead to reduced fatigue lives [19–21].

The load vs. displacement data for one complete fatigue cycle was captured at regular intervals during the fatigue test, and the specimen stiffness was calculated [22]. About 50 pairs of load/displacement data in the central portion of the rising half of the fatigue cycle were used to perform the regression analysis. For the purpose of comparison, the normalised stiffness of the specimen was defined as the ratio of the initial stiffness (obtained in the first cycle) to the measured stiffness at any given fatigue cycle. The fatigue fracture surfaces of the bulk epoxies were sputter-coated with a thin layer of gold and observed using a high resolution scanning electron microscope (SEM).

2.4. Measurement of crack density

Due to the translucent nature of the GFRP composite, the development of fatigue damage (matrix cracks and delaminations) was visible in the gauge section of the specimen under transmitted light during testing. Detailed investigation of matrix cracking was performed during one of the fatigue tests (at $\sigma_{max} = 150$ MPa) for both the neat and silica nanoparticle-modified GFRP composites.

An area at the centre of the gauge section of the test specimen, about 25 mm^2, was marked. The specimen was mounted in the test machine and the cyclic loading was applied. After the application of a specified number of load cycles, the test was stopped, the specimen was dismounted and the matrix cracks in the marked area were photographed using transmitted light. The specimen was then re-mounted and the test restarted. This procedure was continued until the specimen failed.

A typical sequence of photographs obtained for the GFRP composite with the neat epoxy matrix is shown in Fig. 3. The virgin sample with no matrix cracks is on the far left. The polyester binding yarns in both 0° and ±45° directions can be readily seen as faint thick lines, but the E-glass fibres are not visible. With increasing number of cycles, cracks develop in the ±45° and 90° directions and become visible as dark lines. The higher the number of fatigue cycles, the greater the number of cracks that are formed. Similar observations of the matrix cracking sequence in a GFRP composite under fatigue has been reported previously [23].

Although cracks in the 90° ply were observed in some images, due to greater depth of this ply from the surface, they could not be consistently observed in all the photographs. Gagel et al. [23] observed that the stiffness of the composite in the first two stages of the fatigue life correlates strongly with the ±45° crack density and more weakly with the density of 90° cracks. Hence, only ±45° cracks were considered for the analysis in this investigation.