

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 carbon nanoparticle morphology in epoxy on the mechanical properties is investigated regarding the size effect. Three types of particles are used, representing spherical, tubular and layered morphologies. For neat and carbon black modified epoxy, a clear size effect of increasing true failure strength with decreasing volume is found. Carbon nanotube modified epoxy shows high potential for strength increase, but dispersion and purity are critical. Few layer graphene particles are larger than statistically distributed defects in the epoxy and initiate cracks, counteracting any size effect. Different toughness increasing mechanisms on the nano- and micro-scale depending on particle morphology are discussed.

1 INTRODUCTION

The increasing use of fibre-reinforced plastics (FRP) requires detailed knowledge about failure initiation and propagation within composite laminates. A promising approach for further improvement of FRP mechanical properties, 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 [1–5]. This is attributed to stress relieving mechanisms such as nano- or microdamage at the particles [1,6]. In FRP a nanoparticle modification may result in better resistance to impact damage [7,8] or an increase in fatigue life [9].

In general, for nanoparticle modification dispersion and filling content are important [3]. However, the different types of damage mechanisms on the nano- or microscale, such as particle-matrix debonding, particle fracture or layer shearing in case of multilayer particles, depend on the size and morphology of the particles [6]. These mechanisms differ in their contribution to the reported fracture toughness increase.

The volumes between the fibres in FRP are very small; therefore size effects of the material should be concerned, when discussing the effect on nanoparticle modification of the matrix in FRP. In addition, regarding small volumes allows identifying failure initiation and damaging mechanisms at the nanoparticles. Brittle materials show a size effect due to a statistical defect distribution that results in increasing strength with decreasing volume [10]. This is also valid for epoxy which behaves brittle in this context and exhibits a size effect [11–13].

In this work it is investigated, whether a size effect exists as well for epoxy modified with different types of carbon nanoparticles. Three types of particles are used. These are carbon black (CB) representing spherical, carbon nanotubes (CNT) representing tubular and few-layer graphene (FLG) representing layered particle morphologies.

Polymer nanocomposites based on spherical carbon nanoparticles such as carbon black (CB) were investigated previously with regard to fracture toughness of nanoparticle modified polymer [2,14].

Although modification with CB exhibits no significant improvement in tensile strength, tensile modulus and fracture toughness are significantly improved [2,14]. Impressive increase in mechanical properties is reported for CNT modified polymers [2–4,6,15]. Energy dissipating and thus toughness increasing mechanisms at the CNT particles are nanotube pull-out, nanoparticle-matrix debonding and nanotube breakage [2,16]. Graphene based, layered particles such as few layer graphene and graphite nano-platelets exhibits high potential for improving mechanical properties such as fracture toughness of polymers [1,5,6,17–20]. The fracture toughness and hence strength increase is explained with stress relief due to micro-damage at the nanoparticles. At the particles itself, graphene layer separation, layer shearing and plastic yielding of the matrix that results in plastic voids are reported [1,6,12]. 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 [1,6].

For categorisation of the particles, we use a nomenclature after Tang et al. [21] and define spherical nanoparticles as 0D. They can be regarded as a point with surface area and thus the interfacial volume is 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 [6,21]. Three-dimensional (3D) particles are defined as more complex structures such as aerographite [22,23] or nano-foams, but they are not regarded within this work.

The main aim of this study is to investigate the influence of nanoparticle morphology in polymer nanocomposites on the size effect with regard to mechanical properties. Herewith, the influence of the particle morphology on the true failure strength with decreasing volume as well as on the damage mechanisms at the particles is presented. With an experimental approach representing small volumes, as they are present between the fibres in FRP, the most promising particle morphologies for improving mechanical properties in these small volumes are discussed.

2 EXPERIMENTAL STUDY

Epoxy matrix fibres are produced by mixing the resin Momentive Epikote RIMR 135 with the hardener Momentive Epikure RIMH 134, as recommended from the manufacturer (glass transition temperature $T_g = 93$ °C), as described in [24]. The method of using epoxy fibres is adapted from Hobbiebrunken et al. [13]. The different types of carbon-nanoparticles used to investigate the influence of particle morphology are listed in Table 1. Dimensions are given considering the morphology of the particles: for the single-wall CNT diameter d and length l , for FLG width w and thickness t and for CB the BET surface area.

Category	Type	Name	Supplier	Dimensions
0D	CB	Printex 300	Evonik industries	BET surface area = 80m ² /g
1D	CNT	Tuball (75%)	OCSiAl, Russia	$l \geq 5 \mu\text{m}$ $d \leq 1.9 \text{ nm}$
2D	FLG	AvanGraphene-2	Avanzare, Spain	$5 \mu\text{m} \leq w \leq 25 \mu\text{m}$ $t \leq 2 \text{ nm}$ $n_l \leq 6 \text{ layers}$

Table 1: Types of carbon nanoparticles used (Values from the respective data sheets).

For producing nanoparticle modified fibres, the appropriate amounts of nanoparticles and epoxy resin are mixed inside a glove box and dispersed with a three roll mill (EXAKT Advanced Technologies GmbH 120E). 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 the 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.

Fibres are pulled using a needle from the epoxy when it starts to vitrify. The fibre diameter can be adjusted to a certain point via the pulling speed of the needle. The fibres are cut and glued at one end on paper sheets based on ASTM D3379 for single fibre tensile tests [25] and then cured at 20 °C for 24 h and at 80 °C for 15 h, as recommended for this matrix system. Only one side is fixed in order to avoid tension stresses in the fibres from thermal or chemical shrinkage during curing. After curing the second end of the fibres is fixed on the paper.

The specimens are mounted in a universal testing machine (Zwick Z100) with a 50 N capacity load cell. Before testing the side bars of the paper, which connect the upper and lower part of the specimen are cut. 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). The damage mechanisms at the different types of nanoparticles and the influence of particle size and morphology on failure initiation and propagation is analysed in SEM (Zeiss Leo Gemini 1530 electron microscope). The SE2 detector with a working distance between 5 µm and 7 µm at 1 keV is used. The true failure strength R_f is determined from the measured force at failure and the cross section area obtained by microscopy.

3 RESULTS

The results of the fibre tensile tests are presented in Figure 1 with regard to the influence of specimen volume as well as nanoparticle morphology on true failure strength.

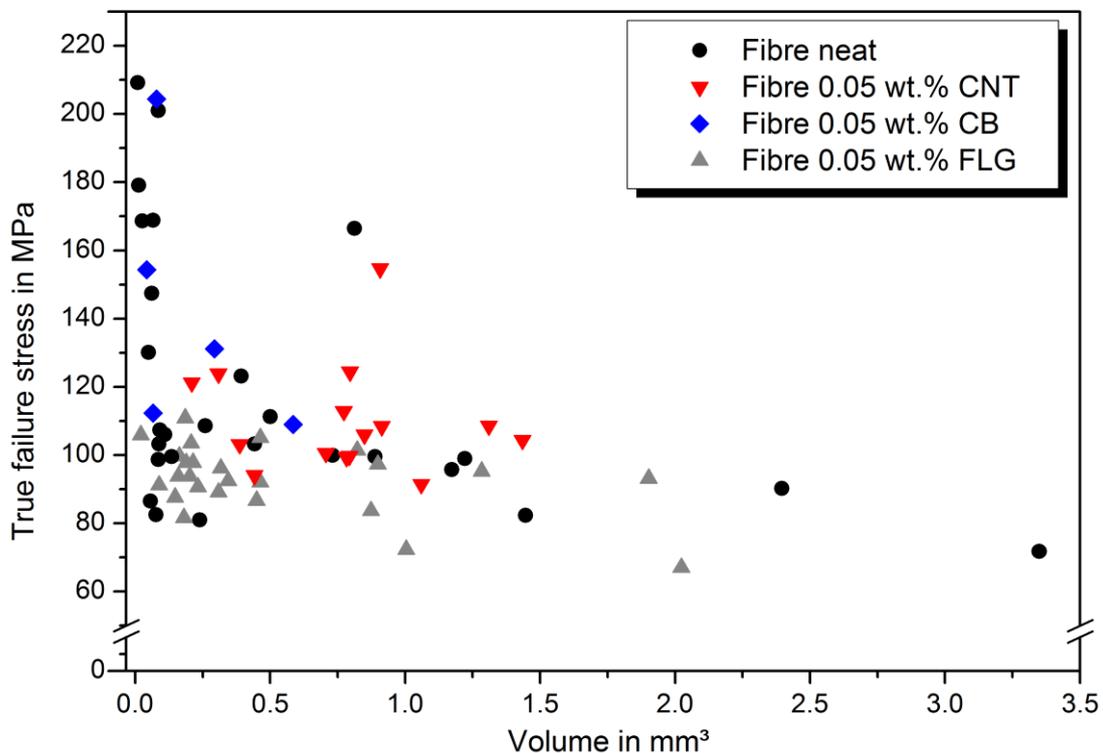


Figure 1: True failure strength versus specimen volume for neat and with 0.05 wt.% carbon nanoparticles modified epoxy fibres showing the influence of nanoparticle morphology.

The test data exhibits a size effect for the neat epoxy and the CB modified epoxy. For small volumes, an increase in true failure strength of approximately 100 MPa is measured. In comparison to the neat epoxy fibres, the CNT modified fibres exhibit slightly higher true failure strength at similar volume. A limitation in true failure strength at approximately 110 MPa is visible for fibres modified with 0.05 wt.% FLG. Most values for true failure strength are between 60 MPa and 110 MPa. This is

attributed to failure initiation at the largest FLG particle or aggregate, which is larger than material defects. Thus a failure initiating particle is always available within the fibre and independent of specimen volume [12]. The true failure strength for FLG modified epoxy is mostly independent of specimen volume but depends on the size and the orientation of the largest FLG aggregate in the fracture surface with regard to loading direction. This is investigated using fractography in SEM. These results are summarised in Figure 2, in which the influence of the largest, failure initiating FLG particle orientation in the respective specimen on true failure strength is shown over specimen volume.

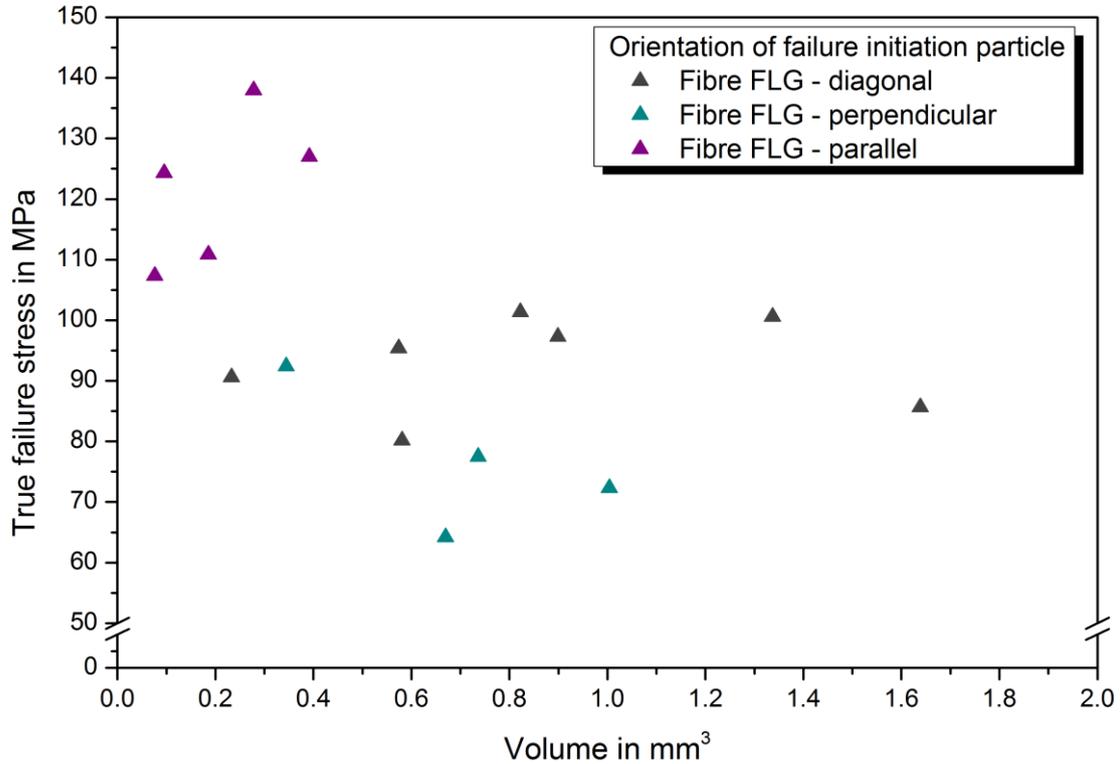


Figure 2: Influence of FLG-particle orientation with regard to loading direction on true failure strength for different volumes.

Assuming that failure always initiates at the largest FLG particle or aggregate in the volume, the orientation of this particle is crucial. True failure strength of fibres with 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 up to $R_t = 140$ MPa. The probability of the comparable large FLG particles to be oriented transverse to loading direction decreases with smaller volume, leading to higher failure stress and the observed occurrence of parallel to loading direction oriented particles only in fibres with smaller volume.

4 DISCUSSION

As modification, carbon nanoparticle morphology has an influence on the size effect in epoxy and the maximum true failure strength. If nanoparticles or nanoparticle aggregates are larger than the statistically distributed defects always existent within the material, they initiate failure and thus neglect any size effect. This is the case for the comparable large FLG particles. If nanoparticles are smaller than material defects, as is the case for CB particles or even small CB agglomerates, a size effect exists. It results in increasing true failure strength for decreasing volume. This may be beneficial in small volumes, such as in FRP between the fibres. According to the experimental results, a size effect

is also observable for CNT modified epoxy. The highest values of true failure strength of neat and CNT modified fibres are in the same range. However, those for CNT modified epoxy are measured in specimens of larger volume. The CNT modification therefore increases the tensile failure strength of polymers. This confirms findings from literature [2–4,15] for very small volumes. As energy dissipating and thus toughening mechanisms at the nanoscale, nanotube fracture, crack bridging and nanotube pull-out are identified in the fracture surfaces, with nanotube pull-out being the dominant mechanism. It can only be effective in dissipating energy along the direction of the tube, thus the aforementioned classification of CNT being a 1D reinforcement seems to be valid. Due to the toughening, a significant increase in strength below a certain volume (size effect) is valid for CNT modified polymer as well, but this critical volume, at which strength increases significantly, is shifted to higher values.

For FLG modified epoxy, a clear influence of the particle orientation with regard to loading direction is quantified (refer to Figure 2). When the covalent bonds within the graphene lay parallel to loading direction, this leads to damage initiation at higher stresses and thus, as failure initiates at the largest FLG particle or aggregate, higher true failure strength of the specimens. In fibres of very small diameter or between the fibres in FRP, a perpendicular orientation of the graphene layers is not possible, if the lateral dimensions of the FLG particles are in the range of the fibre diameter. When the largest FLG particle has diagonal or perpendicular orientation, true failure strength of the specimens is limited. The true failure strength value coincides with the global stress value at which local layer shearing, layer separation or plastic yielding of the matrix occurs at latest and initiates final failure. The results also implicate that in FRP, the particles are oriented along the reinforcing fibres. In 0°-layers, the covalent bonds of the FLG particles are oriented in loading direction, whereas in 90°-layers, the layers are oriented perpendicular to loading direction and may on one hand initiate local failure but on the other hand dissipate energy due to the shearing of the graphene layers and plastic deformation of the surrounding matrix, leading to enhanced mechanical properties observed when incorporated in FRP [9,21].

5 CONCLUSIONS

Whether carbon nanoparticle modified epoxy exhibits a size effect or not, depends mostly on the particle size, because larger particles may initiate failure prior to material defects in the matrix. For CB and CNT modified epoxy, a clear size effect, similar to the unmodified material is found, for the used FLG, particle size is larger than material defects and thus failure initiates at the particles. For FLG, the orientation of the graphene layers with regard to loading direction is critical. Higher true failure strength is measured with the largest particle oriented parallel to loading direction. From a mechanical properties point of view, FLG and CNT are the most promising particle morphologies, if CNT length is high enough and FLG are oriented in loading direction.

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