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Fatigue crack propagation behaviour of epoxy resins modified with silica-nanoparticles

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ABSTRACT

In this study, the effect of nano-SiO_2 (up to 25 wt%) on the mechanical properties of an anhydride cured epoxy resin was investigated with particular attention on the fatigue crack propagation behaviour (FCP). The Young's modulus showed good agreement to the Halpin–Tsai predictions for contents up to 15 wt%. The addition of silica nanoparticles evokes an increase in fracture toughness (up to 74%). However, the augmentation of the critical stress intensity factor rises with respect to the filler loading, although no linear correlation is found. Additionally, a plateau-like behaviour is observed for the fracture energy release rate at filler contents above 15 wt%. The FCP behaviour is improved in all three regimes of fatigue crack propagation. Particle debonding in combination with subsequent plastic void growth and shear yielding of the matrix are identified as major energy dissipating mechanisms in all three regimes of FCP.

1. Introduction

As a consequence of their high Young's modulus and large specific surface area, silica nanoparticles are good candidates to improve the mechanical properties of thermoset polymer matrix nanocomposites [1]. Indeed, the outstanding toughening effect of these rigid, spherically shaped nanoparticles on epoxy resins is widely discussed in literature [2–6]. The general consensus is that the toughening mechanism involves silica nanoparticle debonding [2,3,7] while the energy absorbing mechanisms are the subsequent plastic void growth [2] and the shear band formation [4,5] in the matrix. Crack pinning is not observed.

Prerequisites for having on-plane toughening are particles having a size larger than the crack tip opening displacement. The explanation for the absence of crack pinning is explained through the huge difference between the dimensions of the nanoparticles (in the scale of 20 nm) and the displacement at the crack tip (being in the range of microns) [2], as determined by the Irwin analysis [8]. Due to this large difference (two orders of magnitude), the nanoparticles are not able to interact with the propagating crack so as to induce crack bowing and pinning, as observed for micron sized fillers [9]. Based on the well-understood toughening mechanisms, some models were developed to describe and predict the toughening effect [4,5,7,10]. These models, considering the toughening contribution of shear banding and plastic void growth, are in good accordance to the experimental data for moderate nano-silica contents [4,5]. Though the overestimation of these models at higher filler loadings are considered by partial contribution of nano-silica to plastic void growth [10].

Since the formation and propagation of matrix cracks are highly relevant for dynamically loaded composite materials, the knowledge about the fatigue crack propagation (FCP) behaviour is essential. In contrast to the numerous investigations of the quasi-static fracture toughness of nano-silica filled epoxy resins, very few studies report about the FCP behaviour of epoxy/silica nanocomposites [11,12]. Blackman et al. [11] investigated the influence of up to 20 wt% surface-modified SiO_2 nanoparticles with an average particle size of about 20 nm, on the FCP behaviour of an anhydride cured epoxy resin system. The improved FCP behaviour of the nanocomposites with respect to the increasing amount of nano-silica was related to the significant improvements in the threshold value of crack propagation. Liu et al. [12] presented an extensive study on the influence of nano-silica and rubber particles on the fatigue crack propagation of a comparatively tough amine cured epoxy resin system. The authors used equal silica-nanoparticles as Blackman et al. [11] with concentrations up to 12 wt%. The authors confirmed the improvements in the threshold value of crack propagation. Furthermore, in the region of stable

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crack growth (Paris regime), a systematic decrease of the crack propagation rates, da/dN, for equal stress intensity factor ratios, ΔK, combined with a reduction of the slopes, m, was observed with increasing amount of silica nanoparticles. At low ΔK values, Liu et al. observed crack deflection as major toughening mechanism. While particle pull-out and plastic void growth were observed at higher ΔK values, as reported for quasi-static toughness tests [12].

In the present study the effect of the silica nanoparticles on the FCP behaviour of epoxy nanocomposites is investigated in all three stages of fatigue crack growth. First, the fatigue crack growth rate is determined over five orders of magnitude, allowing for a precise determination of the threshold value for crack initiation, ΔK_{th}, the slope m in the Paris regime and the limit for critical failure ΔK_{cf}. Second, investigations with constant stress intensity ratios, and so constant crack propagation rates are carried out. Fractographic analyses are performed and allow for the determination of the toughening mechanisms in dependency of the applied stress intensity ratio.

2. Experimental

2.1. Materials

Silica nanoparticles were kindly provided as colloidal sol in DGEBA (Nanopox E470, 40 wt% SiO_2, Evonik-Hanse GmbH, Germany). These nanoparticles were synthesised and surface-modified with an organosilane in aqueous solution [1]. The mean particle size is 20 nm [13]. Diglycidyl ether of bisphenol A (DGEBA) epoxy resin (EPIKOTE resin 0162, Momentive Specialty Chemicals, Germany), epoxy equivalent weight 172 g/eq. was used to dilute the masterbatch. The resin was cured with methylhexahydrophtalic anhydride (EPIKURE curing agent 868, Momentive Specialty Chemicals, Germany). Additionally 1 wt% N,N′-Dimethylbenzylamine (Sigma–Aldrich, Germany) as referred to the liquid matrix was added to accelerate curing.

2.2. Sample preparation

Nanocomposites with up to 25 wt% nano-silica were prepared by diluting the epoxy nanosilica masterbatch with pure DGEBA resin, using a conventional stirrer. Previously both components were preheated to 60°C. Subsequently a stoichiometric amount of MHHPA and the accelerator were added. The mixture was homogenised, degassed (10 mbar) and finally poured in a vertically-aligned, preheated (60°C), and release-agent-coated (Loctite Frekote 770-NC, Henkel, Germany) aluminium mould. The samples were cured in a convection oven at 140 °C for 11 h to ensure full curing of the nanocomposites. The materials were demoulded afterwards at room temperature.

Samples required for characterisation were machined from the obtained plates using a circular saw (Diadisc 6200, Mutronic, Germany) equipped with a diamond saw blade. A computer controlled drilling machine (Diadrive 2000, Mutronic, Germany) was used to prepare dog-bone specimens of type 1B according to DIN EN ISO 527-2.

2.3. Characterisation

The dispersion of the epoxy silica nanocomposites was characterised using a LEO 922 A EFTEM transmission electron microscope (Carl Zeiss AG, Germany) applying an acceleration voltage of 200 kV. Thin sections of 50 nm were cut on a Leica Ultracut microtome (Leica Biosystems GmbH, Germany) equipped with a diamond knife.

Fracture surfaces of selected samples were analysed using a Zeiss 1530 (Carl Zeiss AG, Germany) scanning electron microscope possessing a field emission cathode for high-resolution micrographs. An acceleration voltage of 1.5 kV was applied.

Dynamic mechanical analysis (DMA) measurements were conducted with an Advanced Rheometric Expansion System (ARES RDA III, Rheometric Scientific, Piscataway, USA) in torsion mode according to DIN EN ISO 6721-7. The specimens were of rectangular shape ($50 \times 10 \times 2$ mm^3) and excited with an oscillation frequency of 1 Hz and a deformation amplitude of 0.1%. The temperature was varied from 25°C to 200°C with a heating rate of 3 °C/min. The glass transition temperature (T_g) was determined as the temperature at the maximum of the loss factor tan δ. At least three samples were tested for each nano-silica content.

The tensile tests were performed at 25°C according to EN ISO 527-2 using a universal testing machine, Zwick 1475 (Zwick, Germany) equipped with a 10 kN load cell. The crosshead speed was set to 1 mm/min for modulus determination and 5 mm/min subsequently. At least five samples were tested for each nano-silica content.

Based on linear elastic fracture mechanics, the critical stress intensity factor (K_{Ic}) as well as the energy release rate (G_{Ic}) were determined according to ISO 13586 using Compact tension (CT) specimens. The specimen width was $w = 33$ mm, the thickness $t = 4$ mm. For each sample, a sharp crack was generated by tapping a new razor-blade into the machined V-notch. The tests were carried out using a universal testing machine Zwick BZ2.5/TN1S (Zwick, Germany) at constant crosshead speed of 10 mm/min and controlled environmental conditions (25°C and 50% RH.). The crack opening displacement was measured using a clip-on extensometer (632.29F-30, MTS, Germany). At least five samples were tested for each nano-silica content. The K_{Ic} was calculated according to equation 1.

$$K_{Ic} = \frac{F_m}{t \cdot \sqrt{w}} \cdot f\left(\frac{a}{w}\right) \quad (1)$$

F_m represents the maximum force required for crack propagation and $f(a/w)$ the geometry calibration factor which is defined in the ISO 13586 standard and depends on the crack length a.

The G_{Ic} was calculated from knowledge of the values of K_{Ic} and E, using equation 2.

$$G_{Ic} = \frac{K_{Ic}^2}{E} \cdot \left(1 - \nu^2\right) \quad (2)$$

E represents the modulus of elasticity respectively ν the Poisson's ratio, both obtained from tensile testing.

For the determination of the fatigue crack growth behaviour, CT-specimens ($w = 33$ mm, $t = 4$ mm) were used. Testing was performed based on ISO 15850/ASTM E647 at 23°C and 50% relative humidity. The CT-specimens were loaded dynamically in tension–tension mode with a frequency of 10 Hz using a servo hydraulic testing machine (Hydropuls MHF, Schenck, Germany). The FCP tests were performed at increasing stress intensity factor amplitude ($\Delta K = K_{max} - K_{min}$) with a constant ΔK gradient as a function of crack length. Furthermore FCP tests at constant ΔK were performed. For both test methods, a sinusoidal load was applied and the minimum-to-maximum load ratio R (K_{min}/K_{max}) was set to 0.1. An initial pre-crack of about 2 mm in length was introduced into the machined V-notch of the CT-specimens by tapping softly on a sharp razor blade. In order to sharpen the crack tip the initial pre-crack was extended by about 2 mm by increasing the load amplitude under computer control. The compliance of the specimen was continuously measured by the crack opening displacement method using a transducer (632.13F-20, MTS, Germany) fixed