INFLUENCE OF CARBON NANOPARTICLE GEOMETRY IN EPOXY MATRIX ON MECHANICAL PROPERTIES AND FAILURE INITIATION REGARDING THE SIZE EFFECT

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Abstract
The influence of a carbon nanoparticle modification on the damage behaviour and resulting mechanical properties of an epoxy matrix is experimentally investigated. A comparison of different nanoparticle morphologies with regard to their potential use in FRP is carried out. Since the volumes between the fibres in FRP are very small, the focus is set on the investigation of size effects of polymer nanocomposites. The influence of local microdamage at the particles on the mechanical properties in a small volume is discussed by comparing the different energy dissipating damage mechanisms in dependence of the nanoparticle morphology. Crack initiation and damage mechanisms at the different nanoparticles can be clearly identified. For layered particles such as few layer graphene, it is found that the orientation of the graphene layers with regard to loading direction is critical for local damage mechanisms and hence mechanical properties.

1. Introduction

The increasing use of fibre-reinforced polymers (FRP) requires detailed knowledge about failure initiation and propagation within composite laminates. Further improvement of FRP, especially in terms of fracture toughness, can be achieved by a matrix modification with nanoparticles. For carbon nanoparticle modified polymers, superior mechanical properties, compared to the neat material are reported in literature [1–4]. They are attributed to stress relieving mechanisms such as nano- or microdamage at the particles. The different types of damage mechanisms on the nano- or microscale, e.g. particle-matrix debonding, particle fracture or layer shearing in case of multilayer particles, depend on the size and morphology of the particles [2]. For the use of nanoparticles in FRP, size effects of the material should be considered, because the volumes between the fibres are very small. In addition, regarding small volumes allows to identify failure initiation and damage mechanisms at the nanoparticles.

Brittle materials like epoxy matrix show a size effect due to a statistical defect distribution that results in increasing strength with decreasing volume [5]. In this work it is investigated, whether a size effect exist as well for matrix modified with different types of carbon nanoparticles and whether the toughening mechanisms reported for nanocomposite bulk volumes are valid in small volumes. Carbon nanotubes (CNT), few layer graphene (FLG) and carbon black (CB) are used as nanoparticles to represent different nanoparticle morphologies.

2. Experimental methods

The different types of carbon-nanoparticles used are listed in Table 1. Classification of the nanoparticles is according to Tang et al. [6]. This nomenclature defines spherical nanoparticles as 0D, because they can be regarded as a point, with surface area and thus interfacial volume being much smaller compared to tubes or plates of the same volume. Linear particles such as nanotubes are regarded as 1D and planar particles, e.g. graphene or layered structures, as 2D, corresponding to their orientation within a volume [2,6]. Dimensions are given considering the morphology of the particles: for the single-walled CNT (SWCNT) diameter d and length l, for FLG width w and thickness t and for CB the BET surface area.

Table 1. Types of carbon nanoparticles used in this investigation (values from the respective data sheets).

Type	Name	Supplier	Dimensions
CB	Printex 300	Evonik industries, Germany	BET surface area= 80 m^2/g
SWCNT	Tuball (75%)	OCSiAl, Russia	$l \geq 5$ µm $d \leq 1{:}9$ nm
FLG	AvanGraphene-2	Avanzare, Spain	5 µm ≤ w ≤ 25 µm $t \leq 2$ nm $n_l \leq 6$ layers

For the nanoparticle modified fibres, nanoparticles and epoxy resin are mixed inside a glove box and dispersed with a three roll mill (EXAKT Advanced Technologies GmbH 120E) that works on the principle of applying high shear rates on the mixture to disperse the nanoparticles homogeneously [7]. 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 gap widths are adjusted from 120 µm to 5 µm. After dispersion, the hardener is added to the neat or modified resin and the mixture is stirred for approximately 10 min and then degassed under vacuum (15 mbar abs) for 15 min. Uniform nanoparticle dispersion is obtained for the different morphologies and filling contents. Fibres are pulled with a needle from the epoxy when it starts to vitrify. Via the pulling speed of the needle, the fibre diameter can be adjusted to a certain point. The fibres are cut and glued at one end on paper sheets based on ASTM D3379 [8] for single fibre tensile tests and then cured in an oven as recommended at 20 °C for 24 h and at 80 °C for 15 h.

The specimens are mounted in a universal testing machine (Zwick Z100) with a 50 N capacity load cell. The free test length is 25 mm. The side bars of the paper, connecting the upper and lower part of the specimen, are cut before testing. The side bars of the paper, connecting the upper and lower part of the specimen, are cut before testing. Test speed is set to 25 mm/min in order to minimise plasticity effects with necking and assure a more brittle failure mode of the fibres. The cross section after failure is analysed for each specimen by using an optical microscope (Olympus BX51) and by scanning electron microscopy (SEM) to determine the damage mechanisms at the different types of nanoparticles and the influence of particle size, filling degree and morphology on failure initiation and propagation. SEM is carried out using a Zeiss Leo Gemini 1530 electron microscope by using the SE2 detector at 1 kV and without sputtering of the surface. The true failure strength Rt is calculated from the measured force at failure and the cross section area obtained by microscopy. The fracture of the fibres is regarded as brittle.

3. Results and discussion

Representative load-displacement curves for neat epoxy as well as with FLG nanoparticles modified fibre specimens are presented in Figure 1. Fibre diameters are in the range of 150 µm ± 25 µm. The FLG modified fibres exhibit the shortest elongation at break, which hints to a hindering of the polymer to deform plastically and develop necked areas due to the comparable large FLG particles. CNT modified fibres have slightly lower elongation at break compared to the unmodified ones, but show slightly higher maximum load values for similar fibre diameter. The CB modified fibres behave very similar to the unmodified ones. Thus it is concluded, that the small CB nanoparticles have no significant influence on the load versus displacement and accordingly stress-strain behaviour of an epoxy matrix.

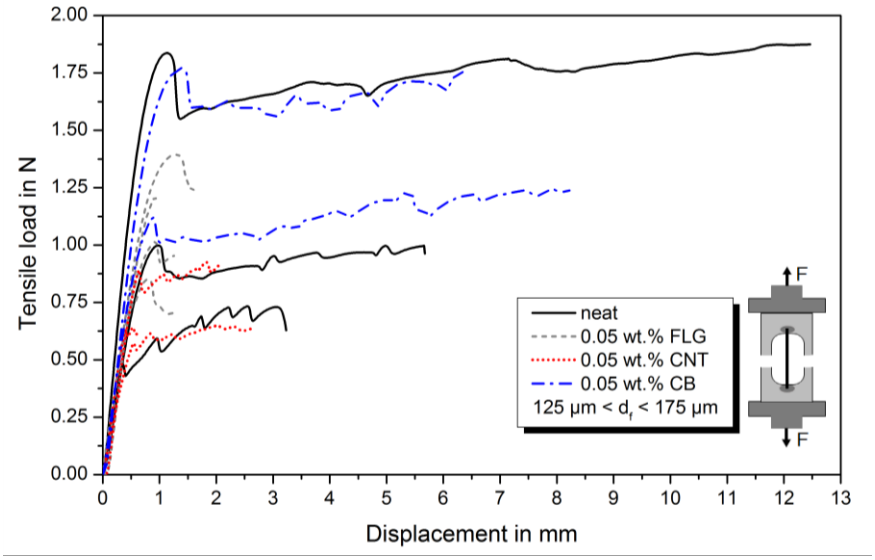

Figure 1. Representative load-displacement curves for neat and carbon nanoparticle modified fibres of comparable diameter between 125 µm and 175 µm.

Figure 2 shows the true failure strength R_t for neat and with 0.05 wt.% carbon nanoparticles modified epoxy as a function of specimen volume. Strength values exhibit a clear size effect for neat epoxy. This is according to Weibull's theory for defect distribution [9] and previous investigations for a different matrix system [10]. A decrease in volume leads to a significant increase in true failure strength. The CB modified epoxy exhibits a clear size effect, comparable to the neat material. For small volumes, an increase in true failure strength of approximately 100 MPa is observed. In comparison to the neat epoxy fibres, the CNT modified fibres exhibit slightly higher true failure strength at similar volume. For a CNT content of 0.05 wt.%, no significant size effect is visible, but for lower particle content, increasing strength with decreasing volume and hence a size effect is observed as well. The FLG modified matrix system shows only a small size effect, with a slight increase in strength with decreasing volume. When compared to the high increase for the neat matrix, the maximum failure strength for the FLG modified matrix is limited at approximately 110 MPa, even in very small volumes. These results implicate, that the nanoparticle modification may act as an enhancement in larger volume, as it is reported in literature [11–14], but initiate failure in very small volumes and thus weaken the material with regard to true failure strength. This is attributed to failure initiation at the largest FLG particle or aggregate, which is larger than any material defects, thus always available within the fibre and independent of specimen volume. As a consequence, true failure strength of FLG modified epoxy depends on two factors. Firstly, the size of the largest FLG particle that initiates failure and secondly, the orientation of this particle with regard to loading direction.

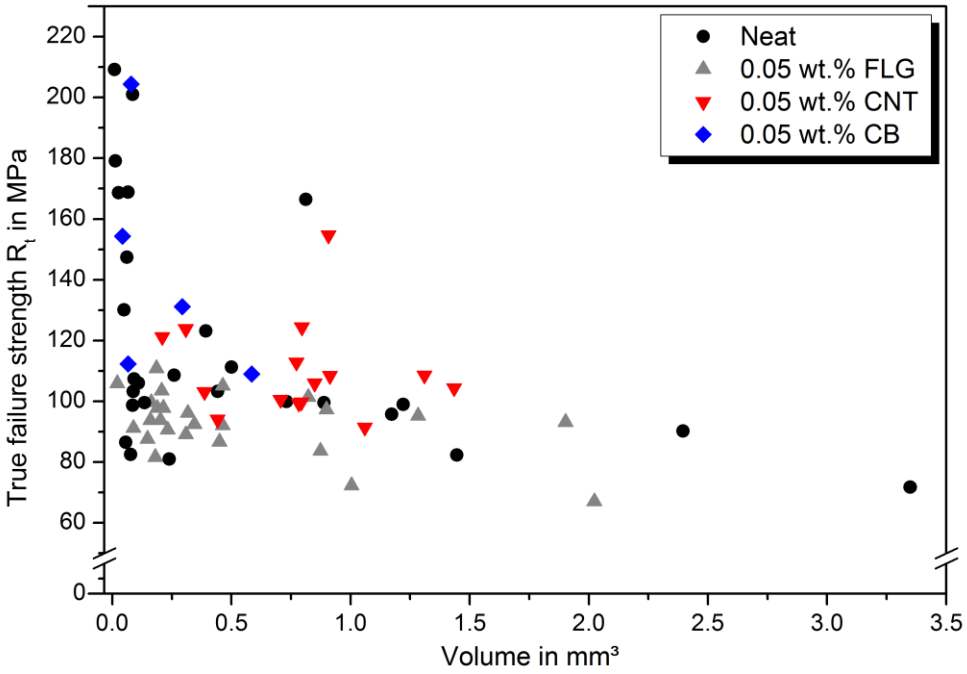

Figure 2. True failure strength versus specimen volume for neat and with carbon nanoparticles modified epoxy fibres showing the influence of nanoparticle morphology at 0.05 wt.% particle concentration.

Different types of microdamage at the FLG nanoparticles are visible in the fracture surfaces that confirm existing models on damage initiation mechanisms at layered particles [15,16]. In, Figure 3, a schematic representation of different types of microdamage at graphene nanoparticles, with SEM images showing these types of damage in the fracture surface of FLG modified matrix fibres, are given together with the corresponding strength of the pictured fibres in a strength versus volume diagram. The schematic representation is based on previous work for layered particles [17] and was already applied for explaining increased fatigue life of FLG modified FRP by Knoll et al. [18]. The type of microdamage depends on the orientation of the layers to the loading direction, as indicated in the scheme. Fibres, in which the graphene layers of the largest FLG particle is oriented in loading direction exhibit a pull-out type of microdamage. They show the highest strength, because their covalent bonds lie in loading direction. When the graphene layers of the largest particle within the fracture surface are orientated perpendicular to loading direction, the Van-der-Waals bonds between the layers carry the load, which results in lower strength. This is visible in the flat, smooth surface, which indicates that two layers of graphene are separated from each other. In Figure 3, also shearing of two graphene layers orientated in an angle of approximately 45° to loading direction is shown. This is the case, when the Van-der-Waals bonds fail before the covalent bonds. Thus, the true tensile strength is mostly determined by the orientation of the largest few-layer graphene nanoparticle with regard to loading direction.

The influence of particle or aggregate orientation on the true failure strength is quantified in Figure 4. Assuming that failure always initiates at the largest FLG particle or aggregate in the volume, fracture surfaces of several FLG modified specimens are analysed with regard to the orientation of the failure initiating FLG particle. The orientation of this particle related to loading direction is correlated with the volume and true failure strength of the respective specimen, as shown in the diagram in Figure 4. True failure strength of the particles oriented perpendicular or diagonal to loading direction is limited to approximately R_t = 105 MPa. The layers oriented perpendicular to loading direction may separate at lower stresses due to the comparable weak Van-der-Waals forces between the layers and initiate

failure. When the FLG particles are oriented with the layers in loading direction, the modified fibres exhibit true failure strength above R_t = 105 MPa and up to R_t = 140 MPa. FLG particles oriented perpendicular to loading direction are observed only in fibres of larger volume. This can be explained by the fibre/FLG particle diameter ratio. If the fibre diameter approaches the lateral FLG dimensions, which may be up to 20 µm, the fibre is prone to break during the manufacturing process. Therefore, in the smaller fibres produced, the largest FLG particles are oriented almost all in loading direction. With smaller volume, the probability of the comparable large FLG particles to be oriented transverse to loading direction decreases, leading to higher failure stress. This leads to the observed occurrence of parallel to loading direction oriented particles only in fibres with smaller volume.

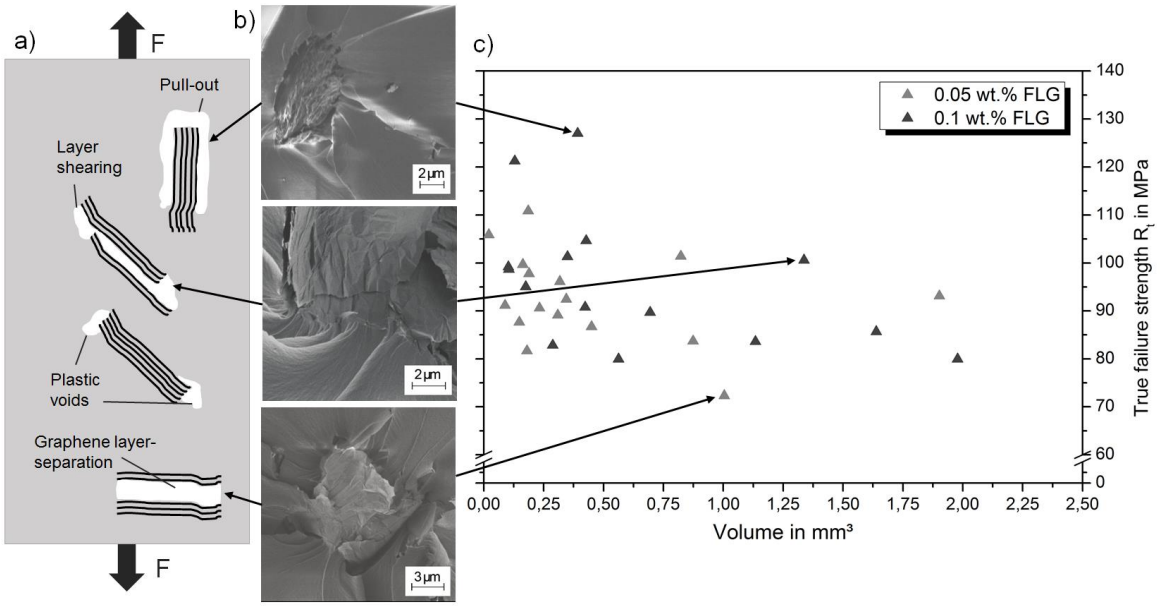

Figure 3. Different damage mechanisms at FLG nanoparticles in dependency of the particle orientation with regard to the loading direction.

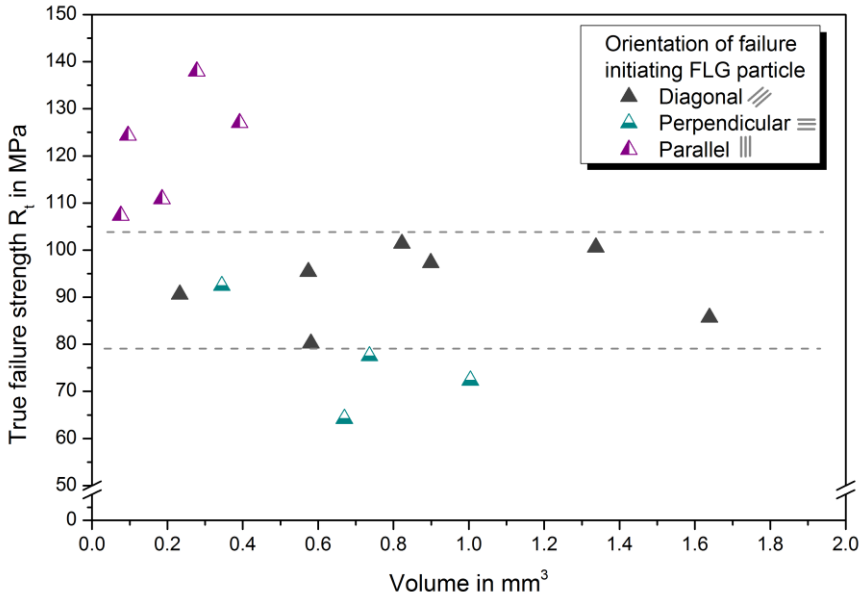

Figure 4. Influence of FLG-particle orientation with regard to loading direction on true failure strength for different volumes.

4. Conclusions

With a carbon nanoparticle modification, multifunctional materials combining electrical conductivity for damage sensing with enhanced mechanical properties can be obtained [19–21]. Particle size and morphology are key factors when regarding small volumes. A significant size effect that shows increasing tensile strength with decreasing volume due to a statistical defect distribution is identified for neat epoxy. A similar size effect is also experimentally proven to exist for CB and CNT modified epoxy, whereas for a FLG modification, the used particle size is larger than material defects. Larger FLG particles initiate failure prior to material defects and act as crack initiators and thus as flaws. For best mechanical properties in a small polymer volume, for example the matrix between the fibres in FRP, the graphene layers should be orientated parallel to loading direction.

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