



In situ multiscale analysis of fracture mechanisms in nanocomposites

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ABSTRACT

Toughening mechanisms in hard, metal oxide nanoparticle reinforced epoxy systems were analyzed using a multi-scale approach. Samples on varying scales were fabricated using a shear mixing device and the dispersion of the particles was characterized. On the macro-scale, four-point bend testing showed a maximum of an 80% increase in fracture toughness over neat resin samples for composites with low filler volume percents. Novel testing completed within the chamber of a focused ion beam provided insight into the mechanisms of fracture on the microscale, providing validation of the existence of micro-cracking and crack pinning in the material. Further analysis of the results was coupled with finite element analysis to determine the feasibility of proposed fracture mechanisms, providing insight for the direction of future analysis.

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1. Introduction

Polymer matrix composites (PMCs) have set the standard in specific strength and toughness in the aerospace industry, but as the needs of aerospace structures become more stringent, fiber reinforced composites must be improved. One possible avenue for improvement began with the discovery of the single wall carbon nanotube by Iijima in the early nineties [1]. Iijima's publication in 1990 was credited with the introduction of carbon nanotubes to the research community (though CNT origins may have predated this work [2]), and has led to the development of nanoparticles (particles with one or more characteristic lengths smaller than 100 nm) as reinforcements in composite materials. Carbon nanotubes are quite expensive though; therefore, other lower cost particles including metal oxides, nanoclays, and nanofibers [3–5] have also been used as additives to modify properties of polymers.

PMC reinforcement phases should be able to withstand large stresses and interact with the matrix to transfer the applied loading. The potential in nanocomposite systems is derived from their small size, which limits the number of defects in each particle and increases the interfacial area between particle and matrix. With fewer defects, the particles have higher strength compared to larger particles of the same material. Typically the force of bonding, and consequently the ability to transfer load, is a function of the amount of surface area between the particle and matrix. Nanocomposite systems have very large interfacial contact areas when

properly dispersed (on the order of 500 m²/g for single wall carbon nanotubes) potentially allowing for efficient load transfer.

Although nanoparticles have potential as a sole reinforcement phase within a polymer matrix, cost and complications in manufacturing (particle agglomerations and alignment of non-spherical particles, for example) restrict the extent that nanoparticles can act as such. One possible method of incorporating nanoparticles into the design of functional materials over the short term is dispersal into fiber reinforced composites. Nanoparticles are useful in this scenario because they can infuse between the sub-micron gaps between fibers. Therefore, the goal of this research is to both determine the properties of materials with nanoparticles as a sole reinforcement phase and use materials that can be incorporated into fabrication procedures used to create fiber reinforced composites, specifically vacuum assisted resin transfer molding (VARTM).

A major challenge in understanding the fracture mechanisms of nanocomposite materials is the vast range of scale. In these systems, important phenomena in understanding and modeling material behavior, which must be accounted for, happen over length scales that range 10 orders of magnitude or more. For this reason, new analysis tools and modeling techniques need to be developed and refined to accurately predict material behavior. The current state of the art in modeling nanocomposite systems attempts to account for these interactions using multi-scale modeling, including aspects from finite element analysis and molecular dynamics simulations [6–8]. Multi-scale simulations attempt to piece together the mechanisms at varying scales into a single model that can explain the behavior of the entire system. This paper will use this multi-scale approach through experimentation, by varying the scale of testing using both conventional and newly developed

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techniques to piece together the varying stages of behavior in nanocomposite systems. Finally, the experimentation was compared to different hypotheses using modeling techniques to fill in some of the gaps in experimental observation.

2. Materials and methods

2.1. Materials

The epoxy used in this study was SC-15 supplied by Applied Pleramic, Inc. It was chosen as a typical, low-cost engineering plastic consisting of a two-part liquid system with a low viscosity of 300 cP at room temperature. The low viscosity allows the particles to be added to the system, dispersed, and cured without the use of solvents which, when not completely evaporated, can change the properties of the system. The two phases of the epoxy are a resin mixture of diglycidylether of bisphenol-A with an aliphatic diglycidylether epoxy toughener and a hardener mixture of cycloaliphatic amine and polyoxylalkylamine. SC-15 is also compatible with most composite manufacturing procedures including vacuum assisted resin transfer molding.

The commercially available particles acquired for use in this study were obtained from Nanophase[®]. ZnO particles were chosen as a typical metal oxide particle used in nanocomposite studies, and the low cost and availability make it a viable option for large scale use. The manufacturer estimated the diameter of each batch of particles as 53 nm.

2.2. Fabrication procedure

Initially, the epoxy resin was heated to 75 °C for 30 min. The nanoparticles were then added to the epoxy resin and manually stirred for 10 min inside a plastic mixing cup. The resin/nanoparticle solution was then mixed in a Hauschild mixer at 3000 rpm for 4 min. The hardener (resin:hardener = 10:2.64 wt.%) was then added into the resin/nanoparticle mixture and manually stirred for 5 min. The epoxy/nanoparticle solution was mixed again for 4 min at 3000 rpm. Finally, the mixture was cast in a mold and cured at room temperature for 24 h. The dispersion state of the nanoparticles was characterized previously [9].

2.3. Macroscale testing

Previous studies on the fracture toughness of nanofiller-reinforced composites have shown the ability to increase the fracture toughness of polymers by adding very small filler concentrations [10–18]. The fracture toughness of the particulate reinforced epoxy mixture was determined using a Mini Bionix II MTS testing machine following ASTM Standard E1820, modified to use a four-point bend fixture. A four-point bend fixture was used to eliminate any alignment errors that may cause unwanted shear force within the sample. Samples are prepared for fracture testing after the curing process by machining the exposed surface to size ($L \approx 114.3$ mm, $W \approx 25.4$ mm, $B \approx 12.7$ mm) and an initial crack ($a \approx 11.43$ mm) was created using a band saw. Following that, a razorblade was inserted into the starter crack and gently tapped with a rubber mallet. The crack was then measured using an optical microscope. The specimen was loaded into the load frame and a pre-crack procedure was completed using a sinusoidal waveform with a frequency of 50 Hz at a load of less than 70% of P_{\max} . The crack length was then re-measured and recorded. Fracture tests were completed using displacement control at a rate of 5 mm/min. To determine the critical stress intensity factor of each sample the following linear elastic fracture mechanics (LEFM) formulas were used [19]:

$$K_{IC} = \sigma_{\infty} \times \sqrt{\pi \cdot a} \left(1.12 - 1.39 \left(\frac{a}{W} \right) + 7.3 \left(\frac{a}{W} \right)^2 - 13 \left(\frac{a}{W} \right)^3 + 14 \left(\frac{a}{W} \right)^4 \right) \quad (1)$$

$$\sigma_{\infty} = \frac{3 \cdot P_{\max} \cdot D}{B \cdot W^2} \quad (2)$$

where a , B , W are specimen dimensions defined above, D is the distance between the four-point bend fixtures ($D \approx 25.4$ mm), and P_{\max} is the maximum load the sample sustains prior to failure.

2.4. Microscale testing

One of the challenges of investigating composites with filler size on the order of nanometers is the inability to image the particles during the loading process. Lourie and Wagner [20] were able to fracture very thin, electron transparent polymer films reinforced with carbon nanotubes within the chamber of a transmission electron microscope (TEM) using thermal expansion by heating the polymer with the electron beam. In an effort to eliminate the thermal component of loading used in that study, a novel procedure was developed to observe mechanical deformation and crack growth within a scanning electron microscope. In these experiments the microscope was a FEI dual-beam focused ion beam. A set of cantilevers was milled using the ion beam of the DB235-FIB. The cantilever had a cross section of approximately $5 \mu\text{m} \times 5 \mu\text{m}$, and was $10 \mu\text{m}$ long. The cantilevers were manipulated using an Omniprobe within the chamber of the microscope, producing a mode III crack within the nanocomposite, a schematic of which is shown in Fig. 1. With this technique, multiple theories, namely microcracking and the pinning of cracks between nanoparticles, can be observed experimentally for the first time, providing experimental validation of toughening theories.

3. Results

The results of the fracture testing are shown in Figs. 2 and 3. From the results, one can notice that the material exhibits linear behavior until catastrophic failure. The nonlinearity at small loads can be attributed to local contact. For small loads the local indentation dominates the global deflection of the beam, and the load-indentation behavior was nonlinear similar to Hertzian contact law. One can also note that the specimens fail in a brittle manner indicated by the sudden drop in load. This indicates that the crack propagation was instantaneous, at least in the macroscopic scale.

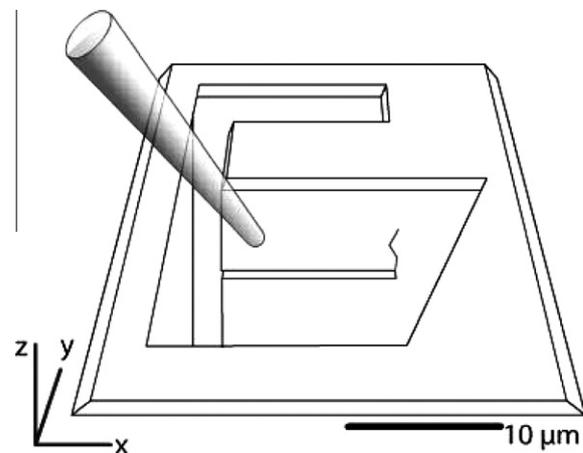


Fig. 1. Schematic of microscale cantilever bending experiment. The probe moves parallel to the upper surface of the cantilever (y -direction).

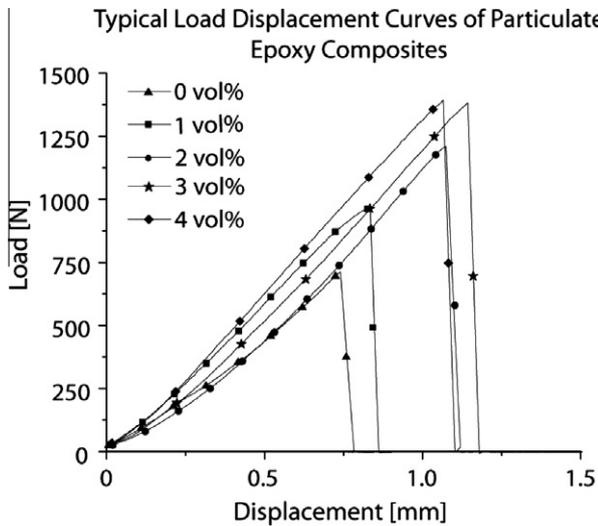


Fig. 2. Typical load displacement curves of nanocomposites.

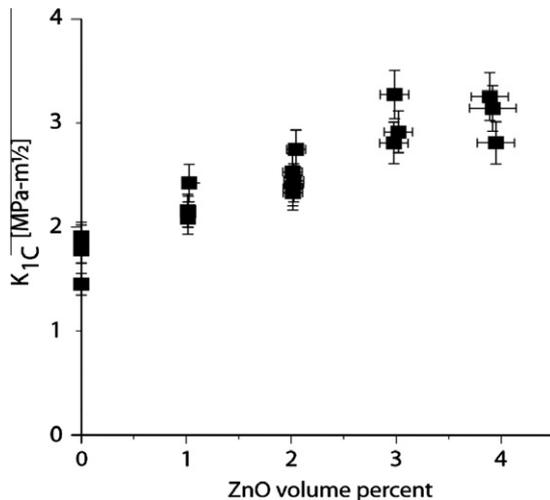


Fig. 3. Results of fracture toughness testing of nanocomposites.

The fracture toughness values calculated, using Eq. (1), for various specimens are plotted in Fig. 3, with the error bars for each test calculated using the law of propagation of uncertainty. There was a monotonic increase in fracture toughness with the volume percentage of particles until 3%, following that the composite seems to reach a plateau between 3% and 4%. The maximum increase in K_{IC} compared to neat resin was about 80%. Another interesting observation from the load–displacement diagram was that the increase in fracture toughness comes from the increase in load to fracture. There was no apparent inelastic behavior similar to yielding in ductile materials prior to ultimate failure. There was a possibility that the process zone ahead of the crack was very small compared to the crack length, and hence there was no significant load drop before failure of the specimen.

The series of images in Figs. 4 and 5 show the results of microscale experiment on a sample with 5 vol.% particles. The formation of microcracks was evident in the images, and through the progression of images the cracks are pinned in many places by particle formations, validating that the crack pinning and microcracking processes are possible in these types of material systems. Additionally, the presence of agglomerated particles within the milled cantilever section should be noted. It appears that the presence of the

agglomerated particles coincide with the larger deviations in the crack path at the microscale, suggesting that these agglomerations have an ability to divert the path of a traveling crack. Particle agglomeration is an important factor in determining the response of the composite and further testing including a wide range of particle dispersions is necessary to quantify these effects. This response was a stark contrast to the unfilled system shown in Fig. 6 where the initial crack quickly propagates through the material and there was no apparent formation of any other cracks on the surface of the composite. It was evident the presence of particle reinforcement results in a more tortuous fracture surface near the crack tip and the cracks tend to both form and terminate near particles.

4. Theory

In an attempt to determine just what mechanical effect that a particle can have on the critical stress intensity factor of an ideal reinforced system, an analysis on a representative particulate reinforced polymer model was conducted using the ABAQUS® software package [21]. A 2D plane stress model was created for the purpose of comparing the stress intensity factor at the tip of a crack in unfilled and multiple configurations of filled polymer systems. The stress intensity factor at the crack tip is measured using both J -integral calculations available in the software package. The simulation used approximately 5000, 8-node quadrilateral elements and the crack tip singularity was modeled using collapsed (triangular) elements with nodes at the quarter point. LEFM was used to determine the stress that should be applied along the boundaries of the model to simulate a specific loading state. The applied stresses on the boundary nodes, shown in Fig. 7, are defined by the following equations [19]:

$$\sigma_{xx} = \frac{K_I}{\sqrt{2\pi r}} \cos\left(\frac{\theta}{2}\right) \left[1 - \sin\left(\frac{\theta}{2}\right) \sin\left(\frac{3\theta}{2}\right)\right] \quad (3)$$

$$\sigma_{yy} = \frac{K_I}{\sqrt{2\pi r}} \cos\left(\frac{\theta}{2}\right) \left[1 + \sin\left(\frac{\theta}{2}\right) \sin\left(\frac{3\theta}{2}\right)\right] \quad (4)$$

$$\tau_{xy} = \frac{K_I}{\sqrt{2\pi r}} \cos\left(\frac{\theta}{2}\right) \sin\left(\frac{\theta}{2}\right) \sin\left(\frac{3\theta}{2}\right) \quad (5)$$

K_I is the applied stress intensity factor, a value of which is arbitrarily set to $1 \text{ MPa m}^{1/2}$. The symbols θ and r designate polar coordinates from the crack tip location.

Initially the model was verified by applying the boundary conditions that correspond to the given K_I to an unfilled system, and comparing the calculated stress intensity factor to the applied value. Using the J -integral approach, the model was able to accurately calculate the applied stress intensity factor within an acceptable 0.1% margin of error. After this calibration, the model was populated with multiple configurations of particles by creating sections within the model with the material properties of the nanoparticles ($E = 50 \text{ GPa}$, $\nu = 0.3$). The interface between the matrix and polymer was assumed to be perfect and all loads are restricted to be within the limits of the elastic region of deformation.

After testing multiple particle configurations, two interesting cases stood out; a single particle of varying size placed at a varying distance from the crack tip, and a random configuration of particles with constant volume percent and diameter. A parametric study was completed for both cases where the particle diameter varied from 25 to 75 μm and the distance from the crack tip ranged from 10 to 50 μm for the single particle simulations. It should be noted that the size of the particles in these simulations are much larger than that of the experiments. This was necessary because of the loading conditions used in Eqs. (3)–(5) which are only valid when outside the range of the crack singularity.

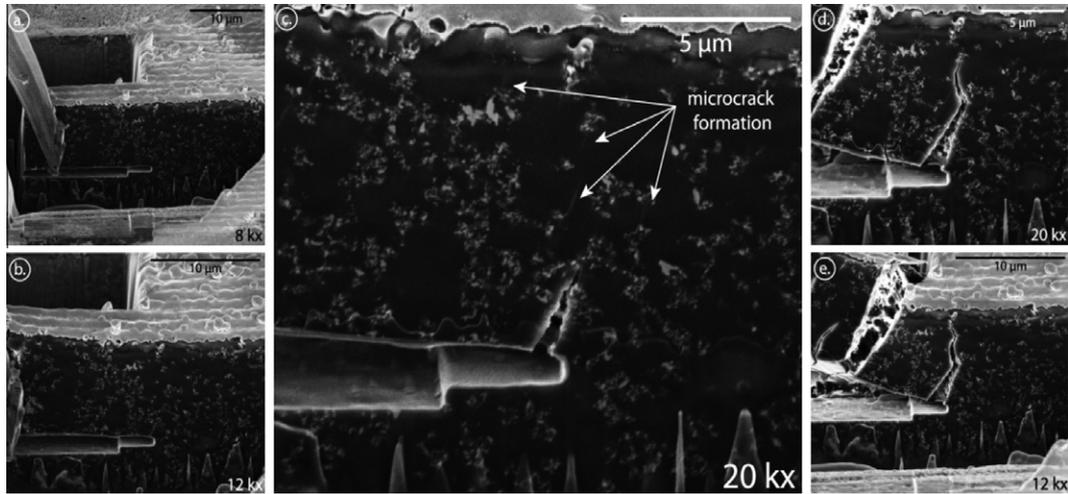


Fig. 4. FIB images of 5 vol.% ZnO/SC-15 10 μm cantilever beam.

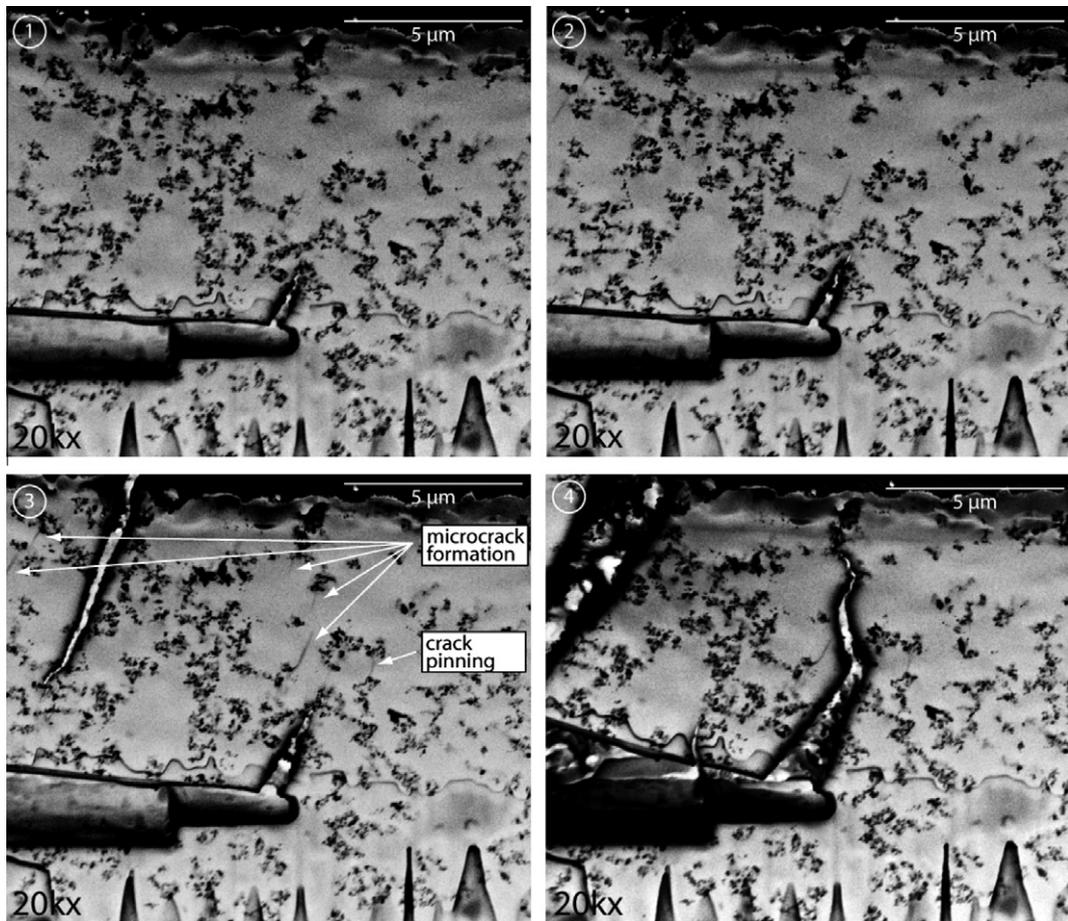


Fig. 5. High magnification images of 10 μm cantilever with inverted color scheme. The inverted color scheme allows for improved imaging of microcracks and crack pinning.

The simulations indicated that a single particle placed directly in front of the crack path can drastically reduce the stress intensity factor at the crack tip, shown in Fig. 8, and the larger the particle and the closer to the crack tip the larger the decrease. The results for multiple random particle fields of a specific particle diameter at a single volume percent are shown in Fig. 9. These results are interesting because the same average increase was seen for varying particle sizes suggesting a strong dependence on percent of filler, but the increase is much lower than that of the experimental data.

Results suggest that the field of particles can influence the stress intensity factor at the crack tip, and that the smaller the particle the more repeatable the increase.

5. Discussion

Macroscale experimentation shows that the mechanism for improving toughness in particulate reinforced composites reduces

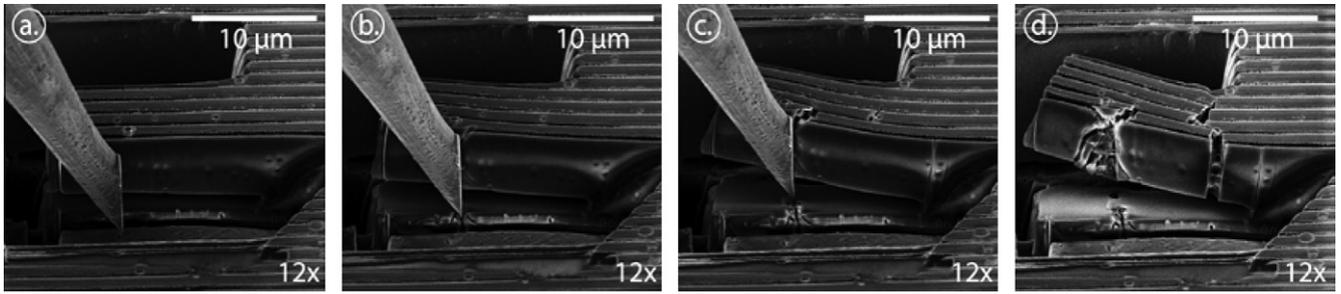


Fig. 6. SEM images of unfilled 10 μm cantilever beam.

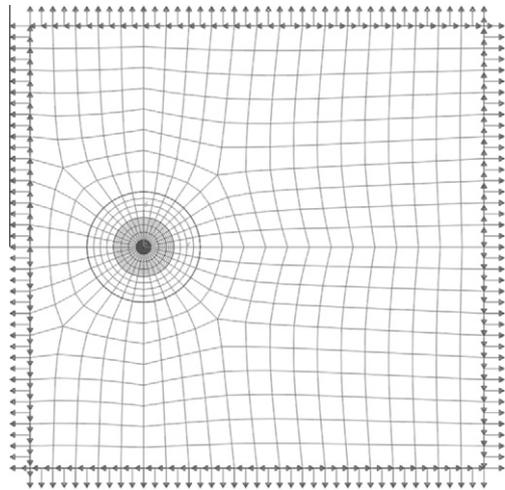


Fig. 7. Finite element mesh and boundary conditions for an unfilled system.

the stress intensity factor at the crack tip and prevents the crack from initial unstable propagation. The formation of microcracks within the region very near the crack tip is one possible avenue to for increase energy dissipation. Cracks in a material generally create stress concentrations and reduce the toughness of a material, although the presence of very small cracks can actually increase the toughness in certain circumstances. This mechanism is dependent on the microcracks absorbing energy during their propagation, but eventually additional propagation must be prevented

somehow (in this case a nanoparticle). If unstable crack growth can be prevented, the load bearing capability of the material will increase, therefore increasing the critical stress intensity factor. A summary of the previous work discussing microcracking in nanocomposites has shown that the mechanism is a distinct possibility [22]. The microscale experiments in this study go a step further validating with experimentation that nanoparticles can be an effective barrier against crack growth assuming that there is a functional interface between the particle and matrix. Microcrack formation happens in a very small region in front of the crack tip, allowing for an increase in the maximum sustainable load, a mechanism that fits with earlier macroscale experimental observations. Furthermore, the images show some agglomerating of the nanoparticles into larger micron sized regions. In a mechanistic sense, it is unclear exactly what quantitative effect that more uniformly spaced particles may have on the bulk composite properties, though simulation has shown that reduced spacing between particles can improve the resistance to fracture of the composite. In contrast, if particle spacing is reduced to the point of interparticle contact, a region of highly reduced interfacial strength can develop causing high stress concentration and ultimately reduced fracture toughness. Additionally, particle agglomeration can provide reduced spacing between the crack and particle in localized regions, but it also provides regions of very large inter-particle spacing, potentially causing variations in response from sample to sample. A more uniform spacing between particles can reduce the inter-particle spacing in a global sense and provide more predictable response, but it is uncertain if the same mechanisms would dominate the fracture of that composite. As particle dispersion techniques improve, tailored designs of nanocomposites, for

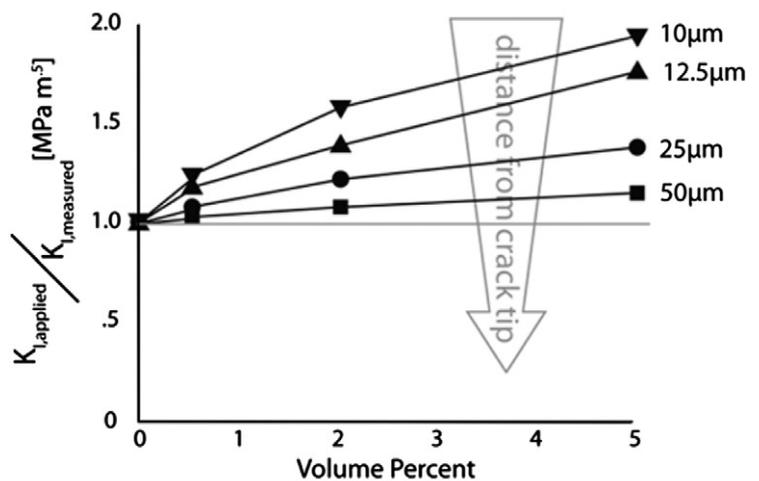
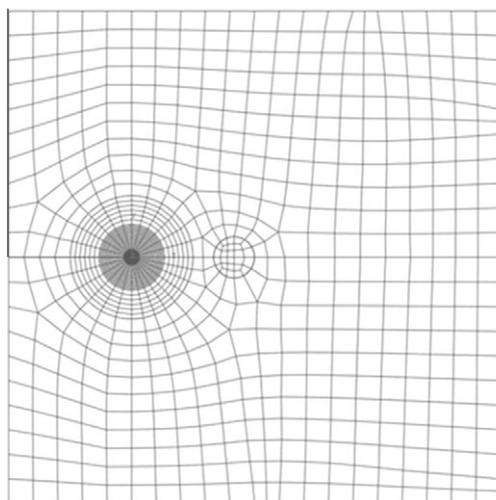


Fig. 8. Results of FEA experiments for a single particle in front of the crack. Each line corresponds to a distance the particle was placed from the crack tip.

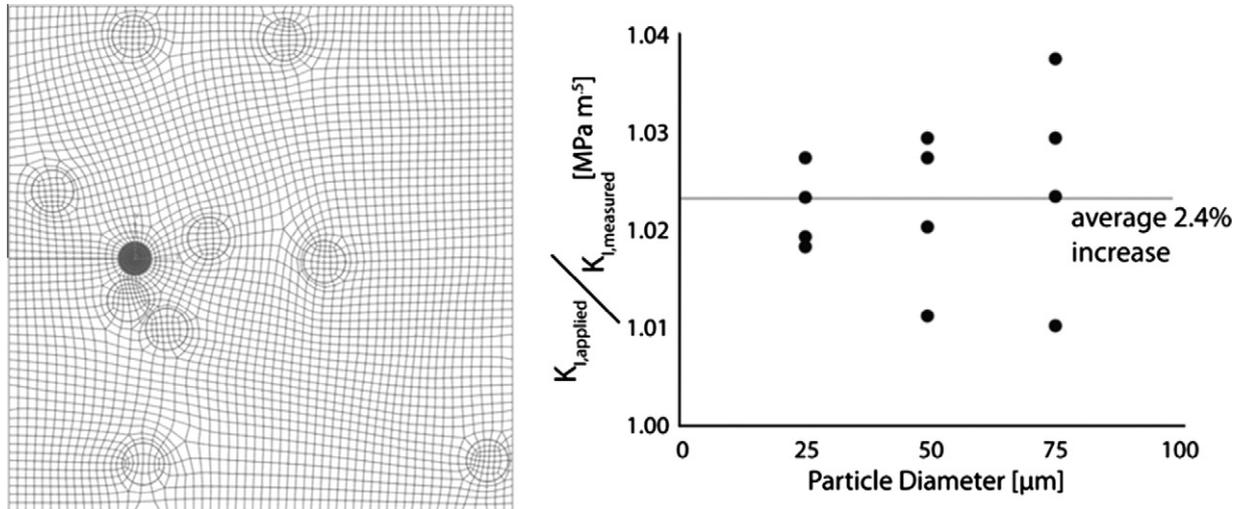


Fig. 9. Finite element mesh and the results for simulations on random particle fields.

instance the grading of particles into regions where fracture is expected, may provide improved performance and microscale experimentation can and should be an invaluable tool to compare and describe material response.

The results of the experimentation and finite element analysis suggest that crack shielding can be a mechanism for toughening, but the method must be refined in order to explain the experimental results. The hypothesis states that the load on the bulk material is transferred to the particles around the crack tip, reducing the actual stress intensity factor at the crack tip. The externally applied load must then be increased for the material to fail, increasing the apparent toughness of the material. FEA results validate that the presence of particles can reduce the apparent stress intensity factor observed very near the crack tip, but results drastically under predict the total increase in toughness, suggesting that a combination of mechanisms is certainly at play. Future work should look to include these combinatory effect and include a move away from linear elastic techniques, looking into other inelastic deformations of the polymer in the crack tip region.

6. Conclusions

A fabrication procedure for nanoparticle reinforced epoxy was developed that is compatible with many of the composite manufacturing techniques used today, specifically vacuum assisted resin transfer molding (VARTM). The addition of nanoparticles into the polymer system provided a repeatable, predictable increase in fracture toughness over multiple loading percentages. The fracture toughness of epoxy increased up to 80% in composites with four volume percent of filler added over the neat resin system. The increase in fracture toughness can be attributed to an increase in maximum load the material can sustain prior to failure, as well as a process zone near the crack tip that displays a more complex region of fracture than that of the neat resin. Multi-scale experimentation was done using an MTS load frame and a Focused Ion Beam electron microscope and hypotheses of the toughening mechanisms of particle addition were examined. Microscale experimentation validated the existence of microcracking and crack pinning in the material system and finite element analysis determined that the stress intensity factor in the region very close to the crack tip can be reduced by the addition of particles. Further analysis is needed to accurately quantify the effects of both crack shielding and microcracking within the composite and the analysis should include non-linear behavior in the crack tip region.

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