



The Adhesive Strength of Epoxy/Sol-Gel Materials Modified by Various Ratio of γ -Al₂O₃ Nanoparticles

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Abstract: In this study, the use of sol-gel/epoxy adhesive based on the combination of organic and inorganic components within the adhesive matrix have been studied. The combination of different amounts of γ -Al₂O₃ nano-particles to the adhesive matrix was evaluated. Mild steel specimens were prepared for lap joints, which were cured in an oven at 200°C for 16 hours.

The bond strength of the sol-gel/epoxy matrix was investigated using a universal tensile test machine. The presence of Al-OH and/or Si-OH bonds increases causing an increase in the strength of the bulk material. This process is seen through the appearance of an absorption peak shoulder which appears in the range of ~ 1088 to 1100 cm⁻¹ which corresponds to Al-O-Si or Si-O-Si. The maximum adhesive strength of composite sol-gel/epoxy adhesive recorded was 23±0.4 MPa. This was obtained when small amounts of γ -Al₂O₃ nanoparticles (4.0 wt%), were incorporated within the matrix. However, as the level of these inorganic materials in the adhesive matrix increased further, the adhesive shear strength gradually decreased. At a high ratio of γ -Al₂O₃ particles, poor interfacial bonding or adhesion between the filler and the adhesive matrix is recorded. Scanning Electron Microscopy (SEM) is used to investigate the fracture surface with 4.0 wt% γ -Al₂O₃, the scanning shows a very small distance of cracks, suggesting the material may act as a barrier to crack propagation and thus increases the energy required for fracture.

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1. INTRODUCTION

In many engineering fields, such as automotive and aircraft industries, the application of adhesive materials to joint and repair parts and components becomes very popular. In many cases this method has successfully replaced bolting and welding, this is due to its numerous mechanical and chemical advantages [1]. These advantages include the low weight, homogeneous stress distribution, low cost, high corrosion resistance and the ease of use compare to other joining applications. It was clearly observed from the literature [2], that the most commonly used type of adhesive materials in producing the structural adhesives is the epoxy-based organic polymer. This type is produced by the modification of epoxy resins based on diglycidylether of bisphenol-A (DGEBA) [3]. These materials have particularly good

adhesion property on different metallic surfaces but have some limitations on their application due to, the brittleness of cured bisphenol-A. Various methods have been reported to improve the toughness of an epoxy resin [4]. The modification of epoxy structures by introducing functional groups into the main or side chain of the epoxy resin is one way to modify the mechanical performance of the adhesive [5]. The use of sol-gel coatings an intermediate layer to bond two materials have been widely studied [6]. These materials offer the advantage of providing an active, uniform and homogeneous bonding layer due to a strong interaction with the substrate and the epoxy-resin-based adhesive primer [7]. Nowadays, the modification of a hybrid silica-based sol-gel formulation to produce adhesives for bonding metallic substrates is increased. The presence of nanostructured materials can be affected on neat polymers in a wide range of properties, such as mechanical performances [8]. The loading of reinforcement phase into the adhesive matrix may improve its fracture properties [9]. It is well known that adhesive

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Table 1: The Chemical Composition of Mild Steel Used

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

Table 2: The Mechanical Properties Of Mild Steel

Materials	Tensile strength	Brinell Hardness HB 500	Elongation%
Mild steel	420 MPa	140	21

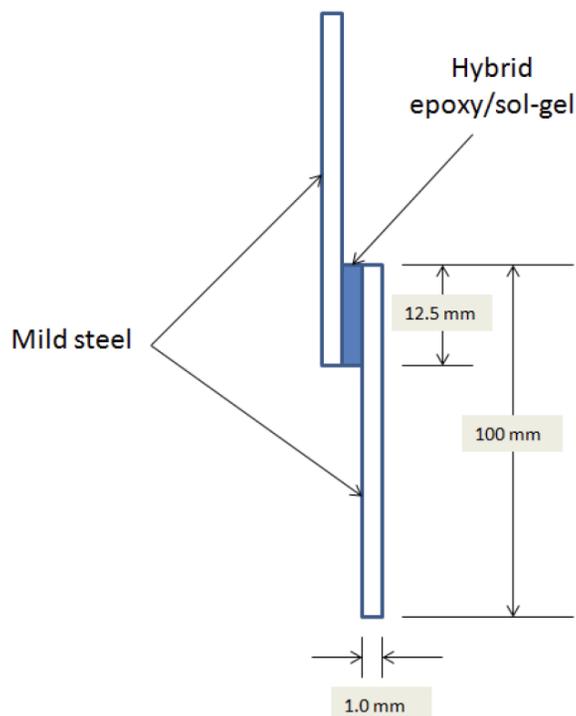
mechanical properties depend on the type, concentration, size, and shape of reinforcement. Other important factors that affect the mechanical behavior of filled systems are the type of dispersion and the kind of agglomeration [10]. In addition, due to the strong bonding between the inorganic nanofillers and epoxy resin chains at the interface zone within the polymer matrix, the material local degradation under the applied load will be reduced [11, 12]. An inorganic material like γ - Al_2O_3 nano-particles can be easily prepared and retains stability in most chemical and biological environments [13]. It has been concluded that the formation of a chemical interaction of inert materials such as silica on the surfaces of aluminum oxide nanoparticles via a sol-gel process could help to prevent their aggregation in liquids and improve their chemical stability [14, 15]. The presence of the γ - Al_2O_3 nanoparticles in the epoxy/sol-gel silica-based system has led to a significant increase in the adhesion properties. The reason attributed to the enhanced crosslinking among the hybrid SiO_2 network through the binding of Si-O-Al, and Si-O-Si in the structure [16]. Numerous works about using γ - Al_2O_3 nano-particles as fillers in the polymer matrix have been extensively reviewed in the literature [17, 18]. However, there are few studies investigating the influences of doping γ - Al_2O_3 in composite epoxy/sol-gel system and affected that upon the adhesive strength [19, 20]. In addition, to our knowledge, there are no data published on the use of sol-gel method for the modification of a hybrid silica-based sol-gel by the addition of a variety of components into the formulation, including different organic-inorganic combined components, i.e., (γ - Al_2O_3 with small amounts of MWCNTs.). In the current work, the influences of doping different ratio of γ - Al_2O_3 nanoparticles on adhesive performance to hybrid epoxy/sol-gel system were discussed. The adhesive performance is investigated using the measurement of shear stress on mild steel samples at room temperature.

2. EXPERIMENTAL WORK

2.1. Materials (Mild Steel)

Mild steel was used as the substrate materials in testing the adhesive strength of the hybrid sol-gel materials. The chemical composition and the mechanical properties of the mild steel are presented in Tables 1 and 2. The steel sample was abraded by a sandpaper grinding with a surface

roughness $R_a = 0.102 \mu\text{m}$ and was then ultrasonically cleaned by using acetone at room temperature. Hybrid epoxy/sol-gel material was then applied as a thin layer (0.03-0.05mm) on the surface of both mild steel specimen and the coated substrates were left to dry for one hour at room temperature. According to ASTM D 1002, the coated steel samples measurement should be (100 mm length, 25 mm width 1.5 mm thickness). These samples were assembled into a single lap shear joint with 12.5 mm of overlap length as shown in Figure 1. In order to ensure (i) full contact between the two specimens ends and the adhesive material and (ii) a uniform adhesive thickness to be achieved between the specimens, constant pressure load was applied to the specimens. The specimen was then placed into an oven for heat treatment at various designated times and temperatures.

**Figure 1:** Schematic of a single lap joint.

2.2. Adhesive Formulations

Hybrid silica-based sols were prepared from silane-based precursors. This hybrid sol was produced by mixing tetraethoxysilane (TEOS), methyltrimethoxysilane (MTMS),

Table 3: Epoxy/Sol-Gel Adhesive Formulation

	DGEBA (ml)	Sol-Gel (ml)	$\gamma\text{-Al}_2\text{O}_3$ (g) with size (10-20 nm)	MWCNT (g) with size (O.D.10-15nm, I.D. 2-6nm, length 0.1-10 μm)
Epoxy/ sol-gel	1.50-2.00	12.00	0.1	0.007

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 adhesives were prepared by mixing the DGEBA with the as-prepared hybrid sol (ratios are listed in Table 3) and then left in an ultrasonic bath for 45 minutes at room temperature to ensure uniform dispersion. Note: the sol-gel systems were not formulated with a curing agent. The sol-gel epoxy adhesives were further modified by doping with 0.007 g multiwall carbon nanotubes (MWCNTs, from Sigma Aldrich) and 0.1 g $\gamma\text{-Al}_2\text{O}_3$ nano-particles (99.98% metal basis, purchased from Alfa Aesar, A Johnson Matthey Company).

2.3. Dispersion of Different Ratio of $\gamma\text{-Al}_2\text{O}_3$ into the Epoxy/Sol-Gel

The sol-gel epoxy adhesive was further modified by doping with a selected ratio of $\gamma\text{-Al}_2\text{O}_3$ (i.e., 1.0, 2.0, 4.0, 6.0 and 10.0 wt%). To achieve optimum dispersion, multiwall carbon nanotubes (MWCNTs) and a selected ratio of $\gamma\text{-Al}_2\text{O}_3$ nanoparticles were first added to 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. Lap Shear Test for Single Lap Joints

Adhesive-bonded single lap joints were produced (see Figure 1) to measure the adhesive strength of the joints. The surface to be adhesively joined was first washed using deionised water, and then cleaned in acetone, and finally air-blow dried for 1 minute. Adhesives were then applied on the surfaces by a spray gun. Specimens were left for 30 minutes at room temperature and then pre-cured in an oven at 95°C for 40 minutes to eliminate trapped air and to evaporate most of solvents and water in the coating. Following ASTM D 1002, mild steel samples were assembled with a single lap shear joint with 12.5 mm overlap, as shown in Figure 1. Finally the joints were placed in a furnace at various designated times and temperatures to achieve a complete cure. For the controlling the adhesive bondline thickness, the bonded area was subjected to an applied pressure of 4 MPa during the curing stage.

2.5. Mechanical Loading and Surface Characterization

Shear mode loading was applied to the specimen to evaluate the adhesive strength of the composite epoxy sol-gel material

on mild steel substrates. The lap joints were tested at room temperature, i.e. $23 \pm 1^\circ\text{C}$, 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. For the surface characterization, 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 type Philips XL 40, operated in the high vacuum mode. The specimen surfaces were coated with the flash- evaporated carbon to prevent charging for the SEM observation. FTIR was used to identify different chemical bonds within the composite matrix.

3. RESULTS AND DISCUSSIONS

3.1. Adhesive Shear Strength

The micrographs confirmed that the $\gamma\text{-Al}_2\text{O}_3$ particles were well dispersed in the epoxy/sol-gel matrix, see Figure 2 (a

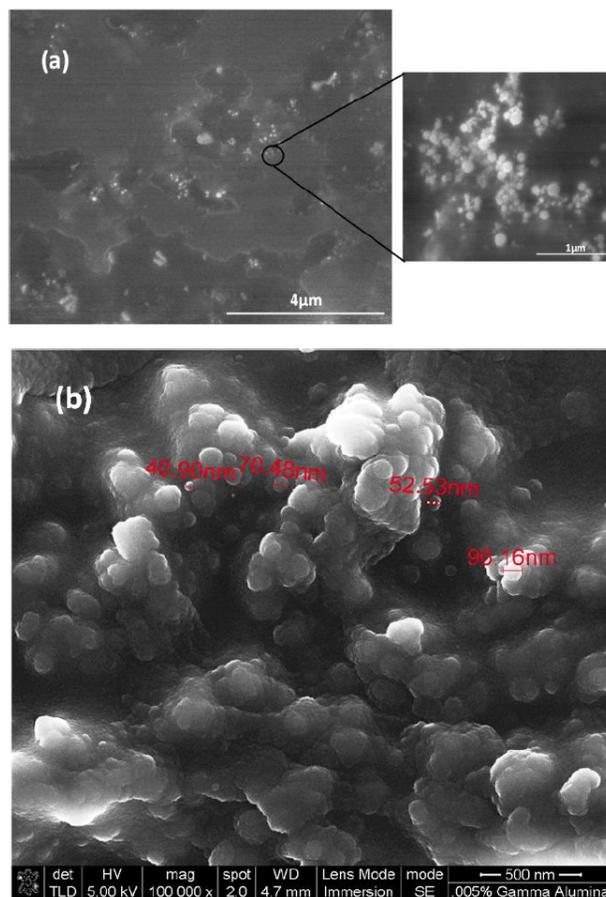


Figure 2: (a & b). SEM images showing the combination of $\gamma\text{-Al}_2\text{O}_3$ within the adhesive matrix.

and b). The incorporation of nano-particles improved the organic/inorganic interaction within the epoxy/sol-gel. The nanoparticles size ranged from 40 to 90 nm and showed to be rather spherical. Due to these nano-size materials, chemical interactions within the formulation such as the formation of Al-O-Al or Al-O-Si bonds increased the degree of adhesive cross-linkage. As a result, improvements in the bond strength of this system were observed. In addition, γ -Al₂O₃ nano-fillers have an important influence on the curing behaviour of the epoxy/sol-gel formulation, including a catalytic effect of the hydroxyl groups of the particles; which increased the local concentration of the activated components, thus increasing the curing reaction rate and the cross-linking density within this doping ratio [21].

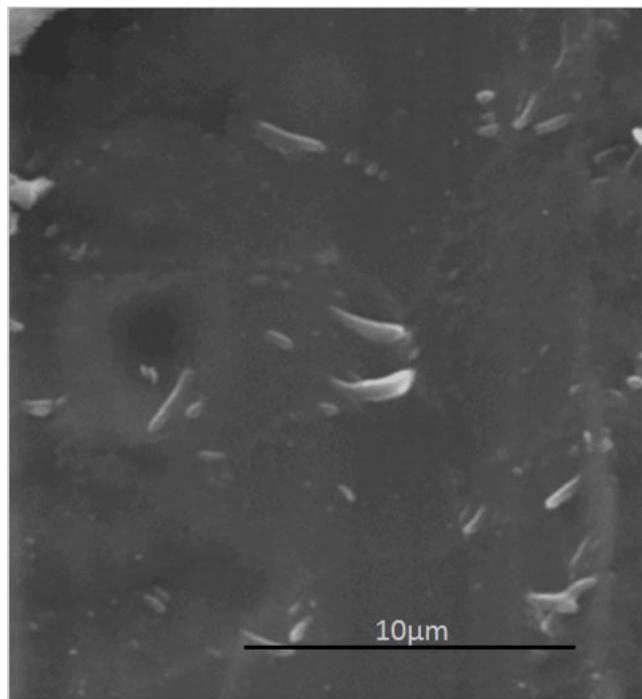


Figure 3. The distribution of MWCNTs within the adhesive matrix.

The doping of small MWCNTs in the adhesive matrix plays a role in the improvements in adhesive performance on metallic substrate. This is related to the uniform distribution of nano-fillers (i.e. MWCNTs) within the matrix which led to an increase of the surface contact area between the nanoparticles and the polymer. The SEM image presented in Figure 3 shows the distribution of MWCNTs, which is thought to be coated and covered with adhesive matrix.

Figure 4 shows the measured adhesive strength after doping the adhesive formulation with different amounts of γ -Al₂O₃. Mild steel specimens were prepared for lap joints, which were cured in an oven at 200°C for 16 hours. Initially there was an increase in the epoxy/sol-gel adhesive shear strength, with the increase of γ -Al₂O₃, this increase in the share stress continue until the value of γ -Al₂O₃ reaches about 4.0 wt%. This may be because the nano γ -Al₂O₃ has increased the crosslinkage where many surface of the hydroxyl group on γ -

Al₂O₃ materials and in silica sol-gel may react during the polymerisation stage as Al-O-Si bond and enhanced the adhesion strength per interaction area within the adhesive matrix. Lambert and Vasconcelos [22] reported that hydroxyl groups in the γ -Al₂O₃ materials can be readily reacted with silanol groups present within sol-gel structure, yielding the production of mixed bonds. The maximum adhesive strength of epoxy/sol-gel adhesive recorded was 23 MPa. However, as the level of these inorganic materials in adhesive formulation increased further, the adhesive shear strength gradually decreased. The reduction in the strength can be attributed to the increase in adhesive viscosity. The behaviour of the adhesive formulation changes from a liquid-like to a more solid-like state, which in return will reduce its wetting ability on the substrate surface, and thus decreasing shear strength. In addition, at high volumes of γ -Al₂O₃ particles, poor interfacial bonding or adhesion between the filler and the adhesive matrix, or the presence of a large free volume phase (un-bonded) of these nano-fillers in the matrix, may have occurred leading to a lower bond strength with the substrate.

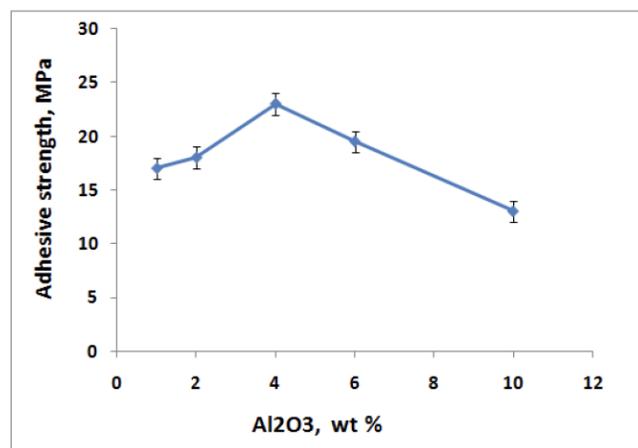


Figure 4: Lap shear strength of epoxy/sol-gel with various percentage of γ -Al₂O₃.

The combination of small amounts of spherical γ -Al₂O₃ nanoparticles within the epoxy/sol-gel formulation, up to 4.0 wt%, caused an increase in joint strength. This increase also related to the distribution in the adhesive matrix allowing greater interaction between the γ -Al₂O₃ and silica network in the form of Al-O-Si bonds. It is also possible that, γ -Al₂O₃ in contact with the polymer segments resulted in less hindrance to the polymer [23] allowing the polymer chains to extend into the matrix and build up strong interaction, which would lower any stress concentrations at the particle/matrix interface, leading to improved adhesive toughness. Figure 5 shows the changes in tensile stress/strain curves for the epoxy/sol-gel adhesive as a function of different amounts of added γ -Al₂O₃. It can be seen that the tensile stress/strain of lap joints increased with the addition of γ -Al₂O₃, exhibiting. A maximum strength value of ~ 23 MPa, and the highest strain value of ~ 0.015 was achieved at 4.0 %wt concentration. However, with an increase in the nano-filler content beyond 4.0 wt%, a

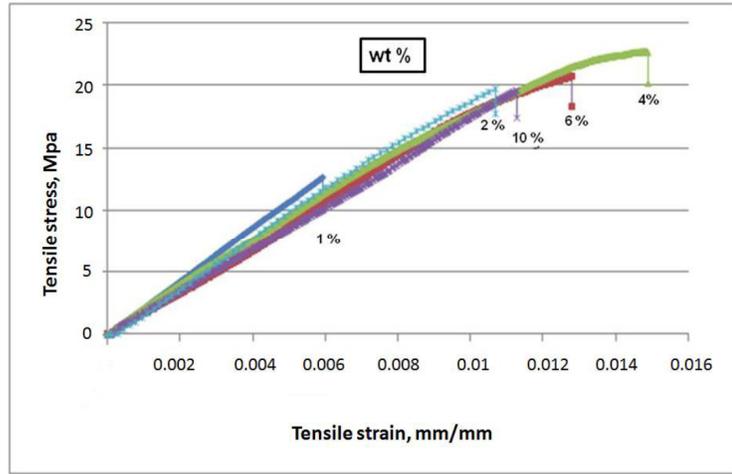


Figure 5: Stress/strain curve of epoxy/sol-gel with the addition of $\gamma\text{-Al}_2\text{O}_3$.

decrease in tensile stress/strain values were observed. As the $\gamma\text{-Al}_2\text{O}_3$ increased from 4.0 to 6.0 and 10 wt%, the areas under the stress/strain curves clearly decreased, suggesting a reduction in adhesive strength. In addition, the total strain decreased as the concentration of $\gamma\text{-Al}_2\text{O}_3$ increased from 4.0% to 6.0% and 10 wt%, indicating increased brittleness. The behaviour may be attributed to the presence of free non-interaction $\gamma\text{-Al}_2\text{O}_3$ nano-particles within the matrix, which

promoted a higher number of stress concentration sites and reduced the adhesive's ability to absorb energy before fracture

3.2. Scanning Electron Microscopy (SEM) Observations

Examination of the adhesive fracture surface of the SEM images in Figure 6a, b, and c, show different failure modes.

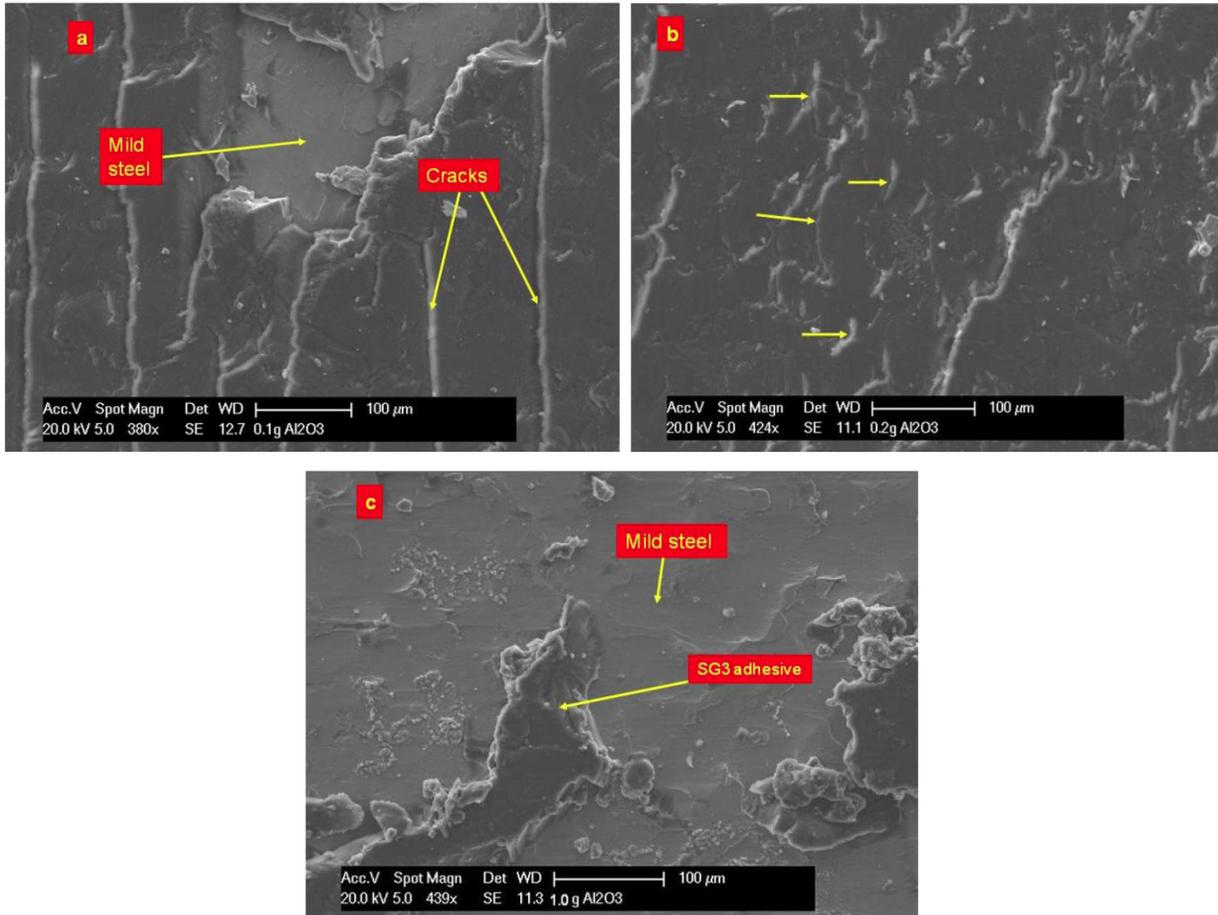


Figure 6: SEM images of adhesive fracture surfaces with the addition of $\gamma\text{-Al}_2\text{O}_3$, (a) 1.0 wt%, (b) 2.0 wt% and (c) 10.0 wt%.

In Figure 6a, can be seen that doping 1.0 wt% of γ - Al_2O_3 into the epoxy/sol-gel adhesive produced a fracture with long cracks within the bulk adhesive, suggesting that the adhesive was brittle and the amount of γ - Al_2O_3 added was insufficient to improve adhesive ductility. The adhesive failure due to this volume of nano-fillers was a mixed adhesive/cohesive mode. Around 70% of adhesive materials remained on the fracture surface (cohesive) and 30% were uncovered surface (adhesive). The fracture surface of adhesive with 2.0 wt% γ - Al_2O_3 added consisted of very small of cracks see Figure 6b, indicating the crack propagation is more restricted compared with Figure 5a. Also, it can be suggested that the γ - Al_2O_3 materials may act as a barrier to crack propagation and thereby increases the energy required for fracture. Here the failure mode was cohesive. The addition of this amount of γ -

Al_2O_3 to the formulation may increase the adhesive ductility due to the increase in adhesive cross-linking, but the addition of higher amounts γ - Al_2O_3 (10 wt%) to the epoxy/sol-gel adhesive decreases adhesive bonding to the substrate surface resulting from 70 to 80% an interfacial fracture mode, see Figure 6c. The failure at the adhesive/substrate interface results from the weakness in the interface where the stress concentrations increased the local stress to levels exceeded the interfacial bonding strength.

3.3. FTIR Characterization

Changes in peak intensities in the Fourier-transform infrared (FTIR) spectra were observed as the cure temperature increased, see Figure 7. With increasing cure temperature for

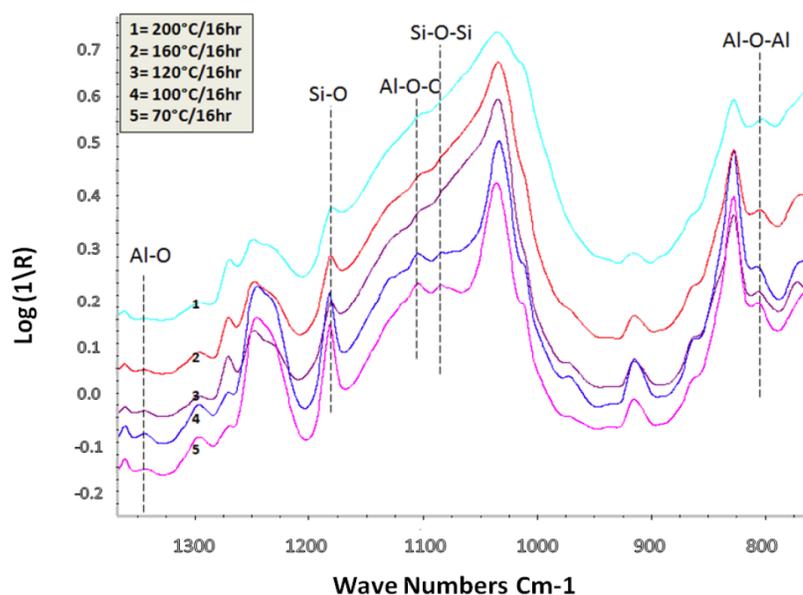


Figure 7: The FTIR spectra of epoxy/sol-gel as the cure temperature.

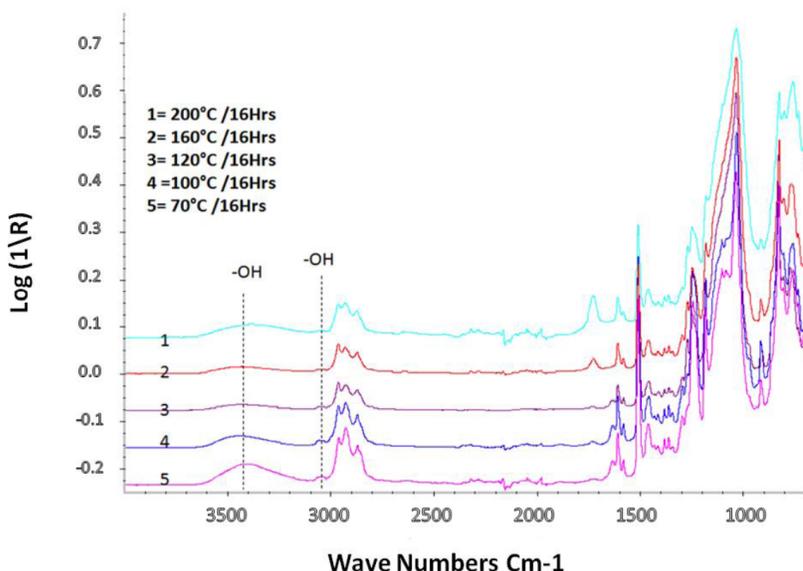


Figure 8: The IR spectra of an -OH stretching band.

the epoxy/sol-gel adhesive, the peak which appears at 1088 cm^{-1} , strongly suggests that temperature is required to promote the cure reaction (leading to improvement in epoxy/sol-gel branching). The gradual disappearance of the Si-OH silanols peak ($\sim 800\text{-}915 \text{ cm}^{-1}$) as the temperature increased, confirms the improved cross-linking via a Si-O-Si bond within the matrix [24]. In addition, the degree of formation of hydrogen bonding of neighbouring inorganic particles via the presence of Al-OH and/or Si-OH bonds increases with temperature causing an increase in the strength of the bulk material. This process is seen through the appearance of an absorption peak shoulder which appears in the range $\sim 1088\text{-}1100 \text{ cm}^{-1}$ which corresponds to Al-O-Si or Si-O-Si bonds as cure procedures increased [25].

Also, Peak shoulder appears in 1125 cm^{-1} is probably related to Al-O-C bonds. In addition, the broad absorption peak from 400 to 1000 cm^{-1} is attributed to the characteristic absorption band of Al_2O_3 . The bands at 1385 and 1124 cm^{-1} are the characteristic absorption band of Al_2O_3 . Also, the conversion of the epoxy/sol-gel adhesive from liquid-like to solid-like state and the release of solvent or water molecules from the process are enhanced. This was confirmed by FTIR in the disappearance of the -OH peak, corresponding to removal of water molecules, see Figure 8. The IR spectrum of an O-H stretching band is assigned in the region between 3000 and 3500 cm^{-1} . It can be clearly seen from these spectra that the intensity of the band in the OH stretching region decreased gradually with increasing the curing temperature.

4. CONCLUSIONS

The measured adhesive strength of hybrid epoxy sol-gel showed an increase in shear strength with increase in $\gamma\text{-Al}_2\text{O}_3$ content up to 4.0 wt%. This because the nano $\gamma\text{-Al}_2\text{O}_3$ increased the crosslinkage where many surface hydroxyl group on $\gamma\text{-Al}_2\text{O}_3$ materials and in silica sol-gel may react during the polymerisation stage. The presences of Al-O-Si bonds enhance the adhesion strength per interaction area within the adhesive matrix. As the $\gamma\text{-Al}_2\text{O}_3$ increased from 4.0 to 6.0 and 10 wt%, the areas under the stress/strain curves clearly decreased. This can be resulted from a reduction in adhesive strength. In addition, the total strain decreased as the concentration of $\gamma\text{-Al}_2\text{O}_3$ increased from 4.0% to 6.0% and 10 wt%, indicating increased brittleness. The behaviour may be attributed to the presence of free non-interaction $\gamma\text{-Al}_2\text{O}_3$ nano-particles within the matrix. This is promoted a higher number of stress concentration sites and reduced the adhesive's ability to absorb energy before fracture.

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