

THE EFFECT OF MICRON-RUBBER AND NANO-SILICA PARTICLES ON THE FATIGUE CRACK GROWTH BEHAVIOR OF AN EPOXY POLYMER

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A thermosetting epoxy polymer was hybrid-modified by incorporating 9 wt. % of CTBN rubber micro particles and 10 wt. % of silica nano-particles. The unmodified and the hybrid-modified resins were poured into steel moulds and cured to produce bulk epoxy polymer sheets from which standard compact tension test specimens were machined. Fatigue crack growth tests were conducted using a 50 kN servo-hydraulic test machine, with following test parameters: stress ratio, $R = \sigma_{\min}/\sigma_{\max} = 0.1$, sinusoidal waveform and frequency, $\nu = 3$ Hz. The crack length was monitored by compliance technique. The fracture surfaces were observed in a high resolution scanning electron microscope. The fatigue crack growth rate of the hybrid epoxy polymer was observed to be significantly lower than that of the unmodified epoxy polymer. The threshold stress intensity factor range, ΔK_{th} , of the epoxy polymer was observed to increase by the addition of micron-rubber and nano-silica particles. The energy dissipating mechanisms viz., (i) cavitation of the rubber microparticles followed by plastic-deformation and void growth of the epoxy and, (ii) silica nanoparticle debonding followed by plastic-deformation and void growth of the epoxy, were observed to be operative and contribute for the reduced crack growth rate in the hybrid epoxy polymer.

Key Words: rubber particle; silica nano particle; thermosetting epoxy; fatigue crack growth.

1. Introduction

The fiber reinforced plastic (FRP) composites, due mainly to their high specific strength and stiffness, are widely used in structural applications such as airframe, wind turbine, ship hull etc. Such composites invariably experience various types of cyclic-fatigue loads in service. Safe operation of the structures requires that these composites possess high fracture toughness and enhanced fatigue-durability.

The majority of engineering composites generally contain continuous fibres of glass, or carbon, reinforced in a thermosetting epoxy polymer. The epoxy polymer is amorphous and highly cross linked material and exhibit many useful properties such as high modulus and failure strength, low creep etc. However, it is relatively brittle and has a poor resistance to crack initiation and growth which significantly affect the overall fatigue and fracture performance of FRP composite.

One of the ways to enhance the fatigue and fracture properties of FRPs is to improve the properties of the epoxy matrix material by incorporating second phase fillers in it. Various types of micro and nano sized and particulate, fibrous and layered shaped fillers have been employed in composites to enhance the mechanical properties.¹⁻¹⁴ The addition of rubber micro particles has been shown to improve the fatigue and fracture behavior of epoxies and FRPs.^{7,9,15-19} The beneficial effect of silica nanoparticles on the fatigue and fracture toughness of epoxies and FRPs has been widely reported.³⁻¹⁰ In recent investigations^{7,9,20} it has been shown that FRPs with epoxy polymer matrix containing both rubber micro particles and silica nano particles exhibit significantly improved fracture toughness and fatigue behavior. However, detailed investigations on the fatigue crack growth behavior of hybrid epoxy polymer are limited. Hence, the main aim of this work was to investigate the fatigue crack growth behavior of a hybrid-modified epoxy polymer with emphasis on understanding the micromechanisms of crack growth behavior.

2. Experimental

2.1. Materials and processing

The materials were based upon a single-component hot-cured epoxy formulation. The epoxy resin was standard diglycidyl ether of bis-phenol A (DGEBA), LY556 with an epoxy equivalent weight (EEW) of 185 g/mol. The silica nano-particles were obtained at a concentration of 40 wt.% in DGEBA epoxy resin. The reactive liquid carboxyl-terminated butadiene-acrylonitrile (CTBN) rubber (which give rises to micrometre-sized particles upon curing) was obtained as CTBN-epoxy adduct with a rubber concentration of 40 wt.% in DGEBA epoxy resin. The curing agent was an accelerated methylhexahydrophthalic acid anhydride, HE 600.

The required quantities of the DGEBA epoxy resin, silica nano particle-epoxy resin mix and CTBN-epoxy adduct were individually weighed and degassed at 50 °C and -1 atm. All the resins were then mixed and the stoichiometric amount of curing agent was added, stirred and degassed once again. The resin mixture was then poured into release-coated steel mould. The filled mould was placed in a circulating air oven, cured at 100 °C for 2 hours and

post-cured at 150 °C for 10 hours. Thus, bulk sheets of both the unmodified and the hybrid-modified epoxy polymers were produced.

2.2. Microstructure

Atomic force microscope (AFM), as explained in Ref. 5 was employed to observe the microstructure of epoxy polymers. The AFM phase image of the hybrid epoxy polymer is shown in Fig. 1. The rubber particles were evenly distributed and had an average size of 0.5 to 1 µm. The silica particles of about 20 nm in diameter were somewhat agglomerated to give a ‘necklace-type’ structure with an average width of about 1 µm.

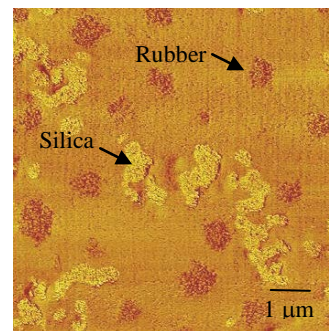


Fig. 1. The atomic force microscopic phase image of the hybrid epoxy showing micron-rubber and nano-silica particles

2.3. Tensile properties

The tensile properties of the bulk epoxy polymers were determined according to the ASTM D638 test standard specification²¹ using dog bone shaped test specimens having a total length of about 165 mm and a gauge cross section of 10mm x 5 mm. The tests were performed using a 100 kN computer-controlled screw-driven test machine with a constant crosshead speed of 1 mm/min. Five replicate tests were conducted for each material and the average tensile properties determined are shown in Table 1. The addition of micron-rubber and nano-silica particles decreases the tensile strength and modulus of the epoxy polymer by about 12% and 10% respectively.

Table 1. The tensile properties of the epoxy polymers

Material	σ_{UTS} (MPa)	E (GPa)
Unmodified epoxy	73.3 ± 1.44	2.62 ± 0.05
Hybrid-modified epoxy	64.4 ± 0.40	2.35 ± 0.06

2.4. Fatigue crack growth testing

The standard 50mm wide compact tension test specimens were machined from the bulk epoxy polymer sheets. All the fatigue crack growth tests were performed in a computer controlled 50 kN servo-hydraulic test machine as per ASTM E647 test standard specifications.²² The crack length was monitored by compliance technique using a COD gage. The fatigue test parameters employed were as follows: stress ratio, $R = \sigma_{\min} / \sigma_{\max} = 0.1$, sinusoidal waveform, frequency = 3 Hz. The failed fatigue fracture surfaces of the test specimens were examined in a high resolution scanning electron microscope fitted with field emission gun (FEG-SEM).

3. Results and Discussion

The fatigue crack growth rate curves determined for both the unmodified and the hybrid-modified epoxy polymers, at a stress ratio, $R = 0.1$ are shown in Fig. 2. The crack growth rate of hybrid epoxy polymer was significantly lower than that of the unmodified epoxy polymer. The threshold stress intensity factor range, ΔK_{th} , of the neat-epoxy polymer was about $0.25 \text{ MPa}\sqrt{\text{m}}$. The addition of micron-rubber and nano-silica particles was observed to increase the ΔK_{th} by about 100% to $0.5 \text{ MPa}\sqrt{\text{m}}$.

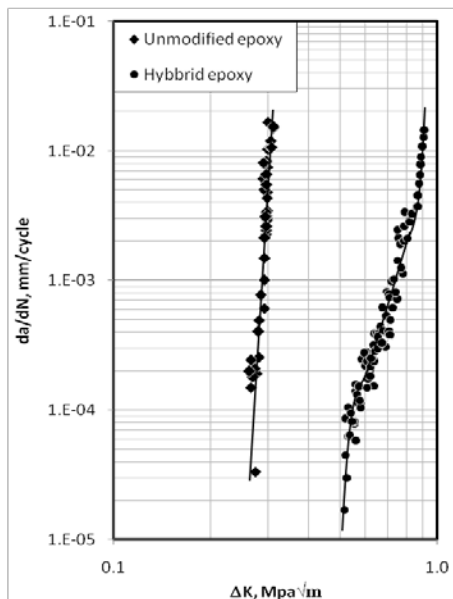
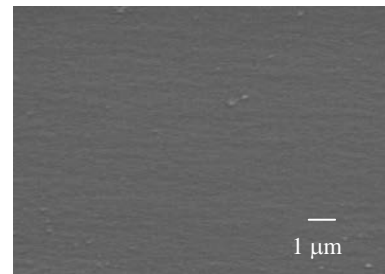
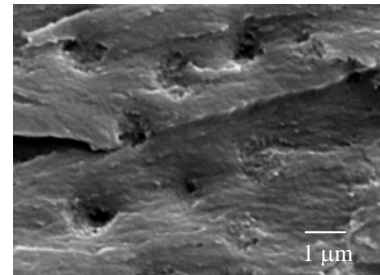


Fig. 2. The fatigue crack growth rate curves determined for unmodified and hybrid modified epoxy polymers

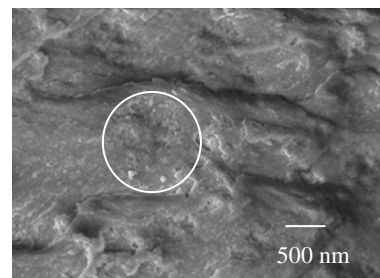
The FEG-SEM images of the fatigue fracture surfaces of both the unmodified and hybrid-modified epoxy polymers are shown in Fig. 3. It can be seen in Fig. 3(a) that unmodified epoxy polymer has a relatively smooth fracture surface and is devoid of any indications of large-scale plastic deformation. However, the hybrid-modified epoxy polymer exhibits a relatively rough fracture surface (Fig. 3(b) and 3(c)). The cavitation of rubber particle is clearly evident in Fig. 3(b) and presence of a cluster of nano-voids is observed in Fig. 3(c). The measured void size was slightly greater than the average diameter of the silica nanoparticle indicating that plastic void growth had occurred during fatigue crack propagation and after the nanoparticles had debonded.



(a) Unmodified epoxy polymer, Approx. $\Delta K = 0.28 \text{ MPa}\sqrt{\text{m}}$



(b) Hybrid epoxy polymer showing rubber particle cavitation, approx. $\Delta K = 0.7 \text{ MPa}\sqrt{\text{m}}$



(c) Hybrid epoxy polymer showing a cluster of voids (encircled) due to debonding of silica nano particles, $\sim \Delta K = 0.7 \text{ MPa}\sqrt{\text{m}}$

Fig. 3. The high resolution scanning electron micrographs of the fatigue fracture surfaces of epoxy polymers (crack growth direction is from left to right).

The toughening micromechanisms in rubber-modified epoxy polymers have been extensively investigated.^{15,18,24-26} Essentially, the cavitation of the rubber particles leads to enhanced plastic-shear deformation of the epoxy polymer via shear banding and void growth in the epoxy. This energy dissipating micro-mechanism has been shown to reduce the crack propagation rate significantly.¹⁸

It has also been observed that the fracture toughness is significantly increased³ and the fatigue crack growth rate is considerably decreased^{5,6} in a silica-nanoparticle modified epoxy polymer. Various toughening micro-mechanisms have been proposed to explain such observations. Rosso *et al.*²⁷ observed that the nano-particles caused a high deflection of the crack growth. Zhang *et al.*²⁸ observed that the nanoparticle induced dimples which might cause energy dissipation. Ma *et al.*⁶ proposed the initiation and development of a thin dilatation zone and nano-voids as the dominant toughening mechanisms. However, Johnsen *et al.*⁵ identified the major toughening micromechanism as arising from the nanoparticle debonding and so enabling subsequent plastic void growth of the epoxy polymer.

From the test results obtained in the present investigation, it is clear that both the micromechanisms of (i) cavitation of the rubber microparticles followed by plastic-deformation and void growth of the epoxy and, (ii) silica nanoparticle debonding followed by plastic-deformation and void growth of the epoxy are operative. These toughening micromechanisms contribute to reduced fatigue crack growth rates observed in the hybrid-epoxy polymer, compared to the neat-epoxy-polymer.

4. Conclusions

Based on the results obtained in this investigation, following conclusions may be drawn:

- The addition of 9 wt.% micron-rubber and 10 wt.% nano-silica particles to a thermosetting epoxy polymer decrease the fatigue crack growth rate and increase the threshold stress intensity factor range, ΔK_{th} , significantly.
- The energy dissipating mechanisms of (i) cavitation of the rubber microparticles followed by plastic-deformation and void growth of the epoxy and (ii) silica nanoparticle debonding followed by plastic-deformation and void growth of the epoxy are operative and contribute

to observed reduction in fatigue crack growth rates.

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