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Adhesive joining of copper using nano-filler composite adhesive

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ABSTRACT

Effect of well dispersed nano particles filled epoxy based adhesive prepared by an innovative ultrasonic dual mixing on lap joint of copper was investigated. Effect of mechanical and chemical treatment of copper substrate on lap shear strength of its adhesive joint produced by using composite adhesive containing 5, 10, and 15 wt.% TiO_2 particles of size 30 ± 5 nm. The lap shear strength of the joint was also studied as a function of bond line thickness of the adhesive. Fracture behavior of the joint under the lap shear loading has also been studied. Characteristics of the nano particles filled epoxy adhesive joints were compared with the adhesive joints of neat epoxy. Adhesive joint of chemically treated copper shows relatively higher lap shear strength than that of the mechanically treated copper while the joint of composite adhesive shows considerably higher strength as compared to that of the neat adhesive.

1. Introduction

Adhesive bonding is widely used in various industries including aerospace, automotive, electronics and electric etc. because of its several advantages such as large area of bonding, possibility of joining dissimilar materials, relatively lighter weight, uniformity of stress distribution, improved sealing and elimination of distortion or residual stresses caused by heating [1–9]. Fusion welding of copper is difficult because of its high thermal conductivity causing excessive heat loss that demands large heat or power input for required fusion at any location. Thus in order to produce high strength copper joint adhesive bonding has often been considered as a more favoured option.

Epoxies are widely used as high performance structural adhesive because of their ability to cure without producing volatile by-product, resistance to chemicals and environments and their low shrinkage during curing [10,11]. However, in order to further improve various properties of structural adhesive metallic and non-metallic filler is used. The addition of nano filler in epoxy based adhesive reduces shrinkage during curing and enhances toughness and strength of adhesive. It is reported [12–14] that use of nano filler composite adhesive improves fatigue strength and lap shear strength of the joints over the joints prepared by using conventional adhesive. In recently reported studies on adhesive joining of metals it is amply justified that the use of epoxy based nano-filler adhesive processed by an innovative ultrasonic dual mixing (UDM) technique significantly enhances the joint strength [15,16]. The UDM process is basically a process of mixing with the help of simultaneous use of ultrasonic vibration and mechanical stirring which is highly efficient to produce a practically cluster free homogeneously distributed nano-filler composite [17–21].

The strength of single lap shear joint also largely depends upon various factors such as thickness of adherent, modification of faying surface of the substrate in order to improve its wetting and adhesion with the adhesive and bond line thickness of adhesive. To address different interface problem of different metallic substrate various surface modification treatments such as solvent cleaning, abrasion and chemical treatment have been used [22–24]. Mechanical treatment of substrate enhances the adhesive bond strength primarily by removal of gross contamination such as oils and greases and creation of surface roughness providing larger contact area for bonding and mechanical interlocking with the adhesive. Chemical treatment of copper surface with sodium chlorite ($NaClO_2$) and sodium hydroxide (NaOH) results formation of black or red oxide on it depending on period of treatment, where the presence of later one provides relatively higher adhesive joint strength than the former one [25]. But, one of the major difficulties in adhesive bonding of copper is that it forms brittle amine compounds with the amine curing agents [26,27]. However it is reported that the effect of amine can be offset by creating a barrier layer by using the process of black-oxide formation [28,29] or formation of chromate conversion coating [30] on the copper surface.

Due to relatively brittle nature of epoxy adhesive the adhesive

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bond strength largely depends upon bond line thickness of cured adhesive [31]. However, the effect of bond line thickness on adhesive performance of single lap shear joint is still not well understood. The classical analyses predict that joint strength increases with the adhesive thickness, but experiments show opposite trend. Various theories have been developed to explain this discrepancy. Somewhere it is reported that joint strength decreases with increase in adhesive thickness because thicker adhesive contain more defects such as voids and micro crack [32] while the thicker adhesive layer develops higher interface stress [33]. Experimental and FEM analysis on lap joints show that joint strength decreases with the increase of bond line thickness due to development of higher bonding stress [34].

Primary objective of the present work is to study the characteristics of adhesive joint of mechanically and chemically treated copper substrate produced by using titanium dioxide (TiO_2) nanoparticles reinforced epoxy based adhesive treated by UDM process. The characteristics of adhesive joint have been studied as a function of bond line thickness of composite adhesive containing varying amount of nano-filler TiO_2 powder in commercial epoxy adhesive. The joint characteristics have been studied by its lap shear strength and fracture behavior of the adhesive joint in case of the mechanically and chemically treated copper substrate. Mechanical properties of the nano-particles filled epoxy adhesive joints of copper were compared to those of its adhesive joints of neat epoxy adhesive.

2. Experimental

2.1. Materials used

Commercial copper sheet of thickness 1.65 mm was used to produce lap joint by applying epoxy based nano-filler adhesive. Chemical composition of the copper sheet was analyzed by vacuum emission spectroscopy as shown in Table 1. A two component adhesive system containing epoxy resin LY556 (Bisphenol-A) and hardener AD 5200 (Aromatic based diamine) supplied by Fine Finish Organics Pvt. Ltd. (India) was used for joining the copper substrate. The TiO_2 powder of average aspect ratio particle size 25–45 nm, confirmed under TEM observation as shown in Fig. 1(a), was used to prepare the nano-filler adhesive.

2.2. Preparation of nano-filler adhesive

The epoxy resin was dissolved in a solvent as ethyl methyl ketone (MEK) in appropriate proportion to obtain a desired fluidity. Slurries of epoxy resin, nano-particle and MEK containing 5, 10 and 15 wt.% TiO_2 nano-particle was processed by the ultrasonic dual mode mixing (UDM) process. A Vibra Cell ultrasonic processor of maximum output power of 750 W was operated at optimum parameter [19] for preparation of a practically cluster free homogeneously distributed nano-filler adhesive. The process was using a 13 mm diameter titanium alloy (Ti–6Al–4V) tip operated at constant frequency of 20 kHz, where ultrasonic amplitude of 60% was applied with a pulse of 5 s on and 15 s off for about 1 h. After UDM processing the slurry was kept inside a vacuum oven at 70 °C for 2 h to remove the solvent. The removal of MEK was confirmed by comparing the weight of the epoxy resin and TiO_2 mixture before and after removal of MEK to an accuracy of 0.1 mg. Hardener was added to the TiO_2 nano filled epoxy resin in a ratio of 1:4 respectively and was thoroughly mixed with the help of a spatula to produce the nano-filler adhesive. During manual mixing of epoxy with hardener by using glass rod, there is possibility of trapping of air bubble inside the adhesive. Vacuum degreasing was used to ensure complete removal of air bubble in epoxy matrix for better bonding. The presence of pores in the manually mixed neat epoxy and its absence in the vacuum degassed one is typically evident in the photographs shown in Fig. 2(a) and (b) respectively. The freshly prepared TiO_2 nano-filler adhesive was vacuum degasified prior to its application on the copper substrate in order to produce the adhesive joint. FESEM image of 10 wt.% TiO_2 reinforced epoxy matrix has been shown in Fig. 1(b). The average cluster size for TiO_2 (10 wt.%) nanoparticles in epoxy matrix was measured between 28 and 60 nm by FESEM .

Wettability of the epoxy based conventional adhesive and 10 wt.% TiO_2 nano-filler adhesive was studied by measuring their contact angle on the mechanically and chemically treated copper substrate by sessile drop technique as typically shown in Fig. 2. The contact angle was measured by a built in facility of a camera system operated through software (Drop Shape Analyzer – DSA25E).

Table 1
Chemical composition of the copper sheet.

Element	Mg	Ni	P	Al	Cu
Weight (%)	0.008	0.088	0.085	0.018	Rest

2.3. Surface treatment of copper substrate

Surface of the copper substrate was treated mechanically as well as chemically. The mechanical treatment was carried out by polishing the faying surface of copper using 220 grade emery paper as recommended in literature [35] of the adhesive manufacturer and wiped with acetone. The faying region of the copper substrate was chemically treated according to ASTM D2651 standard. Prior to chemical treatment the relevant faying location of the copper substrate was mechanically polished followed by degreasing by acetone. Then this region was immersed for 1–2 min at room temperature in a solution containing 88 g distilled water, 10 g nitric acid (sp.gr. 1.42) and 2 g ferric chloride by weight. The chemically treated surface was rinsed with DI water followed by washing in running water until its chemical neutrality is confirmed by litmus paper test. Finally the chemically treated surface was dried by air blowing at room temperature.

Characteristics of the mechanically and chemically treated surface were studied under the Scanning Electron Microscope (SEM) with the facility of energy-dispersive X-ray spectroscopy (EDAX) analysis. Characteristics of the non-treated and chemically treated surfaces of the copper sheet were also studied by X-ray diffraction (XRD) analysis operated with CuK_α at $\lambda = 1.5418$ Å. XRD analysis tests were performed on the surface of mechanically and chemically treated copper strip of dimension 20×20 mm^2. Roughness values of the mechanically and chemically treated copper surfaces, defined by their average roughness (Ra) and mean roughness depth (Rz) asperities, were measured by profilometer (Mitutoyo SJ 400).

2.4. Preparation of adhesive joints

Single lap joint of the copper sheet, as shown in Fig. 3 confirming the ASTM D1002 standard, was prepared by applying the epoxy based TiO_2 nano-filler adhesive on both the faying surfaces of the mechanically or chemically treated sheet. The adhesive was allowed to spread smoothly on the substrate by wetting in order to avoid air entrapment at the interface followed by placing two copper sheets together in proper position of lap joint confirming the dimensions as shown in Fig. 3. A uniform layer of adhesive was obtained in between the two members of the joint by applying rolling pressure on the joint with the help of roller setup moved at a speed of 1 mm/min under different load varying from 2 to 25 N.