

Wedge Test of Carbon-Nanotube-Reinforced Epoxy Adhesive Joints

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ABSTRACT: Epoxy adhesives reinforced with carbon nanotubes (CNTs) were developed. The distribution of the CNTs in the epoxy matrix was observed with transmission electron microscopy. Joints were formed by unclad 2024-T3 aluminum adherents bonded with the CNT-filled epoxy adhesives. The durability of the joints was studied with a wedge test under water at 60°C. The addition of CNTs to the epoxy greatly improved the adhesive joint durability. The initial crack length of the joint with 1 wt % CNTs, which was obtained before the wedge specimen was put into water, was only about 7% of that with neat epoxy. After immersion of the specimens in 60°C water, the joint with neat epoxy failed after 3 h, but all of the joints adhered with different fractions of CNTs were still bound together after the experimental time of

90 h. The significant enhancement by CNTs of the adhesive joint durability was mainly attributed to the high mechanical properties of the CNTs and their ability to resist water. Nevertheless, the experimental results also reveal that the durability of the joints showed an optimum value at approximately 1 wt % CNTs, beyond which a decrease in the property was observed. In addition, the failure mechanism of the joints was also investigated in terms of interfacial failure and cohesive failure. Cohesive dominated failure was found for the joint bonded with 1 wt % CNT-filled epoxy. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 2957–2962, 2009

Key words: adhesion; adhesives; composites; nanocomposites

INTRODUCTION

Polymer adhesive bonding has been widely used in aerospace, automotive, transport, packaging, and other industries because of the high strength-to-weight ratio and low cost of the polymer adhesives.^{1,2} In aerospace, these adhesives have been used to manufacture primary aircraft fuselage and wing structures. As such, polymer adhesive bonding is a competitive process for riveted structures although it is still not dominant. Compared to riveted joining, the use of polymer adhesives results in a more uniform distribution of stresses over the continuous bonded area. However, the durability of the bonded components is one of the major concerns. It is widely believed that polymer adhesives usually suffer from poor mechanical strength and poor adhesion, especially on metal substrates.¹ Additionally, polymer adhesives, such as epoxy adhesives, absorb water easily when they are continually exposed to humid conditions.^{3,4} The absorbed water may degrade the adhesive joints by (1) inducing plasticization and/or hydrolysis of the adhesives, (2) inducing

stresses in the adhesive/adherent interface, and (3) causing the formation of hydrates on the metal adherent.⁵

Many technologies have been used to increase the bond strength between metal substrates and polymer adhesives, including the modification of the metal substrates by chemical (sol-gels), electrochemical (phosphoric acid anodization), and mechanical (abrasion) methods.^{6–9} In this study, an alternative technology was used to improve the joint bond strength. In this approach, the polymer adhesive instead of the metal substrate was modified by the addition of carbon nanotubes (CNTs).

CNTs are a new form of carbon; they consist of rolled up graphene sheets that form long concentric cylinders. Generally, there are two types of CNTs, single-walled CNTs and multiwalled CNTs. Single-walled CNTs consist of a single atomic layer, and multiwalled CNTs consist of several atomic layers. Both types of CNTs have the combination of high aspect ratio, small size, high conductivity, high strength, high stiffness, and low density. CNTs are considered the ultimate reinforcement in polymers, and their nanocomposites have attracted tremendous attention in both the industrial and academic worlds since they were discovered in 1990.¹⁰ CNTs can greatly improve

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the electrical, thermal, and mechanical properties of polymers at very low loading levels, which results in a significant reduction in the weight of the nanocomposites. For example, Khare and Bose¹¹ reported that the elastic modulus of epoxy was increased by 20% with less than 2 wt % CNTs (with respect to the mass of resin). Wang et al.¹² also reported that the elastic modulus of epoxy composite was increased by about 25% with only 0.5 wt % loading of CNTs.

In this study, CNT-reinforced epoxy adhesives were prepared. The distribution of the CNTs in the polymer matrix, which is crucial to the improvement of the adhesive properties, was studied. The durability of the adhesive-bonded aluminum alloy joints was determined with a Boeing wedge test subjected to humid conditions.^{13,14} The effect of the CNT fraction on the durability and failure mode of the joints was investigated systematically.

EXPERIMENTAL

Materials

Epoxy based on a blend of bisphenol A resin and bisphenol F resin (EPIKOTE 240, Hexion Specialty Chemicals) [Columbus, OH] was used as the polymer adhesive matrix. An aliphatic amine (EPI-KURE 3274, Hexion Specialty Chemicals) was used as a curing agent for the epoxy. Multiwall CNTs, purchased from Chinese Nanofiller Co. (Beijing), were used as nanofillers for the epoxy adhesive. They were generated by chemical vapor deposition with a purity of 92%.

Unclad 2024-T3 aluminum alloy with an aluminum fraction of 90.7–94.7% was used as a metal substrate for the adhesive joints. This alloy had good mechanical properties with an ultimate tensile strength of 448 MPa, a tensile yield strength of 310 MPa, and an elastic modulus of 73.1 GPa.¹⁵ 2024-T3 aluminum alloy has commonly been used in the aerospace industry; the unclad aluminum alloy was selected here to simulate aircraft components that may have been heavily abraded.

Before application of the adhesives, the metal surface was pretreated with degreasing and alternating-current (ac) and direct-current (dc) anodization. ac anodization was conducted in an electrolyte consisting of diluted phosphoric acid and sulfuric acid; it produced a thin and porous oxide layer that was electrochemically stable and hydration resistant on the surface of the metal. The further dc anodizing, conducted in the same electrolyte, produced a thick barrier oxide layer capable of offering corrosion protection to the base metal. The pretreated metal surface would promote bonding strength, as compared to the untreated surface.¹⁶

Preparation of CNT-reinforced epoxy adhesives

There were two steps in the preparation of the CNT-filled epoxy adhesives. In the first step, the proportional CNTs were added to the curing agent of EPI-KURE 3274. EPI-KURE 3274 had a much lower viscosity than the EPIKOTE 240 resin; thus, it could facilitate the dispersion of the CNTs. The mixture was mechanically stirred at 1500 rpm for about 1 h at room temperature; then, it was ultrasonicated for a further 30 min for better dispersion of the CNTs. The mixer used was a D10/CV2-01 dispermat mixer [Plasmost (S) Enterprise] (BYK-Gardner GmbH, Germany). The ultrasonication was conducted in a Sonicor ultrasound bath. In the second step, the EPIKOTE 240 resin was added to the mixture obtained in the first step. The weight ratio of the epoxy resin and curing agent was about 5 : 3. Again, the mixture formed was subjected to mechanical mixing at 1500 rpm for 30 min, followed by ultrasonication for another 30 min. An ice bath was used during ultrasonication to reduce temperature and prevent early curing of the mixture. After ultrasonication, the mixture was put into a vacuum oven for about 30 min to remove bubbles trapped in the mixture during stirring. Epoxy adhesives with CNT fractions of 0, 0.5, 1, 2, 3.5, and 5 wt % (with respect to the mass of resin and curing agent) were prepared.

Fabrication of adhesive joints with the aluminum alloy

Joints were formed by unclad 2024-T3 aluminum adherents bonded with the CNT-filled epoxy adhesives. The dimensions of the aluminum substrates were 150 mm (length) × 25 mm (width) × 3.2 mm (thickness). The adhesives were applied on the immediately pretreated metal surfaces with a draw-down block to control the thickness of the adhesives. The drawdown block was designed and fabricated to be able to produce a coating thickness of 0.25 mm. First, the adhesive was applied uniformly on one piece of the metal surface, it was then bonded carefully to another piece of uncoated substrate. No pressure was used in the joint fabrication. The two bonded pieces of the aluminum alloy formed a specimen for the wedge test. The specimen was cured at room temperature for 16 h and further postcured in a vacuum oven at 100°C for 12 h.

Characterization

The microstructure of the CNTs was observed with field emission scanning electron microscopy (FESEM; Jeol JSM 6340F) [Tokyo, Japan]. The dispersion of the CNTs in the epoxy matrix was studied by transmission electron microscopy (TEM; Philips CM300) [Eindhoven, The Netherlands].

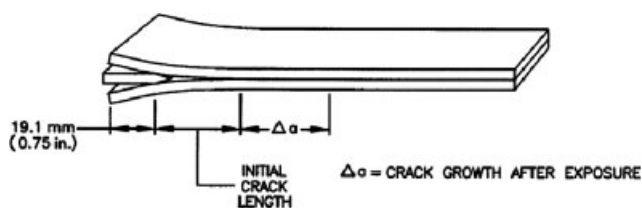


Figure 1 Configuration of the wedge-tested specimen.¹³

The wedge test was performed in accordance with ASTM D-3762¹³ and Boeing wedge test.¹⁴ The specimen was about $150 \times 25 \times 6.4 \text{ mm}^3$ in dimension, and the wedge was about $25 \times 25 \times 3.2 \text{ mm}$ in dimension. In the test, the wedge was first forced into the bondline of the flat-bonded aluminum specimen with a Hounsfield tensometer [Nottingham, UK] under a constant load and speed; tensile stress was thereby created in the region of the resulting crack tip. The configuration of the specimen with the wedge is shown in Figure 1.¹³ The initial crack length, resulting from the insertion of the wedge, was recorded after the specimen was equilibrated at ambient conditions for several hours. After that, the specimen was put into 60°C water, and the crack length development was measured for a period of up to 90 h to establish the relative bond durability performance in a humid environment. Aluminum joints with 0, 0.5, 1, 2, 3.5, and 5 wt % CNT-reinforced epoxy were wedge-tested. For each joint, three testing pieces were fabricated and tested under the same conditions.

The microstructures of the failure surface of the wedge-tested specimens were investigated with scanning electron microscope (Zeiss EVO 50) [Carl Zeiss NTS GmbH, Oberkochen, Germany].

RESULTS AND DISCUSSION

Microstructures of the CNT-reinforced epoxy adhesives

The microstructures of the multiwall CNTs used in this study were observed with FESEM and are shown in Figure 2. The CNTs were randomly oriented, and the diameter was about 15–20 nm. The microstructures of the CNT-filled epoxy adhesives were observed by TEM. Figure 3 shows the TEM microstructure of 1 and 5 wt % CNT-filled epoxy adhesives. The CNTs were oriented randomly in the epoxy polymer matrix. With regard to the dispersion of the CNTs at the two loadings, the dispersion of 1 wt % CNTs in the epoxy was more uniform than that of 5 wt % CNTs. There was no apparent aggregation of nanotubes at 1 wt % CNT loading; however, a certain degree of nanotube aggregation was seen clearly at the 5 wt % CNT fraction. This phenomenon suggests that simple mechanical mixing

was not enough to distribute the nanofiller uniformly in the epoxy when the filler loading was relatively high.

Durability of the aluminum alloy joints bonded with CNT-reinforced epoxy adhesives

The wedge test has a relatively high stress concentration at or near the interface of the joint and is sensitive to environmental attack.¹⁷ Therefore, it is usually used to provide quantitative durability data for a joint. Figure 4 shows the crack propagation as a function of time for the aluminum specimens bonded with neat or CNT-filled epoxy up to 90 h of immersion in 60°C water. The crack developed in three steps for almost all of the specimens: initial crack length, crack propagation in about the first 3–8 h of immersion, and crack propagation after the first 3–8 h of immersion.

The initial crack length, measured after the wedge was inserted at an immersion time of 0 h, was very different from specimen to specimen. For the joint with neat epoxy, the initial crack length was about 37 mm. For the specimens bonded with CNT-filled epoxy, the initial crack length depended greatly on the CNT fraction. It decreased with increasing CNT fraction from 0 to 1 wt % but increased with increasing CNT fraction from 1 to 5 wt %. The initial crack length was about 11 mm for the joint with epoxy filled with 0.5 wt % CNTs, which was about a 70.3% decrement compared to that for the joint with neat epoxy. The initial crack length further decreased to about 2.7 mm for the joint with 1 wt % CNT epoxy; this was the lowest initial crack length among all of the specimens, and it was only about 7% that of the neat epoxy. Obviously, the addition of CNTs into the epoxy significant improvement in the bond

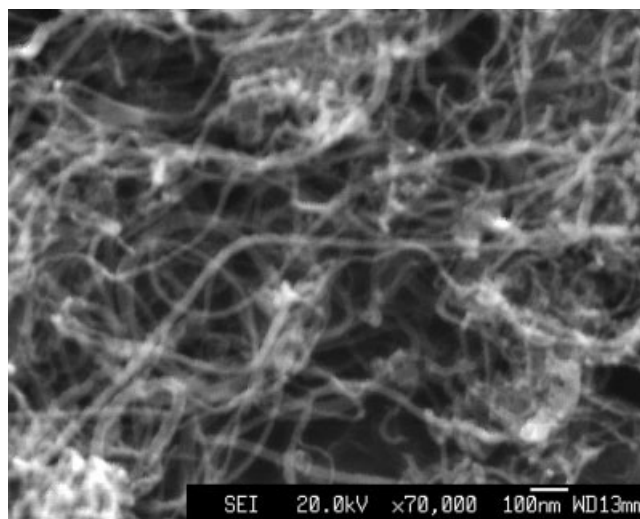


Figure 2 FESEM micrograph of the multiwall CNTs.

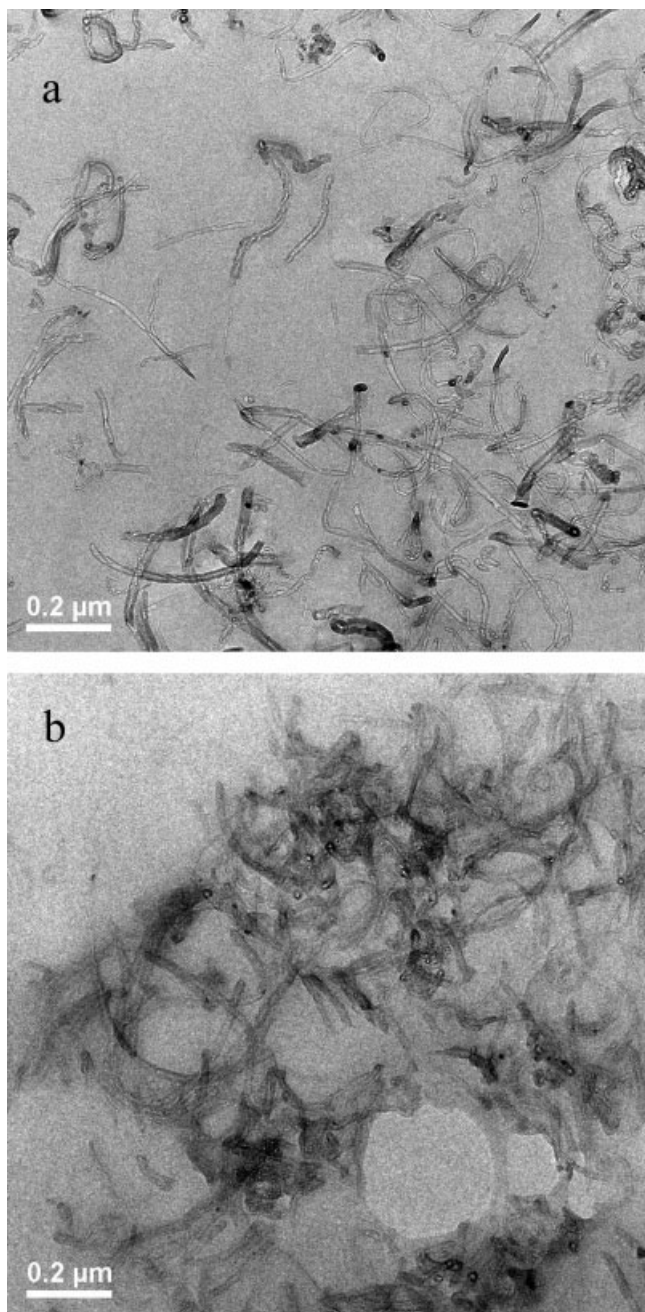


Figure 3 TEM micrographs of the CNT-reinforced epoxy adhesives with (a) 1 and (b) 5 wt % CNTs.

strength of the joints. This was attributed to their excellent mechanical properties. Multiwall CNTs themselves have very high mechanical properties with Young's modulus and yield strength values of about 1 TPa and 150 GPa, respectively;^{18,19} thus, even a small amount of CNTs incorporated into an epoxy will greatly enhance its mechanical properties.^{11,12,20}

From a theoretical point of view, the strength of the adhesives should have monotonously increased with increasing CNT loading; thus, the initial crack length of the specimen would have monotonously

decreased with the CNT fractions. This was true for the joints with CNT fractions from 0 to 1 wt %, but beyond 1 wt %, an adverse effect of CNTs on the initial crack length was found. The joint with 3.5 wt % CNTs had a similar initial crack length to that of the neat epoxy. The joint with 5 wt % CNTs had an initial crack length of about 64 mm, which was much higher than that of the neat epoxy. The adverse effect of CNTs might have resulted from the aggregation and poor dispersion of CNTs in the epoxy matrix. It is known that CNTs tend to be agglomerated because of a strong van der Waals attraction force. The agglomerated CNTs in the epoxy might have acted as defects and lowered the strength of the adhesives. The TEM microstructure shown in Figure 3 revealed that CNT agglomeration occurred for the 5 wt % CNT-filled epoxy. Gojny et al.²¹ also reported that both the modulus and tensile strength of an epoxy nanocomposite with 0.5 wt % multiwall CNTs were lower than those of a nanocomposite with 0.1 wt % multiwall CNTs.

The crack of all of the joints developed with time in about the first 3–8 h of immersion of the specimens into the water. Obviously, the propagation rate was much higher for the neat epoxy joint than for all of the CNT-filled epoxy joints. Actually, the neat epoxy joint failed and broke apart after 3 h of immersion. In contrast, all of the joints bonded with epoxy filled with CNTs stayed in the bonded state. After the first 3–8 h of immersion, the crack propagation slowed down, and all of the joints with different fractions of CNTs remained bonded after 90 h of testing.

The initial crack lengths increased with CNT fraction when the CNT loading was more than 1 wt %: they were about 23, 36, and 64 mm for the joints with CNT fractions of 2, 3.5, and 5 wt %, respectively. However, crack propagation decreased with

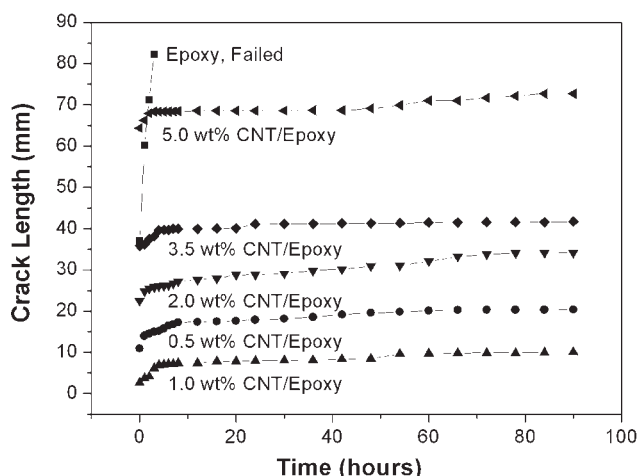


Figure 4 Crack propagation of the CNT-filled epoxy adhesive joints as a function of immersion time.

CNT fraction when the specimens were in water; the crack increments after 90 h of water immersion were about 51.7, 16.3, and 12.9% for 2, 3.5, and 5 wt % CNT-filled epoxy joints. This suggested that the water resistance of the adhesives increased with CNT loading. It is believed that water has an adverse effect on the bonding strength of joints bonded with polymer adhesives such as epoxy. It may deteriorate bonds by inducing the plasticization of the epoxy and stress the interface between the adhesive and adherent.⁵ CNT-reinforced epoxies must be able to resist water attack, so the adverse effects of water on their joints were not so significant. This was not unexpected, as CNTs are hydrophobic in nature; the addition of CNTs greatly enhanced the water resistance of the adhesives, so the crack propagation developed very slowly for joints with CNT-reinforced epoxy adhesives. In the first few hours of immersion, some relaxation took place by movement of the two metal substrates, which resulted in crack development. However, after the relaxation of the inherent stresses from the bonding process, the bondline was nearly free of residual stresses, or only a low level of residual stresses remained. This was why only very little crack propagation occurred and why the whole bonded specimens did not break apart for the joints with epoxy adhesives filled with CNTs.

Failure mode of the CNT-reinforced epoxy adhesive joints

Understanding the failure mechanism of adhesive joints is very important for improving the bonding strength; the wedge test can provide such information besides presenting the durability behavior. Usually, there are two types of failure mode: one is interfacial failure, and the other is cohesive failure. *Interfacial failure* refers to crack propagation on the adhesive–adherent interface; it can be identified by a lack of adhesive on one piece of the adherent failure surface. *Cohesive failure* refers to crack propagation purely in the polymer adhesive itself; it can be determined by the presence of adhesive on both pieces of the adherent failure surfaces. Figure 5 shows the images of the wedge specimens after immersion in 60°C water for 90 h. The specimen bonded with neat epoxy was completely fractured after immersion for 3 h. The other specimens bonded with CNT-filled epoxy were forced to fracture after the completion of the test. The failure mode was easily observed for the CNT-filled joints as they were black in color. For the neat epoxy bonded joint, glossiness on both failed metal surfaces helped to identify the failure mode.

The microstructures of the failure surfaces shown in Figure 5 were various among the specimens, which suggested different failure mechanisms. Nevertheless,

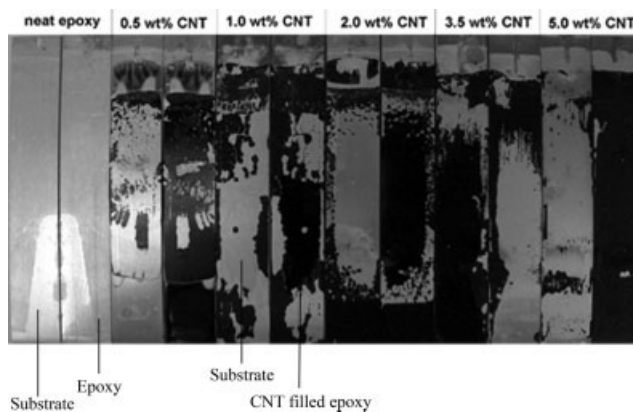


Figure 5 Photomicrograph of the wedge specimens after immersion in 60°C water for 90 h. The specimen with neat epoxy was fractured during the wedge test; others were forced to open upon completion of the test.

all of the specimens bonded with either neat or CNT-filled epoxy adhesives demonstrated a mixture of interfacial and cohesive failures. For the joints with CNT-filled epoxy adhesives, more interfacial failure developed with increasing CNT fraction. For example, for the two fractured surfaces of the joint with 5 wt % CNTs, only one surface was covered with adhesive in most areas; another surface mainly showed its bare metal surface. Thus, interfacial failure dominated. For the two fractured surfaces of the joint with 1 wt % CNTs, both pieces consisted of adhesive in large areas and bare metal in small areas; thus, cohesive failure dominated.

Interestingly, cohesive failure was also dominated for the specimen bonded with neat epoxy. This was indicative of the effectiveness of the ac/dc surface treatment. However, as shown in Figure 4, the durability of the joint with neat epoxy was very low compared to that of CNT-filled epoxy adhesives because of the low mechanical strength and weak water resistance of the epoxy.

Figure 6 shows three scanning electron micrographs of the wedge-testing failure surfaces with CNT fractions of 0, 1, and 5 wt %. For the specimen with neat epoxy, the surface was covered by the epoxy adhesive in large areas, and the fractured surface was quite smooth, which indicated low bonding strength. For the specimen with 1 wt % CNTs, the failure surface was coarser, and the nanotubes were clearly pulled out, which suggested a stronger bonding strength. For the specimen with 5 wt % CNTs, however, the failure surface became less rough. Although the CNTs could still be seen in the interface, most of them were embedded in the epoxy matrix. Thus, the joint with 5 wt % CNT-filled epoxy showed reduced bonding strength compared to the 1 wt % CNT-filled epoxy joint.

By comparison of Figures 2, 3, and 6, it can be seen that the diameter of the CNTs shown in Figure 6

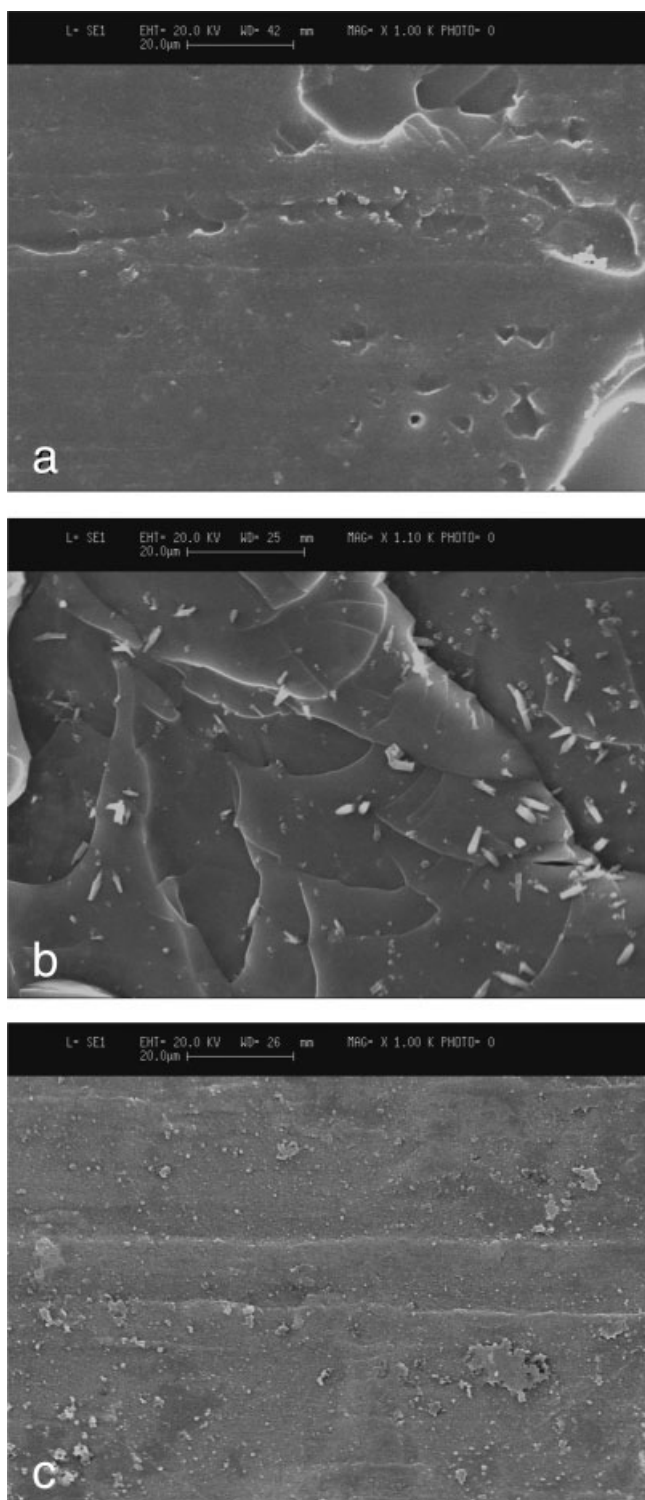


Figure 6 Microstructure of the fractured surfaces of the wedge-tested specimens: (a) neat epoxy, (b) epoxy with 1 wt % CNTs, and (c) epoxy with 5 wt % CNTs.

was greatly increased. Actually, they were not pure CNTs any more, but CNTs wrapped in a layer of epoxy. This was also an obvious indication of the high bonding strength of the CNT-filled epoxy adhesive joints.

CONCLUSIONS

To increase the bonding strength and durability of polymer adhesive joints, multiwall CNTs were used as nanofillers to produce epoxy adhesives. The uniform dispersion of CNTs in the epoxy was achieved by simple mechanical mixing and ultrasonication at low CNT loading. The durability of aluminum alloy substrates bonded with CNT-reinforced epoxy adhesives was studied with a Boeing wedge test in a humid environment. The incorporation of CNTs increased the bonding strength and durability of the epoxy joints remarkably because of the high mechanical strength and hydrophobic nature of the CNTs. The joint with 1 wt % CNT-filled epoxy showed the lowest initial and final crack lengths among the specimens tested. The experimental results also reveal that there was a critical CNT fraction; the bonding strength of the joints decreased with CNT fraction beyond that point. The microstructure analysis on wedge-tested fractured surfaces indicated that the difference in the properties of the joints resulted from different failure mechanisms.

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