Properties of adhesive joint of inorganic nano-filler composite adhesive

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The characteristics of adhesive joints of aluminium sheet containing epoxy based composite adhesives containing nano-filler of ZrO$_2$ powder have been studied. The composite adhesives containing 10, 15 and 20wt.% of about 20±3 nm size ZrO$_2$ powder are applied to mechanically treated aluminium substrates. The single lap joints of the composite adhesive are characterized by their tensile lap shear strength as a function of the bond-line thickness as well as the amount of filler. The characteristics of the composite adhesive joint have been compared to those of the conventional epoxy adhesive joints. The bond-line thickness of the adhesive with respect to the amount of the ZrO$_2$ nano-filler has been optimised for maximum tensile single lap shear strength of the adhesive joint of mechanically treated aluminium substrate. In comparison to conventional epoxy adhesive joints, the nano-filler epoxy based adhesive joint of aluminium shows significantly improved lap shear strength as a function of bond line thickness of adhesive and amount of filler in it.

Keywords: Adhesive joints, Aluminium substrate, Mechanical polishing, Epoxy adhesive, ZrO$_2$ nano-filler adhesive, Bond line thickness, Lap shear strength

The joining of comparatively thin sections of metals using appropriate adhesive of improved properties are very much in demand over other conventional joints primarily due to its higher joint efficiency index (a measure of relative strength to weight ratio of the bonded region) with better stress distribution and ability to handle dissimilar materials at lower fabrication costs$^{1-6}$. The excellent thermal and insulation properties, superior damping and noise reduction ability along with improvement in corrosion resistance are also appreciable advantages of adhesive joints$^{7,3}$. Out of the commonly used structural adhesives, the epoxy-based adhesives are widely employed for joining of various components largely because of their relatively high modulus and tensile strength. But, the pure epoxy based adhesives do not possess appreciable toughness and resistance to crack propagation$^{1,4}$. Thus, it threatens safety of adhesive joint and hence often is not preferred to use in joining of thick metallic components unless the bonded area is large. Due to its relatively brittle nature the adhesive bond strength largely depends upon bond-line thickness of the adhesive and curing cycle of time and temperature$^7$. Prior to application of adhesive a suitable surface treatment of the substrate by mechanical process has been found relatively superior to using chemical process with respect to improvement in strength of the adhesive joint$^7$-$^9$. The surface treatment generally improves joint properties by modification of substrate surface resulting a better wetting and bond strength between the substrate and the adhesive$^9$. In certain cases the surface roughness created by various treatments especially the mechanical polishing also introduce positive contribution to the bond strength by initiating mechanical locking between the substrate and adhesive giving rise to maximum strength at optimum level of surface roughness$^7$-$^9$. The positive influence of mechanical polishing on the substrate-adhesive bond strength may be effective to any ferrous and non-ferrous metals. But, it works more significantly on aluminium substrate primarily due to formation of aluminium oxide with deficiency of oxygen$^5,9,11-16$ at the mechanically polished surface of the substrate prior to application of adhesive on it, which becomes more reactive to the adhesive and provide stronger bonding with the adhesive and the substrate giving rise to improved joint strength.

To improve various properties of structural adhesives the metallic or non-metallic powders as filler have been widely used$^{17}$. The addition of fillers reduces shrinkage while curing as well as enhances strength and toughness of adhesive$^{18}$. A variation in type, amount and size of powders influences the mechanical properties of the powder reinforced epoxies. It is observed that the use of nano-filler adhesive enhances the wear, shear tensile strength and fatigue properties of adhesive joints of aluminium at

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ambient temperature over that observed in case of the adhesive joints of aluminium prepared by using conventional epoxy adhesive. It is also reported that the addition of nano-particles of molybdenum oxide in epoxy adhesive improves its elevated temperature strength. However, the fracture behaviour of nano-filler composite adhesive at different temperature significantly depends upon the characteristics of adhesive base and the type of nano-fillers as well as their hybrid mixture. During curing of adhesive joint in an oven or autoclave a differential thermal stress may generate at the adhesive layer due to difference in coefficient of thermal expansion (CTE) between the adhesive and the metal adherent. Although any appreciable reduction of shrinkage in presence of suitable filler may significantly influence the development of residual thermal stresses in adhesive layer but, its magnitude may largely depend upon bond line thickness of adhesive adversely affecting the mechanical properties of adhesive joint. In view of the potentialities of nano-filler composite adhesive to improve the properties of adhesive joints, it is imperative to know about the flow characteristics of the nano-filler composite adhesive governing the bond line thickness and its influence on the adhesive joint strength. But the paucity of data in order to have a clear understanding about the criticality and mechanism of these aspects affecting the mechanical properties of adhesive joints of inorganic nano-filler epoxy adhesives necessitates further studies in this area.

Amongst many other inorganic nano-particles the ZrO₂ has been found quite effective in enhancement of mechanical and wear properties of thermoplastic polymeric material by improvement of membrane performance. This behaviour of nano-particles is well known due to their strong activities of unique electronic, magnetic and optical properties in dispersion with small size and large surface area. In this investigation an attempt has been made to study the effect of epoxy based zirconium oxide (ZrO₂) nano-filler composite adhesive on the characteristics of adhesive joints of mechanically polished aluminium sheet. The bond line thickness of the particulate composite adhesives containing varying amount of nano-fillers of the ZrO₂ powder in a commercial epoxy adhesive has been studied as a function of rolling load in order to understand their flow characteristics under the rolling pressure of joint preparation. The adhesive joints are also characterised by their lap shear strength as a function of the bond line thickness of the particulate composite adhesives containing varying amount of nano-fillers. The characteristics of the adhesive joints of the ZrO₂ nano-filler composite adhesive are compared to their counterpart of the base epoxy adhesive.

Experimental Procedure

The lap joints of extruded commercial aluminium (ASTM specification SB-209 grade 1100) sections of thickness 2.0 mm were prepared using conventional epoxy adhesive and particulate composite adhesive. The vacuum emission spectroscopy shows that the sheets containing (wt.%) about 0.3Si, 0.02Ti and 0.43Fe as impurities. Prior to preparation of all the joints the faying surfaces of the sheets were polished mechanically by thoroughly rubbing with 400 grade emery paper so that the surface contamination due to presence of excess oxide layer is practically removed and flat smooth surface all along the faying surface is physically ensured. The mechanical polishing was followed by wiping with acetone to remove any adhering dirt or grease from the surface. The selection of this grade of emery paper for mechanical rubbing of the substrate was made in agreement to an earlier observation in respect to optimum strength of the adhesive joint.

Preparation of adhesive

The conventional and particulate composite adhesives were prepared by using commercial adhesive containing epoxy resin Araldite AW 106 and hardener HV 953U manufactured by Huntsman Advanced Material (India) Pvt. Ltd. The adhesive was having good stability under humid environment and service temperature up to about 120°C. The conventional adhesive was prepared by thorough mechanical mixing of the resin and hardener in equal amount by weight. The filled composite adhesives were also prepared on the same base of the epoxy resin and hardener of the commercial adhesive as stated above. They were prepared by thorough mechanical mixing of sparingly sprinkled particles of desired amount on the epoxy resins in about 4-6 min followed by further mechanical mixing of the slurry for about 4-6 min in the hardener with the help of a spatula rotating at a speed of about 60 rpm. Although a thorough mixing of particles was confirmed by a change in optical appearance of the adhesive but, the elimination of agglomerates of filler nano-particles in it cannot be ensured in this process. The entire mixing operation was carried out at ambient temperature and relative
humidity lying in the range of 20-30°C and 45-55% respectively. The composite adhesives were prepared by using about 20 ± 3 nm size zirconium oxide (ZrO₂) particles in three different amounts (10, 15 and 20 wt.%) in the adhesive. The crystallinity and size of the nano-particles were confirmed under transmission electron microscope (TEM) by studying the electron diffraction pattern and micrograph of the nano-powder as shown in Figs 1a and 1b respectively. The particles used were practically round in shape with surface characteristics in as manufactured condition. Prior to their use both the conventional and composite adhesives were always freshly prepared and degassed for 5 min under vacuum of the order of 0.01 mbar.

**Preparation of adhesive joints**

The adhesive joints of all the conventional and composite adhesives were prepared at ambient condition as stated above by applying them on the faying surfaces of the aluminium sheets and putting them together in proper position of lap joint confirming the dimensions as shown in Fig. 2. A uniform layer of adhesive of different thicknesses was obtained by rolling the freshly prepared joint with a speed of about 3 mm/min at different loads of 10 to 60 N applied through a roller set-up. Finally, these joints defined as green adhesive joints were cured at 120°C for 60 min by putting them in an oven to facilitate wetting and setting of the adhesive. During curing the bond line thickness of the adhesive introduced in the joint was controlled by leaving the green adhesive joints freely with appropriate support of levelling the sheets under application of no external load on them.

**Optical microscopy**

The transverse sections of the adhesive joints were thoroughly polished up to metallographic standard and studied under optical microscope to measure the bond line thickness of adhesive with the help of a micrometer mounted in it. The fracture behaviour of the specimens failed under the single lap shear tests was studied under optical stereomicroscope to find out the mode of fracture in different specimens.

**Single lap shear test**

The single lap shear test of the adhesive joints was carried out on a universal testing machine at a cross-head speed of 1 mm/min. The ultimate shear tensile load carrying capacity of the joints was recorded and single lap shear strength of the joints was estimated on dividing it by the area of lap joint and compared. Reproducibility of the joint properties was checked by testing at least three specimens for each type of joints and average of the result has been correlated with various characteristics of the adhesive.

**Results and Discussion**

**Bond line thickness**

The bond line thickness of adhesive in an adhesive joint largely depends upon its flow characteristics in between two faying surfaces of the joining substrates. The flow characteristics of an adhesive can be primarily understood as a function of the mode and magnitude of pressure applied on it, surface characteristics of the substrate and most importantly the viscosity of the adhesive. In this investigation the bond line thickness of the conventional and composite adhesives in mechanically polished aluminium substrate has been primarily affected by the rolling
load and viscosity of the adhesive. The viscosity of the adhesive varied with the addition of the nanoparticles of zirconium oxide in different amount. At the low and high rolling load of 20 and 60 N the typical nature of variation of the bond line thickness of the composite adhesive as a function of the amount of particle reinforcement has been shown in the optical macrographs presented in Figs 3a and 3b respectively. The figure shows that the rolling loads significantly influences the bond line thickness of both the conventional and nano-filler composite adhesive where the amount of particle reinforcement further affects the bond line thickness of composite adhesive by influencing its viscosity. The variation in flow characteristics of different amount of nano-filler containing adhesive under rolling pressure primarily dictates its bond line thickness in adhesive joint.

The influence of the rolling load on the characteristic change in bond line thickness of the conventional adhesive has been shown in Fig. 4. Similarly the influence of rolling load on the nature of variation of bond line thickness of the composite adhesive containing varying amount (10, 15 and 20 wt.%) of zirconium oxide particles has been shown in Fig. 5. In Fig. 4 it appears that the increase of rolling load up to 40 N significantly reduces the bond line thickness followed by a relatively insignificant decrease in it with the further increase of the rolling load up to 60 N. Fig. 5 depicts that unlike it observed in case of the conventional adhesive (Fig. 4) the increase of rolling load from 20 to 60 N relatively steadily reduces the bond line thickness of the composite adhesive and at a given rolling load it enhances with the increase of particle content of the adhesive from 10 to 20 wt.%. The enhancement of bond line thickness of the composite adhesive with the increase in amount of particle reinforcement is primarily attributed to rheological behaviour and viscoelastic properties of the film influencing resistance to flow of the epoxy adhesive. Thus, in agreement to the earlier observation it may be inferred that the nature of reduction in adhesive layer thickness with the increase of rolling load varies with the type of adhesive as the conventional (Fig. 4) or particulate composite (Fig. 5), being comparatively sharper in case of the former one up to the rolling load of 40 N. Whereas, at a higher rolling load the reduction in adhesive layer thickness reacts more sharply to the increase of rolling load in case of the particulate composite adhesive. However, at a given rolling load, the bond-line thickness of the nanoparticulate composite adhesive (Fig. 5) has been found comparatively higher than the conventional adhesive (Figs 4) especially in case of the particle content beyond 10 wt.%.

The lowering of bond line thickness with the increase of rolling load primarily happens due to squeezing out of the adhesive under the pressure in between the substrates resulting from the enhanced

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Fig. 3—Typical nature of variation of bond line thickness of the composite adhesive as a function of amount of particle reinforcement at different rolling loads of 20 and 60 N

Fig. 4—Effect of rolling load on bond line thickness of the conventional adhesive

Fig. 5—Effect of rolling load on bond line thickness of the composite adhesive containing varying amount of ZrO₂ nanoparticles.
rolling load. However, at a given rolling load the observed higher bond line thickness of the composite adhesive than that of the conventional adhesive may have caused by comparatively higher resistance to flow of the composite adhesive imposed by the presence of particle and its amount. At a larger layer thickness the flow of adhesive is predominantly governed by the viscosity of the adhesive. But, at a lower layer thickness of adhesive layer its flow is largely controlled by the interfacial dragging force imparted by the substrate covering a substantial part of the thickness of adhesive layer. The substrate-adhesive interaction offers a significant resistance to the flow of adhesive and thus it predominantly impairs the spreading of adhesive with the increase of rolling load lowering its response to reduction in bond line thickness of adhesive. This phenomenon has been found effective at a bond line thickness of adhesive maximum of the order of 0.1-0.08 mm as revealed (Fig. 4) in case of the conventional adhesive. In case of using particulate composite hardly any situation of such a low bond-line thickness of adhesive has generally been resulted during the increase of rolling load up to 60 N to activate an effective interaction of the substrate with the adhesive restricting its flow in between the substrates.

Single lap shear strength

The effect of bond line thickness on lap shear strength of the conventional adhesive joints of aluminium has been shown in Fig. 6. Similarly the effect of bond line thickness on lap shear strength of the composite adhesive containing varying amount (10, 15 and 20 wt.%) of nano-particles of zirconium oxide has been shown in Fig. 7. Figure 6 shows that the bond line thickness of the conventional adhesive of the order of about 0.1 mm which gives rise to relatively higher joint strength with respect to that observed in case of deviation in bond line thickness from it. In case of the adhesive joint of nano-filler composite adhesive (Fig. 7) the maximum joint strength has also been found to achieve at low bond line thickness of the order of about 0.1 mm followed by a steady reduction in it with a significantly faster rate than that observed in case of the conventional adhesive (Fig. 6) with a further increase of bond line thickness. Fig. 7 also depicts that at a given bond line thickness the strength of the adhesive joint enhances with the increase in amount of particle in the composite adhesive from 10 to 15 wt.% followed by a decrease in it with a further increase of particle reinforcement to 20 wt.%.

![Fig. 6—Effect of bond line thickness of conventional adhesive on tensile lap shear strength of the adhesive joint](image1)

![Fig. 7—Effect of bond line thickness on tensile lap shear strength of the composite adhesive joint containing varying amount of ZrO2 particles](image2)

The results presented in Fig. 7 in general show that the adhesive joints prepared by applying nano-filler composite adhesive gives considerably higher strength than that of the conventional adhesive joint (Fig. 6). But the significant variation in lap shear strength of the adhesive joints of the composite adhesive with the bond line thickness and the amount of particle reinforcement in the adhesive primarily arises due to their considerable influence on fracture characteristics. In agreement to earlier observation the comparatively thicker bond line of the composite adhesive giving considerably higher joint strength than that of the conventional adhesive shows that the particle reinforcement enhances resistance of the adhesive to cohesive fracture. However, it is interesting to note that at a thin bond-line thickness also of the order of less than 0.8 mm the nano-filler composite adhesive joint gives comparatively higher joint strength than the conventional adhesive joint. It shows that the nanoparticles may also provide positive influence on the adhesive joint strength up to certain extent.
At higher bond-line thickness of adhesive with uniform spreading at the interface a more susceptibility to development of residual thermal stresses a competitive nature of predomination of the strengths of three regions of an adhesive joint, such as the interface/inter-phase bond strength, shear strength of adhesive adjacent to its interface and cohesive strength of the adhesive, primarily dictates the joint strength\textsuperscript{10,18}. The presence of residual stresses may also adversely influence the strength and fracture behaviour of these regions. In case of the conventional adhesive it is reported\textsuperscript{17,26,27} that the inter-phase region of adhesive adjacent to the interface with the substrate possesses maximum strength out of the three regions as stated above and the performance of the bond depends upon net work structure of the adhesive influenced by the surface treatment of metal like aluminium\textsuperscript{15,16,28}. A comparatively high strength of the adhesive adjacent to its interface with the substrate may arise from a relatively larger resistance to deformation of this region under the influence of its good interfacial strength. But, the situation can be different in case of the composite adhesives, where the cohesive strength of the adhesive under the influence of reinforcement may primarily dictate the joint strength. This phenomenon has been marked by predominantly cohesive fracture of the high strength adhesive joint as typically shown in Fig. 8 depicting the fracture of the particulate composite adhesive containing 15 wt.% of ZrO\textsubscript{2} nano-particles. In reference to an earlier work\textsuperscript{10} it is interestingly observed that the use of nano oxide particles instead of micron oxide particles enhances the lap shear strength of the adhesive joint of particulate composite adhesive. This may have primarily attributed to the considerable increase in surface area-to-volume ratio of nano-particles over the micron particles facilitating the more wide spread bonding at large interfacial area of the particles with the epoxy matrix and creation of small size of stress concentration sites resisting the fracture of the matrix.

At a given bond line thickness the lap shear strength of the adhesive joints prepared by using the composite adhesive has been found to enhance (Fig. 7) with the increase in amount of ZrO\textsubscript{2} nano-particle reinforcement from 10 to 15 wt.% followed by a decrease in it with a further increase of particle reinforcement to 20 wt%. In agreement to an earlier observation\textsuperscript{79} the increase of adhesive joint strength with the increase of particle content in the epoxy adhesive up to 15 wt.% may be primarily happened due to well known resistance to fracture provided by the particle with the help of crack blunting mechanisms\textsuperscript{28,30}. It happens through suitable modification of stress distribution in the matrix under an effective inter-particle distance affecting the localised shear yielding and damage formation due to crack diversion and particle-matrix debonding\textsuperscript{31,32}. But the relative decrease in joint strength with the increase of particle content to 20 wt.% possibly primarily attributed to aggregation of the particles\textsuperscript{29} and adverse interaction amongst the particles resulting from lowering of inter-particle spacing beyond a critical level for the matrix\textsuperscript{25}. The resistance to fracture offered by the particle with the help of crack blunting mechanisms also justifies the maximum strength of adhesive joints (Fig. 7) at higher bond line thickness of composite adhesive containing larger amount of particle. However, to characterise the adhesive joint of the nano-filler composite adhesive for its maximum strength the mechanism of fracture is still not well understood especially with respect to glass transition temperature ($T_g$) and interaction of the polymer chain and nano-fillers.

**Conclusions**

The use of epoxy based nano (20±3 nm) filler composite adhesive considerably improves the lap shear strength of the adhesive joints of aluminium with respect to that of the conventional epoxy adhesive joints. However, the strength of the adhesive joints of both the conventional and nano-filler composite adhesives is a function of bond line thickness being comparatively more sensitive to the
composite adhesive. At a given bond line thickness the strength of the adhesive joint of the composite adhesive enhances with the amount of particle reinforcement up to 15 wt.% followed by a decrease in it with further increase of particle content to 20 wt.%

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References