The bonding performances of carbon nanotube (CNT)-reinforced epoxy adhesively bonded joints on steel substrates

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Abstract

Carbon nanotubes (CNTs) are generally considered as a promising particle reinforcement of incorporating advanced properties and characteristics into epoxy nanocomposites. This paper investigated the bonding performances of CNT-reinforced epoxy adhesively bonded joints on steel substrates using the single lap shear (SLS) tests. The bonding performances (including bonding strength, fracture strain, toughness, and failure mode) were studied with three adhesive thicknesses (1 mm, 0.5 mm, and 0.25 mm) and three CNT weight fractions (0%, 0.375%, and 0.75%). The experimental results indicated that thinner bondlines and higher CNT additions could significantly improve the bonding performances and modify the failure mode of CNT-reinforced epoxy adhesively bonded joints. However, the effects of adhesive thickness became less significant with the increase of CNT weight fractions. In addition, the plastic behaviour of CNT-reinforced epoxy, CNTs pulling-out, and the aggregation of CNTs were observed by scanning electron microscopy (SEM) image analysis on the fracture surfaces of CNT-reinforced epoxy adhesively bonded joints, indicating the potential effectiveness of the CNT reinforcement.

Keywords: Carbon nanotubes (CNTs); Epoxy resin; Bonding performance; Adhesive thickness; Single lap shear (SLS) joints; Scanning electron microscopy (SEM)

1. Introduction

Epoxy resin is one of the most common structural adhesives due to its easy application, lightweight, high tensile strength, and good chemical and environmental resistance. Adhesively bonded joints using epoxy resin have been widely applied to bond different materials as laminar composite structures in various industries [1]. Compared to traditional joining methods, epoxy adhesively bonded joints yield lower joint weight, stronger corrosion resistance and more uniform stress distribution [2-4]. However, epoxy adhesively bonded joints also suffer from certain weaknesses such as the brittleness of epoxy resin along with the variation of material properties at the adhesive-substrate interface, which makes it difficult to maintain a solid adhesive bonding [5, 6]. In fact, the adhesive bonding between the adhesive matrix and the substrate material is often the weakest part of the whole laminar composite structure, leading to the increasing demand of improving the bonding performances of epoxy adhesively bonded joints [7, 8].

Nanocomposites consist of a polymer matrix embedded with at least one kind of inorganic particles in nano-dimension [9]. Introducing nanoparticles into the epoxy resin has become a promising method to reinforce the mechanical properties of epoxy and synthesizing epoxy adhesively bonded joints with enhanced bonding performances [10-12]. Since first discovered by Iijima in 1991 [13], carbon nanotubes (CNTs) have intrigued exclusive research attentions due to their outstanding mechanical, thermal and electrical properties, which are recognized as an ideal reinforcement for epoxy composites [14-16]. Extensive applications of the CNT-reinforced epoxy composites can be found in many different industries such as corrosion protection coatings [17], transparent heating films [18], and self-sensing components [19] in transportation, automotive, and aeronautics engineering. In civil engineering applications, since CNTs with extremely high tensile strength and elastic modulus are expected to overcome the weaknesses of neat epoxy and improve the adhesive bonding of the joints [23], the CNT-reinforced epoxy adhesively bonded joints have become more and more popular compared to the traditional joining methods [20-22]. The great potential of the CNT-reinforced epoxy adhesively bonded joints requires an effective bonding performance as a prerequisite [24, 25]. For instance, if the CNT-reinforced epoxy adhesively bonded joints are applied as the protective coatings on steel structures in marine areas or corrosive environments and steel pipelines for corrosion mitigation and prevention, a better bonding performance means less coating delamination. Delamination is one of the major damaging modes for these coatings, which would induce hidden corrosion beneath epoxy coatings and is very challenging to detect and mitigate in field.

Previous studies reported that mixing CNTs into epoxy resin could improve the adhesion properties of neat epoxy adhesively bonded joints by increasing the fracture toughness of the epoxy [26, 27] and restricting the crack propagation within the bondline layer [28–30]. Furthermore, the extraordinary high aspect ratio of CNTs could create an extraordinarily large contact area with the surrounding epoxy, resulting in a good load transfer to guarantee a sound cooperative work between CNTs and the epoxy adhesive matrix [23, 24]. However, the reinforcing efficiency of CNTs varies from case to case [31, 32], the effect of CNT fractions on the bonding performance of epoxy adhesively bonded joints is still an essential research topic.

In addition to the particle reinforcements, the bonding performances of epoxy adhesively bonded joints can also be influenced by many other factors, such as geometrical dimensions, substrate treatments, and curing conditions [33-35]. Among these influencing factors, the adhesive thickness of the epoxy layer is an of vital importance parameter which can greatly impact the bonding performances of epoxy adhesively bonded joints [36, 37]. For adhesively bonded joints using neat epoxy resin, state of art and a previous study by the authors shared the same conclusion; The bonding strength of neat epoxy joints usually decreased with the increase of the adhesive thickness [38-40]. The neat epoxy resin is usually regarded as a brittle material because of the voids and micro-cracks generated within the epoxy matrix during the curing process, which could cause stress concentration and weaken the material properties. Epoxy adhesively bonded joints with thicker bondline layers tend to have more voids and micro-cracks, implying a higher porosity and higher possibility of a brittle failure [41, 42].

However, for CNT-reinforced epoxy adhesively bonded joints, the addition of CNTs was found to lower the porosity of epoxy bondlines which could deviate and bridge the crack within the epoxy matrix [43, 44]. Thus, the negative effect of thicker adhesive thickness could probably be reduced or even reversed with the CNT reinforcement. Because when the epoxy bondlines are free of any imperfections, the classic theoretical analysis showed that thicker bondlines positively influence the bonding performances of neat epoxy adhesively bonded joints as a result of a more uniform stress and strain distribution within the bondline layer. A number of researches have reported the investigations on the bonding performances of CNT-reinforced epoxy adhesively bonded joints, but they mostly focused on the impact of changing CNT weight fractions in the reinforced epoxy adhesively bonded joints. There is a severe lack of relevant studies on CNT- reinforced epoxy adhesively bonded joints with different adhesive thicknesses.

Thus, in this paper, the bonding performances of CNT-reinforced epoxy adhesively bonded joints on steel substrates with different CNT weight fractions and adhesive thicknesses were investigated using the single lap shear (SLS) tests. To the best of the authors' knowledge, for the first time, the effect of adhesive thickness is revealed systematically. The following bonding performances of epoxy adhesively bonded joints were evaluated included bonding strength, fracture strain, toughness, and failure mode.

In addition, scanning electron microscopy (SEM) image analysis was also performed on the fracture surfaces of epoxy adhesively bonded joints to understand the reinforcing mechanisms of the CNTs in the epoxy adhesively bonded joints and reveal the potential effectiveness of the CNT reinforcement.

2. Methodology and Experimental Plan

2.1 Materials

The steel substrates are made of mild A36 steel (provided by Mid America Steel Inc) as the steel substrate of epoxy adhesively bonded joints. The neat epoxy adhesive to be tested in this study was a general two-part epoxy resin (provided by East Coast Resin), consisting of a bisphenol A based resin and the polyamide curing agent. The mechanically stirred resin and curing agent with a weight ratio of 1:1 were prepared as the neat epoxy adhesive matrix. Selections of these most common materials for steel substrates and the epoxy adhesive were to make this study more representative.

To prepare the CNT-reinforced epoxy adhesive, the multi-walled carbon nanotubes (MWCNTs) (supplied by Skyspring Nanomaterials Inc) was gradually added into the neat epoxy during mechanical stirring. The CNT-reinforced epoxy was further mixed by ultrasonic sonication for 15 minutes to deeply disperse the CNTs into the neat epoxy adhesive matrix. The detailed properties of the MWCNTs are presented in Table 1. The CNT weight fractions of most existing researches were no higher than 1%, because the CNTs are more likely to be agglomerated with higher weight fraction, which had a detrimental effect on the adhesive properties [43]. According to the literature [45], the optimal CNT reinforcement could be achieved at the percentage of 0.75%. Thus, adhesively bonded joints with three different weight fractions of 0%, 0.375%, and 0.75% were fabricated to investigate the influence of CNT weight fractions on the bonding performances of epoxy adhesively bonded joints when different adhesive thicknesses were considered.

Table 1. Properties of MWCNTs

Purity	>95 wt%	SSA	> 60 m2/g
Outside Diameter	50-100 nm	Amorphous Carbon	<3.0%
Inside Diameter	5-10 nm	Electrical Conductivity	>100 s/cm
Length	5-20 um	Bulk Density	0.28 g/cm3
Ash	<1.5 wt%	True Density	2.1 g/cm3

2.2 Adhesively bonded joint preparation

Figures 1(a, b) show the sample configurations of the SLS joint, following the ASTM D1002-10 [46]. In a SLS joint, two steel sheets were bonded together by the neat epoxy or the CNT-reinforced epoxy adhesives which were prepared following the description in last section with an overlap length of 12.7 mm. The steel sheets were thickened to 3.18 mm to prevent early buckling of the steel sheets before shear debonding. To investigate the influence of adhesive thickness, adhesively bonded joints with each CNT fractions were manufactured in three different adhesive thicknesses of 1 mm, 0.5 mm, and 0.25 mm. The different adhesive thicknesses were controlled using steel shims. As also seen in Figure 1(b), two steel attachments were attached on the edge of each sample to minimize the bonding moment so that the epoxy bondline was dominated by shear stress under tensile loads. The detailed dimensions and sample configurations are demonstrated in Figures 1.

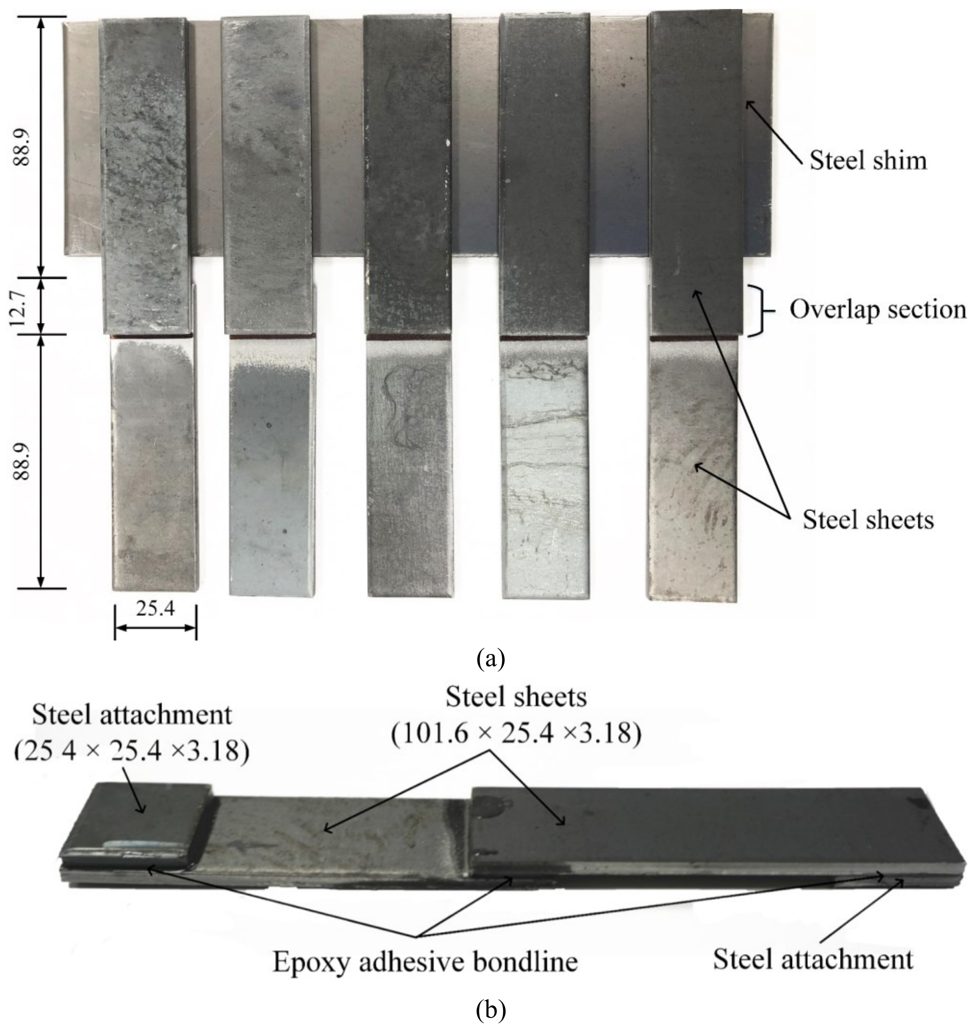


Figure 1. The sample configurations of the SLS joint (unit: mm).

To obtain a strong interfacial interaction at the adhesive-substrate interface, a series of surface preparations and treatments were carried out on the steel substrate. At first, 15-minite ultrasonic cleaning using pure acetone was carried out on the steel sheets. The temperature was kept constant at 20°C during the sonication. Then, girt blasting using 60-grit aluminium abrasives were performed on the overlapped section of the steel sheets, followed by surface cleaning using compressed air. The detailed grit blasting parameters are listed in Table 2. Finally, before applying the prepared adhesive, the blasted steel substrates were again ultrasonically cleaned under the same conditions to remove any possible dusts or contaminants remaining on the surfaces. All adhesively bonded joints were completely assembled within 24 hours after grit blasting to prevent corrosion in the blasted areas. The well-prepared adhesively bonded joints were cured at a warm room

(32°C) for 24 hours, and they were tested after one week curing outside the warm room. Table 3 (Column 1 ~ 4) shows the test matrix for the SLS tests in this study. 9 testing conditions were considered covering three different adhesive thicknesses (0.25 mm, 0.5mm, and 1 mm) and three different CNT weight fractions (0%, 0.35%, 0.75%). For each testing condition, to restrict random error, five samples were made, resulting in a total of 45 samples.

Table 2. Grit blasting parameters

Blasting pressure	Blasting abrasive	Standoff distance	Blasting angle	Blasting time
500 kPa	Aluminum oxides	150 mm	90°	3 min

Table 3. The SLS test results

Testing condition	Sample quantity	Adhesive thickness (mm)	CNT addition (%)	Toughness (MPa)	Bonding strength (MPa)	Fracture strain
E1	5	1	0	0.78	6.54 ± 0.43	0.195 ± 0.007
E0.5	5	0.5	0	3.41	11.72 ± 0.82	0.614 ± 0.037
E0.25	5	0.25	0	15.36	17.66 ± 1.35	1.474 ± 0.107
HC1	5	1	0.375	5.01	12.26 ± 1.04	0.699 ± 0.037
HC0.5	5	0.5	0.375	10.41	17.31 ± 1.60	1.210 ± 0.072
HC0.25	5	0.25	0.375	21.89	18.48 ± 1.23	1.982 ± 0.145
C1	5	1	0.75	7.50	15.56 ± 1.13	0.853 ± 0.041
C0.5	5	0.5	0.75	16.65	18.27 ± 1.45	1.372 ± 0.095
C0.25	5	0.25	0.75	32.45	19.25 ± 1.87	2.079 ± 0.165

2.3 Testing

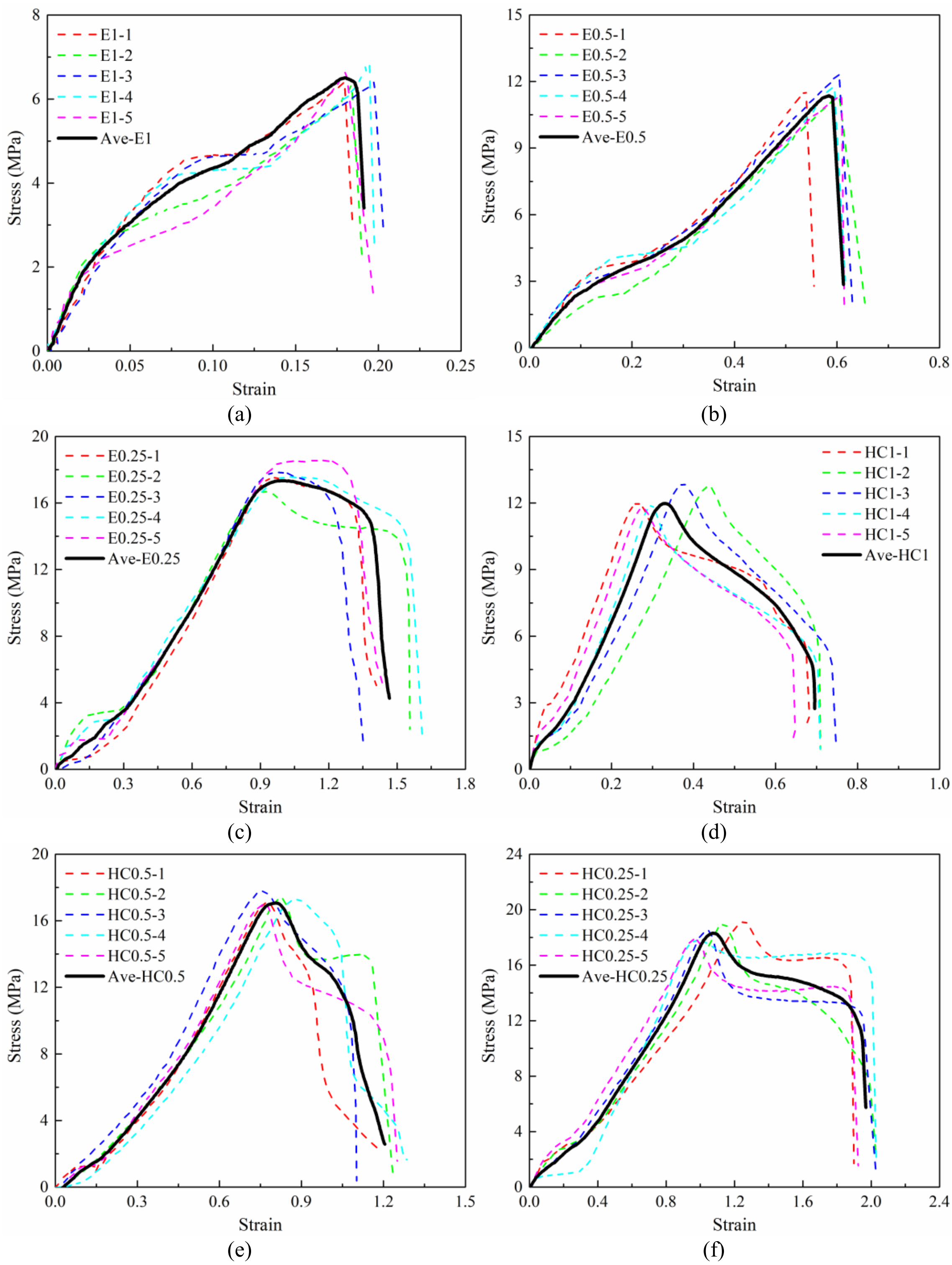
The SLS tests were carried out using the MTS Flex Test® SE loading frame (Figure 2), which could record the real-time tensile loads and displacements automatically during testing. The loading speed was set to be 1.3 mm/min using displacement control mode under monotonic tensile loading. To compare the bonding strength and the fracture strain of neat or CNT-reinforced epoxy adhesively bonded joints with different adhesive thicknesses and CNT weight fractions, the shear stresses (τ) and strains (γ) were calculated based on the recorded tensile loads and displacements as the equations displayed in the previous paper of the authors [40]. Thus, the recorded real-time load-displacement curves of all the adhesively bonded joints could be converted into the stress-strain curves. In addition to the SLS tests, SEM image analysis was also conducted on the all the fracture surfaces of adhesively bonded joints after the SLS tests to study the failure mode and the bonding mechanisms of the neat and CNT-reinforced epoxy adhesively bonded joints.

Figure 2. SLS test setup.

3. Results and discussions

3.1 Stress-strain curve

Figures 3 (a ~ i) show the original experimental stress-strain curves in each testing condition with three different adhesive thicknesses and three different CNT weight fractions following the termination of the test matrix as shown in Table 3. To clearly compare the stress-strain curves in different testing conditions, the five-individual stress-strain curves from the five samples in each testing condition were fitted mathematically into one average stress-strain curve as also illustrated in Figures 3 (a ~ i). The applied fitting algorithm was called trace interpolation which was able to compute the average curves whose shapes were similar to those of the five experimental curves in the same testing conditions. From Figure 3, it can be seen that the five individual curves and the corresponding average curve in each testing condition followed the same traces with similar peak stresses and ultimate strains. Therefore, in the further analysis, the typical stress-strain curves in each testing condition were represented by the corresponding average curves.



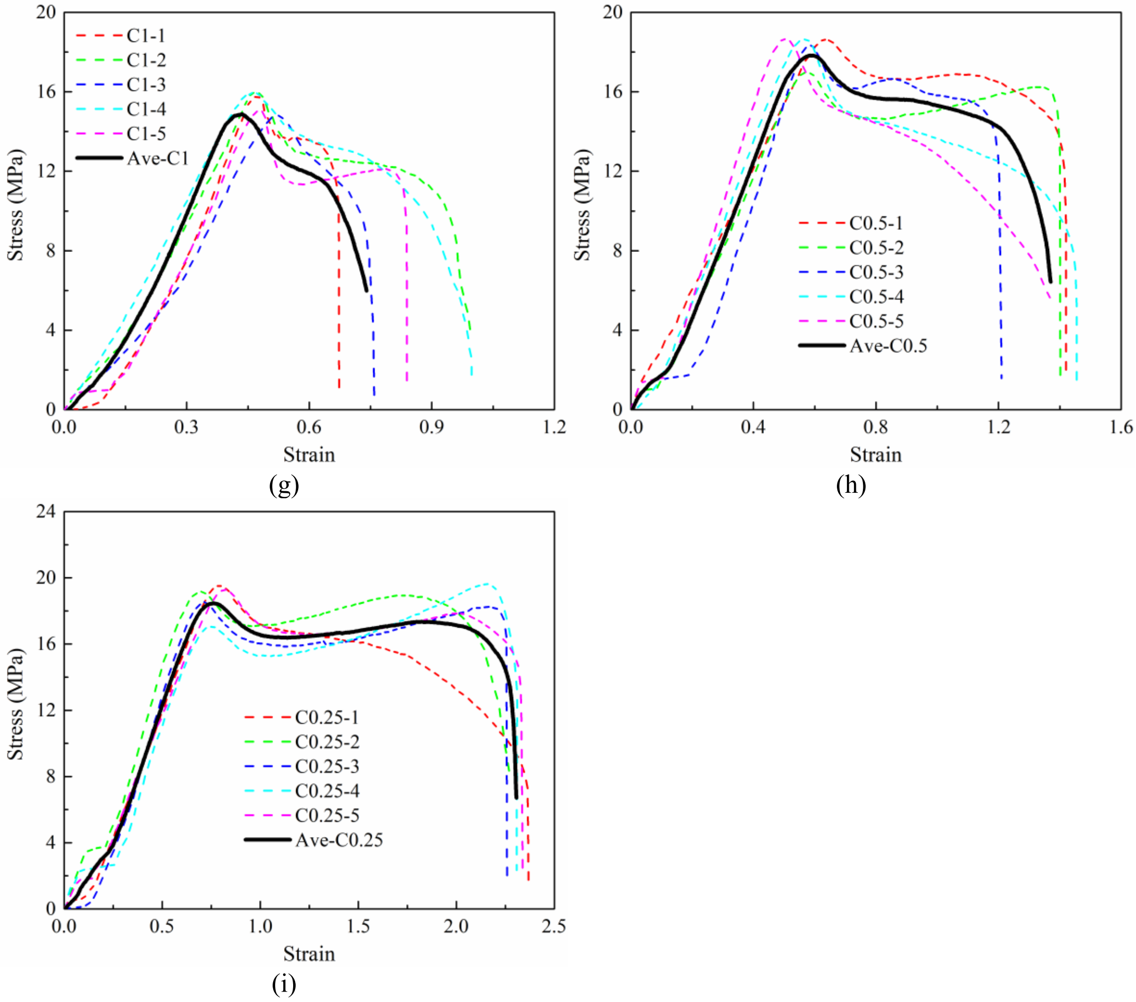


Figure 3. Comparisons between original experimental stress-strain curves and the average fitting curves in each testing conditions: (a) E1; (b) E0.5; (c) E0.25; (d) HC1; (e) HC0.5; (f) HC0.25; (g) C1; (h) C0.5; (i) C0.25.

Figures 4(a ~ c) plot the average stress-strain curves of 0%, 0.35% and 0.75% CNT-reinforced epoxy adhesively bonded joints with the three different adhesive thicknesses of 0.25 mm, 0.5 mm, and 1 mm. As shown in Figure 4(a), the stress-strain curves of neat epoxy adhesively bonded joints (0% CNT addition) with different adhesive thicknesses showed significantly different changing traces. For the neat epoxy adhesively bonded joints with the adhesive thicknesses of 1 mm and 0.5 mm, the shear stress increased almost linearly with the increase of strain, and then decreased suddenly after reaching the peak stress, ending up with a sudden failure. However, when the adhesive thickness was reduced to 0.25 mm, the average stress-strain curve showed a typical nonlinear pattern, with the stress dropping gradually after the peak stress. For the CNT-reinforced epoxy adhesively bonded joints with 0.35% and 0.75% CNT additions, as shown in Figure 4(b) and 4(c), respectively, the shapes of the stress-strain curves were not obviously affected by neither CNT weight fractions nor adhesive thicknesses. All the stress-strain curves exhibited nonlinear patterns which were very similar as the neat epoxy adhesively bonded joints with an adhesive thickness of 0.25 mm. However, the degrees of nonlinearity varied with different adhesive thicknesses and CNT weight fractions. In general, a higher level of nonlinearity of the curves was observed with higher CNT additions and thinner adhesive thicknesses, indicating more plastic deformations generated by the epoxy adhesively bonded joints.

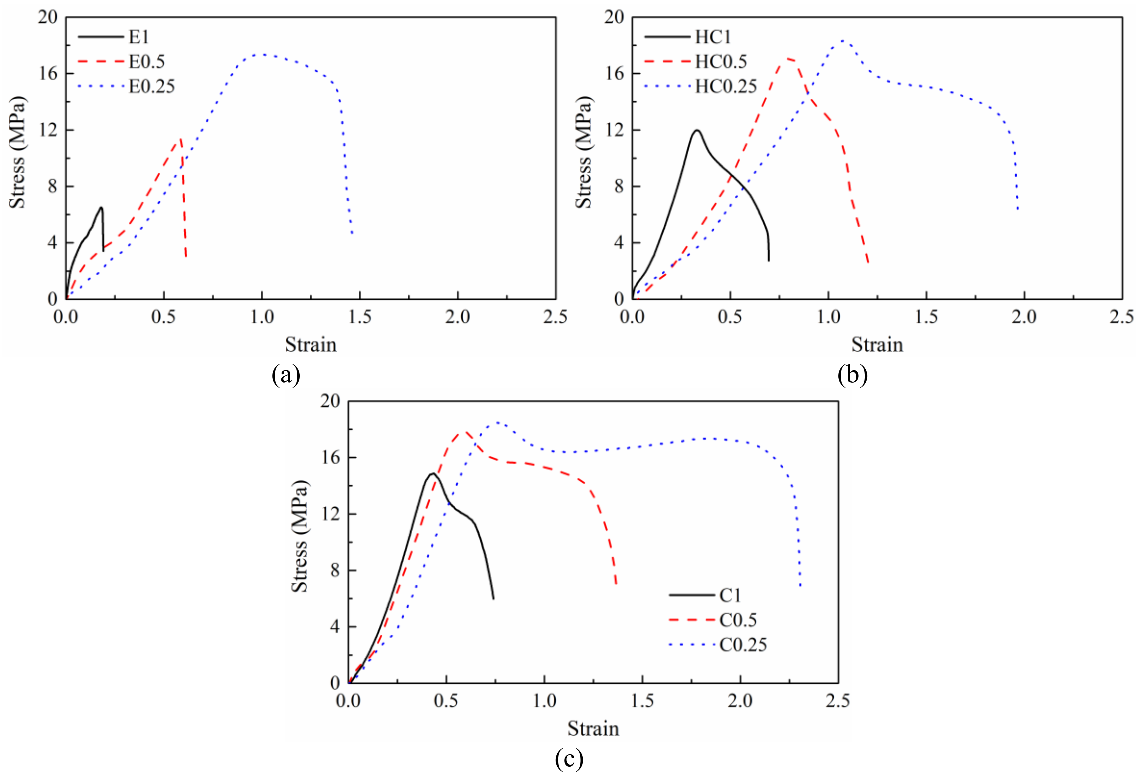


Figure 4. Average stress-strain curves of epoxy adhesively bonded joints: (a) neat epoxy; (b): 0.375% CNTs; (c) 0.75% CNTs.

The plastic behaviour of the neat and CNT-reinforced epoxy adhesively bonded joints could quantitively be reflected by the area under the stress-strain curve, which is an indication of the toughness as the ability of plastically deforming and absorbing energy. Epoxy adhesively bonded joints with higher toughness could generate more plastic deformations and consume more energy while deforming, indicating the improved bonding performances. Based on the average stress-strain curve in each testing condition as shown in Figure 4, the toughness of epoxy adhesively bonded joints among the different adhesive thicknesses with each CNT addition can be calculated and the values of the toughness are presented in Table 3 (Column 5) and compared in Figure 5. According to Figure 5, the reduction of adhesive thickness could remarkably improve the toughness of epoxy adhesively bonded joints with the same CNT fractions. For the neat epoxy adhesively bonded joints, as the adhesive thickness decreased from 1 mm to 0.5 mm and from 0.5 mm to 0.25 mm, the toughness increased by 337% and 350%, respectively. However, for the CNT-reinforced epoxy adhesively bonded joints, the improvements of toughness by the same decreases of adhesive thicknesses reduced to 108% and 110% with 0.375% CNT addition, and 122% and 95% with 0.75% CNT addition, respectively. Compared to neat epoxy adhesively bonded joints, the increments of the toughness among CNT-reinforced epoxy adhesively bonded joints with different adhesive thicknesses became smaller and smaller due to the increase of CNT fractions.

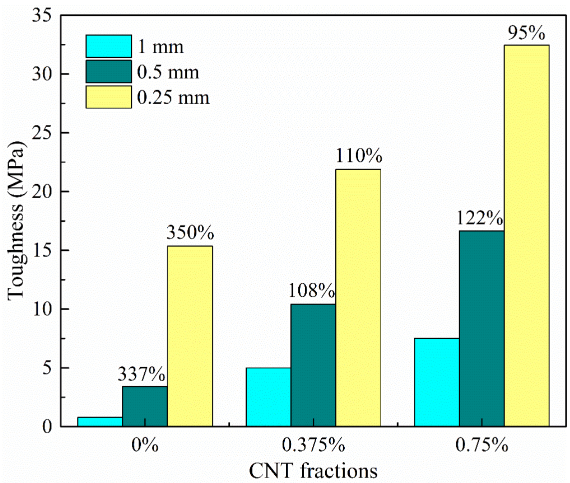


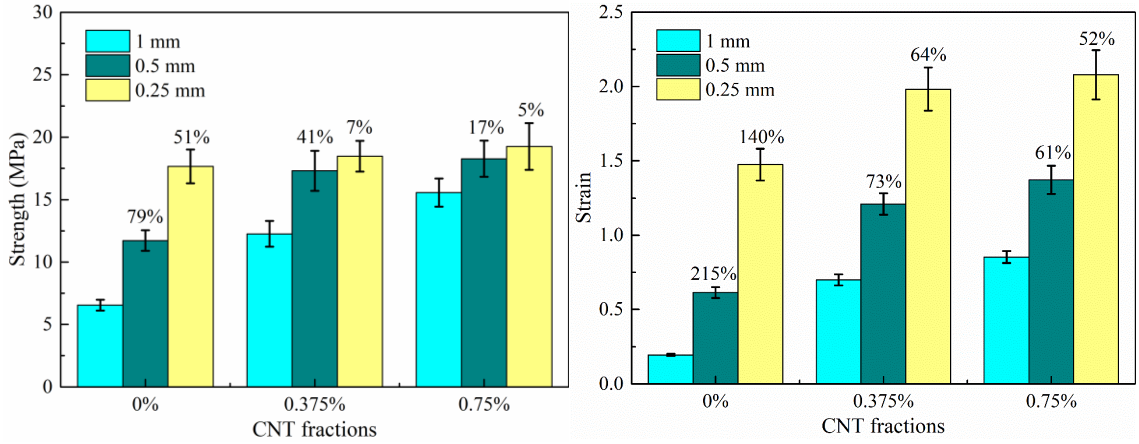
Figure 5. Comparisons of toughness between different adhesive thickness (including increments from 1 mm to 0.5 mm and 0.5 mm to 0.25 mm) with each CNT addition.

Moreover, it was clearly indicated Table 3 (Column 5) that when comparing epoxy adhesively bonded joints with the same adhesive thicknesses, the toughness appreciably increased as the increase of CNT fractions. According to Table 3, as the CNT fraction increased from 0% to 0.375%, the toughness of epoxy adhesively bonded joints with the adhesive thickness of 1 mm and 0.5 mm increased by 542% and 205%, respectively. For the rest epoxy adhesively bonded joints with different adhesive thicknesses and CNT fractions, the increments of the toughness were only around 43% ~ 60%. The improvements were more significant by increasing the CNT fractions from 0% to 0.375% when the adhesive thicknesses were 1 mm and 0.5 mm compared to further increasing the CNT fractions from 0.375% to 0.75% or when the adhesive thickness was 0.25 mm. The influence of the CNT addition was more effective on the epoxy adhesively bonded joints with thicker adhesive thicknesses.

3.2 Bonding strength and fracture strain

Table 3 (Columns 6-7) also includes the influence of adhesive thickness and CNT fraction on the bonding strength and fracture strain of the epoxy adhesively bonded joints. The bonding strength of the joints was identified as the peak stress in the stress-strain curves, and the fracture strain was determined as the ultimate strain when the joints fractured or failed, based on Figure 4. Figures 6(a, b) displays the increments of bonding strength and fracture strain with standard deviations of epoxy adhesively bonded joints among different adhesive thicknesses with various CNT weight fractions. It was found that both bonding strength and fracture strain of neat epoxy adhesively bonded joints increased significantly as the decrease of adhesive thickness, which is the agreement with the literature [40, 47]. The similar trend was also seen for both 0.375% and 0.75% CNT-reinforced epoxy adhesively bonded joints among different adhesive thicknesses.

Specifically, as shown in Figure 6(a), for the neat epoxy adhesively bonded joints, when the adhesive thickness was reduced from 1 mm to 0.5 mm and from 0.5 mm to 0.25 mm, the bonding strength increased by 79% and 51%, respectively. For the CNT-reinforced epoxy adhesively bonded joints, the corresponding increments of bonding strength improved by 41% and 7% for 0.375% CNT reinforcement, and 17% and 5% for 0.75% CNT reinforcement, respectively. The increments in fracture strain also showed a similar trend as those in bonding strength, as shown in Figure 6(b). For the neat epoxy adhesively bonded joints, by reducing the adhesive thickness from 1 mm to 0.5 mm and from 0.5 mm to 0.25 mm, the fracture strain increased 215% and 140%, respectively. For CNT-reinforced epoxy adhesively bonded joints, the corresponding improvements were restricted to 73% and 64% with 0.375% CNT addition, and to 61% and 52% with 0.75% CNT addition, respectively. It was worth noticing that the improvement of both bonding strength and fracture strain became less significant from 0% to 0.75% CNT-reinforced epoxy adhesively bonded joints, indicating that the impact on the bonding performances of epoxy adhesively bonded joints by adhesive thickness was restricted with the addition of CNTs. The restricted impact of adhesive thickness with the addition of CNTs could be possibly related to the reinforcing mechanism of CNTs on the epoxy adhesively bonded joints. Existing studies found that voids and micro-cracks inside the bondline layer could be deflected, pinned and bridged with the incorporation of CNTs [14, 28, 32]. In terms of the influence of adhesive thickness, porosity is one of the most critical reasons for thicker bondlines yielding weaker bonding performance [41]. The voids and micro-crack could be possibly cured by the added CNTs, so that the adverse impact of adhesive thickness might be mitigated or even minimized with the addition of CNTs. Thus, the increments of bonding strength and fracture strain became smaller among CNT-reinforced epoxy adhesively bonded joints with the reduction of adhesive thickness.



(a) (b)

Figure 6. Comparisons between different adhesive thickness (including increments from 1 mm to 0.5 mm and 0.5 mm to 0.25 mm) with each CNT addition: (a) Bonding strength; (b) Fracture strain.

On the other hand, previous researches [27-30] found out that the bonding strength of CNT-reinforced epoxy adhesively bonded joints increased as the CNT fractions increased to around 0.75%, and then decreased gradually with further additions of CNTs owing to the aggregation of CNTs [32, 43-44]. The experimental results in Table 3 (Columns 6-7) confirmed that for epoxy adhesively bonded joints with the same adhesive thicknesses, as the CNT fraction increased from 0% to 0.75%, both bonding strengths and fracture strains increased continuously. By increasing the CNT fractions from 0% to 0.75%, more CNTs were incorporated to reinforce the epoxy bondlines, which could surely improve the bonding performances of the epoxy adhesively bonded joints.

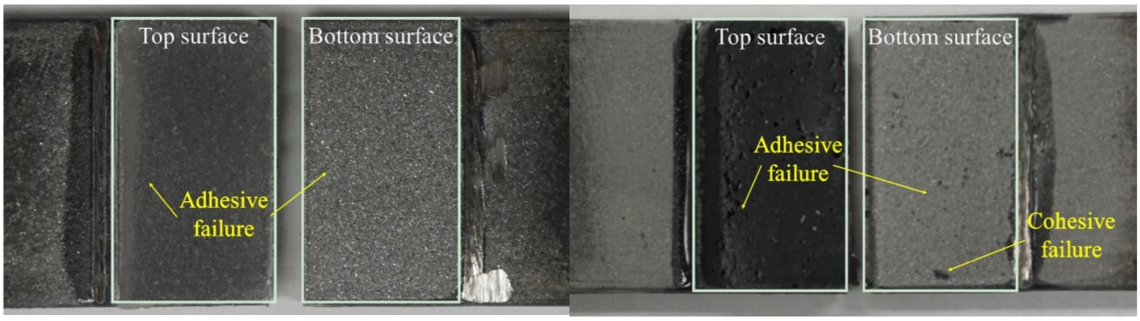
To further investigate the influence of CNT fractions on the bonding strength and fracture strain of epoxy adhesively bonded joints with different adhesive thicknesses, it was noted that when the adhesive thickness was 1 mm, adding the CNT fraction from 0% to 0.375%, the bonding strength and fracture strain increased by 87% and 258%, respectively. and further increasing the CNT fraction from 0.375% to 0.75%, the improvements of bonding strength and fracture strain were 27% and 22%, respectively. When the adhesive thickness was 0.5 mm, the corresponding improvements reduced to 48% and 97% from 0% to 0.375% CNT additions, and 6% and 13% from 0.375% to

0.75% CNT additions. When the adhesive thickness was 0.25 mm, except the fracture strain increased by 34% with the increase of CNT addition from 0% to 0.375%, the other increments were only around 5%. It was observed that the increments of bonding strength and fracture strain by increasing CNT fractions were reduced with the decrease of adhesive thicknesses. The literature showed that thicker epoxy bondlines are prone to have more voids and micro-cracks than thinner bondlines [48]. Thus, more imperfections in thicker bondlines could be fixed by the CNTs, resulting in more significant improvements of the bonding performances.

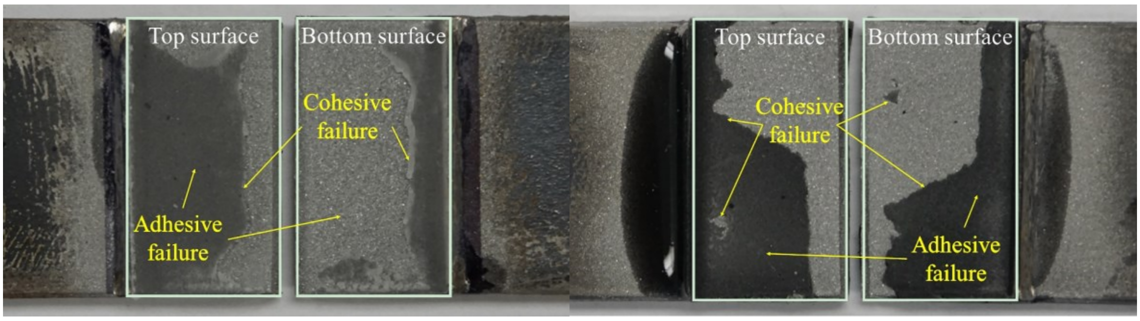
3.3 Failure mode analysis

Generally, the debonding failure of epoxy adhesively bonded joints may fall into three categories: (1) adhesive failure at the interface between the adhesive and the substrate; (2) cohesive failure within the adhesive bondline; and (3) the combination of these two modes. Figures 7(a, b) compare the fracture surfaces of the neat and the 0.75 % CNT-reinforced epoxy adhesively bonded joints with the adhesive thickness of 1 mm. As shown in Figure 7(a), a complete adhesive failure occurred for the neat epoxy adhesively bonded joint with 1 mm adhesive thickness because the epoxy bondline was completely attached on the top surface of the neat epoxy adhesively bonded joint, and there was no visible epoxy remaining on the bottom surface. For the 0.75% 1 mm thick CNT-reinforced epoxy adhesively bonded joint, adhesive failure was also the dominant failure mode with most of the epoxy remaining on one fracture surface. However, as shown in Figure 7(b), some spots of CNT-reinforced epoxy could be found on the bottom surface indicating the existence of cohesive failure. Then the overall failure mode turned into a combination of both adhesive and cohesive failure. It could also be noticed that there were several visible small cracks on the CNT-reinforced epoxy bondline on the top surface. These cracks might be generated due to the plastic behaviour of CNT-reinforced epoxy. Given that the addition of CNTs increased the bonding capacity and toughness of the epoxy adhesively bonded joints, it indicated that adding CNTs into the epoxy could improve the failure mode of epoxy adhesively bonded joints.

In addition, Figures 7(a, c) and Figures 7(b, d) compare the typical fracture surfaces of the neat and 0.75% CNT-reinforced epoxy adhesively bonded joints with adhesive thicknesses of 1 mm and 0.25 mm, respectively. Specially, for the CNT-reinforced epoxy adhesively bonded joints with the adhesive thickness of 0.25 mm, the bondline was penetrated by a big crack thoroughly, and the two separated parts of epoxy remained on both fracture surfaces. Although a large part of the bondline area still belonged to adhesive failure, cohesive failure occurred on the cracking areas including the big crack and some smaller cracks inside the adhesive area. The similar failure mode modification was also observed between the neat epoxy adhesively bonded joints with the adhesive thicknesses of 1 mm and 0.25 mm. The preferred partial cohesive failures were achieved for both the neat and CNT-reinforced epoxy adhesively bonded joints with the adhesive thickness of 0.25 mm, indicating that the change of failure mode was more pronounced between the neat epoxy adhesively bonded joints with the adhesive thickness of 1 mm and 0.25 mm compared to the change between the CNT-reinforced epoxy adhesively bonded joints with those different adhesive thicknesses.



(a) (b)



(c) (d)

Figure 7. Typical fracture surfaces of epoxy adhesively bonded joints: (a) 1 mm neat epoxy; (b): 1 mm 0.75% CNT-reinforced epoxy; (c) 0.25 mm neat epoxy; (d) 0.25 mm 0.75% CNT-reinforced epoxy.

3.4 SEM image analysis

To further analyse the fracture surfaces of the neat and CNT-reinforced epoxy adhesively bonded joints shown in Figure 7, SEM image analysis at a magnification of ×1000 was conducted on the top surfaces of those adhesively bonded joints, which are illustrated in Figures 8(a ~ d). As shown in Figures 8(a, b), the typical fracture surface of neat epoxy adhesively bonded joints with 1 mm adhesive thickness was comparatively smoother and flatter than the fracture surface with the 0.75% CNT reinforcement. Adding CNTs into the 1 mm thick adhesive bondlines could visibly increase surface roughness of the fracture surfaces. Additionally, for the neat epoxy adhesively bonded joints as shown in Figures 8(a, c), the reduction of adhesive thickness apparently increased the surface roughness of the fracture surfaces by introducing more hills, ridges and valleys on the surfaces. The similar roughness improvement was also seen on the fracture surfaces of the CNT-reinforced epoxy adhesively bonded joints between 1 mm and 0.25 mm adhesive thicknesses, while it was less obvious than the improvement between neat epoxy adhesively bonded joints. The influence of adhesive thickness on surface roughness of fracture surfaces became less significant with the increase of CNT additions, which was also echoed with the previous findings in Section 3 of this paper. Rougher fracture surfaces revealed more plastic deformations of epoxy bondlines, resulting in more complex fracture mechanisms with higher energy dissipation and toughness. But when comparing the fracture surfaces of the neat and CNT-reinforced epoxy adhesively bonded joints with 0.25 mm adhesive thickness as in Figures 8(c, d), there was no big difference between the surface morphologies of the neat and CNT-reinforced epoxy adhesively bonded joints, the improvement of surface roughness between them was rather limited.

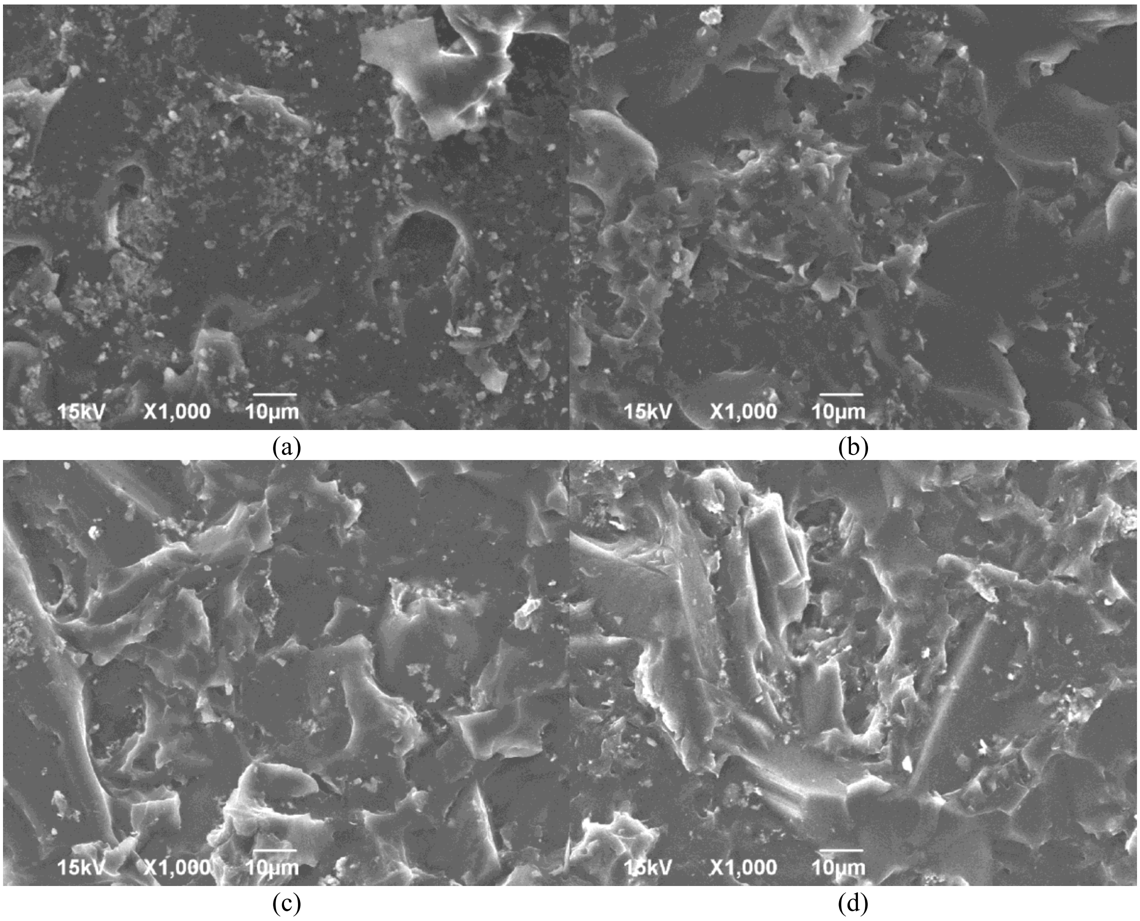
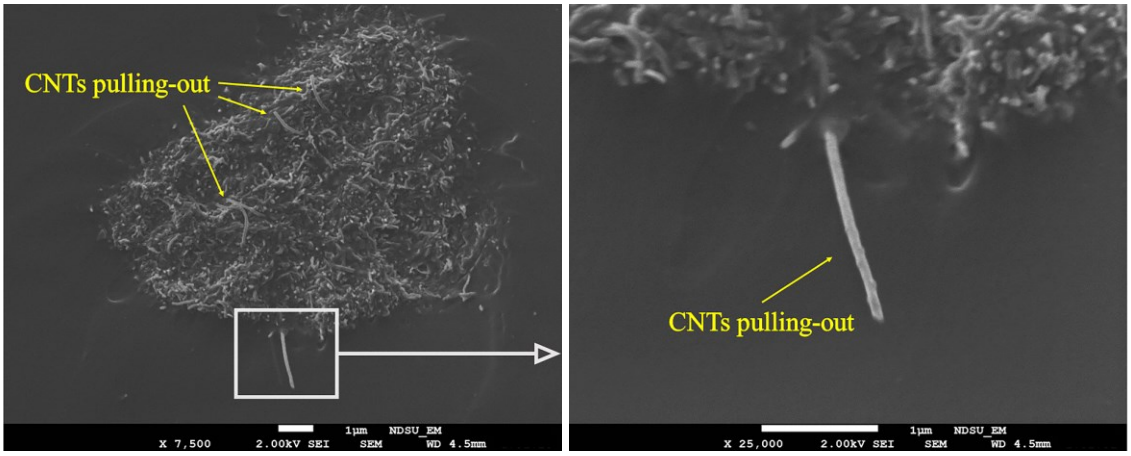


Figure 8. SEM images of the typical fracture surfaces: (a) 1 mm neat epoxy; (b): 1 mm 0.75% CNT-reinforced epoxy; (c) 0.25 mm neat epoxy; (d) 0.25 mm 0.75% CNT-reinforced epoxy.

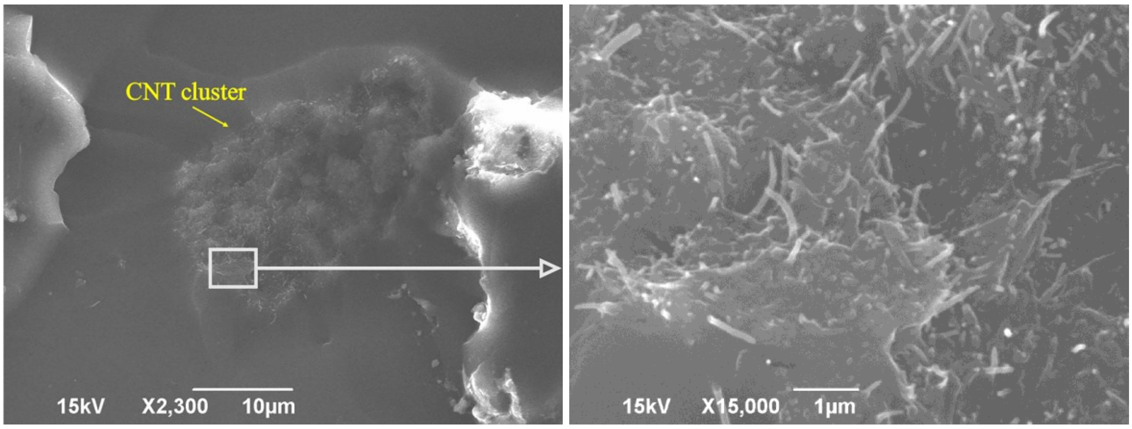
Figures 9(a, b) present the SEM images of the presence of CNTs in the reinforced epoxy bondlines at higher magnifications. Figures 9(a, b) clearly showed that several CNTs were pulled out from the surrounding epoxy bondline, which can be regarded as one of the important reinforcing mechanisms of CNTs. In terms of the CNTs pulling-out, CNTs and the surrounding epoxy matrix are tightly bonded together at the beginning until CNTs started to debond owing to the increase of the pull-out force. During debonding, a part of the CNTs moved along the interface against a friction force between CNTs and the epoxy matrix, with the rest part remaining well-bonded. When the debonding part extended to the whole length of CNTs, slipping occurred and CNTs were pulled out [49]. A lot of energy was consumed during this process, leading to the increase of the toughness and improvement of the bonding performances of epoxy adhesively bonded joints [50].



(a) (b)

Figure 9. SEM images of the presence of CNTs in the epoxy bondlines at higher magnifications: (a) The presence of CNTs; (b): CNT pulling-out from epoxy bondlines.

Although the CNT reinforcement could lower the influence of adhesive thickness on the bonding performance of reinforced epoxy adhesively bonded joints, it still could not eliminate the influence of adhesive thickness, not to mention reverse the influence. This might be induced by the CNT clusters generated in the bondlines, as illustrated in Figures 10(a, b). According to Figure 10(a), the CNTs were not uniformly dispersed in the epoxy matrix even the optimal CNT weight fraction of 0.75%. The CNTs were agglomerated together into a CNT cluster which was restricted in a certain area as evidently shown in Figure 10(b). No recognizable CNT was found in the other area outside the CNT clusters. The CNT cluster played a negative role in the bonding performance improvement of the CNT-reinforced epoxy adhesively bonded joints, acting as defects or imperfections in the bondline layer. The aggregation of CNTs imposed local stress concentration, accelerated the damage process and eventually reduced the bonding performances of CNT-reinforce epoxy joints. In addition, since CNTs were not uniformly dispersed with the CNT clusters, it might be challenging for the CNTs to cure all the imperfections in the epoxy bondline. The improvement of the CNT reinforcement was reduced due to the presence of some unfixed imperfections, resulting in that CNT-reinforced epoxy adhesively bonded joints with thicker bondlines still yielded a little weaker bonding performance compared to thinner ones. The influence of adhesive thickness was expected to be further restricted or even minimized with a more uniform CNT dispersion.



(a) (b)

Figure 10. SEM images of a CNT cluster on the fracture surface of 0.75% CNT-reinforced epoxy adhesively bonded joints: (a) A CNT cluster at a magnification of ×2300; (b): Enlarged view of (a) at a magnification of ×15000.

4. Conclusions

In this study, the neat and CNT-reinforced epoxy adhesively bonded joints with three adhesive thicknesses of 1 mm, 0.5 mm, and 0.25 mm and three CNT weight fractions of 0%, 0.375%, and 0.75% were fabricated and their bonding performances were studied using the SLS tests and SEM image analysis. Based on the experimental results, it was found that the increase of CNT weight fraction (from 0% to 0.75%) and the reduction of adhesive thickness (from 1 mm to 0.25 mm) could significantly improve the bonding strength, the fracture strain, and the toughness of epoxy adhesively bonded joints. The failure mode could be changed from complete adhesion failure for neat epoxy adhesively bonded joints with the adhesive thickness of 1 mm to partial cohesive failure for CNT-reinforced epoxy adhesively bonded joints with the adhesive thickness of 0.25 mm. However, the influence of adhesive thickness on the bonding performances of epoxy adhesively bonded joints become less significant as the increase of CNT weight fractions, which might be explained by the reinforcing mechanism of CNTs. The SEM image analysis also indicated that the addition of CNTs could not eliminate the influence of adhesive thickness, which might be induced by the non-uniform dispersion and the aggregation of CNTs. Thus, in the future, it is promising to optimize the dispersion of CNTs into the epoxy adhesive to see whether the influence of the adhesive thickness would be further reduced or minimized for a better bonding performance of the CNT-reinforced epoxy adhesively bonded joints. With improved bonding performances, the expected reduced potential of delamination of these CNT-reinforced epoxy can extend their applications to be used as protection coatings for wide areas of steel structures such as steel buildings, bridges, pipelines, automobiles, and aircrafts.

CRediT authorship contribution statement

Dawei Zhang: Data curation, Methodology, Formal analysis, Investigation, Roles/Writing - original draft, Writing - review & editing. Ying Huang: Project administration, Funding acquisition, Supervision, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Figure and table captions

Figure 1. The sample configurations of the SLS joint (unit: mm).

Figure 2. SLS test setup.

Figure 3. Comparisons between original experimental stress-strain curves and the average fitting curves in each testing conditions: (a) E1; (b) E0.5; (c) E0.25; (d) HC1; (e) HC0.5; (f) HC0.25; (g) C1; (h) C0.5; (i) C0.25.

Figure 4. Average stress-strain curves of epoxy adhesively bonded joints: (a) neat epoxy; (b): 0.375% CNTs; (c) 0.75% CNTs.

Figure 5. Comparisons of toughness between different adhesive thickness (including increments from 1 mm to 0.5 mm and 0.5 mm to 0.25 mm) with each CNT addition.

Figure 6. Comparisons between different adhesive thickness (including increments from 1 mm to 0.5 mm and 0.5 mm to 0.25 mm) with each CNT addition: (a) Bonding strength; (b) Fracture strain.

Figure 7. Typical fracture surfaces of epoxy adhesively bonded joints: (a) 1 mm neat epoxy; (b): 1 mm 0.75% CNT-reinforced epoxy; (c) 0.25 mm neat epoxy; (d) 0.25 mm 0.75% CNT-reinforced epoxy.

Figure 8. SEM images of the typical fracture surfaces: (a) 1 mm neat epoxy; (b): 1 mm 0.75% CNT-reinforced epoxy; (c) 0.25 mm neat epoxy; (d) 0.25 mm 0.75% CNT-reinforced epoxy.

Figure 9. SEM images of the presence of CNTs in the epoxy bondlines at higher magnifications: (a) The presence of CNTs; (b): CNT pulling-out from epoxy bondlines.

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Table 1. Properties of MWCNTs

Table 2. Grit blasting parameters

Table 3. The SLS test results