

Design and Development of New Nano-Reinforced Bonds and Interfaces

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ABSTRACT

This investigation focuses on the design and development of nano-reinforced adhesively-bonded high performance joints. The influence of homogeneous dispersion of carbon nanotubes and alumina nanoparticles on the cohesive strength, interfacial properties and mechanical behaviour of epoxy adhesives is examined. Mechanical tests and optical measurements are conducted, using carbon fibre/epoxy laminate and aluminium alloy adherends with high performance epoxy adhesives, to evaluate the optimum weight percentage of the nanofillers to be added to induce maximum enhancement in strength and strain energy release rate. The results reveal that the introduction of nanofillers into the epoxy adhesive leads to a dramatic improvement in the debonding and shear strength of the interface without sacrificing its toughness. The presence of nanoparticles plays a major role in determining the fracture toughness of the interface and is typically associated with a significant improvement in the delamination resistance of the joint.

Keywords: nano-reinforced interfaces; carbon nanotubes; alumina nanopowder.

1. INTRODUCTION

Nanomaterials possess high strength and hardness, and excellent ductility and toughness. Undoubtedly, more attention is being paid to the applications of nanomaterials nowadays. Recent works ([1]-[4]) show that the bulk properties of materials can be improved by adding nanoparticles. Gadakaree [5] improved the mechanical properties of fibre-reinforced composites by improving the toughness of the glass matrix with micro-scale particle fillers. Liu and Xu [6] et al. studied the influence of the addition of nano TiN on TiC grains and showed that a wide distribution of nano TiN at the interface of TiC/TiC grains leads to improvement of mechanical properties when the nano additions are below 6 wt.%. Ramanan Krishnamoorti [7] studied the shear properties of polymer-layered silicate nano composites. Sklep [8] successfully prepared a series of

polymer/clay nano composites with the layered silicate clays as the inorganic dispersed phase via intercalation polymerisation. Young and Wang ([9]-[10]) also studied the effect of filler particles in rigid reinforced resin composite systems and observed the toughness improvement. The influence of nanofillers on interfacial properties and bonding region in two-phase materials is not well understood [11]. The authors are unaware of any work that deals with the change in fracture toughness and energy release rate of composite interfaces as a result of dispersing nanoparticles into epoxy adhesives.

The work described herein is devoted to the characterization of the tensile and shear properties, fracture toughness and energy release rate of adhesively bonded interfaces reinforced by nanoparticles. SEM and TEM were also used to elucidate some of the findings.

2. EXPERIMENTAL DESCRIPTION

2.1 Materials and Sample Preparation

Unidirectional carbon fabric (G1157/EFP 100) provided by Hexcel Fabrics was formed into laminate for one of the substrates by autoclave. The carbon fabric has a nominal weight per unit area of 290 g/m², and its laminate has a fibre volume fraction of 55 %. The respective ultimate tensile, compressive and shear strength of the laminate are 1200 MPa, 155 MPa, and 57 MPa. The tensile moduli E_{11} = 180 GPa and E_{22} = 12 GPa, shear moduli G_{12} = G_{13} = 28 GPa, and Poisson's ratio = 0.263. Aluminium 6061-T6 is used as another substrate, and is chosen for its excellent joining characteristics, good acceptance of coatings, and a good combination of relatively high strength, good workability and high corrosion resistance. It has tensile yield strength of 275 MPa, and an elastic modulus of 69 GPa.

A two-component paste epoxy adhesive (Dexter Hysol EA 9330) is used in this study. This adhesive system possesses high peel strength and excellent environmental resistance, and bonds to a variety of substrates.

Nanofillers

Single-walled carbon nanotubes (SWNTs) were used as fillers in the epoxy adhesive, and they are synthesized by

the electric arc technique. Fig. 1 shows the SEM image of a single wall carbon nanotubes. It can be seen that the nanotubes have diameters between 30-60 nm and are a few hundred nanometers long.

Another filler is alumina nanofibre powder, which is approximately 2-4 nm in diameter and a few hundred nanometers in length. The surface area of the alumina nanopowder ranges from 300-700 square meters per gram. Fig. 2 shows TEM images of the fibre powder. As can be seen, they are agglomerated in the longitudinal direction. It can also be seen that the alumina nanofibres have aspect ratios greater than 20 and many of the fibres appear to be hundreds of nanometers long.

Preparation of adherends

The two dissimilar aluminium and carbon fibre adherends were machined from their respective sheets. The carbon fibre reinforced laminates were fabricated by autoclave at specified pressure and temperature. The surface was sand-blasted, cleaned by chemical solvent and dried before bonding. Carbon nanotubes and alumina nanopowders were respectively dispersed into the above-mentioned epoxy adhesive. The dispersion was carried out by stirring the mixture for 30 minutes at 50°C, and then adding and blending the remaining components of the adhesive. This ensured the homogeneous dispersion of the nanofillers into the adhesive. Fig. 3 shows typical micrographs of the epoxy resin with uniformly dispersed carbon nanotubes; the weight concentration in these two cases was 2.5%. Additional nano mixtures with nanofillers at nominal weight percentages of 1.5%, 5%, 7.5%, 10%, 12.5% and 15% were also prepared. The substrates were then bonded together and carefully cured at a controlled room temperature for 7 days.

2.2 Details of Testing

ASTM standard 4541-95 was adhered to during mechanical testing. The tests were carried out using an electro-hydraulic servo-controlled machine at a crosshead speed of 1.0 mm/min. It is worth noting that the load co-axiality was ensured using special crosshead adapters and strain gauged samples. Single-lap tests were carried out as per the ASTM D3162-92 standard.

Double Cantilever Beam (DCB) specimens were used to characterise Mode I interfacial strain energy release rate G and fracture toughness G_{IC} . The specimen contains a non-adhesive polytetrafluoroethylene insert on the interfacial plane, which serves as a delamination initiator. Opening forces are applied to the DCB by means of upper and lower spherical joints bonded to one end of the specimen. The tests were conducted under displacement control on an Instron universal testing. Cross head motion was set at 0.50 mm/min. The specimens are 135 mm long and 25 mm wide, and the test procedure followed ASTM D5528-94a. During the test, a curve of the applied load versus opening displacement is recorded and instantaneous delamination front locations are marked on the chart at different intervals

of delamination growth. Modified Beam Theory (MBT) was used to calculate the energy release rate, such that G_I :

$$G_I = 3P\delta / [2b(a + \Delta)] \quad (1)$$

Where: P is load, δ is load point displacement, b is specimen width, a is delamination length and Δ is a correction factor for rotation at the delamination front, determined experimentally by generating a least squares plot of the cube root of compliance.

3. RESULTS AND DISCUSSIONS

Tensile and shear specimen

Testing results are recorded and compared for three cases: EANP (Epoxy Adhesive with alumina nanopowder), EANT (Epoxy Adhesive with carbon nanotube) and EA (Epoxy Adhesive). Figs. 4(a) and 4(b) show the improvement in Young's modulus and ultimate tensile strength for the cases involving different weight fractions of homogeneously dispersed nanofillers. The increase continues with the increasing weight percentage of the nanofillers, up to a limit of 10%, above which the properties degrade to below those of the EA. These results indicate the sensitivity of the epoxy to the concentration of the dispersed nanofillers.

Fig. 4(c) shows the resulting shear strength for the cases involving different concentrations of dispersed alumina nanopowders and carbon nanotubes. Analogous to the tensile tests, the results also reveal the sensitivity of the shear properties to the concentration of the nanofillers. An increase in the weight fraction of the nanofillers beyond 7-8% results in a reduction in the shear properties of the adhesive.

Energy release rate

Fig. 5(a) shows the energy release rate for the three different cases examined: EA, EANT (2.5% of nanotubes) and EANP (2.5% nanopowder). Compared with bonds containing nanofillers (EANT and EANP), the energy release rate of a joint composed solely of epoxy adhesive (EA) has lower values for G_I for the same delamination length. For nano-reinforced interfaces, the energy release rate G_I is higher, and the improvement is quite significant after the delamination length reaches 75mm. The energy release rate for the carbon nanotube case is on average 16% higher than that of corresponding to pure epoxy adhesive, at a delamination length of 95mm. The interfaces reinforced by alumina nanopowder show even better results at this delamination length, with a 34% improvement in G_I over the unreinforced case.

Effect of weight percentage of nanofillers on G_{IC}

Fig. 5(b) shows the normalised energy release rate G_{IC} for different weight fractions of homogeneously dispersed nanofillers for DCB specimens bonded with prepreg glass reinforced laminate and aluminium sheet. The energy release rates show significant improvement with increasing weight percentage of nanofillers and achieve the best improvement when the weight percentage of fillers is

between 2-5%. However, for percentages above 10%, the properties degrade to below the EA, indicative of the sensitivity of the epoxy adhesive to the concentration of the dispersed nanofillers. The use of alumina nanopowder appears generally more beneficial than the use of nanotubes in the reinforcement of interfaces.

It is worth noting that at a given weight percentage, the presence of nanoparticles plays a major role in determining the strength and toughness of the interface. The phenomenon can be explained as follows: The nanofillers are characterized by large surface areas per unit gram. As the number of adhesively joined sites increase, the cohesive strength of the epoxy increases leading to a higher mechanical strength of the interface. The experimental results show that there is a limit to the number of dispersed nanofillers beyond which a drop in the properties is observed. Once the nanoparticles fully fill the gaps and porosities and all contact points are established, the additional particles cannot interact effectively within the epoxy adhesive and consequently poor matrix infiltration occurs. It is also believed that agglomeration of the nanoparticles may act as failure initiation sites, which results in lowering the strength and toughness of the adhesive.

4. CONCLUSIONS

The influence of the nanofillers in a special epoxy adhesive for the purpose of increasing bond strength and toughness is studied. Two different types of nanofillers were used: carbon nanotubes and alumina nanopowder. The work concentrated on the experimental determination of the tensile, shear and delamination properties of the nano-reinforced interface. The results reveal that at a given weight percent, the presence of nanoparticles plays a major role in determining the strength of the interface. This is attributed to the large surface area and the consequent interlocking of the nanofillers with the epoxy adhesive. Experimental results also show that there is a limit to the number of dispersed nanofillers beyond which a drop in the properties is observed.

REFERENCES:

- [1] Niihara K., and Nkahir A., *Advanced Structural Inorganic Composites*, Elsevier Scientific Publishing Co. Trieste, Italy, 1990.
- [2] Zhang Z., and Cui Z., *Nanotechnology and Nanomaterials*, Defence Technology Press. Beijing, 2001.
- [3] Kim J.K., and Mai Y.W., *Engineered Interfaces in Fibre Reinforced Composites*, Chapter 7. New York, Elsevier, 1998.
- [4] Hodzic A., Kalyanasundaram S., Lowe A.E., Stachurski Z.H., *Composite Interfaces*, 4, 375, 1991.
- [5] Gadakaree K.P., *J. Mater. Sci.* 27, 3827, 1992.
- [6] Liu N., Xu Y.D., Li H., Li G.h. and Zhang L.D., *Journal of the European Ceramic Society*, 22, 2409-2414, 2002.

- [7] Krishnamoorti R., Vaia R.A., and Giannelis E.P., *Chem. Mater.* 8, 1728-1734, 1996.
- [8] Sklep, *Advanced polymer/clay nanocomposites*, report of state key laboratory of engineering plastics, Chinese Academy of Sciences, 2000.
- [9] Spanoudakis J, and Young RJ, *Journal of Materials Science*, 19, 473-486, 1984.
- [10] Wang S.Z, Sabit A. and Bor Z. J, *Composites Part B: Engineering*, 28, 215-231, 1997.
- [11] Hodzic A., Stachurski Z.H., Kim J.K., *Polymer*, 41, 6895-6905, 2000.

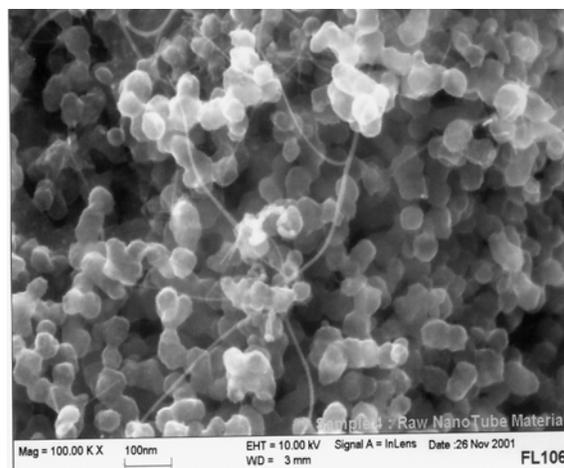


Fig. 1 SEM images of single wall carbon nanotubes

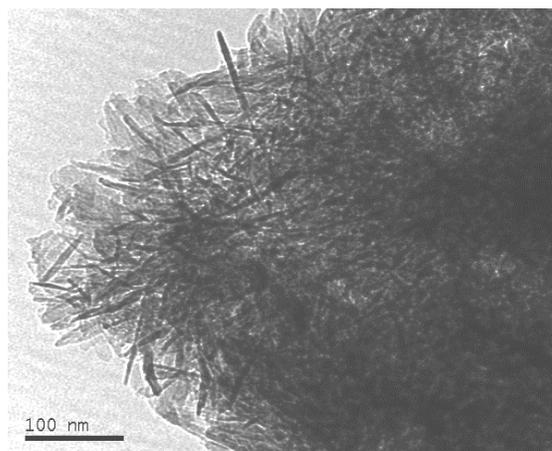


Fig. 2 TEM micrographs of alumina nanofibre powder

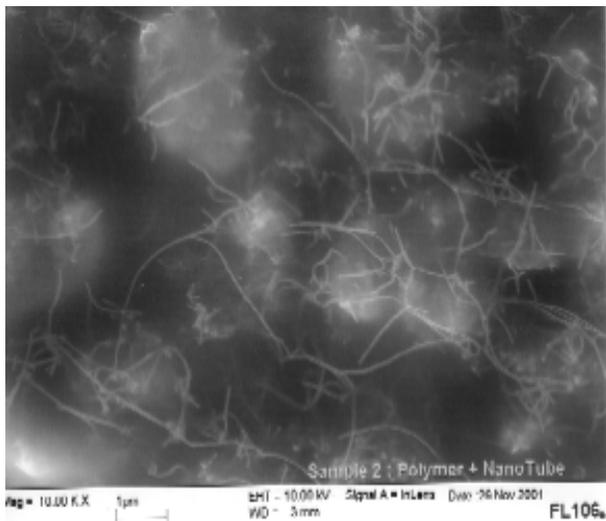


Fig. 3 SEM image of carbon nanotubes dispersed into epoxy adhesive

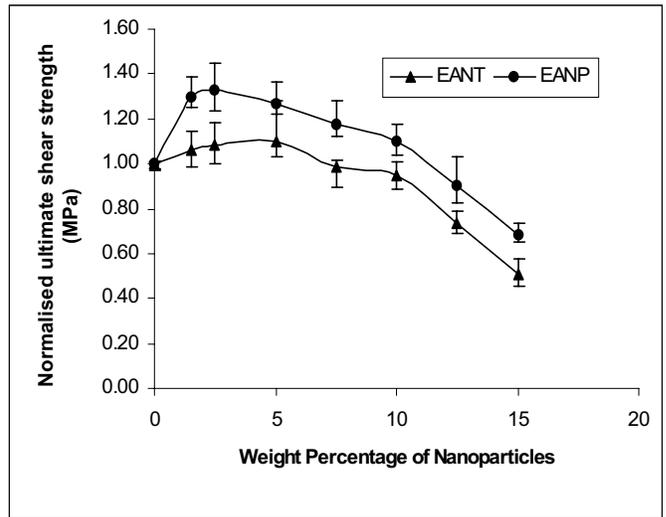


Fig. 4(c) Normalized ultimate shear strength for different weight fractions of nanofillers.

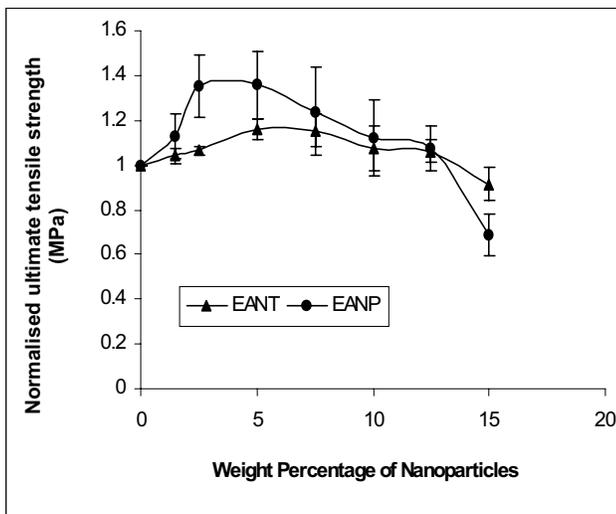


Fig. 4(a) Normalized ultimate tensile strength for different weight fractions of nanofillers.

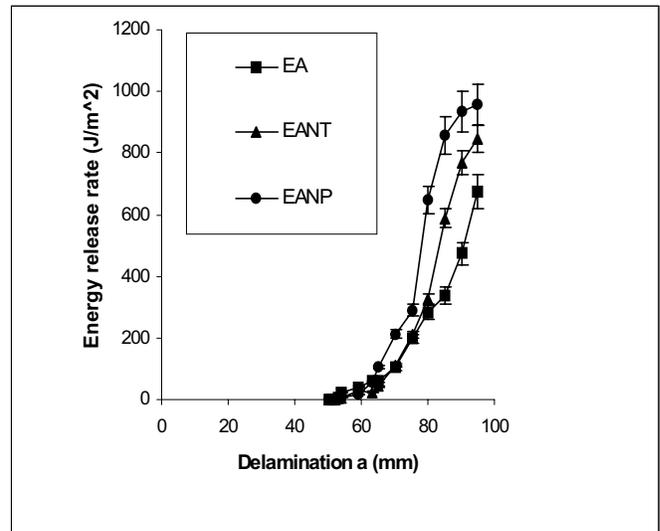


Fig. 5(a) Energy release rate vs. delamination

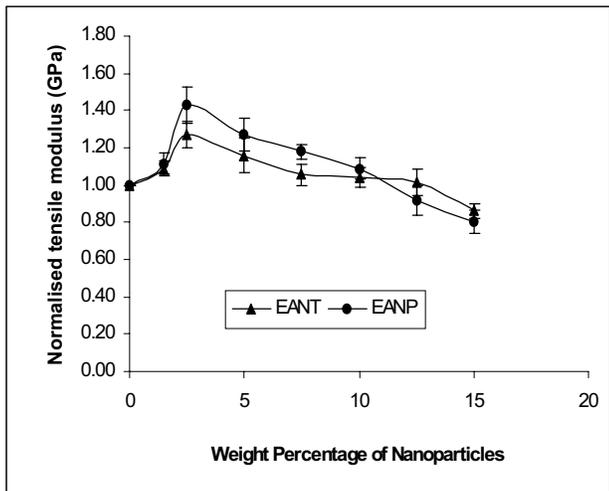


Fig. 4(b) Normalized tensile modulus for different weight fractions of nanofillers.

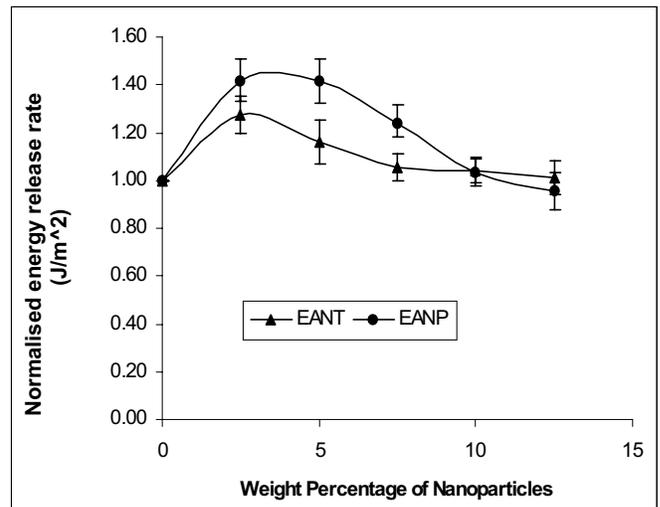


Fig. 5(b) Normalized energy release rate for different weight fractions of nanofillers.