INFLUENCE OF GRAPHENE NANOPARTICLES ON THE SIZE EFFECT OF EPOXY MATRIX

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Abstract
The size effect of unmodified and graphene nanoparticle modified epoxy matrix is experimentally investigated. A significant size effect due to a statistical defect distribution is identified for the neat matrix. The graphene modified matrix shows almost no size effect. Failure initiates at the nanoparticles, counteracting any size effect due to a statistical defect distribution. In a bulk volume, energy dissipation mechanisms play a more important role, therefore higher values for tensile strength, compared to the neat matrix, are obtained with a nanoparticle modification.

1. Introduction

When speaking of a size effect, it means that the strength of a material decreases with increasing volume. Size effects are shown in literature to be present from a large to a smaller scale. On laminate level, the total volume or the thickness of the layers in a laminate influence the strength of a laminate [1–5]. Regarding the substituents, size effects in fibres were first documented by Leonardo da Vinci for iron wires [6] and are shown to exist for different materials such as glass [7], carbon [8, 9] or acrylic [10]. For polymer matrices, the microstructure and the stress state in the pure resin compared to the same material as a matrix in a composite may differ [11]. In an investigation by Hobbiebrunken et al. [12] a size effect for the RTM 6 epoxy matrix system was identified experimentally. By using dog-bone specimens and fibres of the same material, increasing tensile strength with decreasing volume was found. [12]
Since its discovery in 2004 [13], graphene is used as a nanoparticle reinforcement for polymers and fibre reinforced plastics (FRP) with promising results for improving the mechanical properties amongst others. Already the addition of small amounts of graphite nanoplatelets and graphene oxide increase the fracture toughness of epoxy matrix by 25 % respectively 40 % [14]. Rafiee et al. [15] reported ”enhanced mechanical properties” such as Young’s modulus, tensile strength and fracture toughness due to the addition of graphene nanoplatelets in epoxy nanocomposites at low nanofiller content.
The question that arises now is that of a size effect in polymer nanocomposites and whether or not the particles influence the mechanical properties such as ultimate stress in a small volume. Small volumes are of particular interest for the use of graphene in FRP, because the matrix volume between the fibres in FRP is very small. Graphene is only rarely used in commercial products [16], but due to its potential for improving mechanical properties of polymers or FRP, a better understanding of damage mechanisms in small volumes may help finding possible applications for this promising material.

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2. Experimental study

As matrix system, the resin Momentive Epikote RIMR 135 with the hardener Momentive Epikure RIMH 134 is used. Few layer graphene (FLG) Avangraphene-2 from Avanzare is used as nanoparticle reinforcement for the modified fibres. The process for manufacturing neat and nanoparticle modified matrix fibres is shown schematically in figure 1. For the modified fibres, the process starts with the mixing of appropriate amounts of nanoparticles and the epoxy resin inside a glove box before dispersion 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 [17]. The three roll milling process is repeated seven times with the gap widths being adjusted from 120 µm to 5 µm (Refer to figure 1) at a constant rotational speed of the rolls of 33 min^{-1}, 100 min^{-1} and 300 min^{-1} respectively. Three configurations are produced: neat, and graphene nanoparticle modified with 0.05 wt.% respectively 0.1 wt.% . The hardener is added to the resin and mixed manually for approximately 10 min and then degassed under vacuum for 15 min to remove any air inclusions.
The matrix fibre manufacturing process is adapted from Hobbiebrunken et al. [12]. For producing the fibres, the degassed matrix system is heated in a aluminium cup on a heating plate at a constant temperature of 50 °C for about 40 min to increase the viscosity. When the matrix starts to vitrify, the fibres are pulled with a needle and wound around two rods (Refer to figure 1). The diameter can be adjusted to a certain point with the pulling speed of the needle. Fibres with diameters between 22 µm and 350 µm after curing are obtained. The fibres are cut and glued at one end on paper sheets, as shown schematically in figure 1. For avoiding tension stresses in the fibres because of thermal or chemical shrinkage during curing, only one end is fixed. Curing of the fibres is for 24 h at 20 °C and for 15 h at 80 °C as recommended for this matrix system. After curing the second end of the fibres is glued to the paper that is is prepared on the basis of the ASTM D3379 standard for single fibre tension tests [18] with a hole with dimensions of 10 mm × 25 mm. Before testing the side bars of the paper, which connect the upper and lower part of the specimen are cut (Refer to figure 1).
For the tensile tests with a test speed of 25 mm/min, the specimens are fixed in a universal testing machine (Zwick Z10) with a 10 N capacity load cell. The cross section after failure is measured for each specimen in an optical microscope (Olympus BX51). The true failure stress R^t is calculated from the measured force at failure and the cross section area obtained by microscopy.
In order to regard larger volumes, dog-bone specimen are manufactured according to DIN EN ISO 527-2 [19] with a gauge length of $l = 30$ mm and a gauge width of $w = 3{,}86$ mm for the neat and $l = 13$ mm, $w = 4$ mm for the nanoparticle modified specimens respectively. The dog-bone specimens are tested with a universal testing machine (Zwick Z2.5) using a load cell with a capacity of 2,5 kN at a speed of 1 mm/min according to DIN EN ISO 527-2 [19].

3. Results

Figure 2 shows the true tensile stress R^t versus the gauge volume V for both, the neat and the graphene nanoparticle modified epoxy matrix system. Results for fibrous and dog-bone specimens are indicated with circles respectively squares.
The neat specimen show a clear size effect. A decrease in volume leads to a significant increase in failure stress. The median value with standard deviation of true failure stress for the fibrous specimens is ($R^t = 121(36)$ MPa), which is 95 % higher than that of the dog-bone specimens. For the modified matrix, the degree of filling, indicated with different shades of grey in figure 2, has no visible influence on the failure stress. The median failure stress of the modified dog-bone specimen is ≈ 80 MPa, which is an increase of about 20 MPa (+29 %) compared to the neat specimen. The median value for true failure stress of the modified fibres is ($R^t = 93(9)$ MPa), which is only 16 % higher compared to the dog-bone specimens. Thus the modified matrix system shows no significant size effect, although there is a slight increase in strength with decreasing volume. Compared to the high increase for the neat matrix, the

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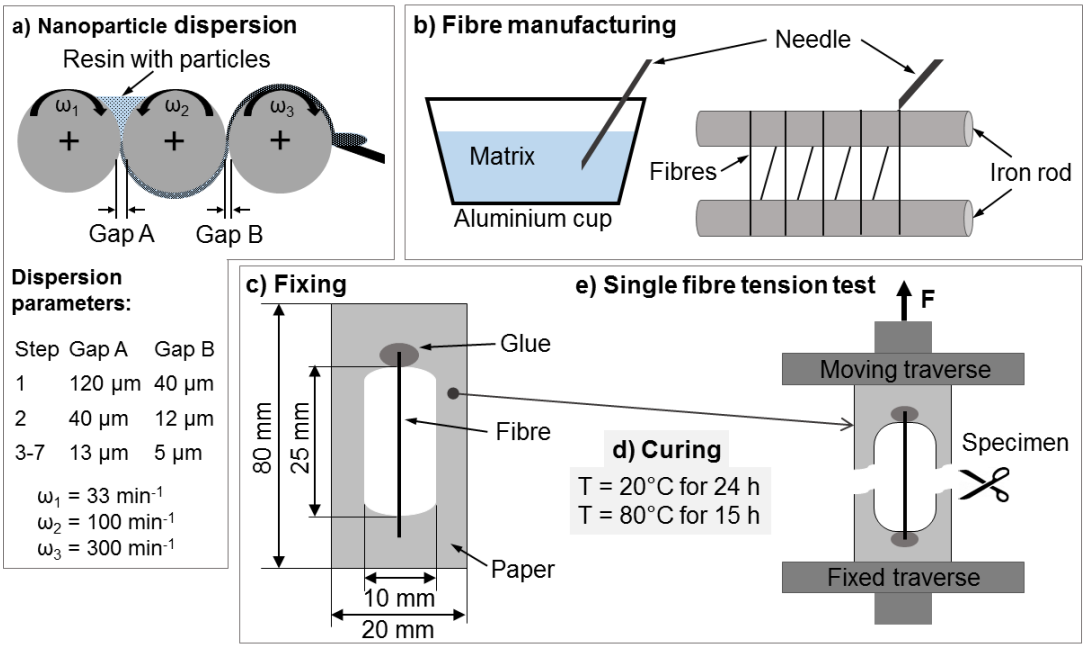

Figure 1. Schematic representation of specimen manufacturing process: a) dispersion of nanoparticles in the resin (only for modified fibres) b) matrix fibre manufacturing c) specimen preparation for curing d) curing parameters e) scheme of test specimen mounted in universal test machine

maximum failure stress for the modified matrix seems to be limited, even in very small volumes. It can be concluded, that the nanoparticle modification acts as an enhancement in larger volume, such as in the dog-bone specimens, but weakens the material in very small volumes regarding the true failure stress. This is explained by fracture initiating at surface flaws that are statistically distributed in the neat matrix, but at nanoparticles in the modified specimens.

4. Conclusion

The size effect of unmodified and graphene nanoparticle modified epoxy matrix is experimentally investigated. A significant size effect is identified for the neat matrix. This is due to a statistical defect distribution according to Weibull's theory [20] and confirms previous investigations for a different matrix system [12]. Since the nanoparticles act as crack initiators and thus as flaws, the graphene modified matrix shows almost no size effect. The size of the particles is independent of specimen volume, so that the failure initiating as well as energy absorbing mechanisms are always available. In the fibres with their small volume, this leads to failure initiation at the nanoparticles, counteracting any size effect due to a statistical defect distribution. In a bulk volume, energy dissipation mechanisms play a more important role, therefore higher values for tensile strength, compared to the neat matrix, are obtained with a nanoparticle modification as also reported in the literature [14, 15, 21, 22].

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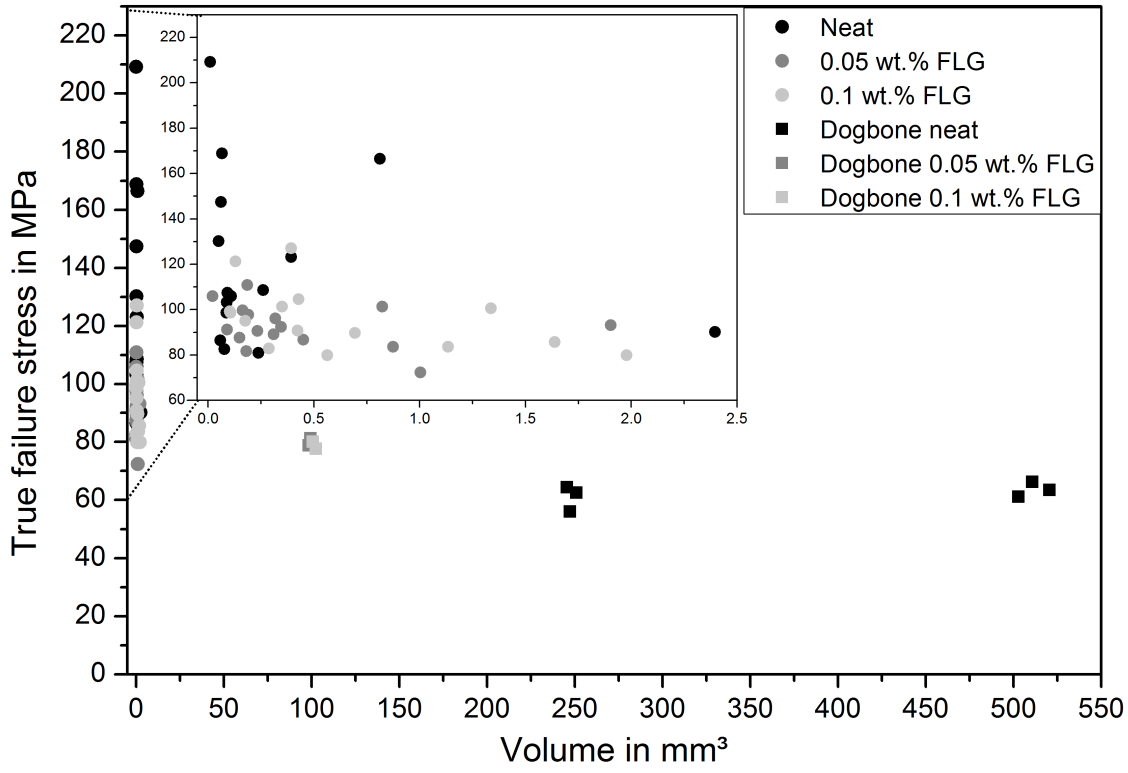

Figure 2. True tensile stress R^t versus gauge volume V for neat and graphene nanoparticle modified epoxy matrix system

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