Enhanced fatigue behavior of glass fiber reinforced composites with nanoparticles

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Abstract

Nanoparticle reinforcement of the matrix in laminates has been recently explored to improve mechanical properties, particularly the interlaminar strength. This study analyses the fatigue behaviour of nanoclay and multiwalled carbon nanotubes enhanced glass/epoxy laminates. The matrix used was the epoxy resin Biresin® CR120, combined with the hardener CH120-3. Multiwalled carbon nanotubes (MWCNTs) 98% and organo-montmorillonite Nanomer I30 E nanoclay were used. Composites plates were manufactured by moulding in vacuum. Fatigue tests were performed under constant amplitude, both under tension–tension and three points bending loadings. The fatigue results show that composites with small amounts of nanoparticles addition into the matrix have bending fatigue strength similar to the obtained for the neat glass fibre reinforced epoxy matrix composite. On the contrary, for higher percentages of nanoclays or carbon nanotubes addition the fatigue strength tend to decrease caused by poor nanoparticles dispersion and formation of agglomerates. Tensile fatigue strength is only marginally affected by the addition of small amount of particles. The fatigue ratio in tension–tension loading increases with the addition of nanoclays and multi-walled carbon nanotubes, suggesting that both nanoparticles can act as barriers to fatigue crack propagation.

Keywords

A. Glass fibres; A. Particle-reinforcement; A. Nano-structures; B. Fatigue; Nanocomposites

1. Introduction

According to Grimmer and Dharan [1] high-cycle fatigue life in aligned glass fibre composites is dominated by fatigue cracking in the matrix, which subsequently propagate and rupture the main load bearing elements, *i.e.*, the fibres. The lower elasticity modulus of glass fibres, when compared to the high-modulus of carbon fibre composites, may impose higher strains in the matrix leading to failure by fatigue. Therefore, the addition of nanoparticles, such as carbon nanotubes (CNTs) or montmorillonite clays (MMTs), is expected to contribute to decrease the scale of damage mechanisms, leading to an increase in the absorption of strain energy through the creation of a multitude of fine nano-scale cracks [1]. Some nanometric particles usually have what is considered to be a high specific surface area (SSA) of more than 1000 m2/g. According to Gojny et al. [2], this property presents an advantage over micro-scaled fillers, since nanoparticles can act as interface for stress-transfer. These authors also state that single wall carbon nanotubes (SWCNTs) have a higher SSA, around 1300 m2/g, but present a tendency to form agglomerates (called nanoropes), as well as present difficulties to separate and blend within the matrix. On the contrary, multi wall carbon nanotubes (MWCNTs) have a smaller SSA, but present a better ability to disperse, although lacking in mechanical reinforcement. According to Yasmin et al. [3] MMTs present a SSA around 750 m2/g. Gojny et al. [4] studied the influence on the mechanical properties of epoxy-based nanocomposites, with several nanofillers, namely single-wall CNTs (SWCNT), double-wall CNTs (DWCNT) and multi-wall CNTs (MWCNT).

The most significant improvements were attained with amino-functionalized DWCNTs with 0.5 wt% filler content: 10% on tensile strength, 15% on stiffness and 43% on fracture toughness.

The main objective of this work was to study the fatigue behaviour of glass-reinforced composites based on epoxy resin. Three types of matrix compositions were analysed, namely neat epoxy resin, as well as epoxy resin enhanced with nanoclays, MMTs, or multi wall carbon nanotubes, MWCNTs. Moreover, two types of fatigue loading modes, namely three point bending and tension–tension loadings, were used.

2. Experimental

Fibres and resin were hand placed in a mould with all fibre layers oriented in the same direction and subjected to low compression. Fibreglass layers and resin were applied alternately, while ensuring the complete impregnation of the fibres until achieving a stack of ten layers. The mould was put into a vacuum bag as illustrated inFig. 1, at room temperature for 8 h. The post-cure process was performed in an oven initially at 55 C during 16 h, then at 75 C during 3 h and finally at 120 C during 12 h.

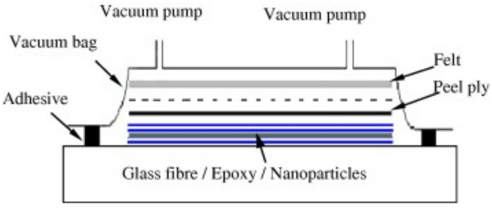

Fig. 1. Schematic view of the vacuum in mould curing process.

Samples were prepared in an ultramicrotome for ultrathin sectioning EM FCS, Leica Company. Morphological analyses were realised in an Ultra-high resolution Field Emission Gun Scanning Electron Microscopy (FEG-SEM), NOVA 200 Nano SEM, FEI Company, using a Scanning Transmission Electron Microscopy (STEM) detector and an acceleration voltage between 15 and 18.4 kV to obtain the micrographs. Fig. 2 shows the typical observation for 1% nanoclays filled epoxy matrix composite, indicating good dispersion and clay exfoliation. However, poor dispersion was obtained for the glass fibre reinforced epoxy composites enhanced with multi wall carbon nanotubes.

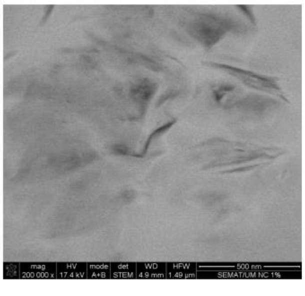

Fig. 2. TEM observation of a composite with the epoxy matrix reinforced with 1% of nanoclay content.

Both uniaxial static and fatigue tests were performed under tension and three point bending (3PB) loadings. Fig. 3 depicts the specimens used in the tests. A referential is also superimposed in the figure to illustrate the considered fibre orientation. The tests performed under tension loading were performed using grooved specimens with the same geometry and dimensions (Fig. 3a) that have been used by other authors[5-8]. Fig. 3(b) shows the specimen dimensions used for tests performed under three point bending loading.

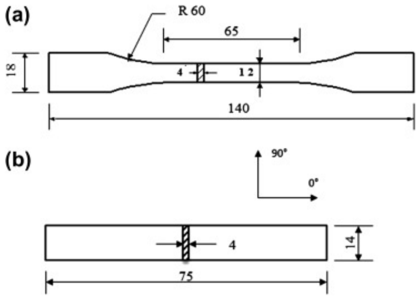

Fig. 3. Specimen’s geometry (dimensions in mm): (a) tension and (b) bending.

3. Results And Discussion

Fig. 4 depicts the typical tensile stress versus displacement curves obtained for the composites under static three point bending loading. The presented curves clearly show that the specimens do not fail immediately at maximum load, keeping some residual strength until final failure. A similar behaviour was also observed under static tensile loading.

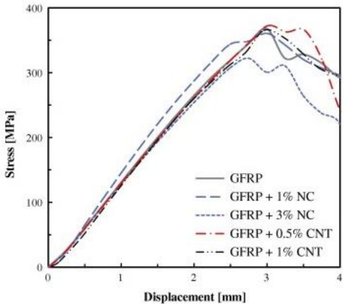

Fig. 4. Typical stress–displacement curves for three point bending static tests.

The fatigue results obtained under three point bending loading, analysed in terms of the stress range of the load cycle against the number of cycles to failure, are depicted in Fig. 5 ; Fig. 6 for glass fibre reinforced polymers (GFRPs) with addition of nanoclays or carbon nanotubes into the epoxy matrix, respectively. The fatigue life for neat epoxy matrix glass fibre reinforced composite is superimposed in both figures for comparison.

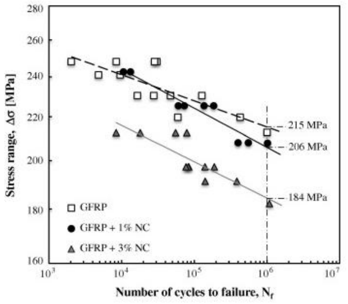

Fig. 5. Effect of nanoclay addition on GFRP composites under three point bending fatigue loading.

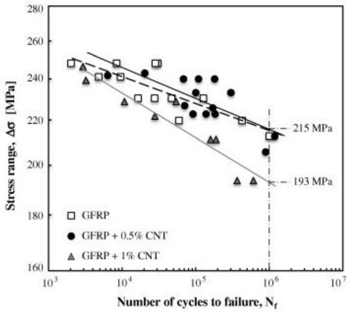

Fig. 6. Effect of carbon nanotubes addition on GFRP composites under three point bending fatigue loading.

Fig. 5 shows that there seems to be a very slight increase in the fatigue strength of 1% nanoclay GFRP composites only for lives lower than approximately 20.000 cycles, while 3% nanoclay GFRP composites present always a significant lower fatigue resistance in comparison to neat composites. The adverse effect of the nanoclay particles on the majority of the fatigue life decreases the fatigue strength at 106 cycles in approximately 4% and 14% relatively to the neat GFRP epoxy matrix, for 1% and 3% nanoclay glass fibre reinforced composites, respectively.

Fig. 6 clearly shows a fatigue life increase of GFRP with 0.5% of MWCNTs, being more significant for short lives and reaching approximately the same fatigue strength at 106 cycles in comparison to the neat glass fibre reinforced composite. The *S*–*N* curve obtained for GFRP composites with addition of 1% of carbon nanotubes is relatively close to the neat composite one at very short lives. However, as fatigue life increases the higher slope of the*S*–*N* curve results in an inferior performance under flexural fatigue loading, reaching a fatigue strength decrease at 106 cycles of approximately 10% relatively to the GFRP with neat epoxy matrix. Both Fig. 5 ; Fig. 6 clearly show that less fatigue resistance is achieved by the laminate composite with increasing percentage of nanoparticles added to the epoxy matrix. Moreover, only 0.5% carbon nanotube GFRP composites achieved a somewhat higher resistance in bending fatigue in comparison to neat matrix composites.

The tolerance to fatigue can also be analysed using the fatigue ratio, which is defined as the ratio between the loading stress range and the respective static strength. Fig. 7a and b presents the comparison between the fatigue ratio of neat glass fibre reinforced polymer (GFRP) with nanoclays and carbon nanotubes GFRP composites, respectively. Obviously, the static strength is the ultimate bending strength (σubs) of the correspondent material.

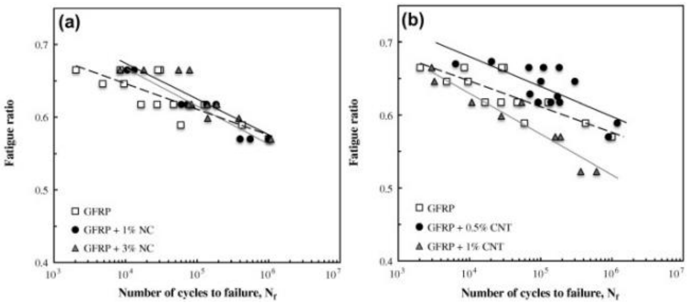

Fig. 7. Fatigue ratio against the number of cycles to failure under 3 PB loading: (a) nanoclay filled GFRP and (b) carbon nanotube enhanced composite.

The fatigue results obtained under tension–tension loading, analysed in terms of the stress range of the load cycle against the number of cycles to failure, are depicted in Fig. 8a and b for glass fibre reinforced polymers with addition of nanoclays or carbon nanotubes into the epoxy matrix, respectively. The fatigue life for neat epoxy matrix glass fibre reinforced composites is once again superimposed in both figures for comparison.

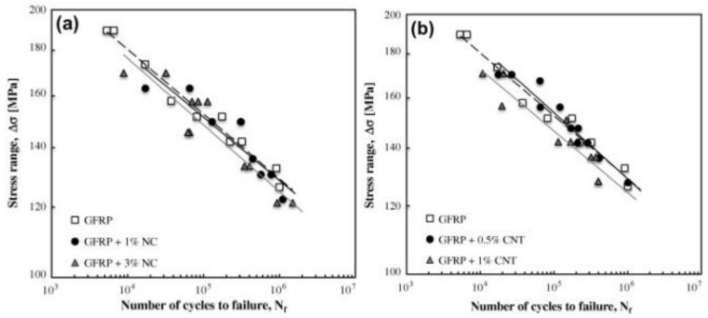

Fig. 8. Effect of nanoparticle addition on GFRP composites under tension–tension fatigue loading: (a) nanoclay particles and (b) carbon nanotubes.

Fatigue results analysed in terms of the fatigue ratio for nanoclay and MWCNT enhanced GFRP composites are plotted in Fig. 9a and b, respectively. The analysis of these figures indicates that nanoclay addition makes the material less sensitive to fatigue damage and that this effect increases with the amount of nanoclays. Moreover, in the case of GFRP with MWCNTs the composite with

0.5% of nanoparticles is the most tolerant to fatigue damage. Contrary to the observed under 3 PB, under tension–tension loading the GFRP with 1% MWCNTs also presents higher fatigue ratio than the neat matrix glass fibre reinforced epoxy composite, indicating that even for this percentage of particle addition the nanotube agglomerates do not have a very detrimental effect on the fatigue strength.

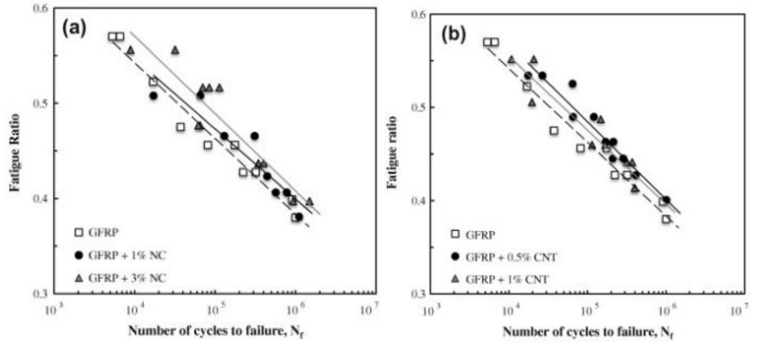

Fig. 9. Fatigue ratio against the number of cycles to failure under tension–tension loading: (a) nanoclay filled GFRP and (b) carbon nanotube enhanced composite.

As already mentioned, in order to control and prevent the possible degradation of the polymer matrix due to the increases of the sample temperature during the fatigue tests, the temperature was monitored at the middle point of the specimen's surface. Fig. 10 depicts the typical temperature rise during cyclic loading, at several stress ranges, against the number of loading cycles.Initially the temperature increases for the earlier fatigue cycles, then grows smoothly for most of the test and finally, nearly the final failure a more intense increase occurs. The value of the stable temperature in the intermediate stage is basically independent of the matrix composition but increases significantly with the stress range, remaining always below 25 °C. Therefore, the degradation of the matrix is not to be expected once the maximum temperature is below the glass transition temperature.

Fig. 11 shows the typical normalised compliance against the number of cycles for the neat glass fibre reinforced epoxy matrix composite under several stress ranges of the loading cycle. As expected, the stress range increase promotes earlier fatigue damage, higher damage rate and lower fatigue life. It was also observed that the fatigue damage just before failure, quantified in terms of the normalised compliance (*C*/*C*0), increases with the stress range.

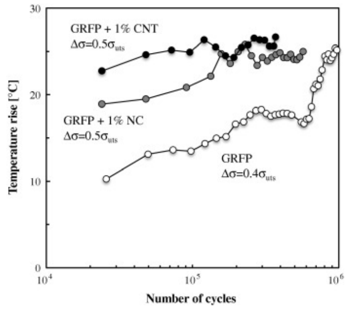

Fig. 10. Temperature rise during tension–tension fatigue loading.

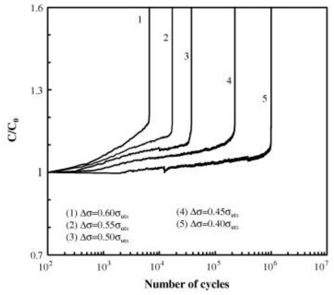

Fig. 11. Normalised compliance for neat epoxy matrix GFRP composite at several stress ranges of the loading cycle.

In order to analyse the effect of the matrix composition in the normalised compliance, Fig. 12presents the comparison of the *C*/*C*0 ratio evolution with the number of loading cycles between the neat glass fibre reinforced epoxy matrix composite, 1% nanoclays GFRP and 1% MWCNTs GFRP composites, tested in tension–tension loading, using as stress range half of the tensile ultimate static strength.

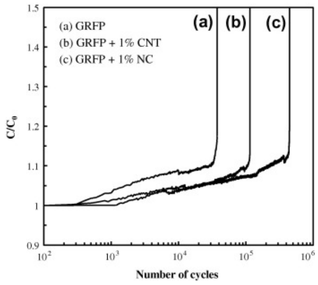

Fig. 12. Normalised compliance for several GFRP matrix compositions. $\Delta\sigma = 0.5\sigma$uts.

4. Conclution

In the present study the effect of the addition of small amount of nanoclays and multi-walled carbon nanotubes into epoxy matrix on the fatigue behaviour of glass fibre composites was analysed. The following main conclusions can be drawn:

Good dispersion into the matrix was achieved for 1% nanoclays, while for higher content and for MWCNTs nanoparticles the dispersion technique was apparently ineffective. Moreover, independently of the efficiency of particles dispersion, both bending and tensile static strength were not improved by the nanoparticles addition.

The fatigue strength, both under 3 point bending as well as under tension–tension loadings, for the composites with matrix filled with only a small amount of nanoparticles (0.5% MWCNTs and 1% nanoclays) is similar to the obtained for the neat glass fibre reinforced epoxy matrix composite. However, for composites with addition of higher percentage of nanoparticles a decrease of the fatigue strength was observed, which is more significant under 3 point bending loading.

The fatigue ratio in bending loading increases slightly with the addition of nanoclays and significantly with 0.5% MWCNTs, but decreases for 1% of MWCNTs as a consequence of the formation of agglomerates.

The fatigue ratio in tension–tension loading increases with the addition of nanoclays and multi-walled carbon nanotubes, suggesting that both nanoparticles can act as barriers to fatigue crack propagation.

Acknowledgements

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References

[1] C. Grimmer, C.K.H. Dharan High-cycle fatigue of hybrid carbon nanotube/glass fiber/polymer composites J Mater Sci, 43 (2008), pp. 4487–4492

[2] F.H. Gojny, M.H.G. Wichmann, B. Fiedler, W. Bauhofer, K. Schulte Influence of nano-modification on the mechanical and electrical properties of conventional fibre-reinforced composites Composites Part A, 36 (2005), pp. 1525–1535

[3] A. Yasmin, J.L. Abot, I.M. Daniel Processing of clay/epoxy nanocomposites by shear mixing Scripta Mater, 49 (2003), pp. 81–86

[4] F.H. Gojny, M.H.G. Wichmann, B. Fiedler, K. Schulte Influence of different carbon nanotubes on the mechanical properties of epoxy matrix composites – a comparative study Compos Sci Technol, 65 (2005), pp. 2300–2313

[5] S.U. Khan, K. Iqbal, A. Munir, J.-K. Kim Quasi-static and impact fracture behaviors of CFRPs with nanoclay-filled epoxy matrix Composites Part A, 42 (2011), pp. 253–264

[6] U.A. Khashaba, A.I. Selmy, I.A. El-Sonbaty, M. Megahed Behavior of notched and unnotched [0/±30/±60/90]s GFR/EPOXY composites under static and fatigue loads Compos Struct, 81 (2007), pp. 606–613

[7] J.A.M. Ferreira, J.D.M. Costa, M.O.W. Richardson Effect of notch and test conditions on the fatigue of a glass-fibre-reinforced polypropylene composite Compos Sci Technol, 57 (1997), pp. 1243–1248

[8] J.A.M. Ferreira, J.D.M. Costa, P.N.B. Reis, M.O.W. Richardson Analysis of fatigue and damage in glass-fibre-reinforced polypropylene composite materials Compos Sci Technol, 59 (1999), pp. 1461–1467