PLY-TAILORED NANOPARTICLE MATRIX MODIFICATION IN CROSS-PLY CFRP LAMINATES

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ABSTRACT

The influence of a matrix modification with few-layer graphene (FLG) nanoparticles in different layers of carbon fibre reinforced plastic cross-ply laminates is investigated. Either the 90°-layers or the 0°-layers are modified with FLG nanoparticles. Quasi-static-tension tests with combined acoustic emission analysis are executed to determine the influence of the nanoparticle modification on tensile strength and stiffness, as well as the stress at inter fibre failure (IFF) initiation. FLG modification of the 0°-layers increases the tensile strength, whereas a modification of the 90°-layers increases the stress at IFF initiation. Fractography analysis of the fracture surfaces using scanning electron microscopy reveals microdamage at the nanoparticles that dissipates energy and is an explanation for the observed delay of transverse cracking in the 90°-layers when modified with FLG nanoparticles.

1 INTRODUCTION

Fibre-reinforced plastics (FRP) and especially carbon fibre reinforced plastics (CFRP) are increasingly used in many industries. The use in structural parts requires detailed knowledge about failure initiation and propagation within composite laminates. Failure initiates at defects in the material as cohesion failure in the matrix between the fibres or as adhesion failure at the fibre matrix interface. Matrix cracks propagate between both characteristics, controlling the design in layers transverse to loading direction. In cross-ply laminates, this inter fibre failure (IFF) occurs first in the 90°-layers reduces the stiffness [1,2]. With increasing load, further damage, such as delaminations may induce at the tips of transverse cracks when the reach the surrounding layers of different fibre orientation.

For graphene based, carbon nanoparticle modified FRP, superior mechanical properties, compared to the neat material are reported in literature [3–5]. Mannov et al. reported enhanced impact resistance and compression after impact strength by FRP matrix modification with thermally reduced graphene oxide [3]. Kostagiannakopoulou et al. improved the interlaminar fracture toughness of CFRP by matrix modification with graphene nano-species. Matrix modification with carbon nanoparticles such as carbon nanotubes or few –layer graphene (FLG) increases the fatigue life in the tension-tension regime, as reported by Knoll et al. [5]. This enhancement is due to damage mechanisms at the particles. Nano- or microdamage at the layered FLG particles, i.e. graphene layer separation, layer shearing and plastic yielding of the matrix that results in plastic voids are reported [5–8]. Furthermore, crack pinning and bifurcation, crack deflection as well as crack propagation at different heights at the graphene nanoparticles decrease the crack growth rate in polymer nanocomposites and therefore increase the fracture toughness [7,8]. These mechanisms dissipate energy that is not available for crack propagation and may therefore increase the fracture toughness of the material.

One promising approach to delay the formation of IFF and increase the mechanical properties of composite laminates is thus a modification of the matrix with carbon nanoparticles such as FLG.

Previous approaches for modifying the matrix of FRP with nanoparticles only compare the unmodified with a completely modified configuration without any investigation of the effects in the respective layers of multidirectional laminates. In this work, the influence of a FLG matrix modification in the different layers of CFRP cross-ply laminates is investigated. Either the 90°-layers or the 0°-layers are modified with FLG nanoparticles. The aim is to investigate the influence this ply-tailored matrix modification on the mechanical properties and damage development within the composite under quasi-static tensile loading. The results contribute to the goal to increase lifetime as well as reliability of composite parts.

2 EXPERIMENTAL

2.1 Materials and specimen preparation

The prepreg material for the CFRP laminates is produced with an in-house prepreg machine. T700S carbon fibres (Toray, Japan) in the form of a 12 k roving with an epoxy resin compatible sizing are used. The epoxy prepreg system Ludeko R470 / H471 (Ludeko, Germany) is used as matrix material. The used nanoparticles are planar few layered graphene avanGraphene-2 (Avanzare, Spain). These FLG particles have less than six layers with a thickness of about 2 nm and lateral dimensions of 5 µm-25 µm (according to the manufacturer). The stacked graphene layers are held together by Van-der-Waals forces and might therefore be separated by transverse tensile stresses, shear loads or if a crack passes through the surrounding polymer [8].

The nanoparticles are dispersed in the resin without hardener in a three roll mill (EXAKT Advanced Technologies GmbH 120E) by the principle of applying high shear rates on the mixture for homogeneous dispersion [9]. Gap size is varied from 120 µm down to 5 µm. The milling process is repeated seven times at constant rotational speed of the rolls of 33 min-1, 100 min-1 and 300 min-1, respectively. The hardener is added before impregnation of the fibres. The components are degassed for 1 h at 30 °C and then mixed and by automated steering in vacuum for 20 min to remove any air inclusions. Nanoparticle content is 0.3 wt.% based on the complete matrix system.

Unmodified and FLG modified CFRP prepregs are manufactured with a custom made fibre impregnation machine. The dry carbon fibre roving is pre-stressed and aligned, before being impregnated with the unmodified or modified matrix system and winded up on a hexagonal roll. A unidirectional tape with straight, aligned fibres of 300 mm width is produced. Nanoparticles are equally dispersed in the matrix between the fibres as confirmed in transmission light microscopy of thin microsection samples.

B-staging is according to the recommendation for this material system. Afterwards, the prepregs are stored at -18 °C until lamination and curing. Glass transition temperature of the cured resin system is determined via differential scanning calorimetry (DSC) to be 121 °C ± 3 °C. For processing of laminates, prepregs are defrosted, stacked to cross-ply laminates with the stacking sequence [0/902]s and autoclave cured at 120 °C for 2 h at -0.2 bar. Three different configurations are laminated. Unmodified laminates are produced for comparison as a reference. For the other two configurations, FLG modified prepregs are used either for the 0°-layers or for the 90°-layers. For the other layers the unmodified prepregs as in the reference are used. This approach of a ply-tailored matrix modification allows identifying the influence of an FLG matrix modification on mechanical properties and damage development in the respective layers of cross-ply laminates without any superimposing of effects.

Ultrasonic inspection is performed after curing to assure manufacturing quality. No larger voids or delaminations are found after curing. The fibre volume content is determined according to DIN EN 2564 and is approximately 65 %. Cured laminates are prepared with 50 mm wide and 2 mm thick GFRP/Aluminium end-tabs using 2-component adhesive. Specimens for static tensile tests are cut with a diamond saw according to DIN EN ISO 527-4 [10] to length l = 250 mm, width w = 25 mm and thickness t = 2 mm. Specimen edges are polished to minimise edge effects.

2.2 Test procedure

Quasi-static tensile tests are performed according to DIN EN ISO 527-4 [10] to determine tensile strength, strain to failure and Young's modulus for each configuration. A universal testing machine type Z100 (Zwick, Germany) with a maximum load of 100 kN is used. Cross-head speed is set to 2 mm/min. Strain is measured with a long-travel extensometer on the specimen surface.

In order to analyse failure initiation in terms of IFF acoustic emission (AE) analysis is used. For the acoustic emission analysis, a Micro II multi-channel acquisition system (Mistras, Germany) is used to record AE data. Two wideband differential sensors are used for AE wave detection. They are mounted on the specimen surface, using silicon grease as a coupling agent between the sensor and the specimen. Internal filters and a static threshold are used to reduce disturbance variables, such as machine vibrations and ambient noise. The setting of the AE acquisition system is shown in Table 1.

Parameter	value and unit
Sampling rate	5 MHz
Preamp gain	40 dB
Threshold	45 dB
HDT	250 µs
HLT	800 µs
PDT	150 µs

Table 1: Parameters of the AE acquisition system (Sensor: WD)

3 RESULTS

Linear elastic stress-strain behaviour is observed until approximately 0.4 % strain. A slight decrease of the stress-strain curve slope at this is simultaneous to an increase in AE-signals of high amplitude and cumulated energy in the AE, indicating the beginning of IFF. Several small drops are visible in the stress-strain curves the unmodified and the 90°-layer modified specimens. These drops correlate with a high increase in cumulated AE-signal energy and singular signals of high amplitude and are identified as breakage of fibres or fibre bundles in the unmodified 0°-layer of the specimens. However, specimens with the 0°-layers FLG modified show a linear stress-strain slope until very short before failure without these aforementioned drops.

The stress at IFF initiation as detected from the slight decrease in the stress-strain slope and the corresponding increase in cumulated energy of the AE signals is compared in Figure 1 for the three configurations. An influence of the 90°-layer FLG modification on the onset of IFF is visible. FLG modification of the 90°-layers increases the stress at IFF, whereas a 0°-layer modification seems to have negligible influence on the initiation of IFF.

In Figure 2 the influence of FLG nanoparticle modification in the different layers of cross-ply laminates on stress at failure is presented. FLG modification of the 0°-layers increases the tensile strength at about 15 %, whereas a modification of the 90°-layers shows no significant change in tensile strength compared to the unmodified material.

Figure 3 shows exemplary Photographs of specimens after final failure with the 90°-layer modified in a) and with the 0°-layers modified in b). A 90°-layer matrix modification results in significantly fewer cracks in his layer spanning the width of the specimen. The unmodified specimens look similar as the 0°-layer modified specimens after final failure, regarding the amount of pieces broken out of the 90°-layer and separated by transverse cracks.

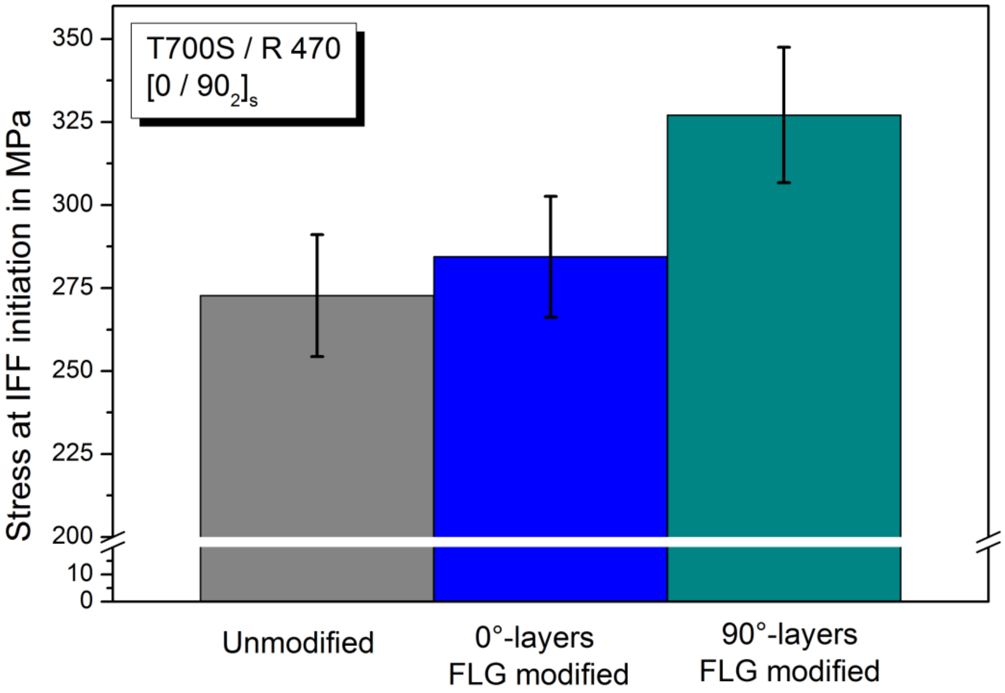

Figure 1: Influence of FLG nanoparticle modification in the different layers of cross-ply laminates on the onset of inter fibre failure (detected with AE-analysis)

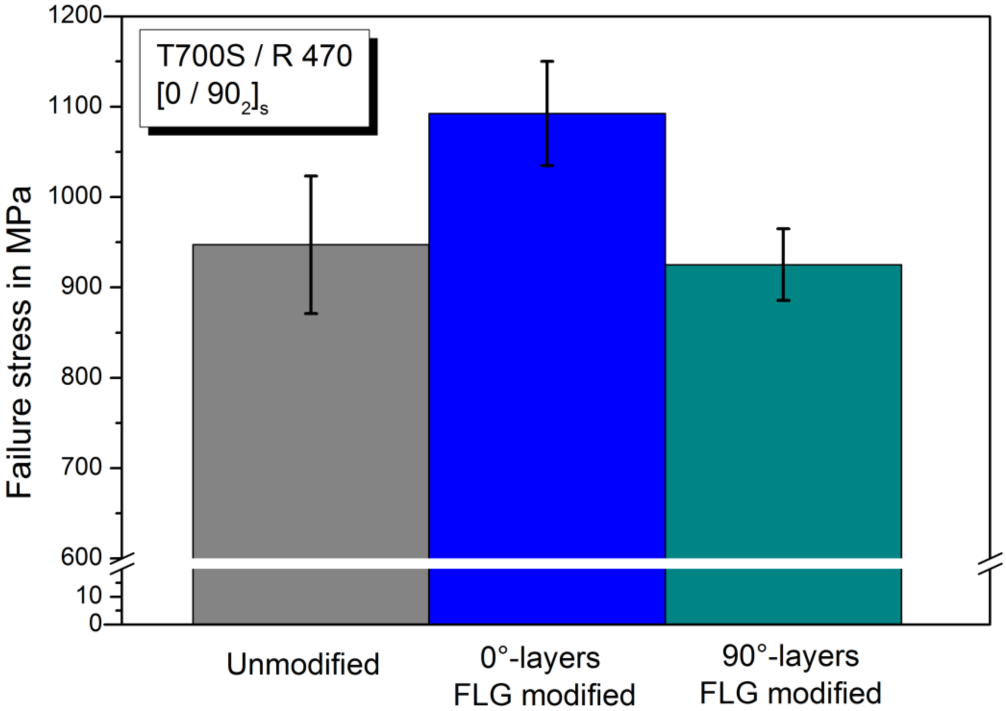

Figure 2: Influence of FLG nanoparticle modification in the different layers of cross-ply laminates on stress at failure

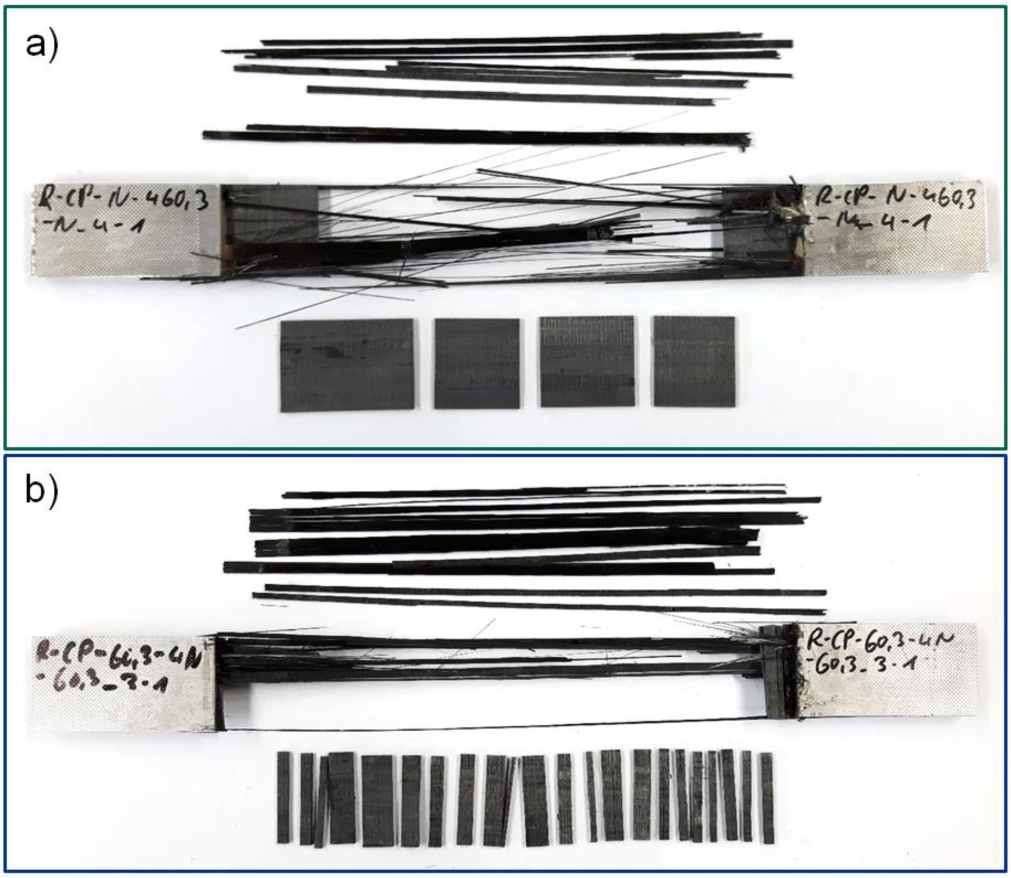

Figure 3: Photographs of exemplary CFRP cross-ply specimens after final failure:
a) 90°-layers FLG modified b) 0°-layers FLG modified, 90° layers unmodified

4 DISCUSSION

IFF initiates first in layers with fibre orientation perpendicular to loading direction, as is the case in the 90°-layers of the cross-ply laminates investigated in this study. Consequently, a modification of the matrix in these layers with FLG nanoparticles results in a delay in the onset of IFF, whereas a modification of the 0°-layers exhibits no significant influence on IFF. The shift of IFF toward higher global stresses is a result of the damage mechanisms at the FLG particles on the nano- and microscale. Graphene layer shearing and plastic deformation of the matrix at the stiff particles dissipates energy that is not available for initiating and propagating inter fibre crack growth. This corresponds well with previous observations from our own and other research groups [4–8,11].

With increasing global stress, delaminations between layers of different orientations initiate at the crack tip of transverse cracks at the interface to the next layer. Due to their size, the planar FLG particles are mostly oriented in fibre direction. Transverse cracks propagating through the thickness of the 90°-layer may be separated at these particles [8], resulting in a larger crack opening displacement and a larger start delamination between the 90°-layer and the 0°-layer. As a consequence, fewer transverse cracks in the 90-layer are formed, as can be seen in Figure 3. Instead of new intralaminar cracks forming in the 90°-layer, cracks propagate as interlaminar delamination damage between the layers.

The increase in tensile strength with a modification of the 0°-layers with FLG nanoparticles can be explained a crack stopping and load redistribution mechanism. Since the lateral size of the planar FLG particles is in the range of the fibre diameter, they are oriented in fibre direction. Matrix cracks in the 0°-layers may thus be stopped or their growth decelerated. Furthermore, after breakage of a single fibre or fibre bundle, the load is redistributed to the adjacent fibres and bundles at the small area of the failure, which may then break as well because of the overload. The FLG particles between the fibres lead to a better redistribution of these local peak stresses. Hence breakage of larger amounts of fibre bundles is delayed until short before final failure, which corresponds well with the linear stress-strain slope, showing no drops at higher stresses as they were observed for specimens with unmodified 0°-layers.

5 CONCLUSIONS

Matrix modification with FLG nanoparticles may improve the mechanical properties of CFRP, but different effects depending on the orientation of the modified layer with regard to loading direction should be considered. A FLG modification of the 90°-layers in cross-play laminates shifts the onset of IFF to higher global stresses, whereas a modification of the 0°-layers increases the tensile strength of the composite. Depending on the design criteria, the load case or simply for cost reasons, it may be beneficial, not to modify the matrix in the whole composite laminate, but just some layers. Further research is carried out for investigating the influence of the presented ply-tailored modification under cyclic loads and for analyzing the observed differences in transverse crack density with theoretical models for transverse crack growth predictions.

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