The effect of rubber micro-particles and silica nano-particles on the tensile fatigue behaviour of a glass-fibre epoxy composite

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Introduction:

Fibre-reinforced polymer (FRP) matrix composites are widely used in airframe structural components. Although composites offer good and useful structural properties, they are brittle. Indeed, the commonly-employed thermosetting epoxy matrices typically have a poor resistance to crack initiation and growth. Therefore, efforts have been made to improve the mechanical properties of the epoxy polymeric matrix, and thereby the properties of FRPs, through the incorporation of second-phase particles in the resin matrix [1-8]. The addition of micrometre-sized rubber particles [1-3] and, more recently, nano-sized silica (SiO₂) particles [4-8], into an epoxy polymer have been shown to improve the fracture energy of bulk epoxies by up to ten to fifteen times, without significantly impairing their other desirable engineering properties [5]. FRPs based upon such particle-reinforced matrices have also shown a remarkable improvement in their interlaminar fracture energy [6,8]. If this enhanced toughness was accompanied by improved fatigue behaviour, then these materials would be highly attractive for structural applications. The present letter addresses the tensile fatigue behaviour of a glass-fibre reinforced-plastic (GFRP) with various particulate-toughened epoxy matrices, and describes some very novel and exciting results.

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Experimental:

The materials were based upon a single-component hot-cured epoxy formulation. The epoxy resin was a standard diglycidyl ether of bis-phenol A (DGEBA) with an epoxy equivalent weight (EEW) of 185 g/mol, 'LY556' supplied by Huntsman, Duxford UK. The silica (SiO_2) nano-particles were obtained at a concentration of 40 wt.% in DGEBA epoxy resin with an EEW of 295 g/mol: 'Nanopox F400' from Nanoresins, Geesthacht, Germany. The curing agent was an accelerated methylhexahydrophthalic acid anhydride, 'Albidur HE 600' also supplied by Nanoresins, and was used stoichiometrically. The reactive liquid carboxyl-terminated butadiene-acrylonitrile (CTBN) rubber (which gives rise to micrometre-sized particles upon curing) from Emerald Performance Materials, Akron, USA, was obtained as CTBN-epoxy adduct with a rubber concentration of 40 wt.% in DGEBA epoxy resin: 'Albipox 1000' from Nanoresins, Geesthacht, Germany. The glass fibre was a non-crimp-fabric (NCF) arranged in a $\pm 45^\circ$ pattern with an areal weight of 450 g/m² from SP Systems, Newport, UK.

The GFRP composite panels were manufactured by the 'Resin Infusion under Flexible Tooling' (RIFT) technique [9]. Fibre-cloth pieces, about 330 mm square, were cut and laid up in a quasi-isotropic sequence $[(+45/-45, 90/0)_s]_2$ with a fluid distribution mesh. The DGEBA-epoxy resin was mixed with the silica nano particle-epoxy and/or CTBN-epoxy adduct to give the required content of silica and/or CTBN rubber. The resin mixture, stirred and degassed thoroughly, was infused into the glass-cloth lay-up at a temperature of 50°C using the RIFT technique and -1 atm. Once infusion was complete, the temperature was increased at 1°C/min and the composite laminate was cured at 100 °C for 2 hours, and then post-cured at 150 °C for 10 hours.

Four different types of GFRP laminates with varying matrix compositions were prepared; (i) neat resin (NR), (ii) resin with 9 wt.% rubber micro particles (NRR) (iii) resin with 10 wt.% silica nano particles (NRS) and, (iv) resin with a 'hybrid' matrix containing both 9 wt.% rubber and 10 wt.% silica particles (NRRS). The atomic force microscopy (AFM) studies on these bulk epoxy matrix materials, as described by Johnsen et al [7], showed that

the rubber particles were evenly distributed and had an average size of 0.5 to 1 μm in both the NRR and NRRS materials. However, the silica particles of about 20 nm in diameter were evenly distributed in the NRS polymer but they were somewhat agglomerated to give a 'necklace-type' structure with an average width of about 1 μm in the NRRS material. The tensile properties, including the ultimate tensile strength, UTS, and modulus, E, of all the materials, determined according to ASTM D3039 [10] using four replicates, are shown in Table 1.

Parallel-sided cyclic-fatigue test specimens of 150 mm x 25 mm x 2.7 mm were machined from the laminate and end-tabbed. The volume fraction of fibres was approximately 57%. Fatigue tests were performed in tension using a 25 kN computer-controlled servo-hydraulic test machine. The fatigue parameters employed were a stress ratio, $R = 0.1$, and a sinusoidal waveform. The frequency used for the low cycle fatigue (high maximum stress) tests was 1 Hz, and for the high cycle fatigue (low maximum stress) was 4 Hz. No significant effect of frequency is expected over this range. The load versus displacement data were obtained at specified regular intervals during the fatigue tests. About twelve tests were performed for each material.

Results and Discussion:

Constant-amplitude, cyclic-fatigue test results at a stress ratio, $R = 0.1$, obtained for the GFRP composites with the various matrices are shown in Fig.1. It may be seen that, over the entire range of stress levels investigated, either the addition of 9 wt.% CTBN rubber micro-particles (NRR) or 10 wt.% silica nano-particles (NRS) alone in the matrix has a similar effect in enhancing the fatigue life by two to three times, when compared to the fatigue life of the NR composite. The addition of both CTBN rubber and silica particles in the matrix, to give a 'hybrid' modified matrix (NRRS), appears to further increase the fatigue life, by about three to eight times compared to the neat (i.e. unmodified) matrix (NR) composites. Further, the enhancement of the fatigue life seen when the 'hybrid' modified matrix is employed is particularly pronounced at the low stress ranges, which is very noteworthy for

obtaining extended fatigue lives from components manufacture using such modified GFRP composites.

The fatigue limit, i.e. the maximum applied stress for a life of 10^6 cycles, of the NR composite was about 95 MPa. The presence of the CTBN rubber or silica particles alone in the matrix raises this fatigue limit by about 15%, to 110 MPa. However, the presence of both these particles further increases the fatigue limit to about 120 MPa, i.e. a total increase of about 26% when compared to the NR composite.

The load versus displacement data obtained during fatigue testing were analysed and the stiffness reduction was evaluated as a function of the number of fatigue cycles. Typical stiffness variation curves obtained at $\sigma_{\max} = 225$ MPa are shown in Fig. 2. In general, all the materials exhibit a stiffness reduction with fatigue cycles, as has been previously observed in FRPs [11,12]. The stiffness reduction was quite steep and very significant in the NR composite. The NRRS showed the slowest rate of stiffness reduction, and exhibited the longest fatigue life. The stiffness reduction curves for the NRR and NRS GFRP composites were observed to be almost similar and lie in-between these two extremes, and these observations agree very well with the trends shown in Fig. 1.

Transmitted-light photography was used to observe a small area of the gauge length of the fatigue-failed specimens. The photographic images of the matrix cracking patterns observed in the $\pm 45^\circ$ plies are shown in Fig. 3, and are very similar to results reported previously [13]. The matrix cracking was most severe in the NR composite and least in the NRRS composite. The crack density (CD), defined as the number of cracks per unit length, was about 3.5 per mm, 2.2 per mm, 2.7 per mm and 1.7 per mm in the NR, NRR, NRS and NRRS composites, respectively. These results are again in good agreement with the observations described above.

From the present results it is clear that modification of the epoxy matrix by incorporating 9 wt.% rubber micro-particles or 10 wt.% silica nano-particles increases the fatigue life. Also, the presence of both of these types of particles, to give the hybrid-toughened matrix, appears to further increase the fatigue life of the GFRP. Now, in a quasi-isotropic GFRP composite under tensile fatigue loads, the most pervasive damage mode is matrix cracking [12] and the particle-toughened matrices appear to suppress the formation of these micro-cracks in the composite material (see Fig. 3). Indeed, the trend in the stiffness reduction (as observed in Fig. 2), which is a direct consequence of matrix cracking, correlates very well with the extent of damage observed in the matrix cracking patterns for the different types of epoxy matrix. Further, interestingly, these observations are in very good agreement with an earlier investigation which also showed that the crack growth rate is significantly decreased in particle-toughened epoxy polymers [14]. Thus, the second-phase particles appear to modify both the crack initiation and crack propagation processes to result in an enhanced fatigue life. During the later stages of fatigue testing, the formation and growth of delaminations, particularly from the specimen edges, were clearly observed, and the continued stiffness reduction (see Fig. 2) is due to initiation and growth of these delaminations [12]. It is noteworthy, that the growth rate of such delaminations also appears to have been reduced in the matrices which contain the second-phase particles.

Conclusions:

It is clear that incorporation of either the CTBN rubber micro-particles or the silica nano-particles alone in the epoxy matrix have almost a similar beneficial effect on the fatigue performance of the GFRP composites. In addition to raising the fatigue limit by about 15%, these particles enhance the fatigue life of GFRP composite by about two to three times, when compared to the neat-resin matrix composite. Furthermore, the presence of both rubber and silica particles in the matrix to give a 'hybrid' modified GFRP results in a further enhancement of the fatigue life, particularly at the low stress ranges. Indeed, the fatigue limit was further raised by about 25% due to the presence of both these types of particles. The suppressed extent of matrix cracking and

reduced delamination growth rate in the composites based upon the modified matrices appears to be the main reasons for the observed enhancement of the fatigue lives of these GFRP composites.

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Table 1. Tensile properties of the GFRP composites, showing mean and standard deviation (SD).

Material	Formulation		Ultimate tensile strength, (MPa)		Modulus, E (GPa)	
	Wt.% CTBN	Wt.% SiO ₂	Mean	SD	Mean	SD
NR	0	0	365	13	17.5	0.1
NRR	9	0	346	25	15.3	0.2
NRS	0	10	381	12	18.8	0.1
NRRS	9	10	380	11	15.9	1.1

List of Figures

- Fig. 1.** Stress versus lifetime (S-N) curves of the GFRP composites.
- Fig. 2.** The stiffness variation during fatigue cycling in the GFRP composites at $\sigma_{\max} = 225$ MPa.
- Fig. 3.** Transmitted light photographic images of matrix cracking in the GFRP composites after testing at $\sigma_{\max} = 150$ MPa.

Fig. 1. Stress versus lifetime (S-N) curves of the GFRP composites.

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Fig. 3. Transmitted light photographic images of matrix cracking in the GFRP composites after testing at $\sigma_{\max} = 150$ MPa.