GRAPHENE MODIFIED CFRP FOR ENHANCED DAMAGE BEHAVIOR

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Abstract
Nanoparticle modification of epoxy matrix systems for advanced (carbon) fibre reinforced polymer (CFRP) components offers promising potential for enhanced service lifetime and improved material properties like electrical conductivity. In contrast to well examined carbon nanotube (CNT) modifications, graphene modified resins offers the potential for liquid infusion processes such as resin infusion or vacuum assisted resin transfer moulding (VARTM) due to nearly unaltered viscosity. In this study we present the impact of graphene modification on fracture toughness of a standard industrial epoxy resin. Starting with the basic characterization of the formed nanocomposites, the transfer to VARTM manufactured CFRP laminates and their compression after impact properties is examined. CFRP coupons were subjected to impact damage and subsequently loaded under compressive load.

1. Introduction

Fibre reinforced polymer composites based on thermoset matrices exhibit superior fatigue behavior for long-term service life in demanding environment [1]. Application of such materials in new generation airplanes, renewable energy powerplants like windmills require safe and reliable operation also in case of damages and very high cycle loading. Thus, a demand for composite materials with the aforementioned properties is given. Prepreg route manufacturing of particle-modified CFRP components was, also industrially, shown to be successful, nevertheless manufacturing costs are extraordinary high. Here, graphene matrix modification offers, beneath superior fatigue performance compared to CNT, broader manufacturing route perspectives as viscosity unalters in case of particle introduction.The upcoming potential to manufacture high performance CFRP components also in infusion processes like VARTM enables cost efficient production.

As impact loadings frequently occur in service life of composite components, compression after impact (CAI) property tests are mandatory for qualification of new materials and structures. Previous studies have shown that nanoparticle incorporation leads to improved residual compressive strength after impact damage. Figure 1 presents an literature overview for improve of CAI strength with modified polymer matrices. Summarizing these results, an increase of ~10% at relatively low concentrations up to 5% is visible. Maximum increase was found for even small amounts of few layered graphene (FLG).

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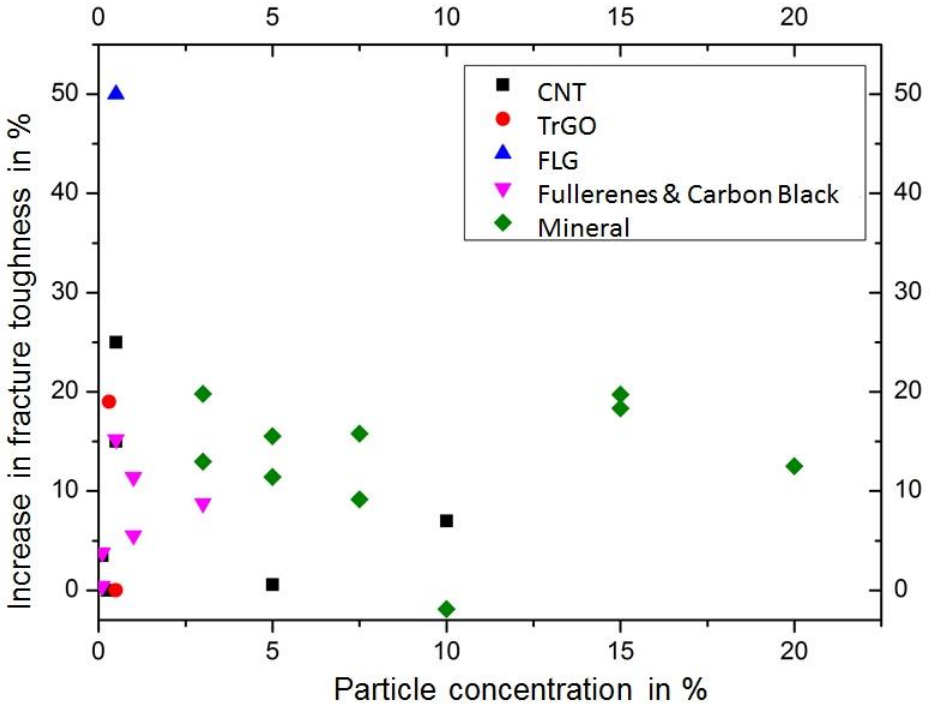

Figure 1. Literature review for relative increase of compressive strength after impact damage for fibre reinforced polymers. [2-12]

2. Materials and dispersion process

In this study, an anhydride based hot curing epoxy system of Araldite LY 556/ HY917/ 1 wt% DY070, Huntsman, Switzerland type was modified with avanGRAPHENE-2 few layered graphene, Avanzare, Spain. A proper dispersing route by three roll milling was developed during this study. A three roll mill of Type EXAKT 120, Exakt, Germany was used. Homogenous dispersion of the particles was achieved after seven cycles at different gap sizes (Table 1).

Table 1. Gap size and roller speed for dispersion process.

Cycle	*Gap size 1* (µm)	*Gap size 2* (µm)	*Temperature* (°C)	Roller speed (rpm)		
				1	2	3
1	120	40	20	300	100	33
2	40	13	20	300	100	33
3-7	13	5	20	300	100	33

Homogeneity was checked by accompanying optical light microscopy, grindometry and viscosity measurements during dispersion process. Figure 2 presents viscosity values for the particle modified resin without hardener during the dispersion steps. It could be seen that viscosity decreases with increasing dispersion state and is equally high as neat resin with its 10-12 Pas viscosity range.

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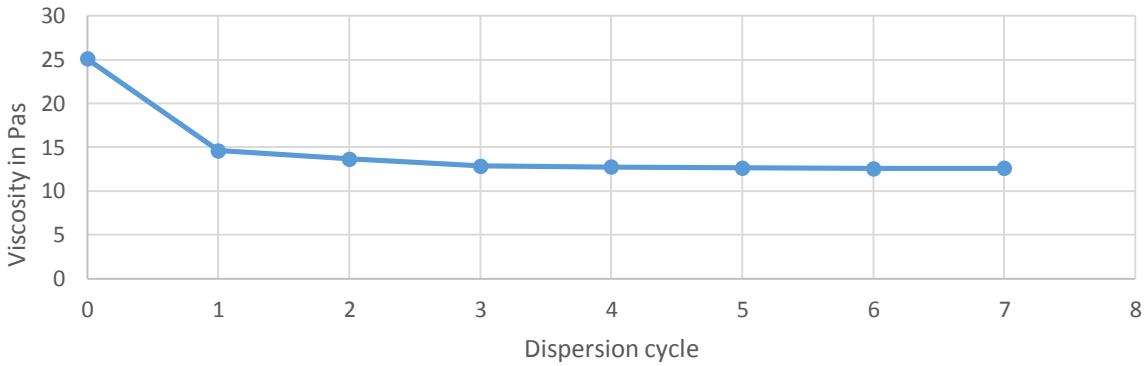

Figure 2. Measurement of the viscosity of 0.1 wt% avanGRAPHENE-2 modified LY556 resin during the dispersion process (measurement parameters: plate-plate configuration, 40 mm diameter, 0.1 mm gap size, 75 1/s shear rate).

Furthermore internal information from the three roll mill like line forces and temperature data were logged and reveal an insight into the dispersion process (Figure 3). Increasing line forces in the first three cycles point to increasing dispersion of the particles. Separation of agglomerates increase interaction between polymer due to higher available surfaces. After the third cycle no significant change of maximum line forces could be observed. This is congruent to the measurements in the rheometer.

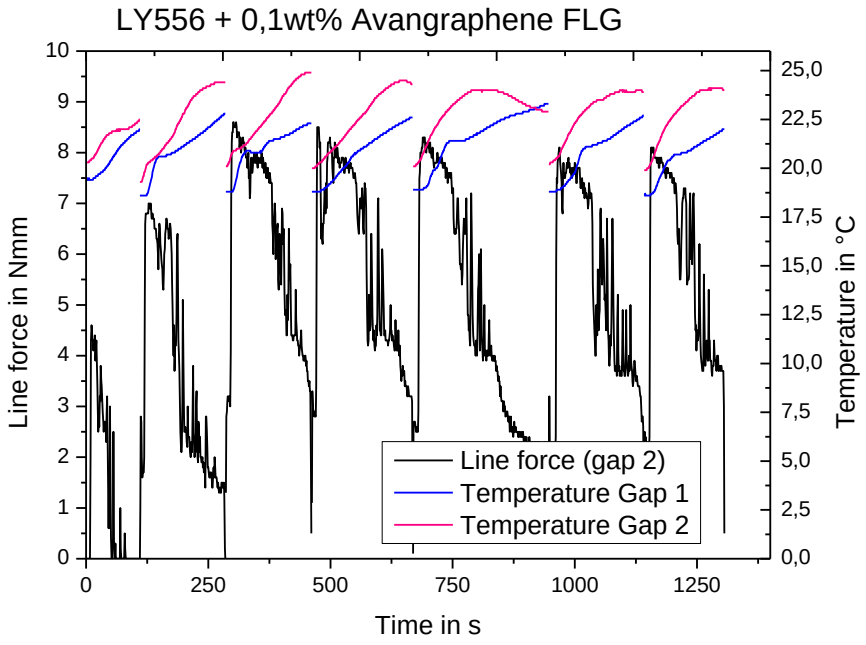

Figure 3. Data acquisition from the three roll mill: Inline- measurement of line force and temperature inside the gaps of the three roll mill measured during dispersion of LY556 resin modified with 0.1 wt% avanGRAPHENE-2. Homogenous dispersion results are achieved after three cycles, steps four to seven are used for further homogenization.

3. Mechanical properties of graphene modified CFRP

3.1. Fracture toughness of neat and modified matrix material in Mode I

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Fracture toughness of the matrix material in Mode I was tested according to ASTM D 5045 on single end notched beam test specimens of 8 mm height, 4 mm depth and 32 mm width in three point bending mode. Samples were primarily notched with a diamond saw blade of 150µm thickness and subsequently sharpened with a razor blade. This manufacturing route leads to high yield rate.
Figure 4 depicts fracture toughness values for nanocomposites made of two tested graphene batchesof type used in this study. Good correlation between the two batches and sample sets proves high repeatability. A significant increase is observable at small concentrations, whereas higher concentrations lead to unaltered or even slightly lower toughness. This fact can be ascribed to strong reagglomeration taking place at higher concentrations and is in good correlation with earlier studies [13,14]. An optimum value of 0.05 wt% avanGRAPHENE-2 modification was revealed and chosen for further application in subsequent CFRP modification.

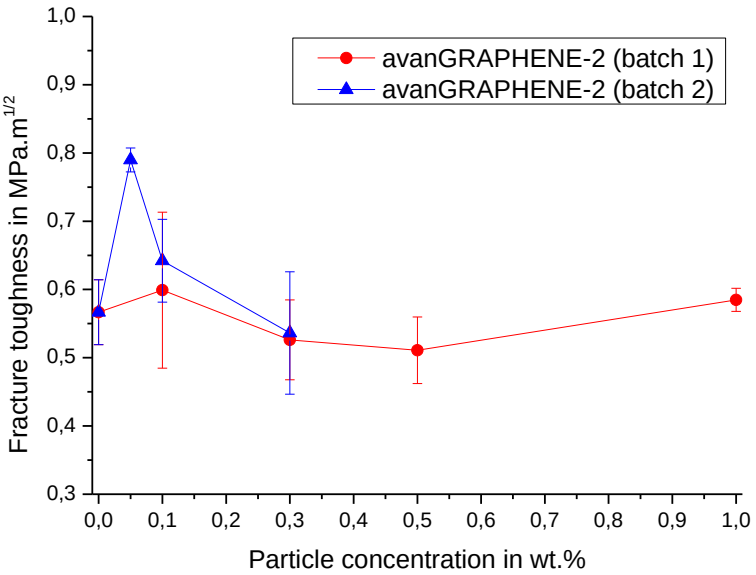

Figure 4. Fracture toughness of the two tested graphene materials with increasing particle content. Measurement of the viscosity of 0.1 wt% avanGRAPHENE-2 modified LY556 resin during the dispersion process.

3.2. Compression after impact strength of modified CFRP

After matrix modification, CFRP plates of 4mm thickness were produced in VARTM method. Here, a 100g/m² unidirectional non-crimped fabric (NCF) made of Tenax HTS45 carbon fibre was used for production of quasi-isotropic laminates with $[45°/0°/-45°/90]_{4s}$ stacking. CFRP plates of constant thickness and high fibre volume content were achieved by this method. CAI tests were performed according to ASTM D 7136. Test specimens were cut to 100 x 150 mm² and non destructively tested in ultrasonic C-scan before impacting with drop weight. Thus, pore-free and homogenous test specimen quality could be guaranteed. Specimens were conditioned to ambient condition before impacting and before final compression test to avoid influences caused by excess humidity from ultrasonic scan bath. Two impact levels of 3 and 10 J energy were chosen for incorporation of defined damage into the laminate. 10 J impact energy level led to distinct damages that are clearly visible in C-scan (Figure 5). Determination of damaged area was performed by image analysis of the bottom echo image. Damage characterization in thickness direction was not possible due to the high number of orientation changes of the 32 thin carbon NCF layers. 3 J impact energy led to barely visible impact damages (BVID) which were not detectable with ultrasonic scan. Thus, X-ray analysis of these specimens were performed to detect inter fibre fracture.

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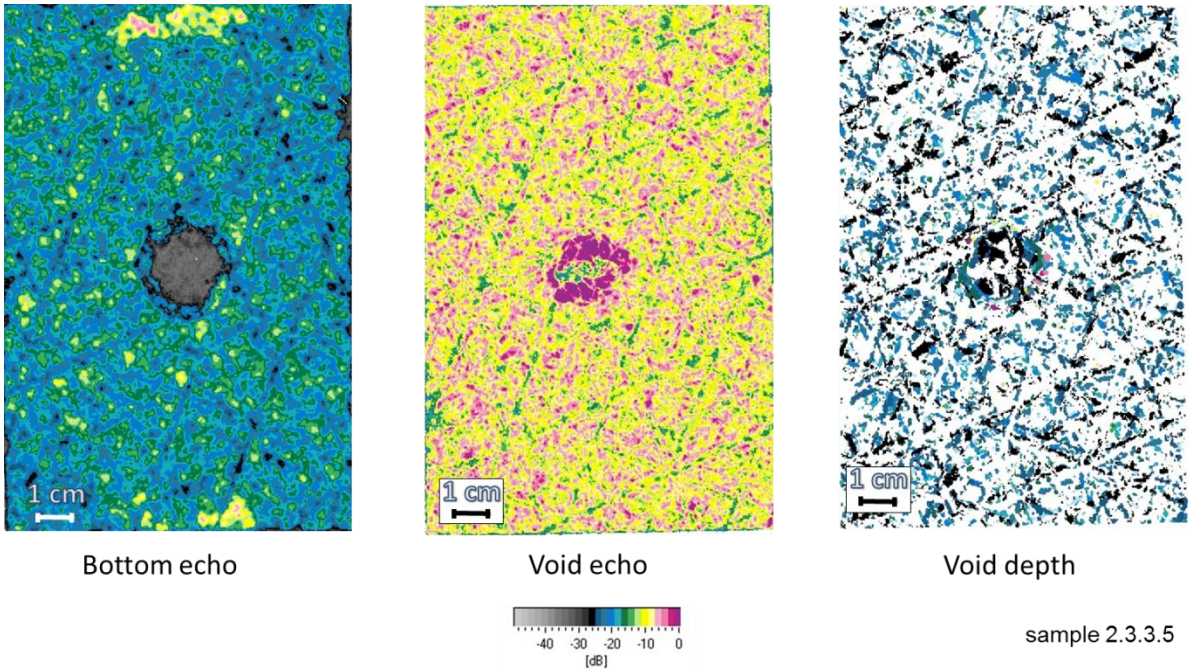

Figure 5. Ultrasonic C-scan of 10 J impact energy loaded test specimens with 0.05wt% graphene modification.

During the impact the contact forces between loading pin and test specimen were measured. No significant differences in force level or response delay are observable comparing unmodified and modified samples. 3 J impacts do not cause severe damage like fibre rupture or delamination. These mechanisms are visible in the 10 J curves, here steep drops of contact force are measured and reveal ongoing damaging.

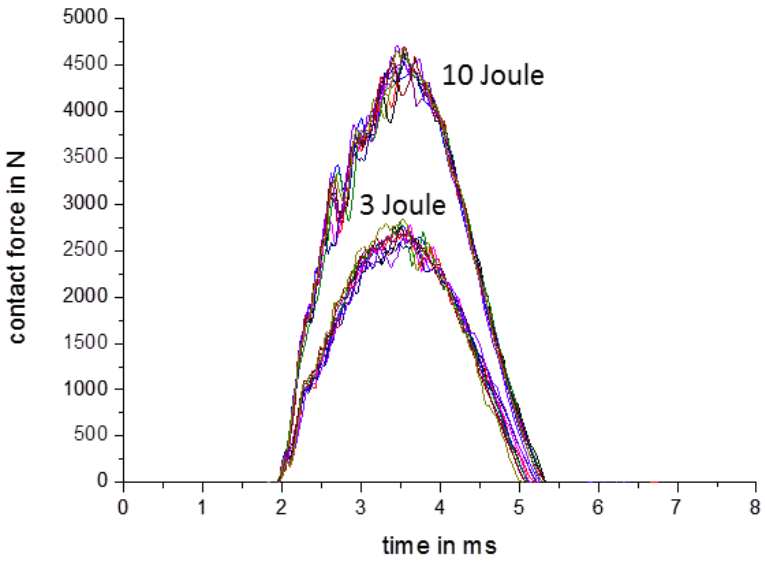

Figure 6. Contact force over time during impact at 3 J and 10 J.

Consequently, as impact energy is constant, delamination areas are again very similar, for unmodified CFRP specimens impacted with 10 J a mean projected area of 471 mm² with a standard deviation of 34 mm² was measured, whereas delaminated areas in modified CFRP were determined with 510 mm² with a standard deviation of 29 mm². For 3 J, delamination area determination was not possible as only single inter-fibre fractures were observed in X-ray.

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Strain field and its direction was measured by an Aramis 3D-Digital Image Correlation (DIC) system, GOM, Germany during compressive load. High frequency image acquisition was triggered shortly before final failure to reveal possible differences in specimens behaviour like buckling or differences in strain field direction or size (Figure 7). No significant changes between all specimens were observed. DIC method offers good opportunities to monitor test quality regarding friction and rectangular specimens and homogenous compression loading.

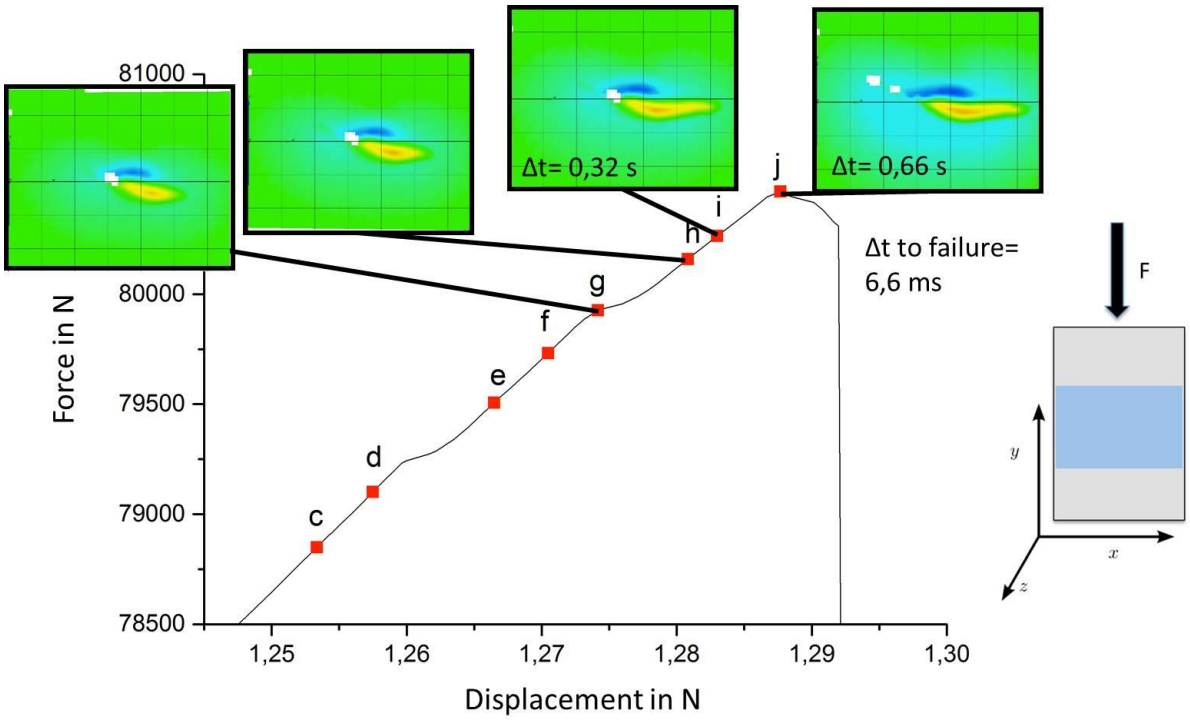

Figure 7. z-direction of the DIC strain field representations of the impacted area during compressive load.

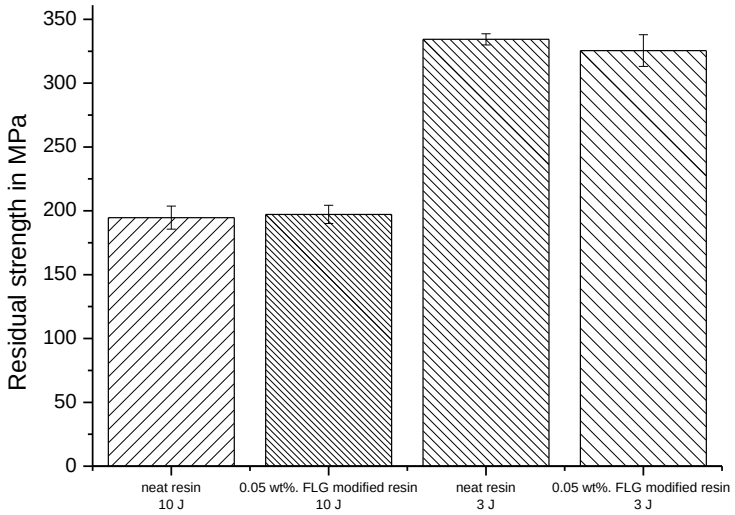

Figure 8. Residual compressive strength of modified and unmodified CFRP after impact loading

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Finally, one can conclude that residual compressive strength properties after impact are unaltered in case of graphene modification (Figure 8 and Table 2).

Table 2. Residual compressive strength values after impact with 3 J and 10 J.

Specimen Type	*Residual compressive strength* (MPa)	*Standard deviation* (MPa)
3 J, unmodified CFRP	334	4,3
3 J, modified CFRP	326	12
10 J, unmodified CFRP		1949
10 J, modified CFRP	197	7

4. Discussion and conclusions

Based on a literature review, graphene or different nanoparticle modified CFRP exhibited at least some improvement in CAI behaviour. In this study no significant increase in residual strength after impact damage could be found. Several likely reasons could influence the results and should be discussed here. First, filtering of the few particles incorporated into the matrix material during the VARTM process is possible. Nevertheless, resin residues were examined in resin inlet and outlet of the mould. No significant change in optical appearance by visual and light microscopy could be observed. Thus, strong filtering as observed for CNT is unlikely. Second, limited percentage of graphene modification could be below a mechanical improve threshold, which means that a direct transfer of modified matrix material properties into fibre reinforced structures is invalid. Third, interaction of superlattice structures from binder yarn or fibre bridging due to the fine material may override the positive contribution of graphene modification. A further look on these aspects have to be performed in future. Accompanying Mode I and II tests of the CFRP material may help to reveal more information.

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