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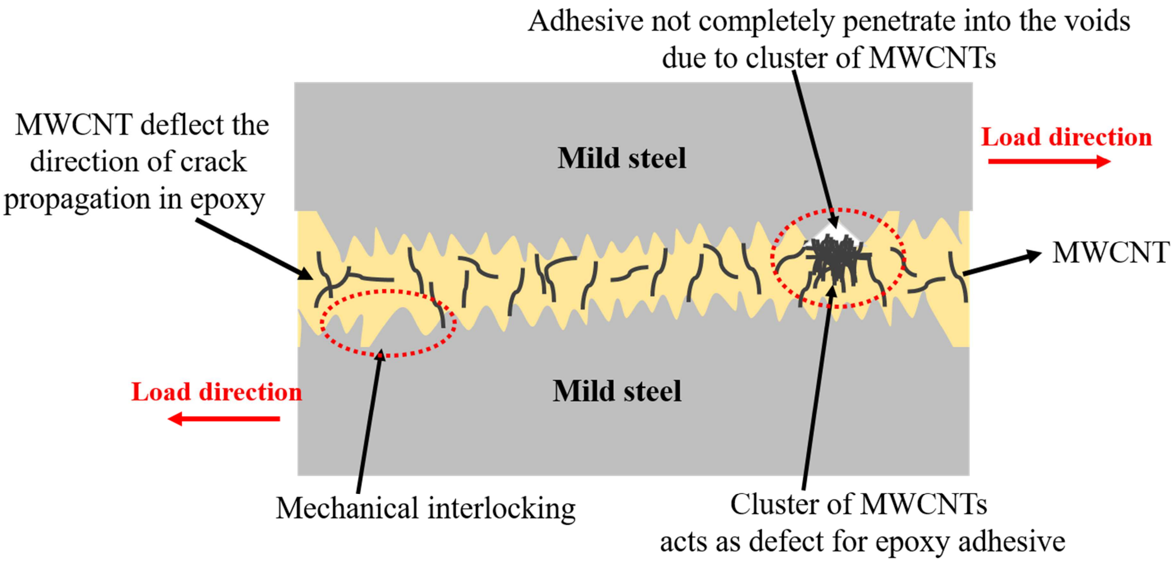
Adhesive not completely penetrate into the voids due to cluster of MWCNTs
MWCNT deflect the direction of crack propagation in epoxy
Mild steel
Load direction
MWCNT
Load direction
Mild steel
Mechanical interlocking
Cluster of MWCNTs acts as defect for epoxy adhesive

MWCNTs toward superior strength of epoxy adhesive joint on mild steel adherent

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Abstract:

In this work, the characteristics of the lap shear joints of MWCNT-epoxy adhesive on mild steel adherend are investigated. In this paper, multiwall carbon nanotubes (MWCNTs) are homogeneously and cluster-freely reinforced in epoxy matrix by simultaneously applying ultrasonic waves and an axial flow impeller on epoxy resin to develop toughened epoxy adhesives. Here, we describe details pertaining to mild steel surface morphology, the bond line thickness of the adhesive, the wettability of MWCNT-epoxy resin on the mild steel surface and the impact of the presence of MWCNTs in epoxy resin on the performance of lap shear joints. The experimental observations indicate that the reinforcement of MWCNTs in epoxy with uniform cluster-free dispersion and a change in the morphology of the mild steel adherend significantly improve the strength of lap shear joints and change their failure mode. The inclusion of 0.75 wt.% of MWCNTs in epoxy adhesive resulted in the largest enhancement in the lap shear strength and as the weight percentage of MWCNTs increased from 0.75 wt.%, the lap shear strength began to degrade.

Keywords: MWCNTs; epoxy resin; adhesive joints; lap shear strength

1. Introduction

Epoxy is widely used as an adhesive for aircraft, automobile, biomedical, electric and electronics industries due to its good tensile strength and modulus, high anti-corrosion properties, low shrinkage and the absence of by-products in curing, good chemical resistance, environmental resistance, good dimensional stability and high adhesion [1–7]. Adhesive joining using epoxy as the adhesive provides several advantages like the ability to join the surfaces of different materials, uniform stress distribution, good sealing and relatively lightweight structures compared with mechanical fastening [8]. The adhesive joints of metal prepared using neat epoxy have certain limitations because of its relatively lower tensile and compressive strength and toughness, along with its highly brittle nature, which indicates lower resistance to crack propagation [9–11]. However, in order to improve the performance of epoxy-based adhesive, various nano fillers are used to reinforce the epoxy, and epoxy nanocomposites have become a promising adhesive for making the joints of various components due to their higher modulus, fatigue strength, toughness and lap shear strength [12–15]. Carbon nanotubes are widely used as nano filler in epoxy to improve its mechanical, electrical, anti-corrosion, adhesion and thermal properties [16–23]. However, not much literature is available about the effect of carbon nanotubes on the adhesive joints of the epoxy when they are used to reinforce epoxy adhesive. Yu et al. [24] reported a significant improvement in fracture toughness and adhesive strength with the addition of carbon nanotubes in epoxy. The performance of a nanocomposite adhesive is influenced by various factors such as dispersion of the nano reinforcements in the polymer matrix, the thickness of the adherent, the morphology of the adherent surface, the bond line thickness of the adhesive, overlap length and the wettability of the adhesive for the surface of the adherent [25–32]. In the past, various techniques like solution casting, melt mixing, in-situ polymerization, electro spinning, surface functionalization of the nano filler, and ultrasonic mixing were applied to obtain cluster-free dispersion of nano reinforcements in the epoxy matrix, and here cluster-free homogeneous dispersion of nano reinforcements significantly enhances the performance of the nanocomposite [33–41].

The surface roughness of the adherent is also a parameter that affects the strength of lap shear joints, because good surface roughness plays a positive role in enhancing the performance of the adhesive by providing a large surface area of the adherent and mechanical inter-locking between the adhesive and adherent [42]. A very high-surface roughness may cause a rise in stress concentration andresulting a decrease in performance of joints [43].Various mechanical and chemical processes were applied on the surface of the metallic adherent to generate a roughness that can improve the wettability and joint strength by inducing physical-chemical changes between adherent surface and adhesive [42–47]. The mechanical treatment removes surface contamination, such as grease, oil, dust and metal oxide layers, and makes the surface rough, which results in improved bond strength.

In the case of epoxy adhesive, the thickness of the adhesive between the metal adherent (bond line thickness) is also a serious factor for the strength of joints due to the relatively high brittleness of neat epoxy. Various theories have been proposed by many researchers to explain the influence of bond line thickness on the strength of joints. Arenas et al [48], Grant et al [49], Banea et al [28] and Da Silva et al [50] reported that the probability of premature failure of the joints increases with increase in the bondline thickness due to generation of voids, microcracks and interface stresses as defects in the lap shear joints.According to classical analyses, the performance of joints improves with increase in the bond line thickness of the adhesive, but this is the opposite of the experimental trends [51,52]. Thus, it becomes necessary to understand how the wettability of the epoxy resin on the adherent and the bond line thickness influence the strength of the joint.The temperature and time of curing for the epoxy adhesive also affect the joint strength [42,47].

So in this work, we try to investigate the effect of the wettability of the epoxy resin on different adherent surfaces, the morphology of the adherent and the bond line thickness of the epoxy adhesive on the performance of epoxy adhesive joints on mild steel adherent. This study also intends to look for any other possibility for further enhancement in already strong neat epoxy adhesive joints with the help of MWCNTs.

2.

Experimental

2.1Materials

Commercially available mild steel (high strength low alloy AISI 4340 steel) strips of thickness 2.0 mm were used as adherent for the preparation of lap joints of MWCNT-epoxy adhesive. The mild steel as adherent in lap shear joints gives elastic deformation within the yield point. However, beyond the yield point it gives plastic deformation, therefore it is the yielding of the mild steel that controls failure and not the adhesive in lap shear joints [53,54]. So, it becomes necessary to use a adherent that does not yield during the test to assess the effect of the adhesive. For this purpose, high tensile strength mild steel (high strength low alloy AISI 4340 steel) was used in this study. The load verses extension curve and stress verses strain curve of used mild steel are given in Fig.1 to confirm the absence of any yielding in mild steel during failure of lap shear joint. MWCNTs (average diameter 30 nm, Fig. 2) synthesized by the chemical vapor deposition (CVD) method, epoxy resin (cam coat 2071) and aliphatic hardener supplied by Champion Advanced Materials Pvt. Ltd, India, were used in this study.

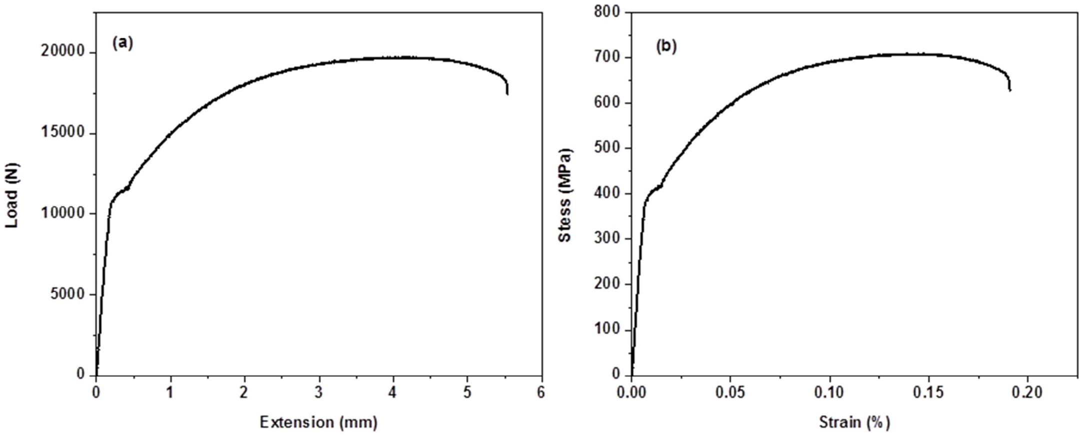

Fig. 1. Load–extension (a) and stress–strain (b) curves for mild steel (high strength low alloy AISI 4340 steel (HSLA AISI-4340))

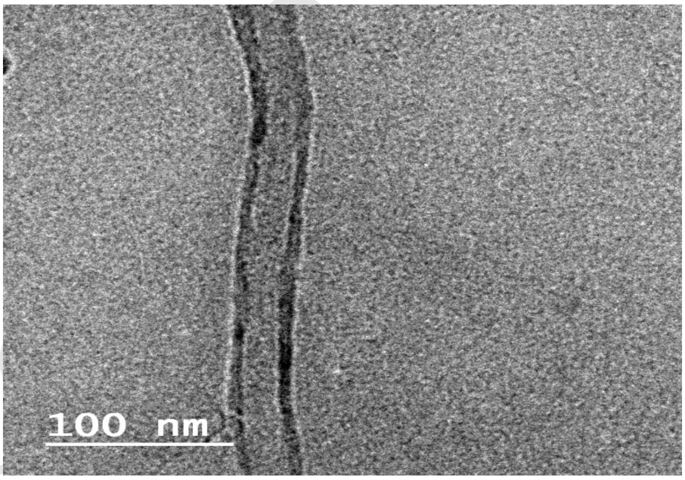

Fig. 2.Diameter of MWCNT

2.2 Preparation of MWCNTs reinforced epoxy adhesive:

Initially, MWCNTs (0.25 wt.%) were loaded in the epoxy resin with 10 wt.% of acetone to reduce the viscosity of the mixture and were thoroughly mixed using a glass rod. Then, ultrasonic waves from a Vibracell ultrasonic processor and axial-flow impeller for shear force were applied simultaneously for 30 min at 60 % amplitude with a pulse (10 sec on and 10 sec off) on the mixture to disperse the MWCNTs (Fig. 3). After processing, the mixture was kept at 50 °C to vaporize the acetone. Then, hardener (10 wt.%) was homogeneously mixed into themixture, followed by vacuum degassing. The same procedure was also followed for the preparation of 0.5, 0.75 and 1.0 wt.% MWCNTs-reinforced epoxy adhesives. The MWCNTs-reinforced epoxy adhesives obtained were used for preparation of adhesive joints on mild steel adherent. The basic mechanical properties of epoxy adhesive with and without MWCNTs have been already published [26] in order to understand the mechanical performance of the lap shear joints and also summarized in table 1.

Table. 1. Mechanical properties of epoxy with and without MWCNTs

MWCNT Content in epoxy (wt.%)	**Tensile Strength (MPa)**	**Elastic Modulus (GPa)**	**Area under stress-strain curve (MPa)**	**Storage modulus at 35 °C (MPa)**	**Tg (°C)**
0	54±1.2	6.6±0.02	0.29±0.01	1026	78
0.25	59±0.6	7.2±0.03	0.32±0.02	1152	81
0.50	63±0.8	7.4±0.04	0.34±0.02	1266	83
0.75	74±0.9	8.0±0.04	0.46±0.01	1387	87
1.00	67±2.7	7.7±0.15	0.37±0.08	1212	81

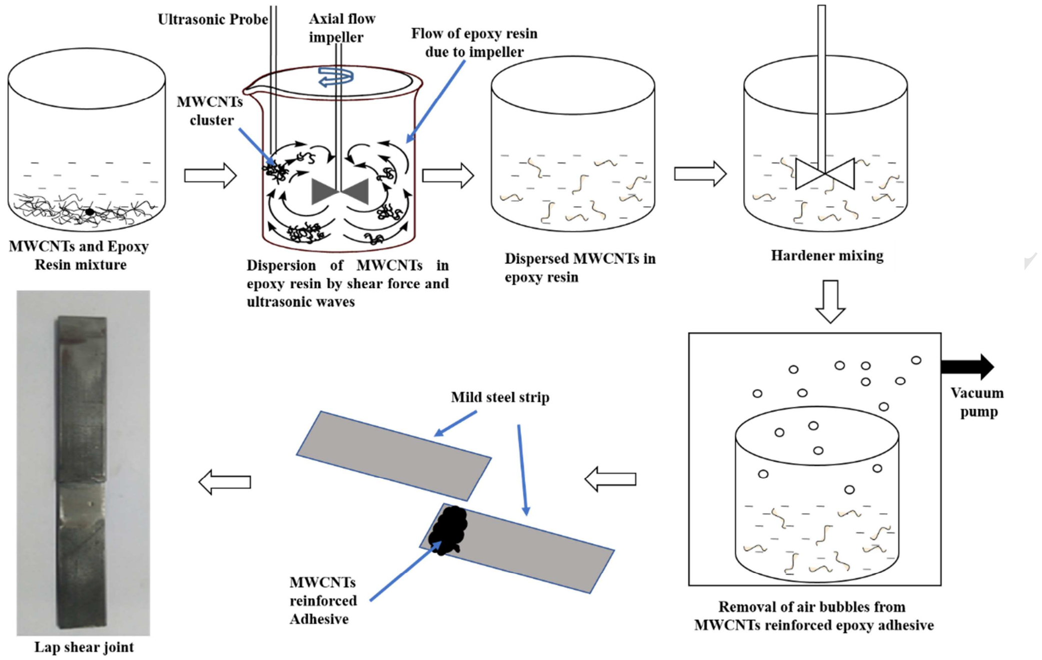

Fig. 3.A Schematic illustration of the procedure for the preparation of MWCNT-epoxy adhesive

2.3 Surface treatment of mild steel adherent

Mechanical and chemical treatments were applied on the faying surface of the mild steel adherent. In the mechanical treatment, the faying surface of the mild steel was polished using 220 grade emery paper [55] to remove contaminants like oxide layers, dirt, grease etc. The chemical treatment was carried out as per ASTM D2651 standard. In the chemical treatment, the strip of mild steel was immersed in a solution containing H_2SO_4 (10 wt.%) and oxalic acid (10 wt.%) in distilled water for 3 min, followed by rinsing with DI H_2O for 4 min. Next, NaOH (2 wt.%) solution was used to neutralize the acidic surface of the mild steel and it was washed in tap water and dried at 65°C. The mechanically and chemically treated surfaces of the mild steel adherent were characterized by FESEM (field emission scanning electron microscopy) at 15 kV accelerated voltage. A Mitutoyo SJ 400 profilometer was used to determine the roughness of the adherent surface.

2.4 Adhesive joint's Preparation on mild steel adherent and Lap shear testing

Single lap shear joints of adhesive (neat epoxy adhesive and MWCNT-epoxy adhesive) on the mechanically and chemically treated mild steel adherent were prepared as per ASTM D1002 standard. The adhesive was applied on both faying surfaces of the mild steel adherent, allowing complete wetting of the mild steel surface by the adhesive. Both surfaces were then put together as per Fig. 4. During the preparation of the adhesive joints, different rolling loads (2.5, 5.0 and 10.0 N) by a Teflon roller set-up (Roller diameter 22 mm and roller length 100 mm) at a speed of 1.5 mm/min were used to obtain different bond line thicknesses of the adhesive joints . Finally, the adhesive joints obtained were put in a hot air oven for curing at 50°C for 12 hr. After curing, all extra edges of the adhesive joints were removed to avoid any damage to the joints and the bond line thickness was measured using an optical microscope.The mechanical performance of the adhesive joints was studied by single lap shear testing. During the test, the cross-head speed of the machine (Hounsfield H25K-S) was 1 mm/min and specimens were gripped on an alignment tab (Fig. 4). The lap shear strength (σs) of joints with various adhesives was determined according to the expression σs = (N/X) x Y, where N stands for the failure load (Newton), X stands for the width of the adhesive joint (mm), and Y stands for the length of adhesive joint (mm). The results reported are the average of at least four measurements and the stress–strain plot was recorded up to fracture of the adhesive joint.

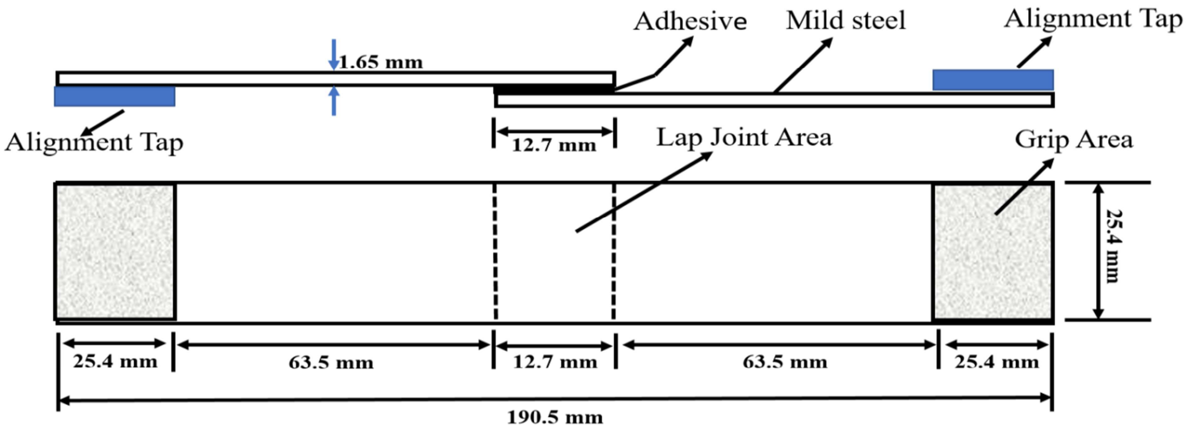

Fig. 4.Dimensions for single lap adhesive joint on mild steel adherent.

3. Results and discussion

3.1 Characterization of mild steel adherent surface

The FESEM images of the mechanically polished and chemically treated surfaces of mild steel adherent at low and high magnification are shown in Fig. 5. Fig. 5 (X1) and (X2) indicate that the mechanical polishing generates parallel scratches with hills and valleys like the pattern on the surface of mild steel (high strength low alloy AISI 4340 steel (HSLA AISI-4340)), while the chemical treatment on the mechanically polished surface creates porosity by a chemical etching process on the hills and valley zones, as confirmed from Fig. 5 (Y1) and (Y2). The chemical reaction releases Fe positive ions in aqueous solution from the mild steel surface and creates roughness in the form of porosity on the surface, as clearly revealed by Fig. 5 (Y1) and (Y2). The roughness of the mild steel surface after the mechanical and chemical treatment was found (Ra = 0.29 µm and Rz = 2.5 µm) and (Ra = 0.88 µm and Rz = 5.6 µm) respectively. This is in agreement with the FESEM images shown in Fig. 5.

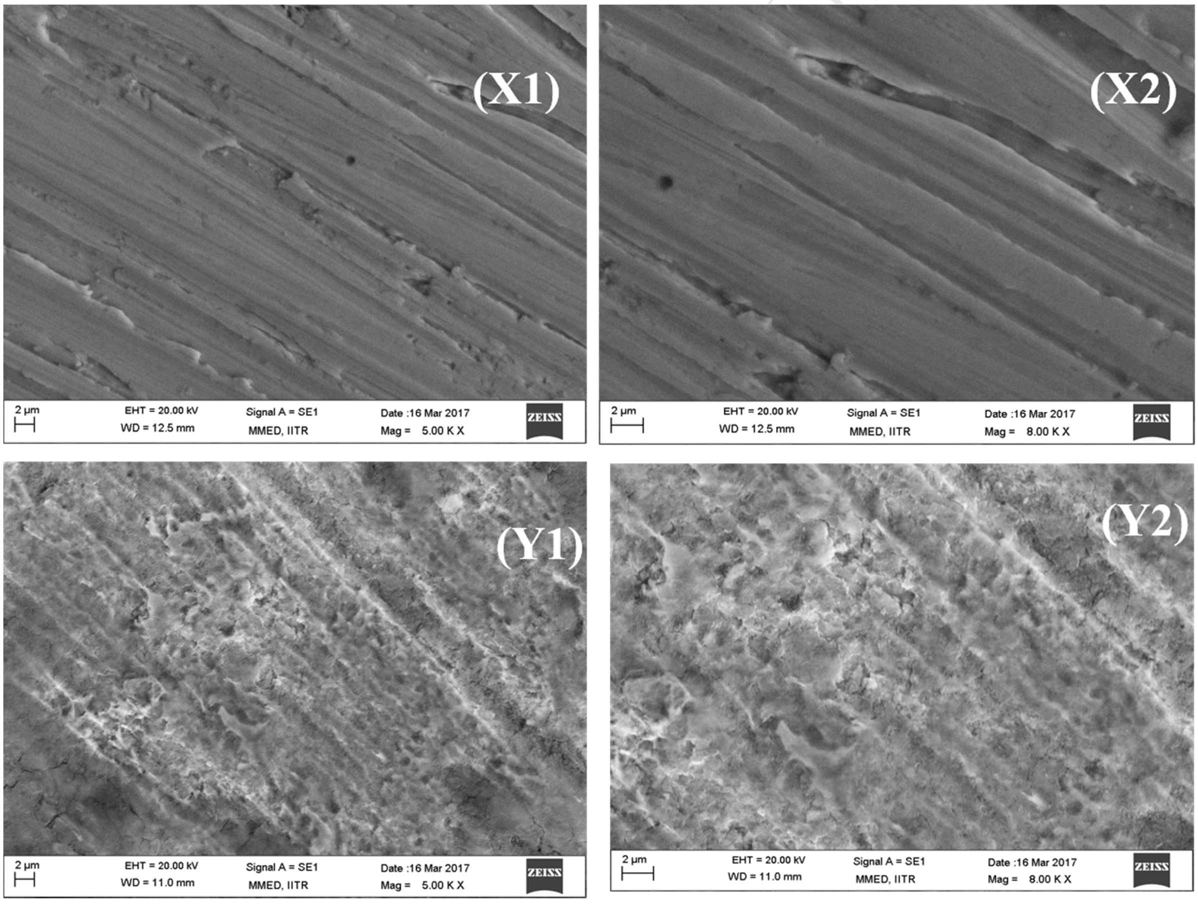

Fig. 5.SEM images of (X1) and (X2) mechanically treated and (Y1) and (Y2) chemically treated mild steel adherent at different magnification.

3.2 Wettability of epoxy adhesive on different surface and bond line thickness

The wettability of the epoxy adhesive on the mild steel adherent is a critical factor for the strength of joints. A mechanically treated mild steel surface with neat epoxy resin, a chemically treated mild steel surface with neat epoxy resin, and a chemically treated mild steel surface with MWCNT-epoxy (0.25 wt.%) resin are considered in the wettability study. The wettability of the adhesives was studied by measuring the contact angle with the help of sessile drop technique. The contact angle was measured by a built-in facility of a camera system operated through software (Drop Shape Analyzer e DSA25E). The contact angle (Q) of various adhesives on different surfaces is shown in Fig. 6. The mechanically and chemically treated surfaces of mild steel adherent show a 62° and 55° contact angle respectively with neat epoxy, which indicates that the chemical treatment improves the wettability of neat epoxy with mild steel compared with the mechanical treatment. However, the chemically treated surface of the mild steel with MWCNTs (0.25 wt.%)-reinforced epoxy resin gave a slightly lower contact angle (51°). This further reduction in contact angle confirmed the improvement in wettability of the epoxy resin by MWCNTs. The chemical treatment generates a porous structure on the mild steel surface for mechanical interlocking and provides a greater adhesion area with improved surface wettability. These illustrations indicate that the strength of the adhesion joint was determined by the surface morphology, adhesion area and wettability. However, the chemical interaction between the mild steel surface and epoxy-based adhesive also plays an important role in enhancing the joint strength. This variation in wettability of the adhesive for different faying surfaces can influence the strength of joints at applied rolling load during preparation of the joints. So, it becomes necessary to study the bond line thickness as a function of rolling load and lap shear strength. However, the viscosity of the adhesive also affects the flow characteristics. But, at very low wt.% loading of MWCNTs in epoxy adhesive, no significant change in viscosity was observed.

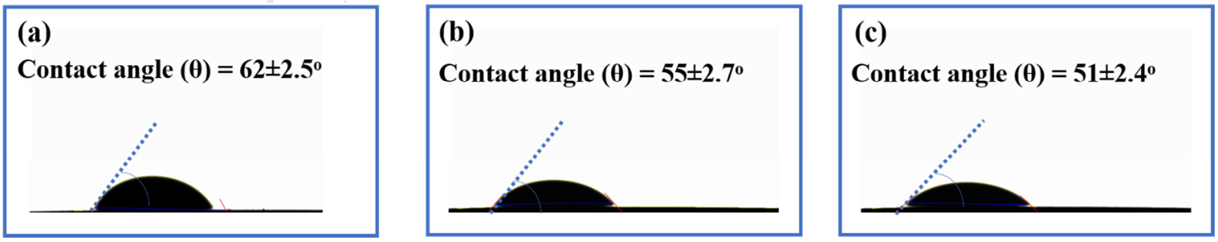

Fig. 6. Photograph of contact angle of (a) neat epoxy resin on mechanically treated mild steel adherent, (b) neat epoxy resin on chemically treated mild steel subs adherent and (c) 0.25 wt.% MWCNT-epoxy resin on chemically treated mild steel adherent.

3.3 Bond line thickness andlap shear strength

The change in bond line thickness at different rolling loads for neat epoxy adhesive on mechanically and chemically treated mild steel adherents is presented in Fig. 7, which indicates that the thickness of the neat epoxy in the adhesive joints is significantly influenced by the applied rolling load during the preparation of joints. Fig. 8 represents the quantitative variation in bond line thickness. Fig. 7 and 8 indicate that as the load increases up to 10 N, the thickness significantly decreases, followed by a moderate reduction with further increase in the load. This indicates that the interfacial drag force of the adherent surface becomes proactive at thicknesses below 80 µm, to grip the epoxy-based adhesive in position by restricting the flow at the applied rolling load. From Fig. 7 and 8, it is noted that the thickness of the adhesive at lower load is approximately the same in both the mechanically and chemically treated mild steel adherents, but at higher loading the bond line thickness in the chemically treated surface is higher than the mechanically treated mild steel adherent. This behavior may be understood as the chemical treatment making the mild steel surface more capable of gripping the epoxy-based adhesive against its flow at relatively low rolling load. This is in agreement with the improved wettability after chemical treatment of the mild steel surface as discussed in the section above (Fig. 6).

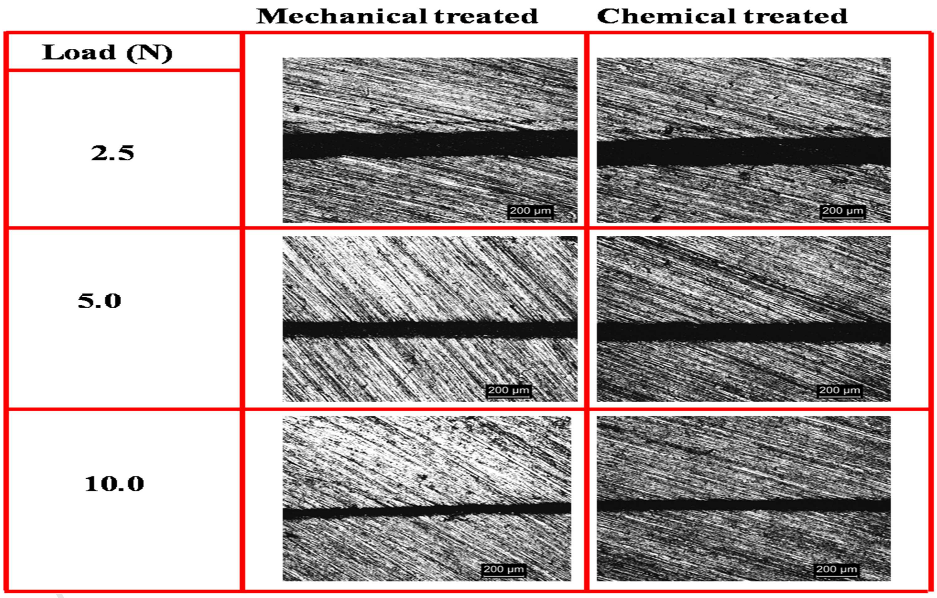

Fig. 7. Optical micrographs of bond line thickness of neat epoxy adhesive joint on mechanically and chemically treated mild steel adherent.

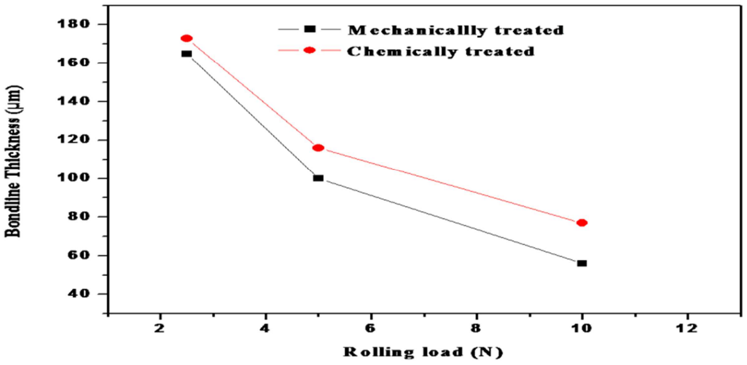

Fig. 8. Bond line thickness's variation withrolling load on different surface.

Table. 2. Lap shear strength and toughness of adhesive joints

Rolling load (N)	Bond line thickness (µm)	Type of Adhesive and surface	Lap shear Strength (Standard deviation) MPa	Area under the stress-strain curve (Standard deviation)(MPa)
2.5	165(±2.55)	Neat epoxy on mechanically treated surface	2.5 (±0.810)	5.5 (±0.974)
5.0	100(±2.91)	Neat epoxy on mechanically treated surface	3.12 (±0.951)	7.43 (±1.334)
10.0	56(±3.12)	Neat epoxy on mechanically treated surface	1.35 (±1.101)	4.7 (±1.244)
2.0	173(±2.85)	Neat epoxy on chemically treated surface	3.5 (±1.121)	6.1(±1.417)
5.0	116(±3.55)	Neat epoxy on chemically treated surface	4.08 (±0.853)	10.04(±1.351)
10.0	77(±2.87)	Neat epoxy on chemically treated surface	2.9 (±0.934)	5.9(±1.223)
5.0	115(±1.98)	MWCNT-epoxy on chemically treated surface (0.25 wt.%)	4.9 (±0.681)	14.00(±1.980)
5.0	116(±2.54)	MWCNT-epoxy on chemically treated surface (0.50 wt.%)	5.32 (±0.993)	15.80(±1.022)
5.0	116(±2.50)	MWCNT-epoxy on chemically treated surface (0.75 wt.%)	6.72 (±0.752)	26.96(±0.981)
5.0	117(±3.02)	MWCNT-epoxy on chemically treated surface (1.00 wt.%)	5.08 (±1.205)	18.21(±1.368)

Table 2 indicates the effect of the rolling load on the lap shear strength of neat epoxy adhesive joints on differently treated adherents. The rolling load is an indication of the bond line thickness; the higher the rolling load, the lower will be the bond line thickness. As the rolling load increases up to 5 N, the lap shear strength also increases, and with further increase in the rolling load, the lap shear strength significantly decreases for the mechanically treated mild steel adherent. A similar trend in strength of joints was also observed in the case of chemically treated mild steel adherent, where the bond line thickness of the neat epoxy adhesive for the maximum strength of joints has been noted as 112 µm. Here, it is noted that the strength of the chemically treated mild steel adherent is higher than the mechanically treated mild steel adherent joints with neat epoxy. The enhancement in wettability and in the area of contact by chemical treatment on the mild steel surface is discussed in the section above. The porosity on the faying surface of the chemically treated adherent provided better mechanical interlocking with the adhesive. These explained phenomena are responsible for the higher lap shear strength on the chemically treated mild steel adherent rate compared with the mechanically treated mild steel adherent.

Fig. 7 and 8 indicate that as the load increases up to 10 N, the thickness significantly decreases and becomes too thin. The reduction in lap shear strength at higher rolling load (lower bond line thickness) may arise due to the greater brittleness of neat epoxy and the tendency of tearing of the adhesive film laid down on the mild steel adherent surface because of surface tension, which has the effect of interrupting its continuity in the adhesive joints. However, the higher bond line thickness of the joint makes it more prone to fracture by escalating the triaxiality of its stress distribution [16,25,53] and prone to the creation of micro defects in adhesive joints, such as air entrapment.

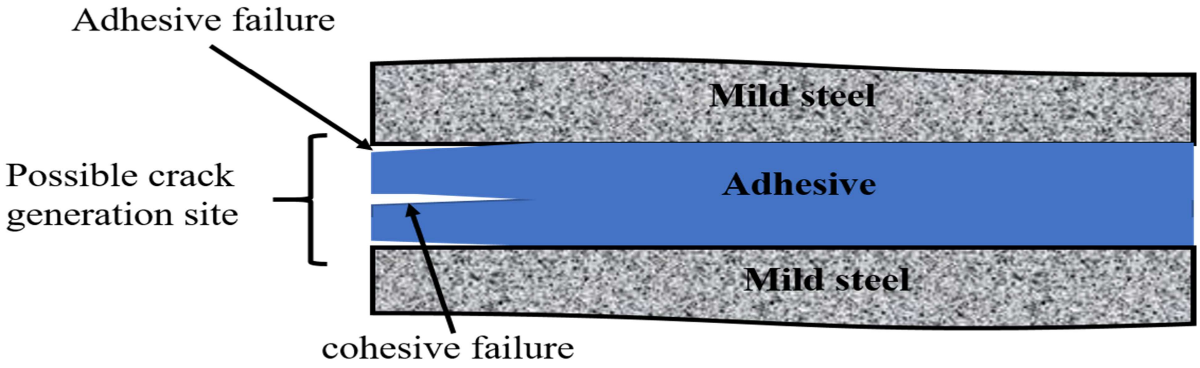

Fig. 9.The possible crack generation site or crack paths.

Generally, there are two most probable means of failure in polymer adhesive joints, as shown in Fig. 9. One is cohesive failure, where cracks grow in the epoxy adhesive. This cohesive failure can be identified by the presence of adhesive on both faying surfaces of the metal after failure of the adhesive joints. The second is adhesive failure, where cracks grow along the interface between the epoxy adhesive and metal adherent. In this failure mode, one faying surface of the metal adherent is completely covered by adhesive and the other faying surface of the adherent completely lacks adhesive. Here, it is noted that adhesive failure takes place for joints of neat epoxy with the mechanically treated mild steel adherents, where only one surface was completely covered with neat epoxy adhesive, as confirmed from Fig. 10. However, for the chemically treated mild steel adherent, the failure is the cohesive type, as confirmed in Fig. 10. So, it is very clear from the fractography results that chemical treatment on the mechanically treated surface shifts the failure mode from adhesive to cohesive, with an enhancement in the lap shear strength. This may be mainly due to the higher wettability of neat epoxy resin on the chemically treated mild steel adherent (Fig. 6) and furthermore because the chemical treatment provided a greater surface area by introducing porosity on the adherent surface, as shown in Figs. 5(Y1) and 4(Y2), which resulted in mechanical interlocking and improved the strength of the joints. The mechanical interlocking is illustrated in Fig. 14.

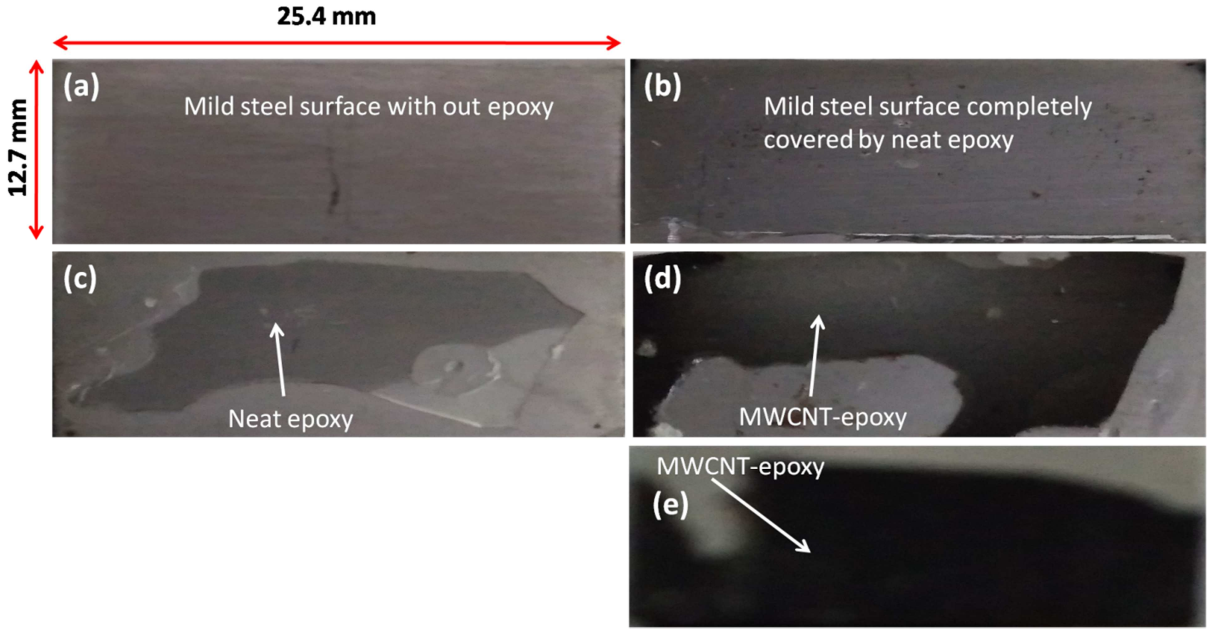

Fig. 10.Typical Shear fracture surface of joints of neat epoxy adhesive on mechanically treated mild steel adherent (a) and (b), neat epoxy adhesive on chemically treated mild steel adherent (c), (0.75 wt.%) MWCNT-epoxy adhesive on chemically treated mild steel adherent (d) and (1.00 wt.%) MWCNT-epoxy adhesive on chemically treated mild steel adherent (e).

Thus, the shear failure site of the polymer-based adhesive joint is determined by whichever is weaker out of the polymer adhesive and the interfacial bonding between the metal adherent and adhesive. The interfacial strength significantly improves with chemical treatment on the metal adherent (Fig. 10). Attention was next mainly focused on strengthening and toughening of the epoxy-based adhesive. For this purpose, 0.25, 0.50, 0.75 and 1.00 wt.% of MWCNTs were homogeneously and cluster-freely dispersed in epoxy by simultaneously applying ultrasound waves and shear force (Fig. 3) and the strength of MWCNT-epoxy nanocomposite as an adhesive on chemically treated mild steel adherent was studied. In this study, the bond line thickness was maintained around 115 µm. At this bond line thickness, neat epoxy adhesive on chemically treated mild steel adherent gives the maximum strength of joints. The effect of the loading of MWCNTs (0.25, 0.50, 0.75 and 1.00 wt.%) on the epoxy adhesive is shown in Fig. 11 for the stress–strain curve of the adhesive joints. The increment in lap shear strength is shown in Fig. 12. From Fig. 11 and 12, it is clear that as the MWCNTs loading in the epoxy adhesive increases from 0.25 to 0.75 wt.%, the lap shear strength of the joints on the chemically treated mild steel adherent appreciably increases, followed by a decrease with further loading of the MWCNTs (1.0 wt.%). Fracture of the MWCNT-epoxy adhesive joints occurred by mixed mode, predominantly including adhesive failure of the MWCNT-epoxy adhesive joints, as indicated by Fig. 10.

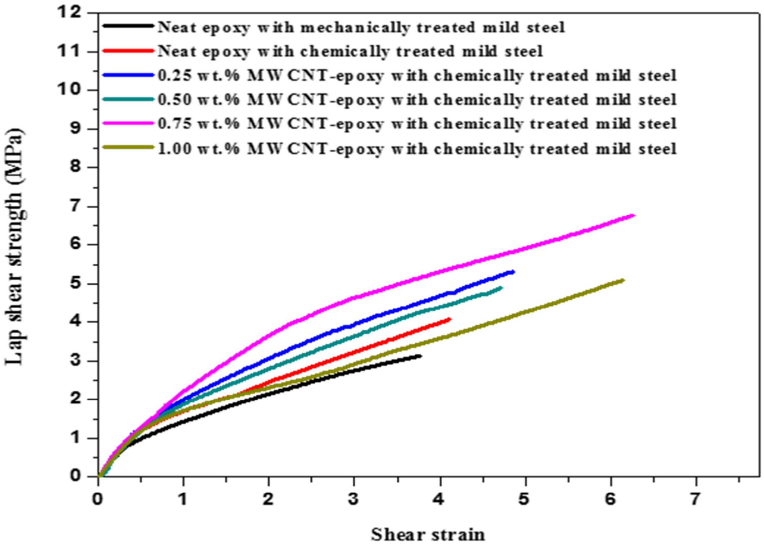

Fig. 11.Stress-strain graphs of MWCNT-epoxy adhesive on mild steel adherent (chemically treated).

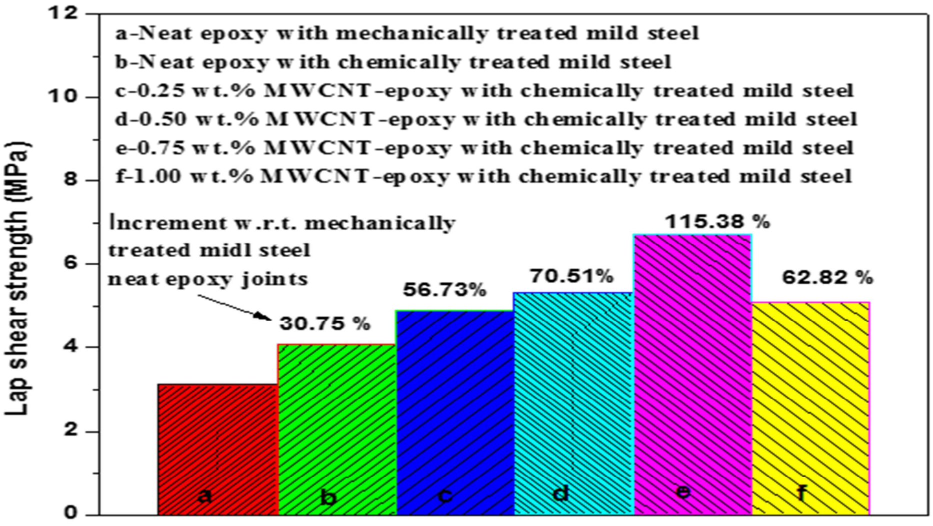

Fig. 12. Increment in lap shear strength

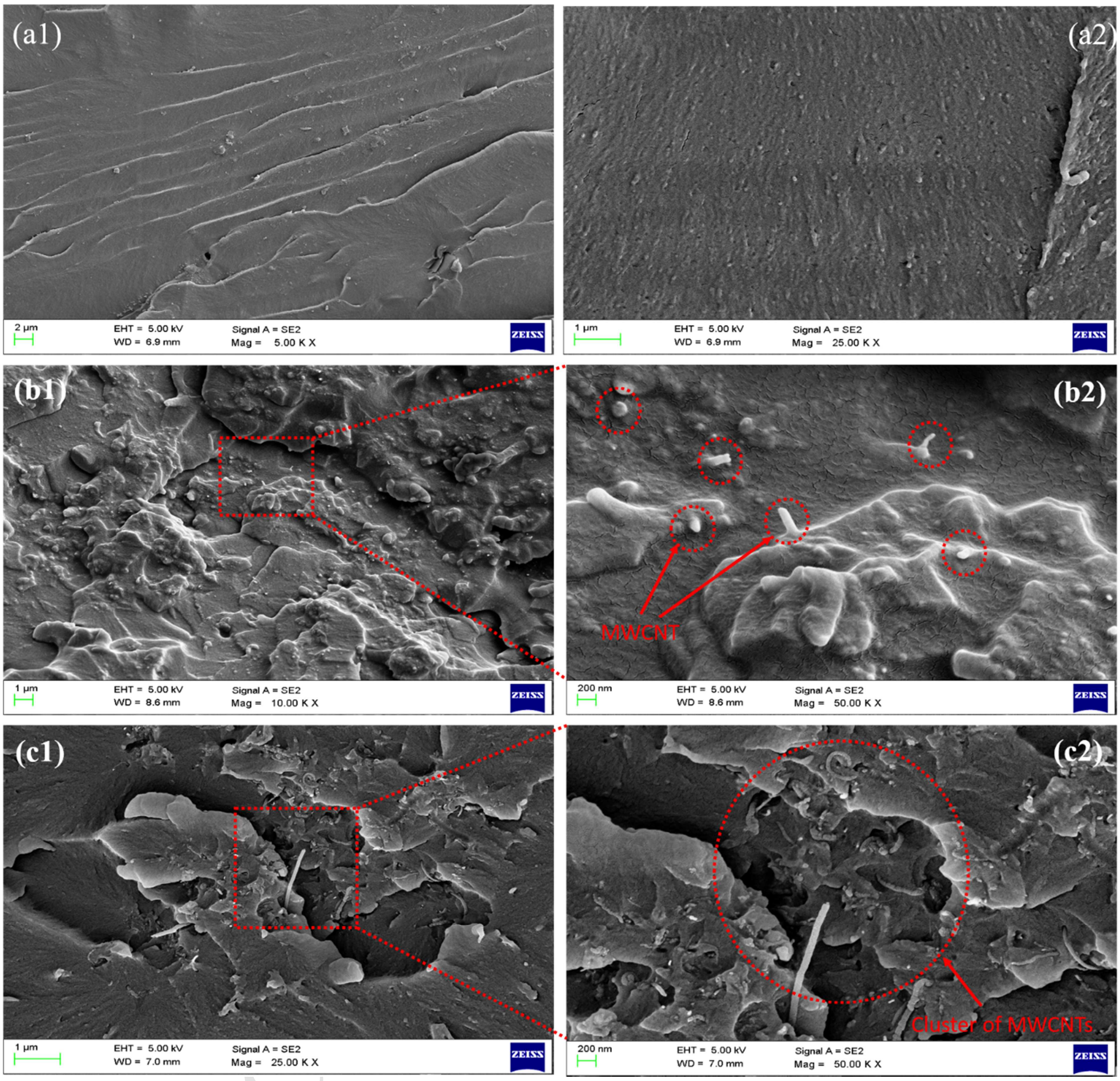

Fig. 13. FESEM image of cohesive failure zone of neat epoxy (a1 & a2), (0.75 wt.%) MWCNT-epoxy (b1 &b2) and (1.00 wt.%) MWCNT-epoxy (c1 &c2) adhesive joints on chemically treated mild steel adherent. Magnification: (a1) x5,000; (a1) x25,000;(b1)x25,000; (b1) x50,000;(c1)x 25,000;(c2)x 50,000.

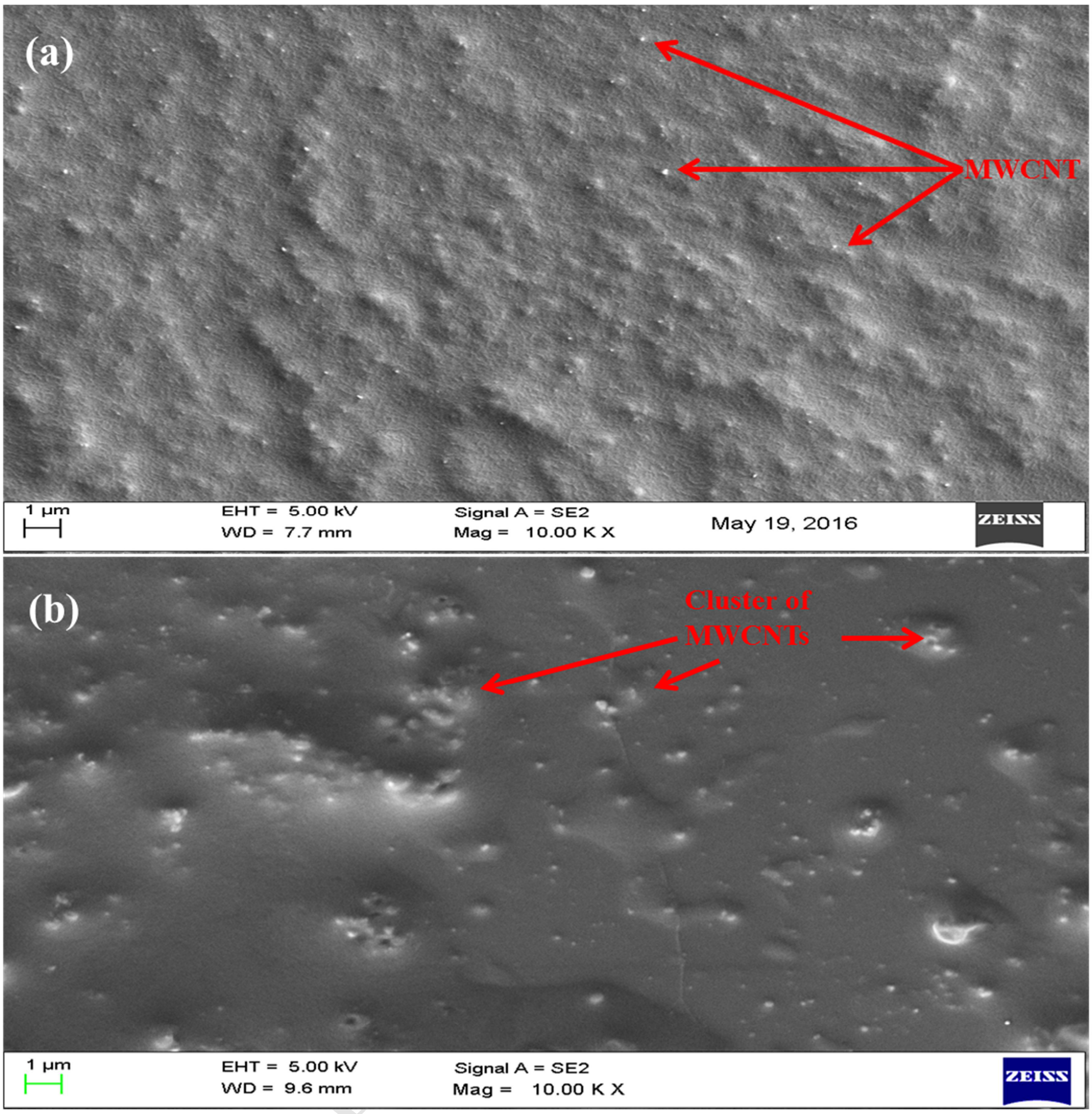

Fig. 14. FESEM image of adhesive failure zone of (0.75 wt.%) MWCNT-epoxy (a) and (1.00 wt.%) MWCNT-epoxy (b) adhesive joints on chemically treated mild steel adherent. Magnification: (a) x10,000; (b) x10,000.

From the FESEM images (Fig. 13 (a1 & a2)) of the cohesive failure zone of the neat epoxy adhesive on the chemically treated mild steel adherent, it is clear that the cracks propagate freely, with the formation of very smooth and river-like patterns. This indicates the weak ability of the neat epoxy to prevent crack propagation, which is the typical brittle fracture of neat epoxy.The increment in lap shear strength with the loading of MWCNTs up to 0.75 wt.% in the epoxy may be credited to the homogeneous and cluster-free dispersion of MWCNTs (Fig. 13 (b1 & b2)

FESEM images of the cohesive failure zone and Fig. 14 (a) FESEM images of the adhesive failure zone), where the fracture surface changes, showing greater roughness with several clusters . Generally, more energy is dissipated for higher surface roughness [26]. Here, MWCNTs resist cohesive fracture by deflecting the crack growth with the help of crack-blunting mechanisms in the matrix, as illustrated in Fig. 15. In this case, the slightly higher wettability of MWCNT-epoxy resin on the chemically treated surface in comparison with the neat epoxy resin, as discussed in section 3.2 on the contact angle, also plays a positive role to improve the strength of joints. The reduction in lap shear strength of joints with 1.0 wt.% loading of MWCNTs may have occurred mostly due to the presence of clusters of MWCNTs (Fig. 13 (c1 & c2) FESEM images of cohesive failure zone and Fig. 14 (b) FESEM images of adhesive failure zone)) in the epoxy matrix, which act as defects in the matrix and result in quicker interaction of the stress field generated in the clusters. From Fig. 13 (c1 and c2) and Fig. 14 (b), it is very clear that MWCNTs are protruding from the cluster-containing surface, confirming the long pull-out mechanism in clusters of MWCNTs, with circular holes generated due to pull-out of the MWCNTs. The de-bonding between the MWCNTs and epoxy matrix in clusters shows that there is not a good interfacial interaction between the MWCNTs and epoxy matrix, and the MWCNTs are not completely wetted by the resin in the clusters. All these observations are marked with red color in the FESEM image. So, the presence of clusters in the epoxy matrix as well as in the interfacial region of the joints has detrimental effects on the mechanical behavior of the MWCNT-epoxy adhesive, as illustrated in Fig. 15.

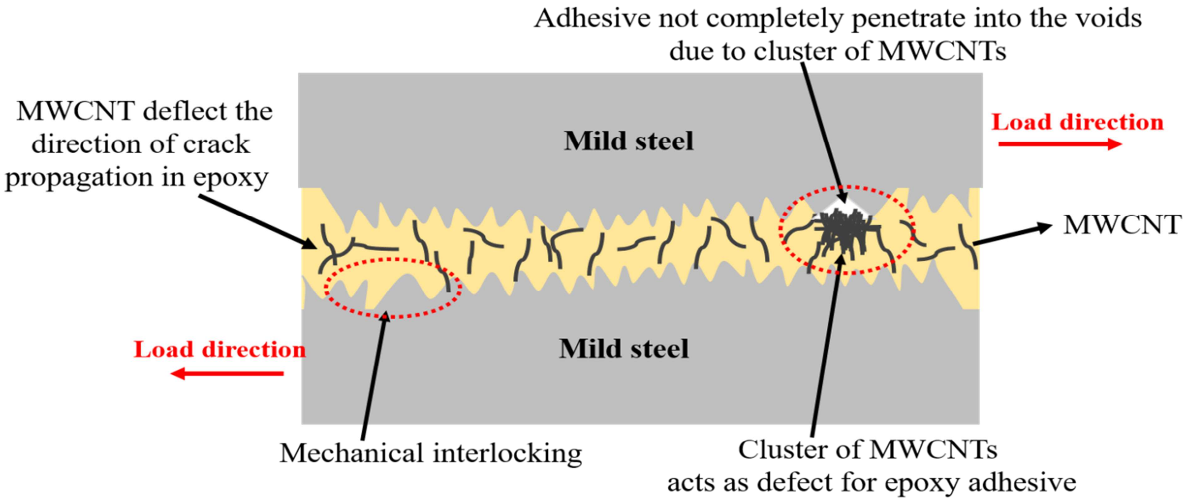

Fig. 15. Proposed mechanism for strengthening and toughening of adhesive joints.

Here, it is also noted that adhesive failure occurred predominantly with the reinforcement of 1.0 wt.% of MWCNTs, as shown in Fig. 10. A possible reason for the weak interfacial bonding in MWCNTs (1.0 wt.%)-reinforced epoxy adhesive is the presence of clusters of MWCNTs, which prevent the epoxy resin from completely diffusing into the micro cavities generated by the chemical treatment, as illustrated schematically in Fig. 15 and confirmed by Fig. 14 (b), which also resulted in lower mechanical interlocking, a smaller area of adhesion and lower surface wetting, as well as a reduction in the lap shear strength. It seems that the presence of clusters of MWCNTs has changed the structural properties in the region near to the clusters, while homogeneous cluster-free dispersion of MWCNTs changes the material properties of the epoxy adhesive joint. However, it is interesting to note that the lap shear strength of joints prepared using 0.75 wt.% MWCNT-epoxy nanocomposite adhesive on chemically treated mild steel adherent increases by 64 % with respect to the joint prepared using neat epoxy on chemically treated mild steel adherent at a similar bond line thickness.

3.4 Area under the stress-strain curves of epoxy adhesive joints

The area under the stress–strain curve is an indication of toughness. The stress–strain curves of all types of joints are shown in Fig. 11. These graphs were used to study the toughness (area under the stress–strain curve) of the adhesive joints. The area under the stress–strain curves is shown in Fig. 16. Fig. 11 shows that the chemical etching on the mild steel adherent appreciably extends the stress–strain curve in comparison with the mechanically treated surface for neat epoxy adhesive, representing an enhancement in toughness by consuming more energy prior to fracture. The improvement in toughness by the chemical treatment is estimated to be of the order of 35%, as shown in Fig. 16. However, the inclusion of MWCNTs from 0.25 to 0.75 wt.% in the epoxy adhesive significantly improves the toughness of joints up to a great level by extending the stress–strain curve. Here it is noted that the addition of 0.75 wt.% MWCNTs in the epoxy-based adhesive increases the toughness of the joints on the chemically treated mild steel adherent by 168 % in comparison with the joints prepared using neat epoxy. However, with the loading of 1.0 wt.% of MWCNTs in the epoxy-based adhesive, the toughness decreases, as shown in Fig. 16. The improvement in toughness of the epoxy joint as a function of the MWCNTs contents may be attributed to the same mechanism as discussed earlier in the case of the variation in the tensile lap shear strength of the epoxy adhesive joints.

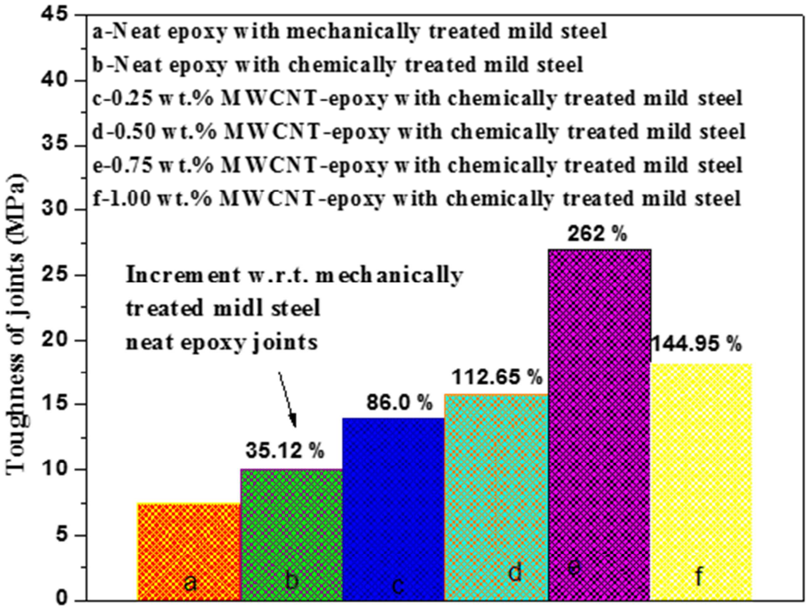

Fig. 16. Area under the stress-strain curves of epoxy adhesive joints

4. Conclusion

The mechanical properties of adhesive joints strongly depend on the surface characteristics of the mild steel adherent and the bond line thickness of the adhesive in between the faying surfaces. The chemical treatment of the mild steel adherent shifts the failure mode from adhesive to cohesive, with higher lap shear strength and toughness. The chemical treatment improves the wettability of the surface with epoxy by decreasing its contact angle. The inclusion of a low content of MWCNTs in the epoxy further reduces the contact angle. The homogeneous cluster-free dispersion of MWCNTs in epoxy adhesive significantly enhances the lap shear strength and the toughness of joints with a mixed mode of failure. The clusters of MWCNTs present act as defects in the epoxy adhesive and also in the interfacial region, which degrades the strength of the joints.

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Highlights

- MWCNTs were homogeneously and cluster freely reinforced in epoxy matrix by applying simultaneously ultrasonic waves and axial flow impeller on epoxy resin.
- The mechanical properties of adhesive joints strongly depend on surface characteristic of mild steel adherend and bond line thickness of adhesive in between the faying surface.
- The homogeneous cluster free dispersion of MWCNTs in epoxy adhesive significantly enhances the lap shear strength and toughness of joints with mixed mode of failure.
- The presences of clusters of MWCNTs act as defect in epoxy adhesive and also in interfacial region, which degrades the strength of joints.