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Influence of adding multi-walled carbon nanotubes on the adhesive strength of composite epoxy/sol-gel materials

M. May^{1*}, H. M. Wang^{2**}, R. Akid³

1. Material Engineering Department, Faculty of Engineering, Sebha University, Sabha - Libya

2. Materials and Engineering Research Institute, Sheffield Hallam University, Howard Street, Sheffield S1 1WB, UK.

3. School of Materials, the University of Manchester. Oxford Road, Manchester M13 9PL, U.K

Corresponding authors:

* hsammay1@hotmail.com;

** h.wang@shu.ac.uk.

Abstract

The tensile shear strength of a composite epoxy/sol-gel system modified with different ratios of multiwall carbon nanotubes (MWCNTs) was evaluated using an mechanical testing machine. The experimental results showed that the shear strength increased when lower than ~0.07 wt% of MWCNTs were added in the composite solution. The increase of the shear strength was attributed to both the mechanical load transfer from the matrix to the MWCNTs and the high specific surface area of this material that increased the degree of cross-linking with other inorganic fillers in the formulation. However, a decrease in the adhesive shear strength were observed after more than ~0.07 wt% MWCNTs was added to the composite. The reason for this may be related to the high concentration of MWCNTs within the matrix leading to excessively high viscosity, dewetting of the substrate surfaces, and reduced bonding of MWCNTs with the matrix, thereby limiting the strength. SEM observation of the fracture surfaces for a composite epoxy/sol-gel adhesive materials with 0.01wt% MWCNTs showed a mixed interfacial/cohesive fracture mode. This fracture mode indicated strong links at the adhesive/substrate interface and interaction between CNTs and the matrix was achieved; therefore, adhesion performance of the composite epoxy/sol-gel material to the substrate was improved. An increase of a strong peak related to the C-O bond at ~ 1733 cm⁻¹ in the FTIR spectra was observed. This peak represented cross-linking between the CNT surface and the organosilica nano-particles in the MWCNTs doped composite adhesive. Raman spectroscopy was also used to identify MWCNTs within the adhesive material. The Raman spectra exhibits peaks at ~ 1275 cm⁻¹ and in the

range of $\sim 1549\text{-}1590\text{ cm}^{-1}$. The former is the graphite G-band while the latter is the diamond D-band. The D-band and G-band represent the C-C single bond and C=C double bond in carbon nanotubes respectively.

Keywords: MWCNT, adhesive strength, sol-gel materials

1. Introduction

In recent years, filler-filled polymeric components have been widely used in a range of applications due to their numerous properties including mechanical strength and adhesive characteristics [1,2]. The use of small additions of carbon nanotubes (CNTs) are expected to be effective in improving the desired properties, such as mechanical, thermal and electrical properties. In addition, CNTs can be used as multifunctional components to develop new materials used in many different fields. Modified adhesive materials based upon the addition of CNTs have received considerable attention because of their potential to achieve property enhancement significantly greater than that attainable using conventional fillers. It has been reported [3,4] that the introduction of CNTs into some thermoplastics can enhance stiffness of the polymeric materials without sacrificing ductility. Sager and co-workers [5] found that the increase in interfacial shear strength of carbon fiber in an epoxy matrix was obtained with the addition of CNTs. This improvement can be attributed to an increase in the interphase yield strength as well as an improvement in interfacial adhesion due to the presence of the CNTs. Also, due to high modulus and low weight of CNTs these materials were ideal reinforcing agents in a variety of adhesive and composite materials used in the aircraft and sport industries [6].

Adhesive bonding, as an alternative to riveting, bolting, or welding is increasing in many industries, e.g. automotive and aircraft, due to its numerous advantages [7]; for example, low weight, homogeneous stress distribution, low cost, high corrosion resistance, ease of application and excellent thermal and insulation properties. Adhesives can be used to join many different materials including metals, composites, ceramics, films and damage-sensitive materials, singly and in combination. It has the

valuable capability of joining and fabricating complicated shapes to produce a smooth aerodynamic surface that gives an improvement in corrosion and/or fatigue resistance [8]. Due to their visco-elastic properties adhesives can reduce the vibration of the bonded parts compared with conventional joining techniques. All these features have encouraged scientists to investigate the production of new adhesives. However, due to some defects; for example, porosity, voids, and incorrect cure within the adhesive structure, these adhesively bonded joints may crack and then fail at low loading. Adhesive bonded joints can fail upon exposure to aggressive environments via under film corrosion, which can lead to catastrophic failure of the adhesive structure in service [9,10].

The incorporation of a second component in the adhesive matrix such as multiwall carbon nanotubes (MWCNTs) can enhance the load bearing capacity of reinforced adhesives, which greatly improves the structure and strength. In addition, using CNTs as a reinforcing component in polymer materials requires the ability to tailor the nature of the CNT walls in order to control the interfacial interactions between the CNTs and the polymer chains. It has been well known that [11] the surface interface between CNTs and the polymer matrix should be optimized. Covalent linkages achieved through chemical functionalization have been utilized in CNTs reinforced polymers. These interactions govern the load transfer efficiency from the polymer to the CNTs and hence the reinforcement efficiency. Numerous work about using carbon nanotubes as fillers in polymer matrix has been extensively reviewed in literatures [12, 13, 14]. In this work, we investigated influences of adding MWCNTs on the shear strength of composite epoxy/sol-gel materials. Adhesion of a single lap joint in the combined mild steel was evaluated according to ASTM D1002.

2. Experimental work

Table 1 Composition of the mild steels.

Composition	C	P	S	Mn	Fe
Mild steel wt%	0.15 -0.2	0.04 max	0.05 max	0.6-0.9	Rest

2.1 Materials

Mild steel was used as the substrate material in testing the adhesive strength of the composite epoxy/sol-gel materials. Table 1 presented the composition of mild steels used in measuring the lap shear adhesive strength. The substrate sample was abraded using grinding with sandpaper having a surface roughness $R_a = 0.102 \mu\text{m}$ and then ultrasonically cleaned by using acetone at room temperature. It should be pointed out that a more complicated surface treatment was not used as it was of interest to assess the 'surface tolerance' of the composite adhesive system. Composite epoxy/sol-gel was then applied as a thin layer on the surface of both mild steel specimens and the coated substrates were left for dry for one hour at room temperature. According to ASTM D1002, the coated mild steel samples (100 X 25 X 1.5 mm) were assembled into a single lap shear joint with 12.5 mm of the overlap length as shown in Figure 1a.

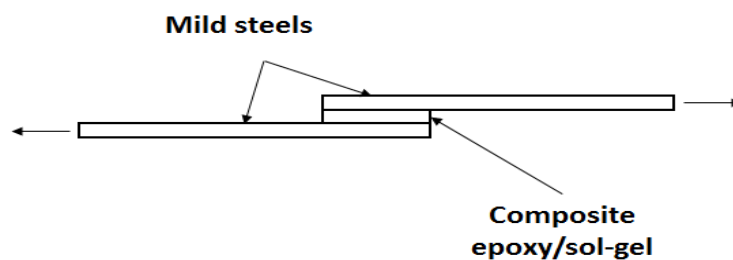
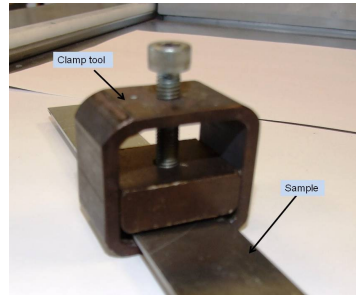


Figure 1a single lap joint

To achieve the lap joints and control the adhesive bondline thickness, a simple clamping arrangement was designed, see Fig 1b. The applied contact pressure (~4MPa) was constant, which allowed a uniform adhesive thickness to be achieved. This procedure produced lap joint specimens with the same adhesive thickness layer ~

0.1mm. The specimen was then placed into an oven for heat treatment at various designated times and temperatures.

Figure 1b The clamp tool for the lap joint.



2.2 Composite epoxy/sol-gel solution preparation

Hybrid organosilica-based sols were first prepared from the silane-based precursors. This hybrid sol was produced by mixing tetra-ethoxysilane (TEOS), methyl-trimethoxysilane (MTMS), ethanol, and deionised water at a mole ratio of 2:3:40:60. Nitric acid (HNO_3) was added as a catalyst to promote the hydrolysis and condensation reactions. The sol-gel modified epoxy adhesive was prepared by mixing the DGEBA (Diglycidyl ether of bisphenol-A resin (D.E.R 324, DGEBA) from Dow Chemicals with an average molecular weight of 700 g/mol) with the as-prepared hybrid sol and then left in an ultrasonic bath for 45 minutes at room temperature to ensure an uniform dispersion. Note: the sol-gel systems were not formulated with a curing agent. The epoxy groups in the sol-gel system are opened up by the nitric acid [15]. Additional reaction products due to esterification between the OH groups and epoxy groups of DGEBA are possible in the presence of metal alkoxide, as reported in [16]. This is further supported by the observation of weak FTIR absorption peaks attributed to the presence of an ester group [17].

2.3 Dispersion of MWCNTs into the epoxy/sol-gel material

The sol-gel epoxy adhesive was further modified by doping with a selected ratio of MWCNTs (i.e. 0.01, 0.05, 0.07, 0.2, 0.5 and 1.0 wt%), (MWCNTs, from Sigma Aldrich with size, O.D.10-15nm, I.D. 2-6nm, length 0.1-10 μm) and small amount of $\gamma\text{-Al}_2\text{O}_3$ nano-particles ~ 0.1g (99.98% metal basis, purchased from Alfa Aesar, A Johnson Matthey Company). Due to their hydrophobic properties and the formation of stabilised bundles under the action of van der Waals forces, MWCNTs generally aggregate together after being dispersed in water, resulting in the formation of hollow ropes [18]. Thus, uniform dispersion in a sol is one of the key issues for the application of MWCNTs. MWCNTs were ultrasonically treated by the pure nitric acid for 5 min and then washed by DI water for 5 times to remove the acid. To achieve an optimum dispersion, a selected ratio of MWCNTs and $\gamma\text{-Al}_2\text{O}_3$ nanoparticles was first added into 2-propanol. The solution was then ultrasonically dispersed for 90 minutes at 25°C using an ultrasonic generator (Roop Telsonic Ultrasonic Ltd, TEC-40, Switzerland). After being dispersed, it was mixed with the as-prepared sol-gel/epoxy solution and this mixture was then excited ultrasonically for 2 hours using the same generator, followed by continuous stirring overnight to obtain a stabilised uniform sol.

2.4. Mechanical and surface characterization

Shear mode loading was employed to evaluate the adhesive strength of the composite epoxy sol-gel material on mild steel substrates. The lap joints were tested at room temperature $23\pm 1^\circ\text{C}$, on a mechanically driven test machine (Instron tensile machine) having a capacity of 150 kN, and at a constant cross-head speed of 1 mm/min. Data were taken as an average of at least three measurements. A Brookfield CAP 2000 viscosimeter was used to carry out viscosity measurements at 22 °C with 2.5 mm diameter cone-plate geometry, the cone having an inclination of 0.1 radian. A scanning electron microscope (SEM) was used to observe and to analyse adhesive fracture surfaces of the lap joint on both materials. Images have been taken using an SEM

(Philips XL40) operated in the high vacuum mode. The specimen surfaces were coated with the flash- evaporated carbon to prevent charging for the SEM observation. FTIR and Raman spectroscopy were used to identify different chemical bonds within the composite matrix.

3. Results and discussions

3.1 Adhesive shear strength

The experimental results for effects of doping different amounts of MWCNTs into the epoxy/ sol-gel system on the adhesive lap shear strength are shown in Figure 2 where the shear strength of the joints increased when small amounts of MWCNTs were added. However, with further addition of the MWCNTs into the composite epoxy/sol-gel system beyond 0.07 wt%, a decrease in the adhesive shear strength was recorded. By adding the low-level of MWCNTs fillers in the composite epoxy/sol-gel system improved the bonding, being attributed to both the mechanical load transfer from the matrix to the MWCNTs and the high specific surface area of this material which increased the degree of cross-linking with other inorganic fillers in the formulation.

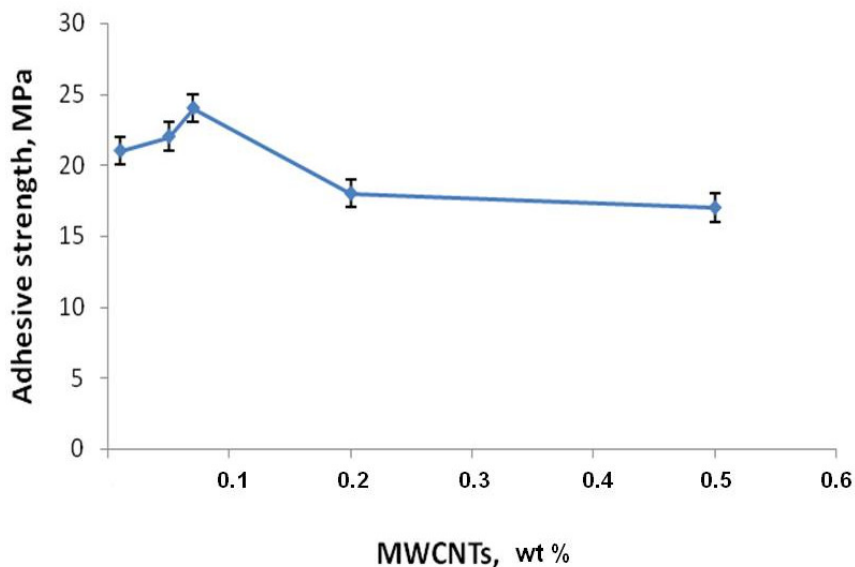


Figure 2. Lap shear strength results with the doping concentration of MWCNTs in the composite epoxy/sol-gel system.

The presence of nitric acid within our sol-gel formulation promoted the formation of carboxylic and hydroxyl groups on the MWCNT surfaces. It was referred [15,16] that nitric acid is extensively used to oxidize CNTs and produces carboxylic groups on its surface, which contributes to the solubilization of nanotubes. In addition, because of high relative surface areas of MWCNTs, this resulted in a strong interaction or anchoring of sites along MWCNTs with the adhesive matrix; therefore, the adhesive structures considerably enhanced. Pitalsky et al. demonstrated [19] that chemical agents such as HNO₃ increased the density of polar functional groups on the CNT surfaces. MWCNTs can also play a role in minimising the formation of micro-cracking by bonding them to organosilica nanoparticles via the interaction of the carboxylic with hydroxyl groups of organosilica. It has been reported [20] that the increase in the load transfer provided by the deformed MWCNTs within the matrix gave rise to the Si-O-CNTs bridges and/or polymer/CNT interactions. Therefore, it finally resulted in the development of a strong interfacial bonding between matrix and MWCNTs. However, when the amount of MWCNTs in the matrix was higher than ~0.07 wt%, the adhesive strength decreased again. One of the reasons may be attributed to the high amount of MWCNTs within the matrix leading to high viscosity, resulting in more difficulty in obtaining a uniform adhesive layer on substrate surfaces, therefore reducing the bonding of MWCNTs with matrix. Table 2 listed viscosity changes of our adhesives with the amount of MWCNTs in the matrix. This performance was also investigated by Loos et al. [21] who reported that the addition of high CNTs contents may reduce the strength of adhesive materials due to the increased viscosity of the adhesive.

Table 2. Viscosity dependent on the doping concentration of MWCNTs in Matrix

Concentration of MWCNTs (%)	0.01	0.05	0.07	0.2	0.5	1.0
Viscosity (cP)	136.3	150.35	169.5	206.34	234.98	267.68

Doping too high a content of MWCNTs in the matrix changed the morphological structures of the adhesives as shown in Section 3.2 below since the presence of high concentration MWCNTs during densification led to a high degree of pores or defects (e.g. microcracks) that were one of another reasons causing the decrease of lap joint strength. The pores were created by the increased viscosity that hindered the removal of the trapped air bubbles. Additionally, too high concentration of MWCNTs in the matrix led to their aggregation because of the difficulty in dispersion, which further resulted in increasing opportunity of forming defects, therefore deteriorating the adhesive strength. Shu-quan et al. [22] conducted their study, which also showed that by increasing the concentration of CNTs in the matrix raised the viscosity of the adhesive matrix, impeding the removal of bubbles. They believed that the trapped air bubbles in the matrix considerably degraded mechanical properties of the adhesives. In Figure 3, the influence of the addition of MWCNTs on the adhesive performance of the composite epoxy/sol-gel materials are further illustrated through a measure of the stress/strain curves. Below 0.07 wt% concentration, MWCNTs were well distributed within the matrix and high degree of cross-linking with the matrix was obtained, therefore enhanced the stretching ability of the adhesive, enabling the transfer of high loads without failure [23,24]. When the amount of MWCNTs increased above 0.07 wt%, a reduction in strain was noted in the stress/strain curves shown in Figure 3.

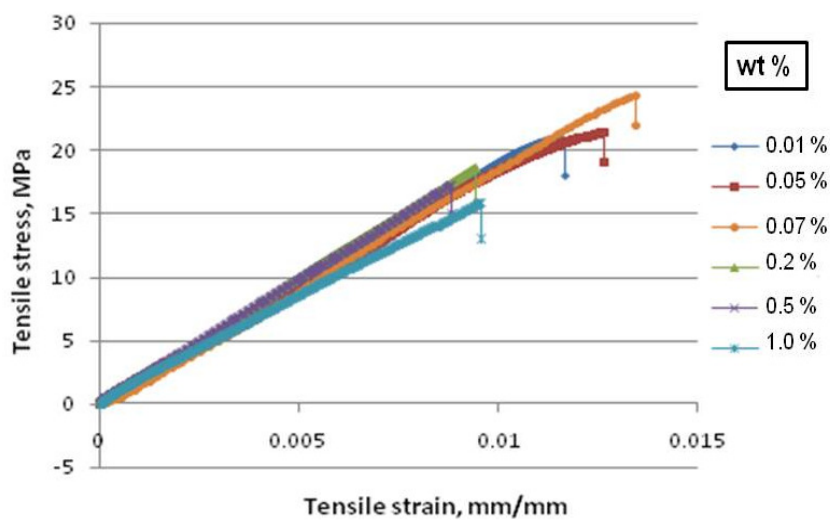


Figure 3. Results of stress/strain curves for the composite epoxy/sol-gel materials

3.2 SEM observation

The introduction of inorganic fillers into the formulation increased the degree of cross-linking within the adhesive matrix and the bonding at the interface, which improved the strength. The SEM image in Fig.4a showed a good distribution of MWCNTs (0.07 wt%) within the adhesive matrix with a consequential effect on the adhesive strength. It should be noted that the diameter of MWCNTs was very large and this was due to the presence of a coating of the adhesive on their surfaces. Achieving a good dispersion of MWCNTs introduced a positive effect on the composite epoxy/ sol-gel adhesive network and increased the chemical interaction bonds [25] (i.e. hydrogen bonds) within the adhesive matrix. Fig.4b illustrated micropores of the adhesive after doping with 1.0 wt% MWCNTs.

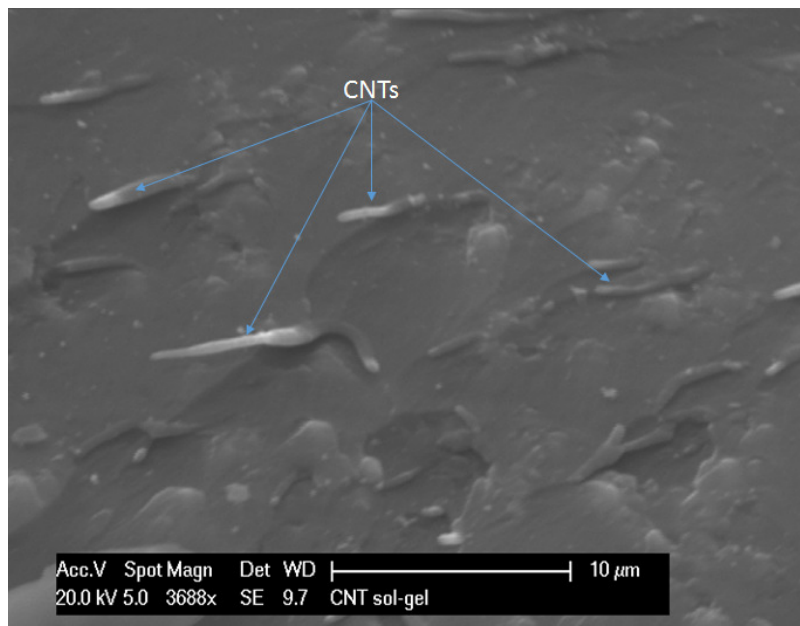


Figure 4a SEM images for distribution of MWCNTs in 0.07 wt% adhesives in the fracture surface.

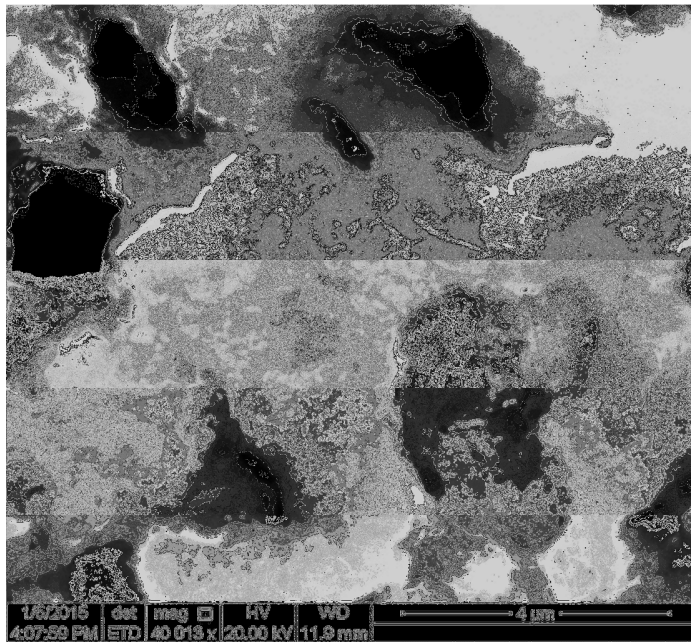
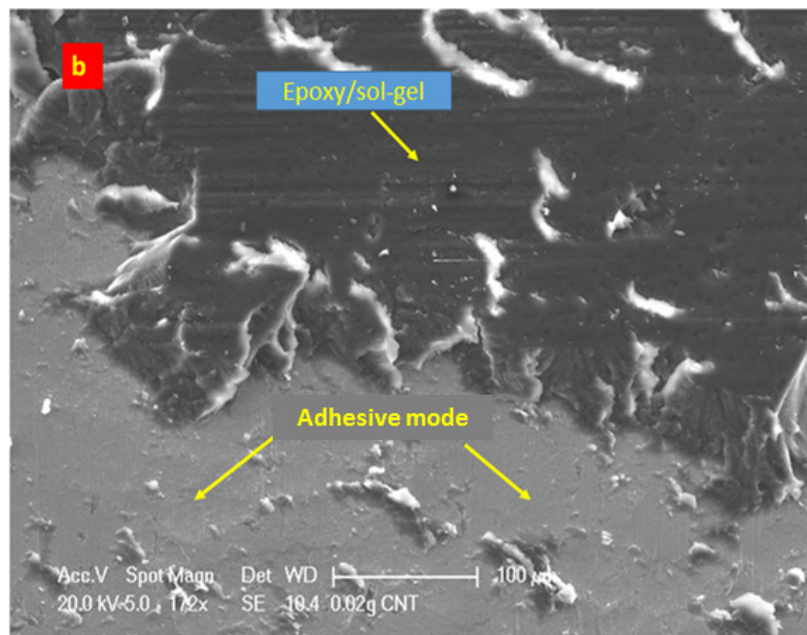
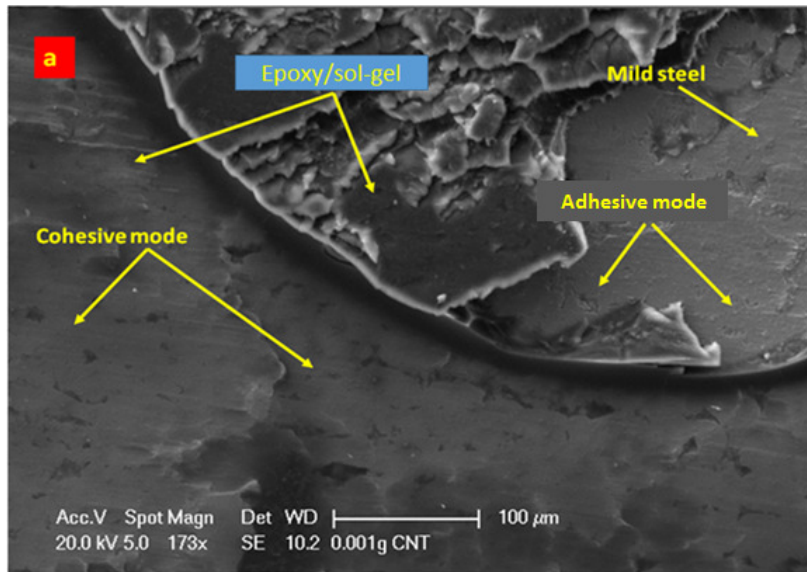


Fig.4b SEM images of micropores observed on adhesives with 1.0 wt% MWCNTs additions.

The fracture surfaces were used to assess the fracture modes of the composite epoxy/sol-gel on a mild steel substrate as shown in Figure 5a, b, and c. Figure 5a showed the SEM micrograph of the fracture surface with 0.01 wt % doped MWCNTs. A mixed adhesive/cohesive fracture mode was observed. This fracture mode indicated strong links at the adhesive/substrate interface. Interaction between MWCNTs and the matrix was achieved as shown in Figure 4, which therefore improved adhesion performance of the composite epoxy/sol-gel material to the substrate. The failure may have been initiated at the adhesive/substrate interface and then transferred within the bulk adhesive, revealing that two adhesion forces controlled the failure system. Figure 5b showed the fracture surface following the addition of 0.2 wt % MWCNTs to the composite matrix. Adhesive fracture mode was presented. With further increase in the amount of MWCNTs up to 1.0 wt %, the fracture mode remained adhesive mode with cracks in the adhesive matrix, as illustrated in Figure 5c. The cracks may be due to the increased free volume of MWCNTs within the adhesive, which weakened the interfacial bonding and reduced the adhesive shear strength.



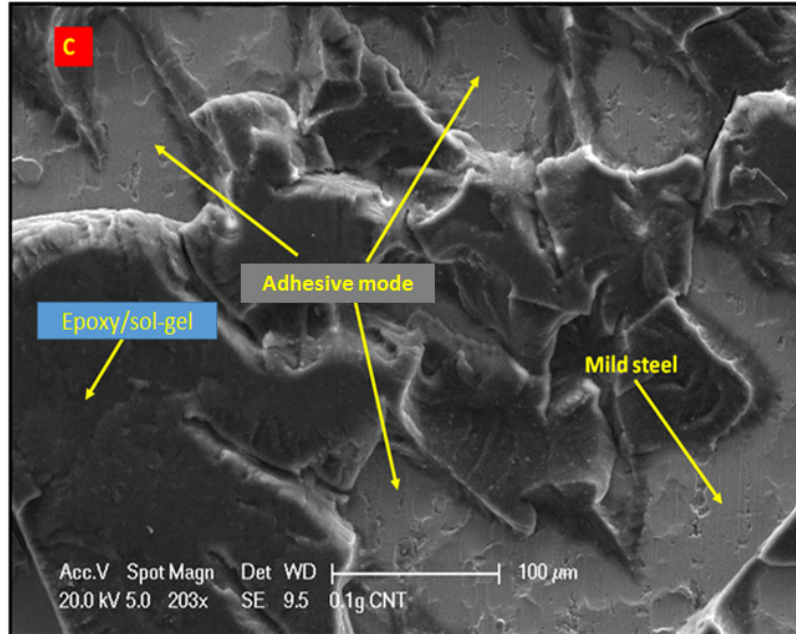


Figure 5. SEM images of the composite epoxy/sol-gel fracture surfaces with an addition of MWCNTs; (a) 0.01 wt%; (b) 0.2 wt%; and (c) 1.0 wt%.

3.3 FTIR spectra of the composite/epoxy sol-gel adhesive

Infrared absorption spectra of the composite epoxy/sol-gel as a function of cure time to understand the chemical changes in the formulation during the curing processes are shown in Figure 6a. FTIR absorption peaks in the range $\sim 800\text{-}1800\text{ cm}^{-1}$ were given. The most interesting bands in the FTIR spectrum were the epoxy ring at $\sim 950\text{ cm}^{-1}$ which disappears on increasing cure time and C-O at $\sim 1733\text{ cm}^{-1}$ that increased when cure time was increased. An increase in cure time improved the adhesive cross-linking via the inorganic nano-filler materials (i.e. Al_2O_3 , MWCNT) within the epoxy/sol-gel system. Figure 6a showed a clear shoulder at $\sim 1165\text{ cm}^{-1}$ that corresponded to the Al-O-Si bond as mentioned in [26]. The introduction of MWCNTs into the adhesive promoted the cross-linking of the adhesive by acting as a reinforcement network, which

restricted and reduced the crack initiation or propagation within the bulk adhesive. Infrared absorption spectra demonstrated that the strong peak related to the C-O-Si bond at $\sim 1733\text{ cm}^{-1}$ was enhanced by extending the cure time. This peak was assumed to be related to the cross-linking between the MWCNTs surface and the organosilica nano-particles in the epoxy/sol-gel matrix [27,17]. In order to further confirm this assumption, a matrix sample without the addition of MWCNTS was prepared after cure for 16 hr for the FTIR analysis. As shown in Fig.6b, only a negligible peak presented at $\sim 1733\text{ cm}^{-1}$, which was due to lack of the C-O-Si bond between the MWCNTs and matrix.

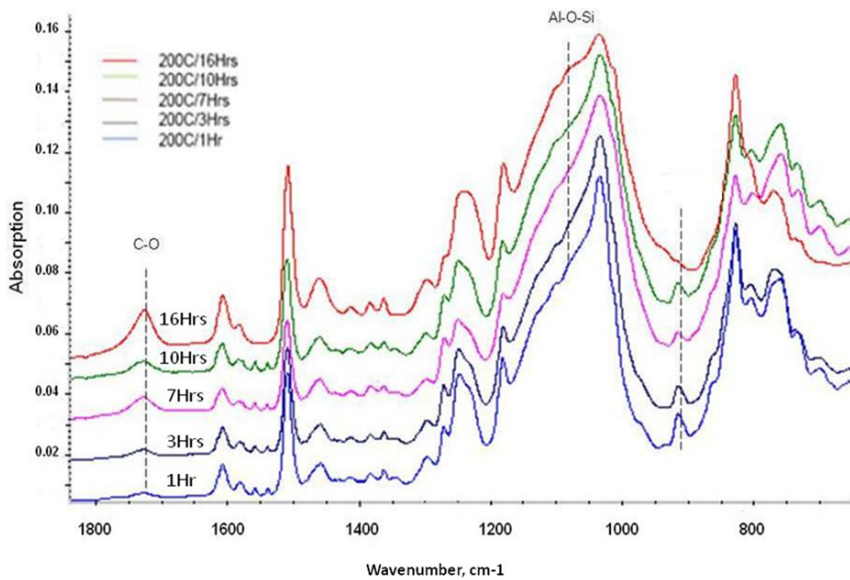


Figure 6a. FTIR spectra of the composite/epoxy sol-gel adhesive from 800 to 1800 cm^{-1}

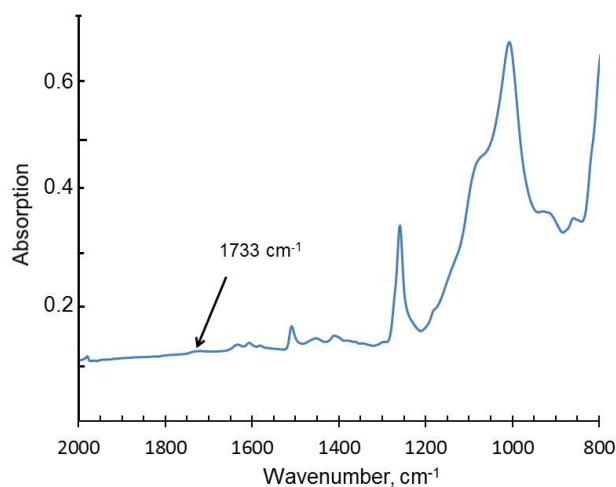


Figure 6b. FTIR spectrum of the matrix without additives of MWCNTs.

3.4 Raman spectra analysis

Raman spectroscopy was used to identify MWCNTs in the composite epoxy/sol-gel adhesive. Figure 7 highlighted the presence of inorganic components, i.e. MWCNTs, in the adhesive matrix. The spectra exhibited peaks at $\sim 1275 \text{ cm}^{-1}$ and in the range of $\sim 1549\text{-}1590 \text{ cm}^{-1}$. The former was the graphite G-band and the latter is the diamond D-band. The D-band and G-band represented the C-C single and C=C double bonds of the carbon nanotubes, respectively [28]. MWCNTs in this system enhanced the adhesive linkage and interacted with other inorganic materials as observed through the formation of Si-O-MWCNT [29]. In addition, weak Raman peaks between 400 and 450 cm^{-1} corresponded to the organosilica network stretch by the sol-gel derived structure. Spectral peaks between 830 and 980 cm^{-1} were attributed to the Si-OH asymmetric bond, indicating the presence of some free silanol groups in the hybrid epoxy/sol-gel system or the Si-O-Si bond [30]. However, Raman spectral peaks of $\gamma\text{-Al}_2\text{O}_3$, which were normally close to the SiO_2 peak locations, were shown here between 605 and 610 cm^{-1} . Similar results were also found by Hernandez [31] and Gnyba [20].

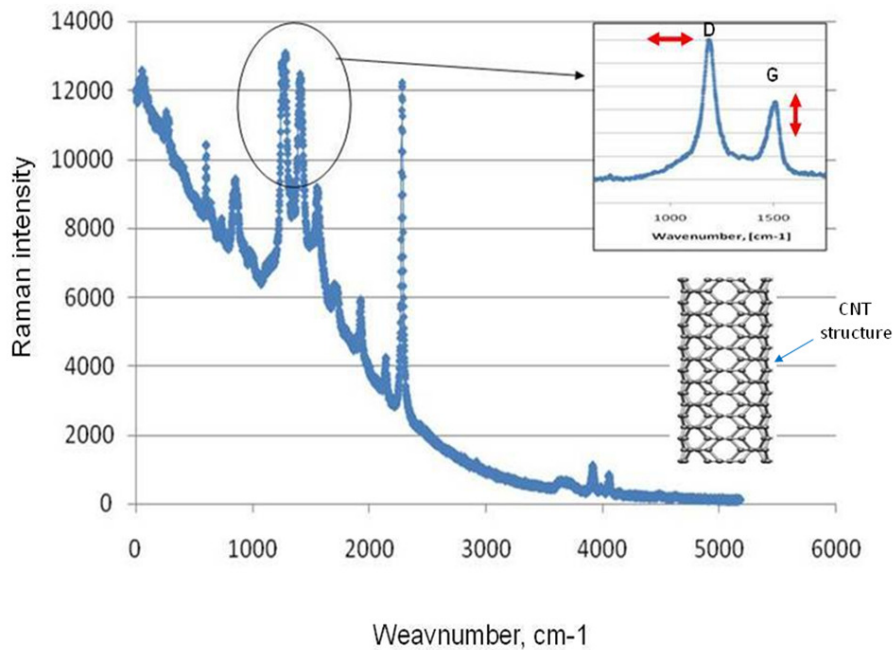


Figure 7. Raman spectra of the SG3 composite epoxy/sol-gel adhesive.

4. Conclusions

An increase in the proportion of the doped MWCNTs (up to 0.07 wt%) within the composite/epoxy sol-gel adhesive resulted in an enhanced shear strength of mild steel coupons bonded with the epoxy adhesive. This increase was attributed to the mechanical load transfer from the matrix to the MWCNTs. The high specific surface area of MWCNTs promoted the cross-linking with other inorganic fillers in the formulation. However, further increase in MWCNTs above 0.07 wt% led to a reduced shear strength. The reason was related to the increased viscosity of the adhesives and the degree of increased microdefects therefore leading to a decrease in bonding. In addition, a strong link at the adhesive/substrate interface indicated that an interaction between MWCNTs and the matrix was achieved, which improved adhesion performance of the composite epoxy/sol-gel material to the substrate.

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