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Static and dynamic properties of single and multi-fiber/epoxy composites modified by sizings

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Abstract

A challenging issue in composite research is to relate microscopic interphase characteristics to macroscopic static and fatigue properties. Here, we systematically analyze fiber surface sizing effects on composites' mechanical performance using the quasi static single fiber pull-out test and a cyclic loading (micro-fatigue) test, dynamic mechanical thermal analysis (DMA), fatigue and other mechanical tests. Our experiments show that the polymer sizing provides the glass fiber with significantly improved both static and fatigue properties. Together, these results demonstrate a correlation between the fatigue behavior and the interfacial adhesion, with the higher interfacial adhesion performing better in fatigue, where the interface should dominate in determining fatigue life. A cooperativity analysis of DMA data reflects constriction effects on molecular mobility of matrix and is consistent with the results of interfacial adhesion and the tendency of fatigue resistance.

Keywords: A. Polymer–matrix composites; B. Interface, mechanical properties, thermal properties; C. Stress transfer; D. Non-destructive testing

1. Introduction

The mechanical properties of composites can vary depending on the interphase between fiber and bulk matrix. A challenging research issue is to relate interphase characteristics and composite static and fatigue properties. One effective way of creating an interphase layer on the nanoscale and in turn, controlling composite properties, is surface sizing for glass fibers. Sizings are multi-component systems mainly consisting of silane coupling agents, film formers, and lubricants, which fulfil both adhesion and wetting relevant requirements in composites and enable prevent damage of the glass fibers during the processing [1–3]. It was also demonstrated that a suitable combination of silane coupling agents and film formers can improve fiber strength by healing surface flaws [4], which in turn, can be effectively utilized under an optimum bonding to improve composites properties.

Many phenomena associated with fatigue loading of microcomposites are not thoroughly understood. Traditionally, the quality of fiber/matrix interphases is determined by quasi static micromechanical techniques, such as quasi-static fragmentation, pull-out, microbond, or microindentation tests. Interfacial parameters can be indirectly estimated from the debond force corresponding to crack initiation taken from pull-out or microbond tests. However, the results regarding dynamic loading conditions are scarce and controversially reported in literature [5,6]. It was reported that the surface treatment effect was insignificant under fatigue loading in tension [5], whereas the magnitude of the interphase shear modulus was sizing and strain rate dependent [6]. Some authors [7–10] came to the conclusion that it is difficult and time-consuming to derive appropriate information from micromechanical tests (perhaps due to the intricate fracture pattern) and to predict the mechanical performance of composites.

In continuous-fiber/matrix laminated composites, the experimental results [11,12] indicated that slightly varied interphases could lead to significantly altered fatigue per-

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formance. It is obvious in fibrous composite materials that energy is dissipated during crack initiation and propagation by a multiplicity of microfracture events like fiber fracture, matrix cracking, fiber/matrix debonding, delamination, interfacial breakdown, fiber and matrix relaxation. Therefore, it is necessary to distinguish the different fiber/matrix systems like brittle or ductile matrix and strong or weak fiber/matrix adhesion, generated by sizing and matrix modification. For a brittle matrix the stress versus load cycle curve (*S–N* curve) is characterized by three regions of fatigue damage before final failure: the first region is due to a stiffness loss without fiber breakage, the second region – the longest fatigue time – is characterized by constant stiffness accompanied by delamination and matrix cracking, the third region is dominated by fiber breakage shown by a great stiffness loss [11]. Ductile matrix composites have a progressive stiffness loss throughout the test and often fail by a "sudden death". In the case of weak interfacial adhesion, the dominating fatigue mechanism is debonding, while the cracks run through the interphase and no fiber breakage occurs. Thus, for unidirectional glass fiber/epoxy specimens, a weak fiber/matrix adhesion may increase the fatigue life by several fold [11]. This effect can be explained by a delamination damage mechanism in the weak fiber/matrix interphase, where the cracks propagate along the interphase, thus, fiber break is delayed and the fatigue life time increased. In the case of a strong adhesion strength, composites designed to possess high transverse tensile strength can fail under cyclic dynamic loading because the interphase does not contribute to energy dissipation in the system, leading to poor stress transfer ability. Besides static performance, therefore, interphase properties are essential for improving fatigue resistance and toughness of composites. However, certain questions remain regarding the critical properties and dimensions of the applied sizing layer that are necessary to bring about the optimum laminate performance. A further clarification seems to be valuable to reveal different influences due to sizing variation and different non-interphase related effects [13–16].

The objective of this investigation is to study the effects of interphase on both the static and dynamic properties of single and multi-fiber reinforced epoxy composites. The glass fiber surface characteristics are varied in a controlled way, i.e. unsized, pure silane coupling agent, model sizings consisting of silane and film former. The conventional fatigue tests are performed to study how the interphases vary the macroscopic mechanical properties of laminate composites. We present data from a novel micro-fatigue test in which the single fiber model composites are loaded under cyclic tension and compression. It can detect interphase related micro-damage without taking into account those issues that make data interpretation complex in fatigue tests of unidirectional composites, such as fiber fracture and loading transfer from broken to unbroken fiber. The dynamic modulus and the inelastic strain are determined using hysteresis curves; the fatigue life is generated by the *S–N* curves. These results are discussed in comparison with moduli and damping behavior derived from dynamic–mechanical thermal analysis.

2. Experimental

2.1. Materials and treatments

A commercial DGEBA-based epoxy resin (resin, Rütapox L20 and hardener, Rütadur SL in a weight ratio of 100:34, manufactured by Bakelite AG) was used in the present study. The epoxy resin and the composites were cured at identical conditions (80 °C, 6 h), as recommended by the manufacturer, taking into account an inhibition of curing by the glass fibers. The cured resin achieved a tensile modulus $E_m = 2.7$ GPa and an average tensile strength $\sigma_m = 75.8$ MPa. The E-glass fibers were manufactured using the continuous spinning devices at the Leibniz Institute of Polymer Research Dresden (IPF). Fibers with a diameter $d = 12$ μm were spun and used either as single fiber for micromechanical tests or yarns of 60 tex fineness for unidirectional composites. During the continuous spinning process, the fibers were sized by the silane coupling agent, γ-aminopropyltriethoxy silane (APS), in conjunction with either polyurethane (PU) or epoxy resin (EP) film formers in the aqueous spinning bath in industry-relevant concentrations. As reference material unsized E-glass fibers (0) were spun without any sizing. To simulate weak adhesion strength, a polyvinaylacetate (PVAc) film former without silane coupling agent was used, representing a film former non-compatible with epoxy resin matrix. Table 1 gives an overview of the designations, concentrations of aqueous solutions and sizing content of the glass fibers.

The unidirectional prepregs with fiber volume content of about 50% were made by continuous impregnation of the filament yarns (4 × 60 tex) and winding-up the impregnated yarns on a heated drum for precuring. To allow sufficient dissolution of the sizing, the contact time for the yarns with the liquid resin and thus the precuring time before gelation was about 1 h at 80 °C. The unidirectional laminates with thickness of 2 mm were prepared by hand lay-up of six plies of prepreg, which were then hot pressed with vacuum at 80 °C, and a pressure of 2 MPa for 6 h. For fatigue testing, the specimens of 190 mm long and 15 mm wide were cut using a diamond saw along the 0° axis of laminates, with end taps to avoid damage failure around the specimen clamps. The gauge length of the specimens was 90 mm.

Table 1
Summary of model glass fiber sizing formulation and content

Sizing	0	APS	APS/PU	APS/EP	PVAc
Solid content in aqueous sizing solution (%)	–	0.25	2.73	3.04	2.71
Sizing content (%)	–	0.19	0.67	0.65	0.74