Effect of Nonwoven Carbon Tissue-Reinforced Epoxy Resin Adhesive Layer on the Single Lap Bonding Strength of Aluminum Alloy Joints

Zhifeng Hu, Haijuan Kong,*, Lei Tao, Mengmeng Qiao, Dongzi Yu, Feiyang Lu, Ahmed Dawelbeit, and Muhuo Yu*

ABSTRACT: The present paper provides a solution to enhance the reliability of bonding. The effect of the nonwoven carbon tissue (NWCT) composite adhesive layer on the bonding strength and reliability of aluminum alloy of single lap joints (SLJ) was investigated by embedding NWCT into the epoxy adhesive layer. The bonding strength, Weibull distribution, metallography of cross section, and fracture surface morphology of NWCT specimens were investigated. The results showed that the average bonding strength and Weibull characteristic strength (WCS) of NWCT-reinforced specimen were 16.78 and 17.17 MPa, which increased by 70.2 and 66.7%, respectively, compared with the neat specimen, and the Weibull modulus increased from 11.46 to 22.83, which indicated that NWCT specimens had higher bonding reliability. The mechanism of microcrack formation was obtained by analyzing the cross section of specimen loaded 95% WCS without macroscopic damage. The metallographic section showed that the microcrack of the neat specimen originated from the adhesive−aluminum interface, while the microcracks of the NWCT specimen originated from the interface between short carbon fibers (SCF) and adhesive. Typical failure modes were gained from visual observation and SEM. The failure mode of the neat specimen included more Al−adhesive interface failure, while the NWCT specimen included more internal failure of adhesive−SCFs with the fracture, pullout, peeling, and slippage of SCFs improving the toughness and bonding strength of the adhesive layer. The bridging effect of SCFs in the adhesive layer reinforced by NWCT can even the load and release the stress to improve the bonding reliability.

1. INTRODUCTION

Adhesive jointing is widely used in metal and fiber-reinforced composite structures such as the automobile industry and aerospace industry. Adhesively bonded joints are an alternative to mechanical joints in engineering applications, which have incomparable advantages over traditional mechanical fasteners. They provide a more uniform stress distribution along the bonded area, which enables to have higher stiffness and load transmission, reducing the weight and the cost. With the development of composite manufacturing technology and nondestructive testing technology, the application of bonding in aerospace, automotive, wind power, and other industries is increasing. However, the bonding strength and bonding reliability of the adhesive have become an important factor in the control of bonding structures because of the low mechanical properties of the adhesive and the instability of the bonding process.

To improve the bonding strength and reliability, numerous studies have been carried out, including different pretreatment methods of the bonding surface of the substrate; toughening of adhesive by adding inorganic particles, carbon nanotubes, and short fibers, the use of functionally graded and mixed adhesive, and so on. Many different surface treatment methods have been used to improve bonding strength by enhancing the roughing of surface roughness or changing the surface free energy of the substrate, such as sandblasting technology, chemical etching, plasma etching, laser activation, and so on. Obviously, the rough surface leads to mechanical locking between the substrate and the adhesive, and the highly active surface is beneficial to the spreading and infiltration of the adhesive resin on the substrate surface. The essence of most of the modification of the adhesive is to improve the toughness and stress uniformity of the adhesive layer to avoid brittle fracture of the local adhesive layer. Among these methods, the short fiber-reinforced adhesive of the bridging
The operation of the short fiber-reinforced adhesive is more friendly, which is easier to disperse uniformly in the resin than nanoparticles. Li et al. studied the effect of SCF reinforced adhesive on the bonding of carbon/carbon composites. When the content of SCF is 0.2 wt%, the bonding strength is 11.43 MPa and the Weibull modulus is 21.56. Sun et al. investigated the effect of short aramid fiber toughening of epoxy adhesive joints between metal substrates and carbon fiber composites, and the results indicated that the performances of aramid fiber interleaved adhesive joints between the carbon fiber composites and aluminum substrates improved. Nonwoven tissue (NWT) is a kind of new supercarbon material, which is a thin nonwoven veil network structure and then reinforced by mechanical, thermal, or chemical methods. Nonwoven carbon tissue (NWCT) is a kind of fabric formed without spinning and weaving, but short fibers or filaments are oriented or randomly arranged to form a network structure and then reinforced by mechanical, thermal, or chemical methods. Nonwoven carbon tissue (NWCT) is a kind of fabric formed without spinning and weaving, but short fibers or filaments are oriented or randomly arranged to form a network structure and then reinforced by mechanical, thermal, or chemical methods.

In this study, the NWCT-reinforced adhesive layer was developed to bond the aluminum alloy joints by interleaving the NWCT into the adhesive layer. The adhesive consisted of epoxy resin and a polyetheramine curing agent. The specimen of the NWCT-reinforced adhesive layer has higher bonding strength and reliability, which provides a solution for the large-scale use of bonding. Meanwhile, NWCT can be easily made into an adhesive film with uniform thickness, which is convenient for preservation and use.

2. EXPERIMENTAL SECTION

2.1. Materials. Bisphenol A diglycidyl ether with an epoxy equivalent of 192–198 g·mol⁻¹ was supplied by Nanya Plastics Industry Co., Ltd. The curing agent was polyetheramine (D230) with an amine value of 570 mg KOH·g⁻¹, obtained from Shanghai Aladdin Bio-Chem Technology Co., Ltd. The silane coupling agent, γ-(2,3-epoxypropoxy) propytrimethoxysilane, was supplied by Shanghai Aladdin Bio-Chem Technology Co., Ltd. Acetone (≥95%) was purchased from Sinopharm Chemical Reagent Co., Ltd. NWCT (CFM-10) with 10 g·m⁻² containing 10% epoxy resin and 90% SCF was purchased from Nanjing Kotech New Material Sci&Tech Co., Ltd. The adherend used in this study was aluminum alloy 6061 with the ultimate tensile strength of 215 MPa, tensile yield strength of 187 MPa, Young’s modulus of 68.90 GPa, and density of 2.78 g·cm⁻³, which was purchased from Bolu Aluminum (Shanghai) Co., Ltd.

2.2. Single Lap Joints Preparation. In this study, 6061 aluminum alloy was used as the adherend, and a kind of epoxy adhesive with two components of epoxy and curing agent made in the laboratory was used as the adhesive. The A component of the epoxy adhesive is Bisphenol A diglycidyl ether and 1 phr silane coupling agent, and the B component is polyetheramine (D230). The ratio of A–B is 10:3.

The effect of the NWCT-reinforced adhesive layer on the SLJ of aluminum alloy was investigated in this study. The mechanical properties of SLJ were changed with the alteration of adhesive thickness, overlap length, and bonding area of adhesive joints. Therefore, for accurately comparing the bonding properties of the joints prepared in this study, the bonding thickness, overlap length, and bonding area of the joints remain unchanged. The bonding joints were prepared according to ASTM D1002 and ASTM D5686 in this study. The geometric parameters of the specimen are shown in Figure 1, and the schematic diagram of the NWCT-reinforced adhesive layer is shown in Figure 2.

Since the performance of the adhesive joints depends on the surface treatment, the surface of aluminum alloy joints was polished by the pneumatic polishing machine at 0.4 MPa pressure with 120 mesh silicon carbide sandpaper in this study. After grinding, a compressed air gun was used to remove the surface contamination, washed with distilled water, then placed in acetone for about 10 min, and finally baked in an oven at 60 °C for 20 min in the vacuum state.

The NWCT was cut into small pieces of about 15 × 25 mm², soaked in 0.5% NaOH solution at 50 °C by an ultrasonic cleaner (SK7200B, Kudos, China) for 30 min to remove grease and other dirt on the surface, then washed to neutral with distilled water, and finally baked in an oven at 100 °C for 20 min in the vacuum state.

The NWCT contained 10 g·m⁻² particles, 1 phr silane coupling agent, and 10% epoxy resin, and the B component is polyetheramine (D230). The ratio of A–B is 10:3.

Figure 1. Geometry of the SLJ specimens (dimensions in mm).

Figure 2. Schematic diagram of NWCT-enhanced specimens (dimensions in mm).
water, and then baked at 105 °C for 2 h in the oven to remove water.

A homemade bonding mold, shown in Figure 3a, was used to prepare the SLJ specimens. The specimens with the desired thickness of the adhesive layer and the overlap length were achieved using the mold and some auxiliary apparatus. For producing the joints, the release agent was first applied to the mold. When the release agent was conjunctival on the surface of the mold, the adhesive was applied to the aluminum alloy joint area and placed at one end of the mold, and then two spacers were placed with the thickness of 1.8 mm (0.2 mm thicker than the adherend) at the off-joint 15 mm (Figure 3b). Then, another piece of adherend was placed at another end of the mold, while the overlap length of the bonding specimen was controlled by the fixed blocks at both ends of the mold (Figure 3b). The pressure-sensing paper (4 LW in the range of 0.05-0.2 Mpa, Fujifilm, Japan) was placed between the adherend and a piece of the transparent glass pane. About 0.15 MPa pressure read from the color of the pressure-sensing paper was applied to the joint area through three bolts during the curing process (Figure 3b).

The specimens were cured at 120 °C for 120 min. The surface preparation and curing conditions of all joint specimens were the same. After curing, the excess adhesive protruding from the overlap area of the joints was cleaned by a cutting tool (Figure 3c).

Table 1. Number of Specimens

|                     | neat epoxy | NWCT-reinforced |
|---------------------|------------|-----------------|
| before aging        | 30         | 30              |
| after aging         | 30         | 30              |
| loading 95% of WCS  | 3          | 3               |
| loading 95% of WCS aged | 3     | 3               |
| cross section without load | 1     | 1               |
| tol                 | 67         | 67              |

The SLJ strength of neat and NWCT-reinforced specimens after hydrothermal aging was also studied. The hydrothermal treatment condition of specimens was soaking in deionized water at 80 °C for 7 days. After treatment, the moisture on the surface of the specimens was dried with absorbent paper.

2.3. Methods and Characterization. 2.3.1. Differential Scanning Calorimetry (DSC). The glass-transition temperature (Tg) of epoxy adhesive is an important parameter to determine the service environment of epoxy adhesive. To analyze the effect of hygrothermal aging on the Tg of adhesive, the DSC (Q20, TA Instruments) method was performed to test the thermal properties of the adhesive. The measured samples were cut from the cured adhesive bulk and in the range of 10−15 mg with an accuracy of 0.01 mg. DSC measurements were carried out in a nitrogen atmosphere at a heating rate of 10 °C/min, from 30 to 150 °C. The thermal history of the sample was eliminated by the first heating run, and the Tg values were obtained from the second heating run. The unaged and aged samples were tested once under the same conditions.

2.3.2. Tensile Test of Specimens. The tensile tests were conducted using a universal testing machine (HPC-63, Changchun New Experimental Instrument Company, China) with a force cell of 100 kN (effective measuring range of the load cell: 0.4 ~ 100% full scale) and 0.0001 N resolution at 23 °C, 30% humidity, and 2 mm/min pulling speed. After tested, the failure surfaces of the specimens were examined. In this study, the loads and displacements of the SLJs of four different groups bonding joints were determined, the bond strength of SLJ is the load per unit bonding area, and the calculation formula is as follows

\[
\sigma = \frac{P_{\text{max}}}{bl}
\]

where \(P_{\text{max}}\) is the maximum load of the specimen, \(b\) is the width of the specimen, and \(l\) is the length of overlap.
2.3.3. Weibull Distribution. In this study, Weibull distribution was used to deal with SLJ data determining the reliability of bonding joints of both neat specimens and NWCT-reinforced specimens before and after aging. The general Weibull three-parameter strength distribution can be written as follows

\[
P_i = 1 - \exp\left(-\frac{\sigma - \sigma_u}{\sigma_0}\right)^m
\]  
(2)

where \(P_i\) is the probability of failure, \(\sigma\) is the fracture strength variable, and \(\sigma_u\) represents the threshold strength parameter, i.e., a minimum strength below which a test specimen will not break. The stress \(\sigma_u\) represents characteristic strength, which depends on the stress configuration and test specimen size. The parameter \(m\) is the Weibull modulus, which stands for the degree of concentrated distribution of \(\sigma\) values. Setting \(\sigma_u\) to zero in eq 2 and taking double logarithms on both sides of the equation, the distribution formula of Weibull’s two parameters is obtained as follows \(^{32,33}\)

\[
P_i = 1 - \exp\left[-\frac{\sigma}{\sigma_0}\right]^m
\]

\[
\ln(1 - P_i) = \left[-\frac{\sigma}{\sigma_0}\right]^m
\]

\[
\ln\ln\left(\frac{1}{1 - P_i}\right) = m\ln\sigma - m\ln\sigma_0
\]

(3)

The characteristic strength is the strength value \(P_i\) is 63.2% when the left side of eq 3 becomes 0. Thus, the Weibull characteristic strength value \((P_i = 63.2\%)\) is slightly greater than the mean strength value \((P_i = 50\%)\).\(^{28}\)

For each of the four different specimens, the strength values were ranked in ascending order, \(i = 1, 2, 3, \ldots, N\), where \(N\) \((N = 30\) in this study) is the total number of test specimens and \(i\) is the \(i\)th datum. Thus, the lowest strength for each represents the first value \((i = 1)\), the next lowest stress value is the second datum \((i = 2)\), etc., and the highest strength is represented by the \(N\)th datum. This enables a ranked probability of failure, \(P_1(\sigma_i)\), to be assigned to each datum according to the following equation \(^{12}\)

\[
P_i(\sigma_i) = \frac{i - 0.5}{N}
\]

(4)

\(N\) pairs of \((P_i(\sigma_i), \sigma_i)\) can be obtained from the SLJ test using eq 4, and then \(N\) pairs were processed by linear regression to obtain the linear relation of \(\ln\left(\frac{1}{1 - P}\right) \sim \ln \sigma\). According to eq 3, the Weibull parameter \(m\) is the slope of the straight line, and the Weibull characteristic strength is obtained by the intercept.

2.3.4. Sectional Analysis by Metallographic Microscope. The SLJ specimen was loaded according to Section 2.3.2. When the load reached 95% of the Weibull characteristic strength and the specimen had no macroscopic damage, the load on the specimen was removed. The adhesive overlap area of the specimen was cut off with a cutter, and the cutting position was 10 mm away from the joint to prevent the cutting stress from damaging the sample. The sample was ground to the bonding area with 120 mesh of sandpaper and then packed in a plastic mold to make a metallographic mosaic sample. The cross section of the sample was polished with 120, 400, 1200, 2400, and 5000 mesh metallographic sandpaper by turns on the polishing machine. Finally, the sample cross section was polished with polishing powder and polishing cloth to make the scratches on the cross section as little as possible. The prepared samples were used for metallographic observation to analyze the distribution of microcracks in the adhesive layer. A schematic diagram of making the mosaic sample is shown in Figure 4. Six kinds of samples under the same conditions were analyzed, namely, the neat specimen and the NWCT-reinforced specimen, the aged neat specimen and the aged NWCT-reinforced specimen, and two kinds of specimens without load as references for the comparison.

2.3.5. Scanning Electron Microscopy (SEM). The fracture surface morphology of the SLJ specimen after failure was observed by a scanning electron microscope (SEM, JSM-5600LV, made by Japan JEOL) with an accelerating voltage of 5 kV before the examination. The surface of the samples was plated with a thin layer of platinum before observation.

3. RESULTS AND DISCUSSION

3.1. DSC Results. It is widely known that the thermosetting resin materials will inevitably experience plasticization due to moisture absorption or be post cured due to high temperature in hygrothermal aging environments, which causes alteration of their \(T^g\).\(^{34,35}\) The DSC curves of the adhesive before and after aging are plotted in Figure 5. The values of \(T^g\) before and after aging were 78.09 and 82.65 °C, respectively. The reason for the higher \(T^g\) of the sample after aging is that additional cross-linking that occurred at 80 °C due to the increased mobility above the glass transition may have contributed to the relatively higher \(T^g\). Generally, \(T^g\) may be related to the density of the cross-linked...
polymer chain, which means that the aged samples have a higher cross-link density and higher mechanical properties.\textsuperscript{36} In fact, when the epoxy resin undergoes hygrothermal aging treatment, the resin has the effects of both added cure and plasticization at the same time. In the early stage of hygrothermal aging, the impact of postcure overpowers the effects of plasticization, but it cannot be considered that the resin has not undergone plasticization.\textsuperscript{34}

3.2. Bonding Strength of SLJs. The SLJ test results arranged in ascending order and the average load of failure tensile strength are shown in Figures 6 and 7. Compared with the neat specimen, the failure strength of the NWCT-reinforced adhesive layer joint increased by 70.2%. When the specimens were treated by hygrothermal aging at 80 °C for 7 days, the failure strength of the NWCT-reinforced specimen was 24.2% higher than that of the neat specimen. For neat specimens and NWCT-reinforced specimens, the failure strength increased by 77.1 and 31.2%, respectively, after hygrothermal aging. The increase of the strength of the specimens after hygrothermal aging is related to the postcuring of the adhesive. When the epoxy resin is cured by ether amine, it is difficult to achieve complete curing, and when the resin is treated by hygrothermal aging, the resin that is not fully cured will continue to be solidified. Therefore, the mechanical properties (modulus, cohesion energy) of the adhesive improved after hygrothermal treatment for a period of time.\textsuperscript{37,38}

Figure 8 shows the average bonding stress–displacement curves of the different groups of SLJ specimens. The slope of the diagram can be related to the toughness of the adhesive layer to some extent, and the area surrounded by the curve can be approximately regarded as the fracture energy per unit area of the specimen in the fracture process. The toughness of the neat specimen is the best, but the bonding strength and the fracture energy are the lowest. The slope of the strength–displacement curve of the adhesive layer reinforced by NCWT is larger, and the failure load also increases greatly. The main reason is that the NCWT-reinforced adhesive layer is actually a kind of carbon fiber composite adhesive layer, and its tensile strength is higher than that of the neat specimen, and the SCF has a bridging effect during failure, which increases the displacement of failure and can absorb more energy.\textsuperscript{27} The failure strength of the neat specimen after hydrothermal aging treatment is greatly improved, and the slope of the load–displacement curve becomes larger, mainly due to the further curing of the
adhesive. However, this kind of increase of the strength and modulus of the adhesive is often not good for the adhesive. Although the adhesive with the large modulus has greater cohesion energy, it is more prone to delamination, which is one of the reasons for people to study gradient adhesive. After hygrothermal aging, although the slope of the strength−displacement curve of the NCWT-reinforced adhesive layer is a little lower than the neat specimen aged, it has the highest bonding strength and the largest fracture energy, which means that the specimen can absorb more energy during failure. It may be due to the simultaneous postcuring of the resin and the plasticization of the interface between the resin and the SCFs. When the specimen is loaded, the SCFs are likely to fracture, slip, break, and pull out, which can absorb more energy.

Figure 9 shows the typical failure surface of bonding joints of SLJ specimens under tensile load. Figure 9a shows the failure surface of the neat specimen, and its failure mode is mainly the interface failure between adhesive and aluminum alloy. Figure 9b shows the failure surface of the neat specimen after aging, and the interface failure between the adhesive and Al alloy alternately appears on both sides of the failure surface. Figure 9c shows the failure surface of the NWCT-reinforced adhesive layer specimen, and its failure surface is all in the middle of the NWCT-reinforced adhesive layer. Figure 9d shows the failure surface of the NWCT-reinforced adhesive layer after hygrothermal aging, and its failure mode is the same as that before aging, which is the cohesive failure of adhesive.

3.3. Weibull Distribution of Bonding Strength. Four groups of data arranged in ascending order in Figure 6 were

---

**Figure 9.** Failure surfaces of adhesively bonded joints subjected to tensile loading. (a) Neat specimen, (b) neat specimen after aging, (c) NWCT-reinforced specimen, and (d) NWCT-reinforced specimen after aging.

**Figure 10.** Weibull plot for SLJ bonding specimens: (a) neat specimens and NWCT-reinforced specimens; (b) neat specimens aged and NWCT-reinforced specimens aged.
analyzed by Weibull distribution according to eq 3. Figure 10 shows the Weibull plots of four groups of specimens. The fitting formulas and $R^2$ values are shown in Table 2. Figure 10a shows the Weibull plot for the neat specimens and NWCT-reinforced specimens, and the linear regression results from this figure show that $m = 11.45$ and $\sigma_\theta = 10.30$ MPa for neat specimens, and $m = 21.56$ and $\sigma_\theta = 17.17$ MPa for NWCT-reinforced specimens. The results show that the WCS of the NWCT-reinforced specimens increased by 66.7%, and the higher $m$ value indicates that the NWCT-reinforced specimen has better bonding stability. The reason for the increase of bonding strength is the bridging effects of SCFs, and the improvement of bonding stability is due to the stress dispersion of SCF in the adhesive layer, which effectively transfers and releases the residual stress. Figure 10b shows the Weibull plot for the neat specimens and NWCT-reinforced specimens after aging, and $m = 9.74$ and $\sigma_\theta = 18.40$ MPa for neat specimens, and $m = 19.08$ and $\sigma_\theta = 22.64$ MPa for NWCT-reinforced specimens. The results show that after aging, the WCS of neat specimens and NWCT-reinforced specimens increased by 78.6 and 31.9%, respectively, and the $m$ values decreased slightly. The increase of bonding strength is due to the postcuring of the resin. And the decrease of $m$ values is due to the increase of adhesive layer defects caused by hygrothermal aging, which reduces the reliability of the adhesive layer. It can be observed that the $m$ values of NWCT-reinforced specimens before and after aging are much larger than that of neat specimens, indicating that NWCT-reinforced SLJ specimens have higher bonding reliability. Figure 11 shows the fitting curves of loading strength and cumulative failure rate of four groups of specimens. It can be observed that the bonding strength and reliability of NWCT-reinforced specimens are better than those of neat specimens before or after aging.

### Table 2. Fitting Formulas and $R^2$ Values of SLJ Specimens

| Specimen       | Fitting Formula | $R^2$ | $m$  | $\sigma_\theta$/MPa |
|----------------|-----------------|-------|------|---------------------|
| Neat           | $y = 11.45x - 26.72$ | 0.97384 | 11.45 | 10.30               |
| NWCT           | $y = 22.83x - 64.71$ | 0.96986 | 22.83 | 17.17               |
| Neat aged      | $y = 9.74x - 28.33$ | 0.97450 | 9.74  | 18.40               |
| NWCT aged      | $y = 19.08x - 59.53$ | 0.96958 | 19.08 | 22.64               |

3.4. Metallographic Cross-Sectional Analysis of Specimens. The metallographic cross sections of the neat specimen and NWCT-reinforced specimen without loading are shown in Figure 12. Figure 12a shows a cross-sectional metallographic section of the neat specimen under the bright field (B.F) view of the optical microscope. It is observed that the thickness of the bonding layer of the specimen is about 0.2 mm, and there are no defects in the bonding layer. Figure 12b shows the metallographic section of the NWCT-reinforced adhesive layer specimen from the perspective of the bright field of the microscope. It is observed that a layer of resin wrapped around the SCFs (the adhesive added in the NWCT manufacturing process) has an obvious interface with the resin of the adhesive layer. Figure 12c shows an enlarged view of Figure 12b. Figure 12d shows another metallographic section picture of the NWCT-reinforced adhesive layer specimen in the bright-field view of the microscope, and Figure 12e is the dark field (D.F) view of Figure 12d. It can be observed that there is an obvious interface between the original resin on the surface of NWCT and the adhesive resin, but the two are connected, and there are no microcracks and delamination.

The metallographic sections of the neat specimen and NWCT-reinforced specimen loaded with 95% of WCS are shown in Figure 13. Figure 13a−c shows the metallographic sections of the neat specimen. From Figure 13a−c, it can be seen that the microcrack of the neat specimen was distributed at the interface between the aluminum alloy and adhesive resin, and no microcracks were found in the middle of the adhesive layer. Figure 13d−f shows the metallographic sections of the NWCT-reinforced specimen. From Figure 13d−f, it can be seen that there were no microcracks at the interface between aluminum alloy and adhesive resin in the NWCT-reinforced specimen. The microcracks were mainly distributed at the interface between NWCT self-coated resin and adhesive resin in the middle of the adhesive layer. As the interaction at the interface between NWCT and adhesive resin is weak, when the specimen was subjected to the external load, more microcracks were generated. The crack propagation needs to consume extra energy, which can protect the interface between the adhesive and the adherend.

The metallographic sections of the neat specimen and NWCT-reinforced specimen loaded with 95% WCS after aging are shown in Figure 14. The cross-sectional morphology of the specimen after aging is very similar to that before aging. Figure 14a−c shows metallographic sections of the neat specimen. From Figure 14a−c, it can be seen that the microcrack of the neat specimen was distributed at the interface between the aluminum alloy and adhesive resin, and no microcracks were found in the bonding layer. Figure 14d−f shows the metallographic sections of the NWCT-reinforced specimen. From Figure 14d−f, it can be seen that there were no microcracks at the interface between aluminum alloy and adhesive resin in the NWCT-reinforced specimen. The microcracks were mainly distributed in the interface between NWCT self-coated resin and adhesive resin in the middle of the adhesive layer. As shown in Figures 12a,b, 13a−e, and 14a,b,d, the thicknesses of the neat specimens and NWCT specimen are all about 0.2 mm. Therefore, the effect of thickness inhomogeneity on the stress distribution and bonding strength of the specimens can be ignored.

3.5. SEM Analysis of Fracture Surface. Figure 15 shows the SEM morphology of four groups of different specimens. As shown in Figure 15a, the residual adhesive on the fracture...
surface of the neat specimen is relatively smooth. Figure 15b shows the fracture surface morphology of the neat specimen after aging. The orientation of the residual adhesive on the fracture surface is more obvious than that of before aging, which may be because the postcuring of the resin results in the increase of the modulus of the resin during the aging. High-modulus
adhesives are more prone to stress concentration, which leads to the obvious orientation of the fracture surface.26 Figure 15c,15d shows the fracture morphologies of the failed specimen of the NWCT-reinforced adhesive layer. As can be seen from Figure 15c, the fracture surface is divided into many irregular areas by carbon fibers, which are filled with adhesive resin. There are many microcracks between carbon fiber and adhesive resin. A special fracture appearance of folding resin is observed, which is usually distributed on one side of the carbon fiber and perpendicular to the SCFs. The reason for this special morphology may be that the growth of the microcrack is limited by the carbon fibers, which forces the direction of the microcracks to change. The turning of the microcrack needs to consume additional energy and increase the total fracture energy of the failure of the adhesive layer. As a result, the adhesive layer is toughened. It also can be seen from Figure 15d that these folded sections have a layered structure and large surface area, which need to absorb additional energy when they are formed. Microcracks at the interface between adhesive resin and carbon fiber can also be observed in Figure 15d. The fracture surface morphology of the failure sample after aging of the NWCT-reinforced adhesive layer is shown in Figure 15e.f. The fracture morphology of the failure sample after aging of the NWCT-reinforced adhesive layer is shown in Figure 15e.f. Compared with that before aging, for the failure specimen after aging, not only the microcracks in the interface and the morphology of folded resin but also the phenomena of fracture, peeling, slip, and pullout of SCFs were observed. These failure modes can absorb additional energy to make the adhesive layer obtain better toughness.29 Slip and pullout of SCF can also explain that the failure of the aged NWCT-reinforced specimen in Figure 8 has the largest displacement.

3.6. Failure Mode. There are usually three types of bonding failure modes, including the cohesive energy of the adhesive, the interface of the adhesive, and the cohesive energy of the adherend, as shown in Figure 16. Based on the failure images of SLJ specimens (Figure 9), metallographic cross-sectional images (Figures 12−14), and SEM fracture surface morphology analysis (Figure 15), the failure modes of the neat specimen and NWCT-reinforced adhesive layer specimen are shown in Figure 17. The main failure mode of the neat specimen before aging is the first kind of interface failure of Mode 2, and the main failure mode of the neat specimen after aging is the second kind of interface failure of Mode 2. The failure mode of the NWCT-reinforced adhesive layer specimen before and after aging is the adhesive cohesive failure of Mode 1. The crack propagation path is along the SCFs and turns or divaricates due to the hindrance of the SCFs in the NWCT-reinforced specimen.

The adhesive–carbon fiber interface is introduced into the adhesive layer using the NWCT so that the original single adhesive/adherend interface is changed into a double-interface system. When the stress load is transferred in the adhesive layer, it will first be transferred to the NWCT/adhesive resin interface and then to the interface of the adhesive/adherend. The bridging of the carbon fiber/adhesive interface acts as a
Figure 15. Fracture surface morphology of the SLJ specimen: (a) neat specimen, (b) neat specimen after aging, (c, d) NWCT-reinforced specimen, and (e, f) NWCT-reinforced specimen after aging.

Figure 16. Schematic description of failure models.

Figure 17. Schematic description of failure models of neat and NWCT-reinforced specimens.
predispersed load to prevent stress concentration,27 which is the reason why NWCT-reinforced specimens have higher Weibull modulus and higher bonding reliability. The failure modes of the interface between carbon fibers and adhesive include micro-cracks at the interface, special morphology of folded resin, fracture, slippage, pullout, and peeling of SCFs. These failure modes need to consume extra energy and greatly enhance the toughness of the adhesive layer. NWCT has a certain thickness, which can control the thickness of the adhesive layer and improve the stability of the bonding.

4. CONCLUSIONS

The purpose of this study is to investigate the effect of the NWCT-reinforced adhesive layer on the SLJs. It is concluded that the NWCT-reinforced adhesive layer can not only improve the reliability of the bonding but also improve the toughness of the adhesive layer and increase the bonding strength. By embedding NWCT into the adhesive layer of SLJs, the bonding strength of the reinforced specimen is increased by 70.0 and 24.2% before and after aging, respectively. The bridging effect of SCFs in the adhesive layer reinforced by NWCT effectively transfers and releases stress and prevents stress concentration results in higher bonding reliability. The failure surface of the NWCT-reinforced specimen is in the adhesive layer, which can protect the interface between the adhesive and the adherends. The fracture surfaces of the NWCT-reinforced specimen, such as resin folding, fiber fracture, fiber pullout, fiber slip, and fiber peeling, need to absorb extra energy and make the adhesive layer obtain additional toughness. This study provides a feasible solution for improving bonding strength and reliability.

■ AUTHOR INFORMATION

Corresponding Authors

Haijuan Kong — School of Materials Engineers, Shanghai University of Engineering Science, Shanghai 201620, China; Email: Konghaijuan@sues.edu.cn

Muhuo Yu — State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University, Shanghai 201620, China; College of Materials Science and Engineering, Donghua University, Shanghai 201620, China; Email: yumuhuo@dhu.edu.cn

Authors

Zhifeng Hu — State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University, Shanghai 201620, China; College of Materials Science and Engineering, Donghua University, Shanghai 201620, China; orcid.org/0000-0003-4150-8663

Lei Tao — State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University, Shanghai 201620, China; College of Materials Science and Engineering, Donghua University, Shanghai 201620, China

Mengmeng Qiao — State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University, Shanghai 201620, China; College of Materials Science and Engineering, Donghua University, Shanghai 201620, China

Dongzi Yu — State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University, Shanghai 201620, China; College of Materials Science and Engineering, Donghua University, Shanghai 201620, China

Feiyang Lu — State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University, Shanghai 201620, China; College of Materials Science and Engineering, Donghua University, Shanghai 201620, China; orcid.org/0000-0003-0640-4973

Shanghai 201620, China; College of Materials Science and Engineering, Donghua University, Shanghai 201620, China

Ahmed Dawelbeit — State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University, Shanghai 201620, China; College of Materials Science and Engineering, Donghua University, Shanghai 201620, China; orcid.org/0000-0003-6040-4973

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c02635

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This investigation was supported by the Construction of National Demonstration Platform for Production and Application of New Materials in 2019, Ministry of Industry and Information Technology of the People’s Republic of China (Demonstration Platform for Production and Application of High-speed Railway Equipment Materials) (Item CLPT-2019-0016).

REFERENCES

(1) Chen, D.; Sun, G.; Jin, X.; Li, Q. Quasi-static bending and transverse crushing behaviors for hat-shaped composite tubes made of CFRP, GFRP and their hybrid structures. Compos. Struct. 2020, 239, No. 111842.

(2) Wang, Z.; Jin, X.; Li, Q.; Sun, G. On crushworthiness design of hybrid metal-composite structures. Int. J. Mech. Sci. 2020, 171, No. 105380.

(3) Banea, M.; Rosioara, M.; Carbaj, R.; Da Silva, L. Multi-material adhesive joints for automotive industry. Composites, Part B 2018, 151, 71–77.

(4) Kwon, D. S.; Yoon, S. H.; Hwang, H. Y. Effects of residual oils on the adhesion characteristics of metal-CFRP adhesive joints. Compos. Struct. 2019, 207, 240–254.

(5) Bishop, J. Aerospace: a pioneer in structural adhesive bonding. In Handbook of Adhesives and Sealants; Elsevier, 2005; Vol. 1, pp 215–347.

(6) Katsiropoulos, C. V.; Chamos, A.; Tsperes, K.; Pantelakis, S. G. Fracture toughness and shear behavior of composite bonded joints based on a novel aerospace adhesive. Composites, Part B 2012, 43, 240–248.

(7) da Silva, L. F. M.; Ochsner, A.; Adams, R. D. Introduction to Adhesive Bonding Technology. In Handbook of Adhesion Technology; da Silva, L. F. M.; Ochsner, A.; Adams, R. D., Eds.; Springer International Publishing: Cham, 2018; pp 1–7.

(8) Lutz, A. Preparation for bonding. In Handbook of Adhesion Technology; da Silva, L. F. M.; Ochsner, A.; Adams, R. D., Eds.; Springer, 2018; Vol. 1.

(9) Sarac, İ.; Adin, H.; Temiz, Ş. Investigation of the effect of use of Nano-Al2O3, Nano-TiO2 and Nano-SiO2 powders on strength of single lap joints bonded with epoxy adhesive. Composites, Part A 2019, 166, 472–482.

(10) Zheng, M.; Ke, C. Mechanical deformation of carbon nanotube nanorings on flat substrate. J. Appl. Phys. 2011, 109, No. 074304.

(11) Borrie, D.; Al-Saadi, S.; Zhao, X.; Raman, R. S.; Bai, Y. Effects of CNT modified adhesives and silane chemical pre-treatment on CFRP/steel bond behaviour and durability. Constr. Build. Mater. 2021, 273, No. 121803.

(12) Sun, Z.; Shi, S.; Hu, X.; Guo, X.; Chen, J.; Chen, H. Short-arimid-fiber toughening of epoxy adhesive joint between carbon fiber composites and metal substrates with different surface morphology. Composites, Part B 2015, 77, 38–45.

(13) Wang, B.; Kang, S.; Wang, G. Mode-II fracture properties of CFRP/steel composite structure reinforced by short aramid fibers. J. Adhes. Sci. Technol. 2020, 34, 949–960.
(14) Delzendehrooy, F.; Ayatollahi, M.; Akhavan-Safar, A.; da Silva, L. Strength improvement of adhesively bonded single lap joints with date palm fibers: Effect of type, size, treatment method and density of fibers. Composites, Part B 2020, 188, No. 107874.

(15) Dadian, A.; Rahnama, S. Experimental and Numerical Study of Optimum Functionally Graded Aluminum/GFRP adhesive lap shear joints using Epoxy/CTBN. Int. J. Adhes. Adhes. 2021, 107, No. 102854.

(16) Kumar, S.; Scanlan, J. On axisymmetric adhesive joints with graded interface stiffness. Int. J. Adhes. Adhes. 2013, 41, 57–72.

(17) Feng, Z.; Zhao, H.; Tan, C.; Chen, J.; Wang, Y.; Chen, B.; Song, X. Modification of surface treatment on the strength of 30CrMnSiA steel adhesively bonded joints. Mater. Res. Express 2019, 6, No. 116521.

(18) Hu, Y.; Yuan, B.; Cheng, F.; Hu, X. NaOH etching and resin pre-coating treatments for stronger adhesive bonding between CFRP and aluminium alloy. Composites, Part B 2019, 178, No. 107478.

(19) Shin, K.-H.; Kim, J.; Kim, J.-H. In Sensors and Smart Structures Technologies for Civil, Mechanical, and Aerospace Systems 2021, Effect on Plasma Treatment on Adhesive Bonding Strength, International Society for Optics and Photonics, 2021; p 115911T.

(20) Sundriyal, P.; Pandey, M.; Bhattacharya, S. Plasma-assisted surface alteration of industrial polymers for improved adhesive bonding. Int. J. Adhes. Adhes. 2020, 101, No. 102626.

(21) Pizzorni, M.; Parmiggiani, A.; Prato, M. Adhesive bonding of a mixed short and continuous carbon-fiber-reinforced Nylon-6 composite made via fused filament fabrication. Int. J. Adhes. Adhes. 2021, 107, No. 102856.

(22) Bello, I.; Alowayed, Y.; Albinmousa, J.; Lubineau, G.; Merah, N. Fatigue crack growth in laser-treated adhesively bonded composite joints: An experimental examination. Int. J. Adhes. Adhes. 2021, 105, No. 102784.

(23) Akman, E.; Erdoğan, Y.; Bora, M. Ö.; Coban, O.; Ortoprak, B. G.; Demir, A. Investigation of the differences between photochemical and photothermal laser ablation on the shear strength of CFRP/CFRP adhesive joints. Int. J. Adhes. Adhes. 2020, 98, No. 102548.

(24) Baldan, A. Adhesion phenomena in bonded joints. Int. J. Adhes. Adhes. 2012, 38, 95–116.

(25) Silva, L. F.; Ochsner, A.; Adams, R. D. Introduction to adhesive bonding technology. Handbook of Adhesion Technology, Silva, L. F.; Ochsner, A.; Adams, R. D. Eds. Springer Berlin Heidelberg: Berlin, Heidelberg, 2011; pp 1–7.

(26) Shang, X.; Marques, E.; Machado, J.; Carbos, R.; Jiang, D.; da Silva, L. Review on techniques to improve the strength of adhesive joints with composite adherends. Composites, Part B 2019, 177, No. 107363.

(27) Li, J.; Luo, R.; Bi, Y.; Xiang, Q.; Lin, C.; Zhang, Y.; An, N. The preparation and performance of short carbon fiber reinforced adhesive for bonding carbon/carbon composites. Carbon 2008, 46, 1957–1965.

(28) Yang, B.; Xiong, Y.; Ma, K.; Liu, S.; Tao, X. Recent advances in wearable textile-based triboelectric generator systems for energy harvesting from human motion. EcoMat 2020, 2, No. e12054.

(29) Lee, S.-H.; Lee, J.-H.; Cheong, S.-K.; Noguchi, H. A toughening and strengthening technique of hybrid composites with non-woven tissue. J. Mater. Process. Technol. 2008, 207, 21–29.

(30) Xu, F.; Yang, B.; Feng, L.; Huang, D.; Xia, M. Improved interlaminar fracture toughness and electrical conductivity of CFRPs with non-woven carbon tissue interleaves composed of fibers with different lengths. Polymers 2020, 12, 803.

(31) Ou, Y.; González, C.; Vilatela, J. J. Understanding interlaminar toughening of unidirectional CFRP laminates with carbon nanotube veils. Composites, Part B 2020, 201, No. 108372.

(32) Abernethy, D. R. B. The New Weibull Handbook; Dr. Robert B: Abernethy, 2004.

(33) Song, D. W.; Lim, J. K. Tensile, bending and shear strength distributions of adhesive-bonded butt joint specimens. Compos. Sci. Technol. 2005, 65, 1421–1427.

(34) Blackburn, B. P.; Tatar, J.; Douglas, E. P.; Hamilton, H. Effects of hygrothermal conditioning on epoxy adhesives used in FRP composites. Constr. Build. Mater. 2015, 96, 679–689.