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The effect of carbon nanoparticles on the fatigue performance of carbon fibre reinforced epoxy

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ABSTRACT

The aim of this study is to investigate the influence of different types of carbon nanoparticles like multi-wall carbon nanotubes (MWCNT) and few layered graphene (FLG) on the damage mechanisms of carbon fibre reinforced epoxy (CFRP) under fatigue loading up to the high cycle regime. Specimens were manufactured from in-house made prepregs to ensure good and reproducible nanoparticle distribution within the CFRP and penetration of the fibre rovings. The quasi-static mechanical properties of the crossply laminates were not affected by the nanoparticle modification. The fatigue life, however, increased significantly for both types of carbon nanoparticles, being most pronounced for FLG at high fatigue loads. Scanning electron microscopy-analysis revealed enormous plastic deformation of the matrix due to the nanoparticles. The fatigue life increasing effect was discussed by means of energy absorption. Nanoparticle-based damage mechanisms in CFRP were displayed and differences due to the varying nanoparticle structures identified.

1. Introduction

Due to their high density specific quasi-static strength and stiffness carbon fibre reinforced polymers (CFRP) are of major importance for applications in lightweight structures like for example in aircraft and wind turbine industry as well as automotive engineering. They additionally feature a superior fatigue performance when compared to the classic metallic construction materials. However, for achieving a maximum profitable efficiency by extended in-service times of fatigue loaded fibre reinforced polymers (FRP) further improvement of the fatigue performance remains an aim of research. Consequently, the fatigue life and the degradation of the mechanical properties are issues of great importance.

The complex structure of FRP causes several different damage mechanisms when loading the composite like fibre–matrix debonding, inter fibre fractures (IFF), delaminations and fibre fractures, which all lead to stiffness degradation of the FRP [1,2]. Under axial and multiaxial tensile fatigue loading, these mechanisms occur in a particular order resulting in the common three phases of degradation [3–5], as shown in Fig. 1 (unmodified). Phase I is characterised by initiation and growth of matrix cracks in-between the reinforcing fibres in off-axis layers, which lead to a rapid increase of FRP degradation. In phase II a saturation of transverse matrix cracks is reached and delaminations and longitudinal IFF begin to form. The degradation rises almost constantly but slowly, before increasing rapidly again in phase III until global failure of the composite due to delamination growth and fibre fractures [3,6]. However, it is evident that the whole degradation process begins with damages in the fibre embedding polymer matrix, therefore suggesting a matrix modification to improve fatigue performance of FRP.

One promising approach to modify a brittle epoxy matrix is the incorporation of stiff nanoparticles like silica, carbon nanotubes (CNT) or graphene based nanoparticles as the fracture toughness is significantly improved. Many experimental studies of non-fibre reinforced polymers, so-called nanocomposites, resulted in these findings by the addition of low nanoparticle contents [7–14]. This effect was always accompanied by a rougher fracture surface of the modified epoxy. Nanoparticle-related toughening mechanisms like crack deflection and crack pinning at the nanoparticles, nanoparticle–matrix debonding followed by plastic deformation of the matrix or nanoparticle pull-out were observed depending on the nanoparticle type and morphology [7–10,12,15,16]. Hence, in nanocomposites increased fracture energy is required, which enables the material to absorb more energy [8]. In addition, fatigue tests with graphene-modified epoxy nanocomposites were carried

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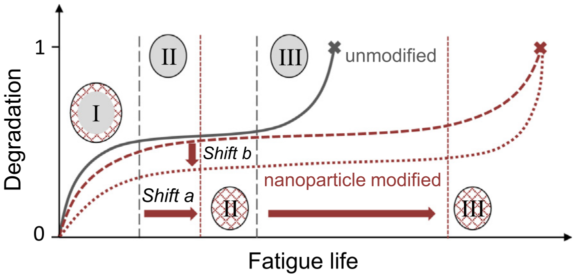

Fig. 1. Schematic of desired changes in degradation development with typical three degradation phases for unmodified and nanoparticle modified FRP loaded in fatigue: fatigue life improvement by an extension of phase I and II (shift a) and a less pronounced degradation increase (shift b). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

out and revealed a significant improvement of the fatigue performance [9,15].

Based on these findings, some studies were performed to reveal whether the incorporation of nanoparticles into the polymer matrix of FRP also results in an improved fatigue performance of so-called multi scale composites. Most of them report a remarkable improvement of the fatigue behaviour of CNT and silica modified carbon and glass fibre reinforced polymers (GFRP) [17–20]. Also for graphene-modified CFRP, there are first results showing a significant enhancement of mechanical properties and fatigue performance [21–23]. It was observed that also in the presence of reinforcing fibres the graphene-nanoparticles restrain the formation and growth of IFF and that the fibre–matrix-interface is enhanced. As a result, the aforementioned three phases of fatigue degradation of FRP should be extended, thus increasing the fatigue life like it is indicated in Fig. 1. The onset of degradation phase II and III is delayed (shift a) and the level of degradation reduced (shift b), which was already shown by Manjunatha et al. [20] for silica nanoparticle modified GFRP.

However, there is little information about how these nanoparticle toughening mechanisms actually affect the fatigue performance of modified FRP in detail on the nano- or micro-scale and which specific damage mechanisms arise from the type of nanoparticle included into the polymer matrix. In this study, we report a theory about how CNT and graphene nanoparticles may affect the micromechanical fatigue fracture process of CFRP and if there are particularities due to the different structure of both types of carbon nanoparticles. Therefore, unmodified and modified CFRP specimens with a homogenous distribution of carbon nanoparticles within the multi scale composites were prepared. An appropriate prepreg-manufacturing-process was used to ensure a dispersion of the nanoparticles in the small inter-fibre-spaces of the composite in order to completely exploit their potential as called for in [21] and [24]. In mechanical experiments the specimens were exposed to quasi-static and tensile cyclic loading to investigate the influence of the carbon nanoparticles on the fatigue damage mechanisms, degradation and lifetime.

2. Materials and methods

2.1. Materials

The FRP tested in this study are fabricated with an in-house fibre impregnation machine. The following raw materials are used:

The fibre reinforcement is based on the T700S carbon fibre, supplied by Toray (Japan). The fibres have an epoxy resin compatible sizing and are arranged as non-twisted 12 k roving on a bobbin. The resin is the epoxy prepreg system Araldite LY 1556/Aradur 1571/Accelerator 1573/Hardener XB 3403 from Huntsman (Switzerland), which is based on chemical B-stage. The components are mixed at the weight ratio of 100:23:5:12 as per the datasheet of the supplier. The B-stage is a chemical pre reaction and reached after storing the system for 24 h at 23–25 °C. Further reaction can be delayed by freezing until final processing and cure.

Two types of carbon nanoparticles were investigated in this work: cylindrical multi-wall carbon nanotubes (MWCNT) Nanocyl™ NC7000 and planar few layered graphene (FLG) avanGraphene-2. Both nanoparticles are commercially available and were purchased from Nanocyl (Belgium) and Avanzare (Spain), respectively. The particles are made of carbon, which is arranged in a hexagonal lattice with covalently bonded atoms, known as graphene. At MWCNT several of these layers form closed tubes with only the outer tube shell having contact to the surrounding matrix whereas at FLG several graphene layers (less than six layers according to the manufacturer) are stacked and held together by van der Waals forces. Because of this structure FLG might be separated by transverse tensile stresses, shear loads or passing through cracks of a surrounding polymer [7] in contrast to MWCNT. The MWCNT have an average tube diameter of 10 nm and length of 0.1–10 μm and are therefore often referred to as 1-dimensional nanoparticle. FLG on the other hand has a thickness of about 2 nm and particle diameter of 5–25 μm and is a 2-dimensional planar, but often creased structure, which hinders the separation of the layers by pure shear.

2.2. Production of multi scale composites and specimens

Before adding the fibre reinforcement the nanoparticles were dispersed in the neat epoxy resin (without hardener) using a three-roll mill from EXAKT 120E (Advanced Technologies GmbH, Germany). The gap size was varied from 120 μm down to 5 μm and the whole suspension was milled seven times in order to achieve a uniform dispersion. The hardener and accelerator components were added just before fibre impregnation. The resin system was mixed by automated steering in vacuum for 20 min. The single components have been degassed beforehand for 1 h at 30 °C. The nanoparticle content for both modifications was 0.3 wt% based on the complete matrix system.

The composite laminates were made of prepregs which have been manufactured on an in-house fibre impregnation machine which is sketched in Fig. 2. The dry carbon fibre roving is prestressed and aligned, before being impregnated with the unmodified or modified resin system and winded up on a hexagonal tool. This way a unidirectional tape with straight, aligned fibres and a width of 300 mm is produced. The advantage of this production method for nanoparticle modified FRP is a very good dispersion of the nanoparticles in the resin in-between the fibres, as it

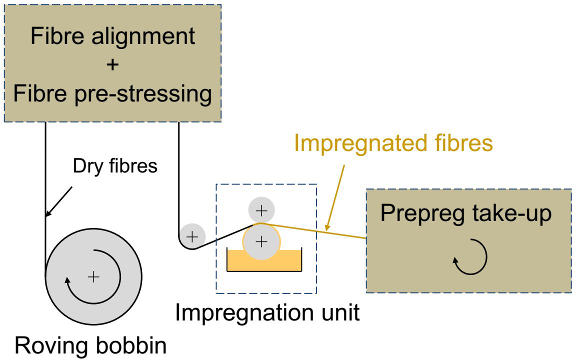

Fig. 2. Schematic set-up of in-house fibre impregnation and winding machine for prepreg production. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)