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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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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 multilayered 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.