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Effects of the addition of inorganic nanoparticles on the adhesive strength of a hybrid sol–gel epoxy system

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ABSTRACT

A combination of inorganic nanoparticles was added as reinforcement to a diglycidyl ether of bisphenol-A (DGEBA)-based epoxy resin modified by a hybrid sol–gel method. Different epoxy/sol–gel systems were prepared to evaluate their adhesive strength. The mechanical performance of different formulations was characterised by shear and tensile tests to define the influence of nano-fillers on adhesive strength performance of the modified epoxy/hybrid sol–gel. The results obtained indicate that the incorporation of a selected ratio of inorganic nanoparticles in the epoxy/sol–gel adhesive improves the adhesion performance between substrate surfaces. A significant increase in adhesive lap shear strength of the sol–gel modified epoxy, compared with that of the neat epoxy, was observed. Butt joint strengths of the modified epoxy/sol–gel were also recorded, showing good adhesion behaviour to mild steel surfaces. Tensile strength of joints up to 28.5 MPa for 16 h/150 °C cure time/temperature was observed. The modified system exhibited a high yield point and large extension compared with that of the unmodified epoxy. The study further showed that doping with small amounts of one type of nanoparticle to the system increases adhesive cross-linking. Epoxy/sol–gel adhesive strength was also evaluated as a function of cure temperature for mild steel and Al2024-T3 substrates. Results showed adhesive strength decreased with increased cure temperature on the Al substrate, while lap joint strength of the mild steel exhibited no significant changes at three different cure temperatures. This may be attributed to good interfacial bonding of the sol–gel adhesive to the mild steel over the designated temperature range.

1. Introduction

Adhesives are among some of the most widely used structural materials due to the variation of formulations that can be prepared, providing a range of properties under conditions that other joining techniques cannot offer. Hybrid inorganic/organic sol–gel systems are materials formed by incorporating a functional organic polymer or organo-functional silane into the matrix of an inorganic network. Organic polymers provide specific characteristics with respect to their toughness, flexibility, and processability [1], while the inorganic component provides good mechanical and temperature-resistance properties. Recently, hybrid inorganic/organic sol–gel materials have been studied by numerous investigators. Yano et al. [2] reported that the combination of an organic polymer within an inorganic network led to an increase of mechanical strength of the bulk material. In addition, the development of nanoparticle reinforced adhesive materials is presently one of the most explored areas in materials science and engineering. The exceptional properties of nanoparticles have led to widespread research in this area. Nano-fillers provide many advantages over classical micro-reinforcements for adhesive materials; for example they allow thin layer bond lines and consequently lower the risk of embrittlement within the bulk adhesive material, resulting in improved adhesive tensile strength [3].

Traditionally micro/nano-fillers have been introduced into epoxy resins to improve their mechanical performance, for example, silicon, titanium, and aluminium oxides. The use of nano-sized γ-Al_2O_3 particles is one approach to improve the mechanical performance of adhesive materials. In these particulate-filled systems, binding at the inorganic filler/epoxy matrix interface has a great effect on the mechanical properties of the adhesive material. Dudkin et al. [4] demonstrated that the strength of the epoxy matrix when reinforced by γ-Al_2O_3 increased due to the interaction between active surface groups of the oxide nanoparticles and functional groups of the epoxy matrix. However, whether the addition of filler particles improves the mechanical behaviour of these adhesives still remains unclear, since their mechanical properties rely on other factors that cannot be studied in isolation using commercial adhesive systems [5,6].

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Carbon nanotubes (CNTs) provide the potential for improving resin-dominated properties, such as interlaminar strength, toughness, and thermal and environmental durability [7]. CNTs are molecular-scale tubes of graphitic carbon with outstanding properties. Multiwalled carbon nanotubes (MWCNTs) are multi-layered graphite sheets in a cylindrical structure, having a size of several microns in length and 5–50 nm in diameter, depending on the number of layers [8]. They are among the stiffest and strongest fibres known and for this reason MWCNTs have the potential to improve the mechanical properties whilst enhancing a material's electronic properties [9].

Epoxy resins are known as brittle thermosetting polymers that need to be toughened in fields requiring high impact and fracture strengths, such as reinforced plastics, matrix resins for composites, and coatings [10]. To overcome their brittleness, a number of researchers demonstrated that dispersing rubber particles as a second phase into the epoxy resin led to an increase of toughness of the brittle matrix and improved its resistance to crack initiation and propagation [10–12]. These resins can normally be applied using two-pack formulations and are cured with common curing agents such as an amino hardener at room temperature. Epoxy resin adhesives can also be made as single-component materials, where the epoxy resin and hardener are already mixed. Marra et al. [13] have shown that this type of system provides single-pack stability and cures rapidly at elevated temperatures (i.e. 170 °C/20 min). In the present work, a hybrid epoxy/sol–gel adhesive based on the bisphenol-A epoxy resin and alkoxysilane chemistry was prepared. The purpose of this work is to assess adhesive strength of this novel adhesive material and influence on adhesion behaviour by adding MWCNTs and γ-Al_2O_3 nanoparticles into this system.

2. Experimental

2.1. Materials

Four adhesives were prepared for evaluation of their adhesive strengths, see Table 1. The choice of a sol–gel system as an adhesive was based on the ability to form Si–O–M bonds and the ease of incorporating nanoparticles and nano-fillers into the sol–gel matrix. The unmodified epoxy adhesive (designated 'neat epoxy') was a diglycidyl ether of bisphenol-A resin (D.E.R. 324, DGEBA) from Dow Chemicals with an average molecular weight of 700 g/mol, which was cured by adding a curing agent based on diethylenetriamine (DETA). The hybrid sol was produced by mixing tetraethoxysilane (TEOS), methyltrimethoxysilane (MTMS), ethanol, and deionised water at the mole ratio 2:3:40:60. Nitric acid (HNO_3) was added as a catalyst to promote hydrolysis and condensation reactions. The sol–gel modified epoxy adhesives used in this work were prepared by mixing the DGEBA with the as-prepared hybrid sol (component ratios are listed in Table 1). Note: the sol–gel systems were not formulated with a curing agent. The effects of doping (0.05 wt%) MWCNTs (from Sigma Aldrich) and (0.71 wt%) γ-Al_2O_3 nanoparticles (99.98% metal basis, purchased from Alfa Aesar, A Johnson Matthey Company) in the hybrid sol–gel adhesives were investigated. To achieve optimum dispersion, multiwall carbon nanotubes (MWCNTs) and γ-Al_2O_3 nanoparticles were first added to 2-propanol. The components within the solution were then ultrasonically dispersed for 90 min at 25 °C using an ultrasonic generator (Roop Telsonic Ultrasonic Ltd, TEC-40, Switzerland). After being dispersed, the solution was mixed with the as-prepared sol–gel/epoxy solution and the mixture was then excited ultrasonically for 2 h using the same generator, followed by continuous stirring overnight to obtain a stabilised uniform sol. An aluminium alloy (Al2024-T3) and mild steel were used as substrates.

2.2. Sample preparation

Lap shear test samples were prepared according to ASTM D1002 and joint tensile strength samples were prepared according to ASTM D2094-00. Fig. 1 shows the geometry and dimensions of the joints. The surface to be adhesively joined was first washed by running hot tap water to remove any dust on the surface, and air-dried at room temperature (~23 °C), further immersed in acetone and ultrasonic for 15 min at ~23 °C, and then air-dried. This procedure was used for both mild steel and aluminium alloys. It should be pointed out that a more complicated surface treatment was not used as it was of interest to assess 'surface tolerance' of the adhesive system. Adhesives were then applied on both surfaces by a spray gun. The neat epoxy/Al specimens modified by DETA were left for 30 min at ~23 °C, for drying. However, the sol–gel/epoxy specimens were first left for 30 min at ~23 °C and then pre-cured in an oven at 95 ± 5.0 °C for 60 min to eliminate the entrapped air and reduce the level of solvent and water. Single-lap and butt joints were then prepared according to the standards given above. To achieve the lap joints and control adhesive bondline thickness, a simple clamping arrangement was designed (Fig. 2). The bonded area was subjected to an applied pressure of 4 MPa during the curing stage. This procedure produced lap joint specimens with the same adhesive thickness layer ~0.1 mm. Finally the joints were placed in a furnace at various cure temperatures for up to 16 h to achieve full curing. Further comments on the thermal behaviour of the system are given below.

2.3. TGA measurements

Thermal stability of neat epoxy/Al, SGA1/Al, SGA2/Al, and SGA3/Al adhesives was assessed by thermo-gravimetric analysis (TGA, Mettler TG-50). Tests were carried out in nitrogen at the heating rate of 10 °C/min in the temperature range 35–650 °C.

Table 1
Epoxy/sol–gel adhesive formulations.

Samples		Formulations				
		DGEBA (m)	Sol–gel (ml)	DETA curing agent (ml)	γ-Al_2O_3 of size 10–20 nm (wt%)	MWCNT of size OD 10–15 nm, ID 2–6 nm, length 0.1–10 μm (wt%)
–	NE/Al	1.50–2.00	–	0.5–1.00	–	–
–	SGA1/Al	1.50–2.00	12.00	–	–	–
SGA2/MS	SGA2/Al	1.50–2.00	12.00	–	0.71	–
SGA3/MS	SGA3/Al	1.50–2.00	12.00	–	0.71	0.05

NE = neat epoxy, Al = Al2024-T3 alloys, MS = mild steel.

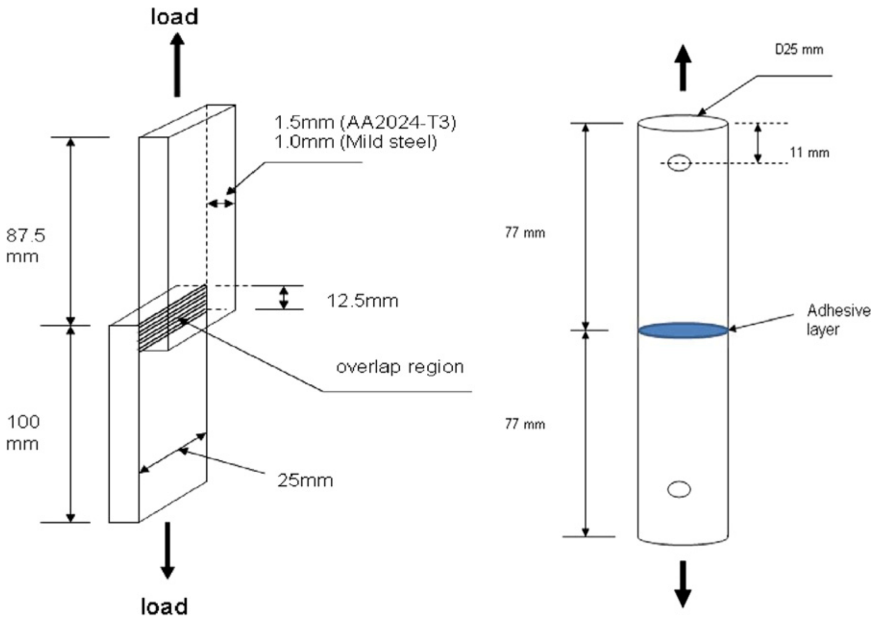

Fig. 1. Geometry and dimensions of (left) lap joint and (right) butt joint.

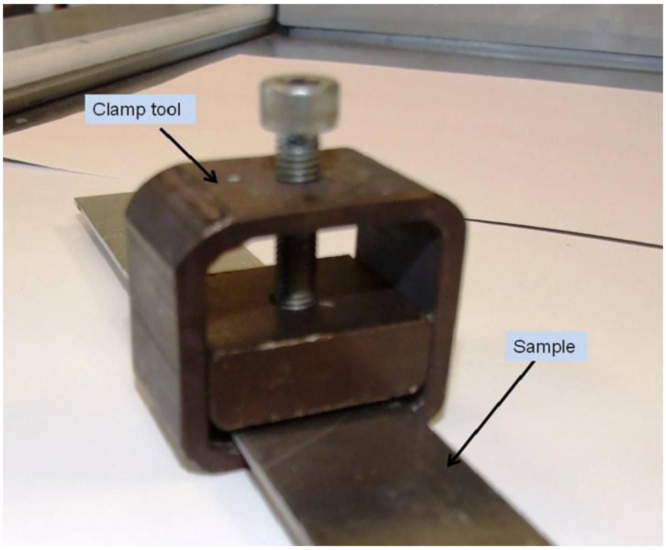

Fig. 2. Lap joint clamp tool.

This method indicates weight loss of the heated sample due to the evaporation of volatile products. Fig. 3 shows changes in weight loss as a function of change in temperature up to 650 °C. Change in the sample weight loss during thermal scan is calculated as follows:

$$\text{Weight loss} = \frac{Wi - Wt}{Wi} \times 100\% \qquad (1)$$

where Wi is the initial weight and Wt the weight at a specific temperature during scan. TGA curves showed only small changes in weight, indicating no loss of volatiles, in the temperature range 35–200 °C, for all the adhesive formulations. Almost all mass of the unmodified epoxy (neat epoxy/Al) was lost above 450 °C due to decomposition. However, the peak temperature weight loss of SGA2/Al and SGA3/Al increased up to 500 and 550 °C, respectively. The differences in percentage total weight loss in the adhesives at 650 °C were 91% in neat epoxy/Al compared with 71% in SGA1/Al, 64% in SGA2/Al, and 50% in SGA3/Al. This difference in weight loss was attributed to the addition of inorganic components. The addition of nano-fillers also significantly improved thermal stability of the sol–gel epoxy adhesive.

2.4. Mechanical and surface characterization

Shear mode loading was employed to evaluate epoxy/sol–gel adhesive strength on aluminium and mild steel substrates. Butt joint geometry was used to evaluate sol–gel adhesive tensile strength on mild steel substrates. The joints were tested at room temperature ~23 °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. Lap shear strength data were taken as an average of at least three measurements. Butt joint tests were carried out in the same machine on a minimum of five specimens. Joint adhesive strength was calculated using the following formula;

$$\sigma = P_{\max}/A \qquad (2)$$

where σ is the adhesive strength in (MPa), $P_{\max}$ the maximum load at fracture in (N), and A the average cross-sectional area in (mm^2). A scanning electron microscope (SEM) was used to observe and 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 flash-evaporated carbon to prevent charging within the SEM.

3. Results and discussion

3.1. Adhesive strength of the lap joints

The presence of hydroxyl groups on the substrate surface and in the sol–gel epoxy adhesive can, via condensation reactions, lead to formation of strong cross-linked bonds within the sol–gel epoxy adhesive, as reported in [14]; the number of metal–oxygen (Me–O) bonds increases with the release of residual water and organic solvent during the early stages of drying. Further increase in cross-linking and Me–O bonding occurs during the high temperature cure regime [15]. The mechanical test results

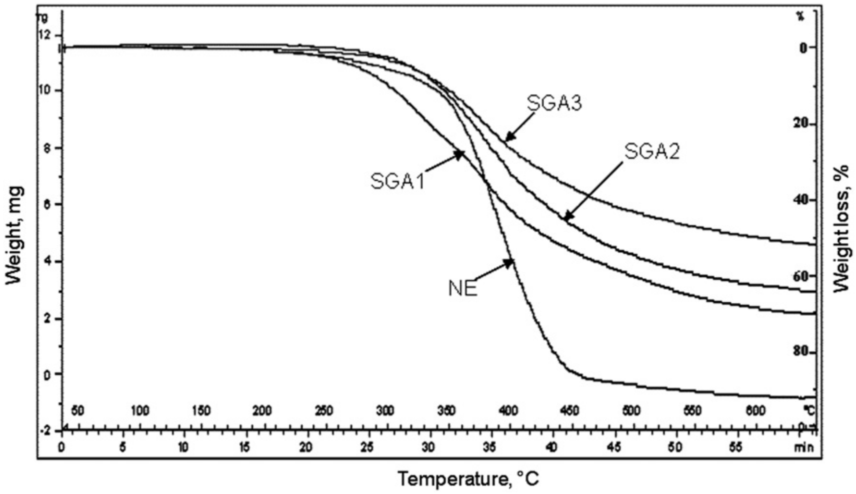

Fig. 3. TGA data for different adhesive formulations.

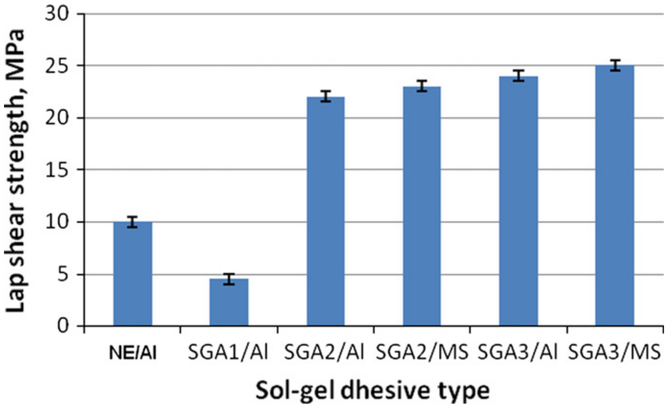

Fig. 4. Adhesive strength of different adhesive formulations on AA2024-T3 and mild steel.

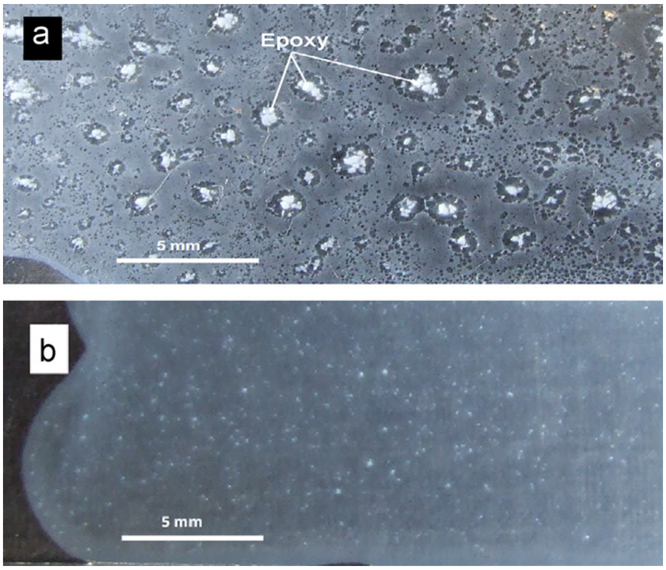

Fig. 5. (a) Phase separation between epoxy and sol–gel matrix on glass slide and (b) effect of addition of γ-Al_2O_3 into epoxy/sol–gel.

obtained from the lap shear tests for different adhesives cured at 140 °C for 16 h on Al2024-T3 and mild steel substrates are shown in Fig. 4. Lap shear strength of the neat epoxy/Al (NE/Al), cured using an amine hardener, was close to 10 ± 0.5 MPa. However, lap shear strength of the sol–gel modified system SGA1/Al reduced to about 4–5 MPa following simple mixing with the sol. This may be due to a lack full cross-linking and phase separation between the epoxy and the sol–gel matrix (Fig. 5a). The incorporation of γ-Al_2O_3 nanoparticles SGA2/Al and a mixture of MWCNTs and γ-Al_2O_3 SGA3/Al in the sol–gel epoxy adhesives led to a significant improvement in the adhesive performance on the AA2024-T3 substrate, where adhesive strength increased up to 22 ± 0.5 and 24 ± 0.6 MPa, respectively. Similar results were obtained for mild steel substrates, where nanoparticle additions resulted in adhesive strengths of 23 ± 0.8 MPa for SGA2/MS and 25 ± 0.9 MPa for SGA3/MS. The modification of an epoxy resin/sol–gel system as a result of doping small amounts of MWCNTs and γ-Al_2O_3 nano-materials has enhanced its adhesion performance for both Al2024-T3 and mild steel surfaces. The matrix of the silica-based sol–gel played a major role in providing three-dimensional networks within the adhesive. The presence of γ-Al_2O_3 nano-fillers in the adhesive may prevent phase separation within the matrix. It was reported [16] that when nano-alumina particles are incorporated into an epoxy resin, cure kinetics of the resin is affected due to the catalytic effect of hydroxyl groups on the particles. Changes in adhesive structure (phase separation) were observed on adding γ-Al_2O_3 nano-fillers into the epoxy/sol–gel matrix (Fig. 5b). A clear solution was produced, indicating the high degree of miscibility and cross-linking, which enhanced the structure of the adhesive and thus increased the lap shear strength performance.

It is well known that properties of the bisphenol-A epoxy are related to the curing agent and the opening of epoxy groups. It has been reported that changing the amount of curing agent will have an effect on degree of cross-linking and formation of chemical bonds in the cured epoxy system [17]. DETA was used as the curing agent in the neat epoxy sample to open the epoxy rings, through the chemical reaction of the epoxide groups in the epoxy resin, with the active hydrogen atoms in the curing agent (hardener). However, the epoxy groups in the sol–gel system are opened up by nitric acid [18], which was used as a catalyst to promote the hydrolysis and condensation reactions. 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 [19]. This is further supported by the observation of weak FTIR absorption peaks attributed to the

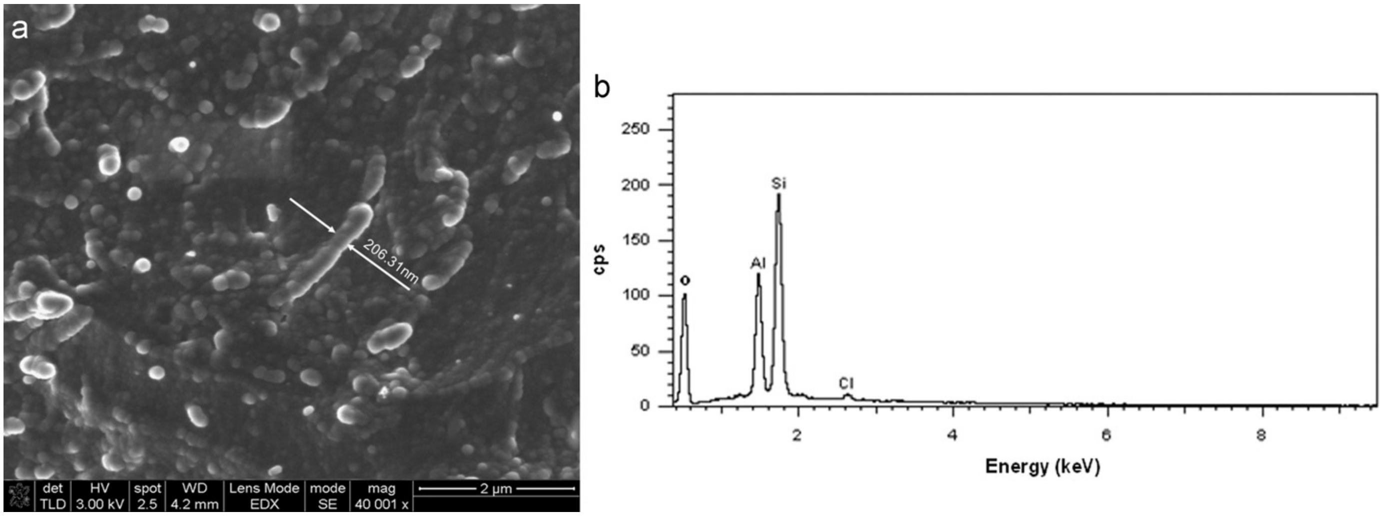

Fig. 6. (a) SEM image of distribution MWCNT and inorganic nano-materials in SGA3/Al and (b) EDX spot analysis of surface of MWCNT.

Table 2
Adhesive tensile strength of butt joints on mild steel substrates. (SGA3/MS cured at 150 °C for 16 h).

Samples	Extension at break (mm)	Tensile stress at maximum load (MPa)	An average tensile stress (MPa)	Fracture mode (%)		
				CO	AD	CO+AD
1	1.110	35.62	28.5	50	40	10
2	0.964	32.27		32	61	7
3	0.930	26.92		22	75	3
4	0.916	25.48		15	80	5
5	0.891	22.47		10	86	4

CO = cohesive failure, AD = adhesive(interfacial failure), CO+AD = mixed cohesive/interfacial mode.

presence of an ester group [20]. In this modified system, the hydroxyl groups generated from the epoxy resin by the opening of the epoxy rings can lead to condensation with the hydroxyl groups in the sol–gel network. This reaction may create some bonding between the sol–gel and the epoxy. The doped γ-Al_2O_3 nanoparticles further strengthen this cross-linking. Hence, the addition of γ-Al_2O_3 nanoparticles has greatly increased lap shear strength of sample SGA2/Al compared with the neat epoxy/Al and the SGA1/Al sample. The doping of MWCNTs in SGA3/Al and SGA3/MS showed a further increase in adhesive strength on AA2024-T3 and mild steel substrates. These improvements of lap shear strength were also related to the uniform distribution of nano-fillers (i.e. γ-Al_2O_3 and MWCNTs) within the matrix. The SEM image presented in Fig. 6 shows the distribution of MWCNTs, which is thought to be coated with adhesive matrix, rich in SiO_2 nanoparticles (i.e. size 40–80 nm) derived from the sol–gel matrix, and γ-Al_2O_3 (i.e. size 10–20 nm). The appearance of silicon, oxygen, and aluminium peaks in EDX spectra confirmed the presence of these materials. The incorporation of nano-filler materials in the epoxy/sol–gel led to an increase of surface contact area between the nanoparticles and the polymer and decreased or minimized gaps and nano-voids within the adhesive matrix compared with that of the unmodified epoxy/sol–gel system (Fig. 5a and b). This was also suggested by Wetzel et al. [21], who demonstrated that large contact areas between the organic and inorganic component within the matrix reduced the presence of voids, leading to improved joint strength. Furthermore, it was found that MWCNTs act as a reinforcing phase in the epoxy/sol–gel system, resulting in an increase of joint strength. However, only a relatively small difference was observed between adhesion strengths of SGA2/Al and SGA2/MS compared with those of SGA3/Al and SGA3/MS samples. The reason for this might be due to the small concentration of MWCNTs added in the matrix. The dependence of strength on concentration of MWCNTs within the adhesive is being further investigated.

3.2. Adhesive tensile strength of butt joint

Due to the complex stress state existing within the adhesive layer, measured adhesive strength of a joint can be highly variable; for example, a small misalignment in a joint operating in the tensile mode will result in cleavage stresses [22]. Hence adhesive strength of a joint is very dependent on sample preparation. A variation in adhesive tensile strength of SGA3/MS may be attributed to the distribution of internal stresses within the adhesive layer (Table 2). Yuichi et al. [23] and Kendall [24] reported that the formation of complex stresses throughout the adhesive layer plays an important role in evaluating adhesive bonding strength of joints. Further factors that may affect adhesive strength of butt joints, as pointed out above, include sample preparation, particularly joint pressure and joint misalignment. An average joint tensile strength of 28.5 MPa was achieved after 16 h cure time at 150°C. The results show that there is a difference between SGA3/MS adhesive tensile and shear strengths. There is indeed evidence that shear strengths of polymers are less than their tensile strengths [25]. da Silva and Adams [26] have recently reported adhesive shear to tensile strength ratios of 0.72–0.83 at room temperature. The measured value of SGA3/MS is relatively close to that obtained by Silva and Adams and a shear to tensile strength ratio between 0.7 and 0.85

was observed for this system. The interfacial tensile strength of SGA3/MS may be attributed to a mechanical interlocking between the adhesive and the substrate surface (Fig. 7), and the possibility of formation of a reaction layer (20–50 nm). This reaction layer has been observed in TEM sections of other sol–gel systems coated onto metal substrates [27]. The release of water and solvent from the adhesive is controlled by cure time and temperature. Initial studies were conducted to determine the optimum time/temperature to obtain maximum strength [20]. Hence, the mechanical properties are related to the adhesive pre-cure stage (95 ± 5.0 °C for 60 min, as selected while drying the system). It is also noted that the presence of γ-Al_2O_3 nano-fillers in the matrix modifies the adhesive structure as the addition of γ-Al_2O_3 reduces the degree of phase separation of the sol–gel/epoxy. Furthermore nano-size fillers may also reduce the density of voids formed within the matrix, thereby reducing stress concentrations within the system, leading to an increase of adhesive tensile strength, as discussed above in Section 3.1.

3.3. *Fracture surfaces*

The adhesive fracture modes of mild steel and Al2024-T3 substrates are presented in Fig. 8a and b, respectively. The results shown are for a lap joint cured at 140 °C for 16 h. It can be seen that the fracture surfaces of mild steel indicated a mixed interfacial/cohesive fracture mode, ~70%:30% (Fig. 8a). The same mixed fracture mode was observed in the Al2024-T3 failed joints, and the interfacial to cohesive mode is ~80%:20%, as shown in Fig. 8b. The failure in the joints was initiated at free edges, where the maximum stress intensity exists in the joint, with cracks propagating along the interface or close to the interfacial region. The SGA3/MS adhesive exhibited three fracture modes for the butt joint samples, as shown in Fig. 9. It can be seen that around 50% of the fracture was via the cohesive mode, 40% via the interfacial fracture mode (adhesive fracture), and the remaining 10% via mixed failure mode (i.e. cohesive/adhesive on

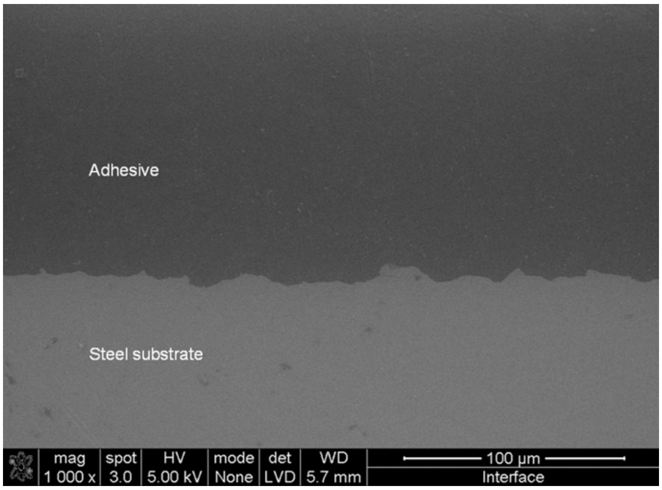

Fig. 7. Adhesive/substrate interface for SGA3/MS.

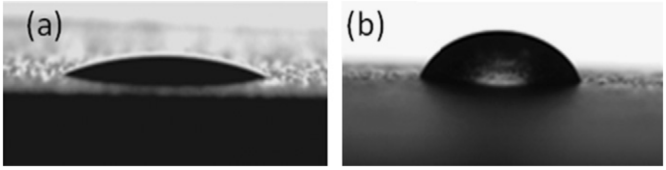

Fig. 10. Sol–gel adhesive drop on Al2024-T3: (a) SGA3/Al and (b) SGA1/Al.

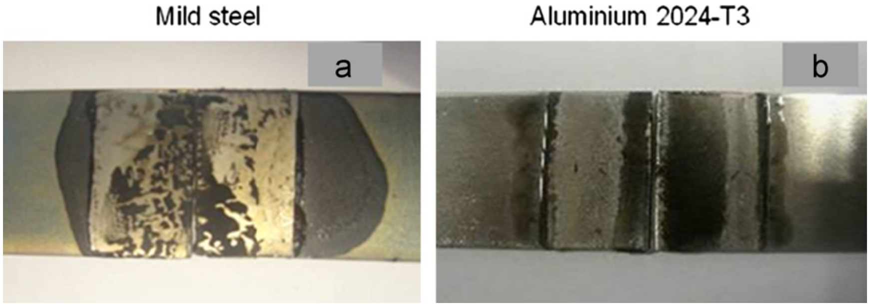

Fig. 8. Interfacial fracture surface of (a) SGA3/MS and (b) SGA3/Al (lap joints).

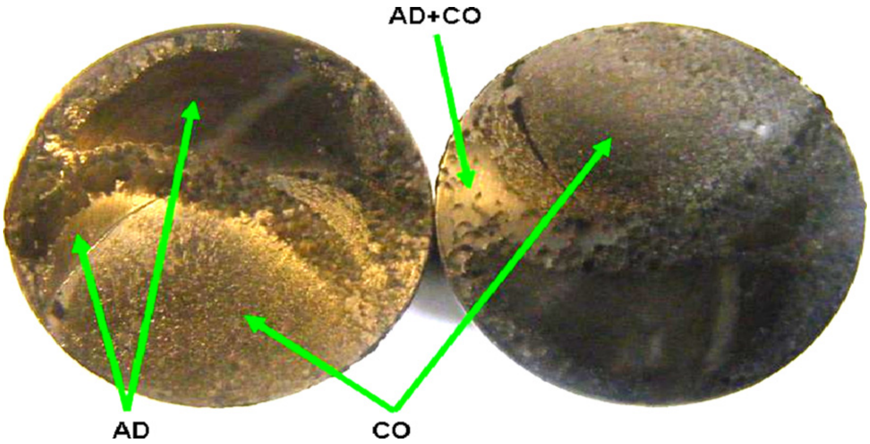

Fig. 9. Interfacial fracture of SGA3/MS (AD~40%), cohesive fracture (CO~50%), and mixed fracture (AD+CO~10%) modes.

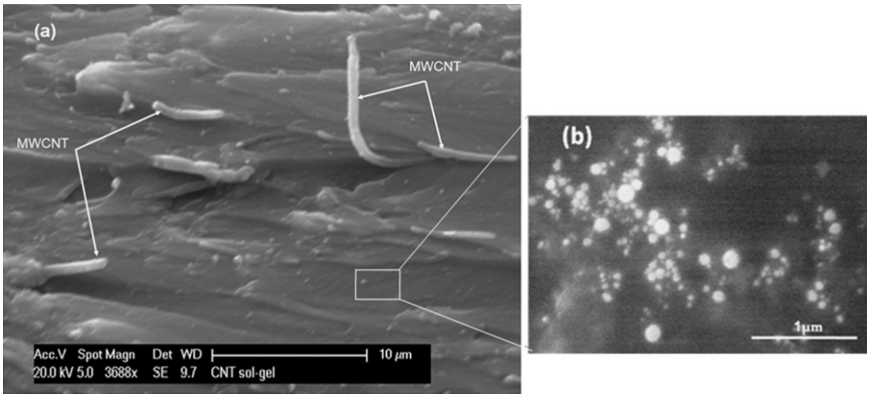

Fig. 11. SGA3/Al matrix: (a) fracture surface showing distribution of MWCNT and (b) distribution of γ-Al_2O_3 nanoparticles.

Table 3
Experimental results for load versus extension at break (lap joint, AA2024-T3).

Samples	Maximum load (N)	Extension at break (mm)	Tensile stress at maximum load (MPa)	Tensile strain at maximum load (%)
NE/Al	3008	1.803	9.63	14.39
SGA2/Al	7401	2.96	23.68	22.16
SGA3/Al	7904	3.89	25.29	29.12

Table 4
Adhesive strength of the lap joints in MPa, as a function of cure temperature. (16 h cure time).

	Cure temperature (°C)		
	140	160	180
SGA3/MS	23.63 ± 0.2	25.01 ± 0.1	24.35 ± 0.4
SGA3/Al	24.95 ± 0.1	19.34 ± 0.5	17.07 ± 0.7

the surfaces). The fracture behaviour can be explained in terms of the improvement in cross-linking within the adhesive itself and at the interface. Adhesive strength is enhanced due to the incorporation of γ-Al_2O_3 nanoparticles in the matrix, where γ-Al_2O_3 is available for catalytic epoxide ring-opening reactions. It was reported [28,29] that the opening of epoxy rings was increased with the addition of catalytically active AlOR/OH groups to the acidic silica-base sol–gel system, which supports the above. Furthermore, the presence of nano-size fillers in the matrix increases wettability of the bonded surfaces when the adhesive was applied. The adhesive droplets on the substrate surface exhibited a different contact angle as shown in Fig. 10a and b, (i.e. (a) SGA3/Al ~ 19.15 ± 1 and (b) SGA1/Al ~ 56.74 ± 1). SEM analysis of the fracture surface was conducted to understand how addition of γ-Al_2O_3 and MWCNTs affected the failure mode of the modified sol–gel epoxy adhesive. The addition of nano-fillers may increase adhesive matrix ductility, see the discussion in Section 3.4 below, and reduce the formation of voids within the adhesive. Therefore, a good distribution of these nano-fillers in the matrix will increase the adhesive's ability to absorb energy during tensile loading and hence improve joint strength. Fig. 11a and b shows the distribution of inorganic nano-fillers within the adhesive matrix on the fracture surface. It should be noted that the MWCNTs are quite thick and this is due to the presence of a coating of the adhesive on the MWCNTs.

3.4. *Characteristics of load versus extension*

Changes in load/elongation data of the modified and unmodified formulations were used to assess the behaviour of different adhesives under shear mode loading. Load/extension at break was obtained for samples cured at the same temperature of 140 °C. A cross-head speed rate of 1 mm/min was used for all tests. SGA2/Al and SGA3/Al adhesives showed a high maximum load and increased strain (extension) compared with that of the neat epoxy/Al, as shown in Table 3. The results for SGA2/Al and SGA3/Al indicated that the fracture point occurred beyond the point of maximum load, implying greater ductility over that of the neat epoxy/Al. As previously stated, doping of γ-Al_2O_3 causes an increase in adhesive strength. This increase in strength, due to the addition of a nano-filler, was further enhanced by the addition of high strength carbon nanotubes, causing a reinforcement of the hybrid sol–gel epoxy system. Ductility of the modified system is attributed to the adhesive's ability to exhibit increased amounts of plastic deformation. We suggest that the presence of inorganic nano-fillers within the epoxy/hybrid sol–gel system leads to an increase in ductility of the adhesive, where the external load is transferred to the inorganic materials, as indicated by higher 'extension at break' values compared with that of the neat epoxy/Al (Table 3).

3.5. *Effects of cure temperature on adhesive strength*

Adhesive strength of the SGA3/Al and SGA3/MS sol–gel epoxy adhesives were evaluated as a function of cure temperature. Three different cure temperatures, at the same cure duration (16 h), were studied to assess cure temperature effects on lap joint strength. The results for SGA3/Al showed that adhesive strength decreased as cure temperature increased as shown in Table 4. This behaviour may be attributed to changes in thermal expansion at the adhesive/substrate interface, where the thermal expansion coefficient (α) value for aluminium alloys is $\sim 23 \times 10^{-6}$/m/°C. This should be compared with lap joint strength of SGA3/MS, where no significant change occurs as cure temperature is increased, suggesting a stable surface under the heat treatment temperatures used for curing. It should be noted that α of mild steel is $\sim 11.7 \times 10^{-6}$ m/°C, around two times less than that of Al2024-T3.

4. Conclusions

A novel adhesive based on a epoxy/sol–gel system has been developed incorporating the use of nano-fillers (γ-Al_2O_3 and MWCNTs). The lap shear and tensile strength properties were investigated using this adhesive system on Al2024-T3 alloys and mild steel substrates. The following may be concluded from this study:

1. Adhesive lap shear strength of the epoxy/sol–gel was increased on both AA2024-T3 and mild steel substrates up to 24 ± 0.6 and 25 ± 0.9 MPa, respectively, compared with 10 ± 0.5 MPa in the neat epoxy.
2. Joint tensile strength of the modified sol–gel adhesive recorded good adhesion performance on mild steel surfaces, showing an average value up to 28.55 MPa.
3. The epoxy/sol–gel adhesive showed greater thermal stability than the conventional neat epoxy adhesive tested, suggesting that this novel adhesive can be used for moderately high temperature environments.
4. High strength and thermal stability of this novel epoxy/sol–gel adhesive were attributed to the addition of inorganic nanocomponents, i.e. silica-based sol–gel, γ-Al_2O_3 nanoparticles, and MWCNTs. This behaviour is attributed to the components added, which play a role in increasing adhesive matrix ductility and reducing formation of voids within the adhesive.

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References

[1] Ochi M, Takahashi R, Terauchi A. Phase structure and mechanical and adhesion properties of epoxy/silica hybrids. Polymer 2001;42(12):5151–8.

[2] Yano S, Furukawa K, Kodomari M, Kurita K, Kobunshi R. Physical properties of poly(vinyl alcohol)/silica hybrid prepared by sol–gel process. Kobunshi Ronbunshu 1996;53(4):218–24.

[3] Jacobs O, Xub W, Scha DB, Wu W. Wear behaviour of carbon nanotube reinforced epoxy resin composites. Tribology Letters 2006;23:1.

[4] Dudkin BN, Zainullin GG, Krivoshapkin PV, Krivoshapkina EF, Ryazanov MA. Influence of nanoparticles and nanofiberes of aluminium oxide on the properties of epoxy composites. Glass Physics and Chemistry 2008;34(2): 187–91.

[5] Conde MCM, Zanchi CH, Rodrigues-Junior SA, Carreno NLV, Ogliari FA, Piva E. Nanofiller loading level: influence on selected properties of an adhesive resin. Journal of Dentistry 2009;37:331–5.

[6] Jong SK, Byeong HC, In-Bog L, Chung MU, Bum SL, Myung HO, Chang GC, Ho HS. Effect of the hydrophilic nanofiller loading on the mechanical properties and the microtensile bond strength of an ethanol-based one-bottle dentin adhesive. Journal of Biomedical Materials Research 2004;72(2):284–91.

[7] Duval K, Davey S. Development of carbon nanotube/carbon fiber multiscale reinforcement composites. MSc thesis, College Of Engineering, The Florida State University, 2005, 〈http://etd.lib.fsu.edu/theses/available/etd1109200201956/unrestricted/kirk_davey_thesis〉.

[8] Hsiao KT, Alms J, Advani SG. Use of epoxy/multiwalled carbon nanotubes as adhesives to join graphite fibre reinforced polymer composites". Nanotechnology 2003;14(7):791–3.

[9] Xiao Q, He S, Liu L, Guo X, Shi K, Du Z, Zhang B. Coating of multiwalled carbon nanotubes with crosslinked silicon-containing polymer. Composites Science and Technology 2008;68(1):321–8.

[10] Jansen BJP, Tamminga KY, Meijer HEH, Lemstra PJ. Preparation of thermoset rubbery epoxy particles as novel toughening modifiers for glassy epoxy resins. Polymer 1999;40(20):5601–7.

[11] Unnikrishnan KP, Thachil ET. Blends of epoxy and epoxidized novolac resins. Journal of Elastomers and Plastics 2005;37(4):347–59.

[12] Harani H, Fellahi S, Bakar M. Toughening of epoxy resin using hydroxyl-terminated polyesters. Journal of Applied Polymer Science 1998;71(1):29–38.

[13] Marra KME, Alvarenga D, Buono VL. Adhesiveness of cold rolled steels for car body parts. Materials Research 2007;10(3):267–71.

[14] Plinio I, Tongjit K. Hybrid organic–inorganic sol–gel materials based on epoxy–amine systems. Journal of Sol–Gel Science and Technology 2005;35: 225–35.

[15] Habsuda J, Simon GP, Cheng YB, Hewitt DG, Lewis DA, Toh H. Organic–inorganic hybrids derived from 2-hydroxyethylmethacrylate and (3-methacryloyloxypropyl)- trimethoxysilane. Polymer 2002;43(15):4123–36.

[16] Ji QL, Zhang MQ, Rong MZ, Wetzel B, Friedrich K. Tribological properties of surface modified nano-alumina/epoxy composites. Journal of Materials Science 2004;39:6487–93.

[17] Wong CP. Polymers for encapsulation: materials, processes and reliability. Georgia Institute of Technology, 〈http://www.chipscalereview.com/9803/home.htm〉.

[18] Shpan IV, Sadovaya IV, Kitaigorodskii AM. Effect of the structures of arylsufonic acids on the kinetics of oxirane ring opening in 4-nitrophenyloxirane. Theoretical and Experimental Chemistry 2000;36(6):338–41.

[19] Chen P, Hu L, Zhang X, Sun D. Enhanced corrosion resistance for silsesquioxane coating by diglycidyl ether of biphenol A. Material Science—-Poland 2007;25(3):843–9.

[20] May M. The use of sol–gel technology for adhesive and structural durability applications. PhD thesis, Sheffield Hallam University, 2010.

[21] Wetzel B, Haupert F, Zhang MQ. Epoxy nanocomposites with high mechanical and tribological performance. Composites Science and Technology 2003; 63(14):2055–67.

[22] de Morais AB, Pereira AB, Teixeira JP, Cavaleiro NC. Strength of epoxy adhesive-bonded stainless-steel joints. International Journal of Adhesion and Adhesives 2007;27(8):679–86.

[23] Yuichi N, Masahide K, Masataka K, Toshiyuki S. Two-dimensional thermal stress analysis in adhesive butt joints containing hole defects and rigid fillers in adhesive under non-uniform temperature field. Journal of Adhesion 1998;65:57–80.

[24] Kendall K. Shrinkage and peel strength of adhesive joints. Journal of Physics D: Applied Physics 1973;6:1782–7.

[25] Souheng W. Polymer interface and adhesion. CRC Press; 1982.

[26] da Silva LFM, Adams RD. Measurement of the mechanical properties of structural adhesives in tension and shear over a wide range of temperatures. Journal of Adhesion Science and Technology 2005;19(2):109–41.

[27] Mostafa M. Hybrid sol–gel/polyaniline coating for the corrosion protection of AA2024. PhD thesis, Sheffield Hallam University, 2009.

[28] Tae HL, Eun SK, Bae BS. Catalytic effects of aluminum butoxyethoxide in sol–gel hybrid hard coatings. Journal of Sol–Gel Science and Technology 2003; 27:23–9.

[29] Hoebbel D, Nacken M, Schmidt H. On the influence of metal alkoxides on the epoxide ring-opening and condensation reactions of 3-glycid-oxypropyltrimethoxy-silane. Journal of Sol–Gel Science and Technology 2001;21:177–87.