Chapter 2

Literature Review

2.1 Electrically Conductive Adhesives

Electrically conductive adhesives (ECAs) are gaining great interest as potential solder replacements in microelectronics assemblies. Basically, there are two types of ECAs, isotropic conductive adhesive (ICA) and anisotropic conductive adhesive (ACA) [1]. Although the concepts of these materials are different, both materials are composite materials consisting of a polymer matrix containing conductive fillers. Typically, ICAs contain conductive filler concentrations between 20 and 35 vol.%, and the adhesives are conductive in all directions. ICAs are primarily utilized in hybrid applications and surface mount technology [2]. In ACAs, the volume fractions of conductive fillers are normally between 5 and 10 vol.% and the electrical conduction is generally built only in the pressurization direction during curing. ACA technology is very suitable for fine pitch technology [2] and is principally used for flat panel display applications, flip chips and fine pitch surface mount devices [3].

Compared to conventional solder interconnection technology, conductive adhesives are believed to have the following advantages [4,5]:

1). More environmental friendly than lead-based solder;

2). Lower processing temperature requirements;

3). Finer pitch capability (ACAs);

4). Higher flexibility and greater fatigue resistance than solder;

5). Simpler processing (no need to get rid of flux);

6). Non-solderable (inexpensive) substrates can be used (e.g., glass).

Despite the advantages of ECA technology, the replacement of solder by this technology has not been widely adopted by the electronics industry. Lower electrical conductivity than solder [6-7], poor impact resistance [3] and long-term electrical and mechanical stability [4,8-11] are several critical concerns that have limited wider applications

of electrically conductive adhesive technology. Numerous studies are being conducted to develop a better understanding of the mechanisms underlying these problems and to improve the performance of conductive adhesives for electronic applications.

2.1.1 Polymer Binders and Conductive Fillers

Electrically conductive adhesives consist of a polymer binder that provides mechanical strength and conductive fillers, which offer electrical conduction. Polymers are commonly classified as either thermosets (such as epoxies, polyimides, silicones and acrylic adhesives) or thermoplastics. With different applications of ECAs, polymer binders can be of either type. For conductive fillers, metallic materials such as gold, silver, copper, and nickel or nonmetallic materials such as carbon have found application in ECA technology.

2.1.1.1 Polymer Binders for Electrically Conductive Adhesives

a. Thermoplastics

Thermoplastics are also referred to as remeltables and hot melts. This class of polymers typically has a long linear molecular structure, which allows these materials to melt and flow when heated to a specific melting point without significantly altering their intrinsic properties. Generally, thermoplastic adhesives are available in film form and in solvent solution pastes. The paste adhesives are applied to the bonded surface by dispensing, printing, or stenciling. The solid film, typically utilized as anisotropic conductive adhesives, is mechanically positioned and bonded by applying heat and pressure. Thermoplastic-based adhesives are believed to have good reworkability and offer a shorter bonding process. On the other hand, because thermoplastic adhesives consist of long polymer chains, their rheological properties must be altered through the substantial use of solvents when utilized in paste form. Because thermoplastics soften or melt if heated to a high enough temperature, they are somewhat limited in service temperature performance [12]. Another concern in the application of thermoplastic adhesives is that thermoplastics tend to flow under the application of force. This flow is referred to as creep, which is thought to be a factor that may cause electrical resistance increases in thermal cycling tests [13].

b. Thermosets

Thermosets are crosslinked polymers and generally have an extensive three-dimensional molecular network structure. Thermoset systems undergo true chemical

reactions and form chemical crosslinks between polymer chains that resist deformation even at relatively high temperature. Many thermoset systems require little or no solvents, and the reduced use of solvents in adhesives is preferred from an environmental point of view, and also minimizes the possibility of formation of solvent bubbles and voids due to solvent emissions during curing. In addition, thermoset adhesives typically are cured from low molecular weight liquids that can wet out a surface and form strong bonds that can improve the durability of adhesive joints. Some drawbacks of thermosets include limited shelf life and poor reworkability.

Thermoset epoxies filled with silver particles are by far the most common adhesive binders for isotropic conductive adhesives used for component assembly. They have been used for decades due to their many superior properties, such as low shrinkage, good adhesion, and good resistance to moisture and chemical attacks [12].

2.1.1.2 Conductive Fillers

a. Silver

Silver is the most commonly used conductive filler for isotropic conductive adhesives because of its high electrical conductivity, chemical stability, and lower cost compared to gold [12]. Unlike many other metals such as copper, that become non-conductive after being oxidized due to exposure to heat and humidity, silver oxides also show high conductivity. The other important attribute is that silver can be easily precipitated into a wide range of controllable sizes and shapes [12]. The silver fillers are typically fabricated into flakes and pretreated with organic lubricants to ensure the proper rheology of the ECAs [14]. The organic lubricant on the surface of silver flakes can greatly affect the performance of ECAs, including the dispersity of the Ag flakes in the ECA [15], rheology, and electrical conductivity of the ECA [14]. A mixture of silver flakes and particles with broad size distribution can offer improved conductance over narrow size distribution [16]. Flakes can provide improved conductivity by allowing the flake-like particles to overlap one another. On the other hand, the voids caused by the overlapping can be filled with the small particles. Other silver systems were also developed to improve the performances of silver-based conductive adhesives. Kottaus, *et al* [17] used highly porous Ag power as filler material for ICAs. They illustrated that the thermo-mechanical properties of the adhesives using porous

Ag were improved because of the infiltration of the resin into the pores. The electrical performance of these systems, however, needs further improvement. Lu and Wong [18] utilized a mixture of silver flakes and low-melting-point alloy fillers (LMPA) as the conductive filler. During the curing of the adhesive, the LMPA filler melts and forms metallurgical interconnections between the Ag flakes and the metallizations of the substrates. The conductive adhesive filled with this newly developed silver system shows much lower electrical resistance than those filled only with silver flakes.

b. Nickel

The ability to resist oxidation allows nickel to be used as stable conductive fillers. However, as a hard, poorly malleable metal, nickel cannot be easily fabricated into optimized geometries. Generally, isotropic nickel adhesives show both higher filler resistance and contact resistance than silver based products [16]. However, nickel has found use in anisotropic conductive adhesives where spherical particles are commonly used.

c. Metal-coated particles

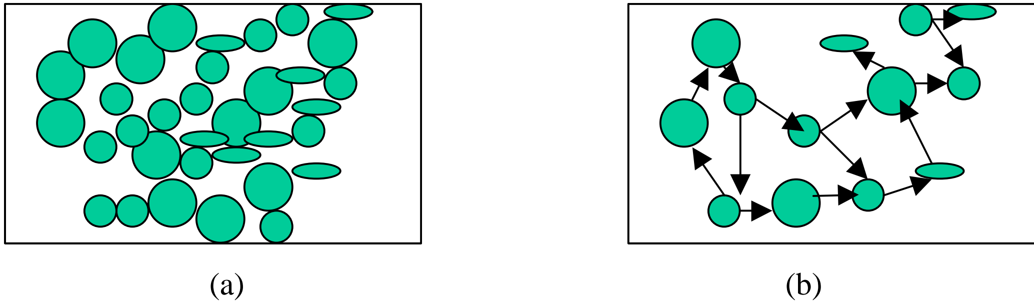
In some applications, metal-plated conductive particles have been used, especially in anisotropic conductive adhesives. Although the original intent of using plated particles was to reduce cost, various types of plated particles have been specially designed for specific characteristics and end uses. Silver, nickel and gold plating on non-metals such as glass and plastic are among the most common types of filler product [11].

Besides the conductive fillers described above, other fillers such as gold and carbon particles are also used in special applications. Due to the high cost, gold filler is mainly used for highly demanding military and space applications [19]. Because of their poor conductivity, carbon-based adhesives are only used for low conductivity applications such as keyboards or shielding [12].

2.1.2 Conduction Mechanisms in Isotropic Conductive Adhesives

In general, there are two conductive pathways for isotropic conductive adhesives as shown in Figure 2. 1. One is genuine conduction, caused by particle-to-particle contact within the polymer matrix. The other is percolation, which involves electron transport brought about by quantum-mechanical electron tunneling between particles close enough to allow dielectric breakdown of the matrix. Ritter [20] has suggested that percolation is the dominant

conduction phenomenon in the early stages of conduction, as the applied current polarizes the conductive adhesive system causing the electrical resistance to drop by charge effects. As currents, especially high currents, continue to be applied, polarized particles migrate and further coalesce, and conduction by particle-to-particle contact overwhelms percolation and becomes the dominant conduction phenomenon.



(a) (b)

Figure 2. 1 Conduction Mechanisms in conductive adhesives; (a) Particle-to-particle, (b) electron tunneling.

For isotropic conductive adhesives, as the conductive filler loading is progressively increased, the electrical resistance does not decrease significantly until the filler loading reaches a critical value, P_c. This point, where the electrical resistance decreases abruptly, is called the percolation threshold. Practical isotropic electrically conductive adhesives are typically manufactured with filler loading P sufficiently greater than the threshold value P_c to guarantee low electrical resistance. The percolation threshold may vary with silver particle sizes and shapes, and silver orientations in the polymer matrix. Ruschau *et al* [21] and Sancaktar and Wei [22] showed that the thresholds for spherical/power particles appeared consistently at around 40% vol.% filler. Lyons [23] investigated the effect of the composition and size distribution of conductive particles on the percolation threshold. He demonstrated that wide particle size distributions and particle types with higher density in adhesive formulations could reduce the percolation threshold.

2.1.3 Cure Effects

The thermal cure is believed to be critical to develop the ultimate mechanical and electrical performance of ICAs. Prior conduction studies [24-26] have shown that the metallic contacts between silver flakes are primarily established during cure. Klosterman *et*

al [24] found that the conduction development during epoxy cure was accompanied by displacement and decomposition of the organic lubricant, which covers the silver flake surface, and by the increase of the contact area between silver flakes by thermal stress and shrinkage. Lu *et al* [25,26] investigated the roles of adhesive shrinkage and silver flake lubricant removal on adhesive conductivity achievement during cure. They found that cure shrinkage, which brings the silver flake particles closer, rather than lubricant, was the prerequisite for conductivity achievement in ICAs, and ICAs with higher cure shrinkage showed higher conductivity. Khoo *et al* [27] investigated the effects of degree of curing on the shear strength and electrical resistance of an epoxy conductive adhesive joint with Sn37Pb bonding surface when exposed to environmental aging. They concluded that a minimum degree of curing was needed to provide a certain level of mechanical and electrical performance in the adhesive joint. Below the critical degree of curing, the electrical resistance of the adhesive joint increased significantly upon exposure to environmental aging, because the adhesive which was not fully cured could absorb a significant amount of moisture which in turn caused oxidation/hydration at the adhesive/substrate interface. In addition, below the critical degree of curing, the shear strength of the adhesive joint was found to be very poor compared with that of the adhesive joint which was cured above the critical degree of curing.

2.1.4 Review of Reliability Studies on Isotropic Conductive Adhesive (ICA) Joints

The reliability of any conductive adhesive joint is a critical issue that must be considered carefully before the adhesives can be widely used in a production setting. Poor electrical and mechanical stability upon exposure to environmental aging conditions, such as elevated temperature and humidity aging, and poor reliability in impact situation, are several major concerns that exist in the ICAs. In most cases, reliability testing is often accelerated by increasing load/stress, humidity, temperature, etc. to simulate environmental influence factors and cyclic thermal loads, shock tests, etc.

Jagt, *et al.* [4] studied the influence of the component and board metallizations on the durability of the conductive adhesive joints. In their research, electrical and mechanical behavior of conductive adhesives was discussed for bonding R 1026 resistors with SnPb or AgPd terminations on bare copper, SnPb or Au plated boards before and after climate testing.

They concluded that with the noble AgPd termination, the increase in electric resistance of the resistors in the climate was significantly less, compared with those with SnPb terminations. They believed that the deterioration of contact resistance on SnPb was due to a significant extent to surface oxidation and adhesion failure as also suggested by other researchers [2,10,24,28]. They also found that there was no clear correlation between mechanical and electrical properties after environmental aging. Liu *et al* [10] investigated reliability and failure mechanisms of ICA joints on Sn37Pb, Cu, and Au plated surfaces upon exposure to the 85°C, 85% RH environment. They observed that the mechanical strength and electrical performance were both reduced with increasing aging time in the Sn37Pb and Cu systems. They attributed these phenomena to the formation of Cu_2O on the copper metallization and the formation of PbO on the Sn37Pb surface, as both Cu_2O and Sn37Pb are both poor conductors and may form weak boundary layers at the interface. On the other hand, the gold metallization system exhibited stable electrical performance after the hot/wet humidity test. The mechanical performance of the gold metallization system after environmental aging, however, was not presented in their study. Studies by Lu *et al* [18,29] revealed that galvanic corrosion rather than simple oxidation of the metal at the interface between an ICA and the non-noble metal was the main mechanism for contact resistance shift. Lu *et al* showed that adding corrosion inhibitors and using low-melting-point alloy fillers to form metallurgical interconnections could be very effective ways to stabilize contact resistance of ECAs during environmental aging. Constable *et al* [30] performed pulling and fatigue tests on lap joints to study bond strength of conductive adhesive/copper joints. Constable used four different metallizations including Cu, Au, Pd and PdNi for the copper substrates and tested four adhesives. Based on the lap joints results, Constable found that no single surface finish gave superior performance for all adhesives tested. He concluded that the choices of adhesive and metal surface finish were interdependent and must be considered together with the application. His study also revealed that typical strains for a 1000 cycle fatigue life for conductive adhesives are on the order of 10%, which is in contrast to 1% for solders, though the operational stress range of conductive adhesives is 5-26 MPa, which is less than 17-42 MPa for solders. Perichaud *et al* [2,31] compared the performance of two thermosetting and one thermoplastic conductive adhesives for surface mount technology assemblies. Perichaud *et al* showed that under thermal cycles from –55°C to +125°C, the thermoplastic adhesive

presented the best electrical stability, which was due to its higher flexibility and similar coefficient of thermal expansion (CTE) to that of component to be connected. On the other hand, their shear tests after thermal cycling showed that the adhesion strength was always higher for both thermosetting adhesives than for the thermoplastic one. They attributed this phenomenon to the nature of the bonds, where thermosetting resins can produce strong covalent and secondary links, while thermoplastic adhesives can form only secondary bonds. Vona *et al* [32] conducted a structure-property-performance study of conductive adhesives to identify the key material properties for improved impact resistance. They concluded that the ability of a material to effectively dissipate energy was essential for better impact performance, which accordingly could be achieved by designing materials with reduced Young's Modulus and increased loss factor (tan δ) under drop test conditions. Lu *et al* [33] developed a class of conductive adhesives with a broad loss factor peak with temperature and a high tan δ at room temperature by combining modified resins and effective additives. Based on the drop test results, Lu *et al* claimed that this class of conductive adhesives showed superior impact resistance. Liu *et al* [4] demonstrated that conformal coating could improve the impact strength of conductive adhesive joints.

2.2 Theories of Adhesion

The actual mechanism of adhesion has been investigated for years. Several theories have been proposed in an attempt to provide an explanation for adhesion phenomenon. However, no single theory explains adhesion in a general, comprehensive way. For a specific adhesive joint, one or more of the adhesion theories may be applicable. In the following, some of the major developments on adhesion theories are briefly reviewed.

2.2.1 Adsorption

The adsorption theory states that adhesion results from intimate intermolecular contact between two materials, and involves surface forces that develop between the atoms in the two surfaces. This theory is believed to be one of the most important mechanisms in achieving adhesion [34]. The most common surface forces that form at the adhesive-adherend interface are van der Waals forces. In addition, acid-base interactions and hydrogen bonds, which are generally considered as a type of acid-base interaction, may also contribute to intrinsic

adhesion forces and have been studied in depth by Fowkes [35-37]. Research conducted by many researchers [38-40] has experimentally demonstrated that the mechanism of adhesion in many adhesive joints only involves interfacial secondary forces. It has also been noted that the calculated attractive forces between two surfaces are considerably higher than the experimentally measured strength of adhesive joints. This discrepancy between theoretical and experimental strength values has been attributed to voids, defects or other geometric irregularities which may cause stress concentrations during loading [41].

To obtain good adsorption, intimate contact must be reached such that van der Waals interaction or the acid-base interaction or both take place; hence good wetting is essential. According to Young's equation, the surface tensions (liquid/vapor: γ_{lv}, solid/liquid: γ_{sl} and solid/vapor: γ_{sl}) at the three phase contact point are related to the equilibrium contact angle θ through:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} Cos\theta$$

Sharpe and Schonhorn [42] have proposed that one important factor that influences the adhesive joint strength is the ability of the adhesive to spread spontaneously on the substrate when the joint is initially formed. For spontaneous wetting to occur:

$$\gamma_{sv} \geq \gamma_{sl} + \gamma_{lv} \quad (1)$$

By ignoring the interfacial free energy, Sharpe and Schonhorn have further proposed the following criteria:

For good wetting: $\gamma_{sv} > \gamma_{lv}$

For poor wetting: $\gamma_{sv} < \gamma_{lv}$

According to Fowkes [37], the total work of adhesion W_A is the sum of the van der Waals interaction W_A^{LW} and the acid-base interaction W_A^{a-b}:

$$W_A = W_A^{LW} + W_A^{a-b} \quad (2)$$

Fowkes also suggested that the van der Waals W_A^{LW} and the acid-base interaction W_A^{a-b} could be expressed as follows, respectively

$$W_A^{LW} \cong W_{12}^d = 2(\boldsymbol{g}_1^d \boldsymbol{g}_2^d)^{1/2} \quad (3)$$

and

$$W_A^{a-b} = -fn^{a-b} \Delta H^{a-b} \quad (4)$$

where $\boldsymbol{g}_1^d$ and $\boldsymbol{g}_2^d$ are the dispersion force components of phases 1 and 2, respectively, f is an enthalpy-to-free-energy correction factor, $n^{a\text{-}b}$ is the surface fraction of the acid-base pair per unit area, and $\boldsymbol{D}H^{a\text{-}b}$ is the enthalpy required for the formation of an acid-base pair.

2.2.2 Chemical Bonding

The chemical bonding mechanism suggests that primary, chemical bonds may form across the interface. Chemical bonding is strong and may make a significant contribution to the intrinsic adhesion in some cases. According to Kinloch [43], primary chemical forces have energies ranging between 60-1100 kJ/mol, which are considerably higher than the bond energies secondary forces have (0.08-40 kJ/mol). The chemical reactions occurring at the interface through the use of coupling agents have been reviewed by Plueddemann [44] and Miller and Ishida [45]. Ho *et al* [46] and Haight *et al* [47] have reported the formation of chemical bonding between metal and polyimide.

2.2.3 Mechanical Interlocking

According to the mechanical interlocking theory of adhesion, good adhesion occurs only when an adhesive penetrates into the pores on the surface of a substrate, and locks mechanically to the substrate. However, the attainment of good adhesion between smooth adherend surfaces in many studies suggests that the interlocking may help promote adhesion, but is not an adhesion mechanism with general applicability. Clearfield *et al* [48] reviewed several common pretreatment methods applied on aluminum surfaces such as the Forest Product Laboratory (FPL) etching procedure, phosphoric acid anodization (PAA) and chromic acid anodization (CAA). He summarized that these pretreatments result in microroughness on the adherend surface, which can improve bond strength and durability by providing mechanical interlocking. It has been found that besides mechanical interlocking, the enhancement of the adhesive joint strength due to the roughing of the adherend surface may

have also benefited from other factors such as formation of a larger surface, improved kinetics of wetting and increased plastic deformation of the adhesive [49,50].

2.2.4 Diffusion

Voyutskii [51] first proposed the diffusion theory, which states that the major driving force for polymer autohesion and heterohesion is due to mutual diffusion of polymer molecules across the interface. This theory requires that both the adhesive and adherend are polymers, which are capable of movement and are mutually compatible and miscible. To describe the self-diffusion phenomenon of polymers, several theories have been proposed: entanglement coupling [52], cooperativity [53], and reptation [54]. The reptation model has been applied to study tack, green strength, healing, and welding of polymers. In accordance with the reptation model, Wu [55] has proposed that for the interfusion between two compatible polymers, the thickness of the interdiffused region $x(t)$ is proportional to the square root of time, $t^{1/2}$, and inversely proportional to the number of monomers per chain, N. Furthermore, the interdiffusion coefficient is proportional to N^{-2}. Although some evidence may have demonstrated that the interdiffusion phenomenon exists in mobile and compatible polymers and may have promoted the intrinsic adhesion, the diffusion theory has found limited application where the polymer and adherend are not soluble or the chain movement of the polymer is constrained by its highly crosslinked, crystalline structure or when it is below its glass transition temperature.

2.2.5 Electrostatic

The electrostatic theory proposed by Deryagin [56] states that electrostatic forces are formed in the form of an electrical double layer (EDL) at the interface, resulting in adhesion, and these forces accounts for resistance to separation. Some controversies have arisen surrounding the electrostatic theory owing to some facts that the EDL could not be identified without separation of the adhesive bond. Also the effect of electrical double layer on the adhesive bond strength was exaggerated, as argued by many researchers. For example, Roberts [57] has indicated in his studies of rubber adhesion that the electrostatic component contributes less than 10%, usually 0.1-1% of the total adhesion. Possart [58] has also revealed that the energy required to peel the LDPE film from the aluminum foil is about 600 times that of the stored electrostatic energy due to the electrical double layer.

2.3 Water Adsorption and Diffusion in Polymer Systems

Adhesive systems may be exposed to various environmental conditions during their service life. The performance of the adhesive systems may deteriorate to a certain extent upon exposure to harsh environments for a certain period of time. Moisture/water is the most commonly encountered service environment, and must be considered a critical factor in determining the long-term durability of adhesively bonded joints. In this section, we will review previous studies on the mechanisms of water absorption into polymeric materials and the effects of water in some commonly used polymer systems.

2.3.1 Kinetics of Water Absorption and Water Distribution in Polymeric Materials

In many cases, the kinetics of water diffusion in a sheet of polymer is assumed to follow the one-dimensional Fick's second law:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \qquad (5)$$

where c is the concentration of the penetrant, t is the time, x is the distance through the plate thickness, and D is the diffusion coefficient. Based on Fick's law, Shen and Springer [59] have derived an appropriate expression for the calculation of the fractional water uptake as follows:

$$\frac{M_t}{M_\infty} = 1 - \exp[-7.3(\frac{Dt}{h^2})^{0.75}] \qquad (6)$$

where M_t and M_∞ are mass percentage of water absorbed at time t and equilibrium, respectively, and h is the thickness of the polymer sheet. For $\frac{Dt}{h^2} < 0.05$, the fractional uptake is approximately linear with the square root of time and the following equation applies

$$\frac{M_t}{M_\infty} = \frac{4}{h}\sqrt{\frac{Dt}{\pi}} \qquad \text{when} \quad \frac{M_t}{M_\infty} <\sim 0.5 \qquad (7)$$

Jacobs and Jones [60,61], in studies of fiber-reinforced composites, have proposed a diffusion model to describe the kinetics of water absorption in a two-phase material consisting

of one dense phase and one less-dense phase. They have suggested that water diffusion in each phase follows the Fickian diffusion process. According to Jacobs and Jones, the fractional water uptake with time in the polymeric material can be described using the following equation:

$$\frac{M_t}{M_\infty} = V_d\{1-\exp[-7.3(\frac{D_d t}{h^2})^{0.75}]\} + (1-V_d)\{1-\exp[-7.3(\frac{D_l t}{h^2})^{0.75}]\} \quad (8)$$

where D_t and D_d are the diffusion coefficients of the less-dense phase and the dense phase, respectively, and V_d is the volume fraction of the dense phase.

Maggana and Pissis [62] have further modified the Jacobs-Jones model by considering the epoxy resin system as a two-phase system with a homogeneous and nonpolar phase, where the major part of water is absorbed, and a second phase with different density or/and hydrophilic character. By assuming that water diffusion takes place independently in the different phases in accordance with the Fick's second law, Maggana and Pissis have proposed the following equation

$$M_t = M_1\{1-\exp[-7.3(\frac{D_1 t}{h^2})^{0.75}]\} + M_2\{1-\exp[-7.3(\frac{D_2 t}{h^2})^{0.75}]\} \quad (9)$$

Where D_1 and D_2 are the diffusion coefficient of the two phases, and M_1 and M_2 are the mass percentage of absorbed water at equilibrium in phase 1 and 2.

In many cases, however, Fick's second law cannot satisfactorily describe water diffusion in polymeric materials as other mechanisms of water absorption that are not taken into account in the Fickian law may be involved. Lefebvre *et al.* [63, 64] have proposed a diffusion model to incorporate temperature, strain, as well as penetrant concentration terms in the equation of the diffusion coefficient. This model is based on free volume theories and assumes that the transport kinetics is governed by the constant redistribution of the free volume that is temperature, strain, and penetrant concentration dependent. In addition, various diffusion models have also been proposed by different researchers to take into account various parameters, such as the formation of hydrogen bonds [65], relaxation phenomenon during hydration [66], degradation of the epoxy resin, and the formation of clusters, crazes and microvoids during hydration [60].

Water absorbed in the polymer is generally divided into free water and bound water [62,67]. Water molecules, which are contained in the free volume of the polymer and are relatively free to travel through the microvoids and holes, are identified as free water, while water molecules that are dispersed in the polymer matrix and attached to the polar groups of the polymer are designated as bound water. Research in [62,68] further suggested that bound water which exists in the polymer network can be recognized as loosely bound water, which can be released easily upon heating and strongly bound water that is "frozen" in the network and difficult to be removed from the polymer. According to the water sorption mode proposed by Adamson [69], the transport of water below T_g is a three-phase process in which the absorbed water first fills the free volume, then is bound to network site, and finally enters the densely crosslinked region. Moy and Karasx [70] reported that at low temperatures, absorbed water in epoxy resins initially interacts with binding sites of the polymer and then exists in the liquid-like state of water. At high temperatures, they proposed that the water sorption mode is associated with simple solution sorption. Antoon *et a.l* [71] found that water absorbed in an epoxy resin usually interacts with the polar groups by hydrogen bonding and the epoxy-water interactions are completely reversible. However, Woo and Piggot [72] suggested that water in certain epoxy systems is not bonded to any polar groups or hydrogen-bonding sites.

2.3.2 Effect of Water on the Adhesive

Moisture absorbed in a polymer matrix can lead to a wide range of effects. Some effects on the polymeric materials are reversible and can be erased on removal of water. Others are irreversible and result in permanent changes in the performance of polymers. Water absorption into polymer materials can cause plasticization and swelling, which are both reversible processes. Water acting as a plasticizer can depress the T_g of the polymer matrix and reduce the strength and modulus of the adhesive. The depression of the T_g of adhesives by water is generally described by the free volume theory using either the equation proposed by Kelly and Bueche [73] or the Fox equation [74]. Ivanova [75] demonstrated that the introduction of water in the polymeric materials causes swelling, which may have introduced swelling stresses into the adhesive system. Many studies have also shown that water causes permanent chemical and physical changes. Antoon and Koenig [76] investigated the effects of moisture on anhydride-crosslinked epoxy resin films by means of Fourier-transform infrared

(FT-IR) measurements. They demonstrated that hydrolytic attack of water takes place on the epoxy films and the hydrolysis effects are enhanced under tensile stress in alkaline water. They have also reported that slow oxidation processes occur in 100% relative humidity air. Liu *et al* [5] reported that on exposure of the electrical conductive adhesives to a hot/wet environment, further curing and hydrolysis and oxidation effects can be observed in the materials at a certain aging time. It has been shown that moisture can also cause structural damage by inducing microcavities or crazes in polymeric materials [77,78] and the formation of these structural damages can further accelerate the moisture diffusion [79]. For resin-filler systems, some research has shown that absorbed water can attack the matrix/filler interface and cause debonding at the interface [80,81,82]. Studies conducted by Ivanova, et al [75] and Gonon, et al [83] showed that absorbed water cannot be totally removed by thermal annealing and the residual water in the adhesive is believed to be the one which is strongly bonded to polar sites.

2.3.3 Effect of Water on the Interface

Water can also weaken the strength of adhesive joints by attacking the adhesive/substrate interface. It has been proposed that there must be a critical water concentration within the adhesive layer below which environmental attack on the adhesive joint does not occur. For an epoxy system, it is estimated that the critical water concentration is about 1.35%-1.45%, and the critical humidity is around 50-65% [38,84]. Lefebvre, *et al* [85] discovered in their study of an epoxy/glass model system that the critical humidity was around 70% RH, at which point an abrupt loss of adhesion, a sudden increase in water solubility and swelling in the epoxy, and a decrease in the mobility of dissolved water occur. They attributed these phenomena to chemical reactions between adsorbed water molecules and the OH groups of the polymer, which cause the breaking of inter-chain hydrogen bonds and displacing adsorbed OH groups from the surface of the substrate, as well as result in other observed changes. Several mechanisms have been proposed to explain the degradation of the adhesive joint interface due to water absorption, though no single mechanism is applied to explain all the failure phenomena. Gledhill and Kinloch [86] suggested that for adhesive joints, where only secondary forces are the mechanism of adhesion, the intrinsic stability of the adhesive/substrate interface in the presence of an absorbed liquid may be evaluated from a

consideration of the thermodynamic work of adhesion. Usually, the work of adhesion for a dry adhesive/substrate has a positive value, indicating thermodynamic stability of the interface. However, the introduction of water may induce a negative value of the work of adhesion, which indicates that the interface is unstable and the adhesive may be easily displaced from the substrate by water. Water can also chemically degrade the interface by interacting with the adhesive and the substrate or probably chemical bonds across the interface. It has been observed by many researchers [87-89] that the presence of water/moisture can hydrolyze aluminum oxide and result in the formation of a hydrated oxide layer between the underlying substrate and the adhesive, which is mechanically weak and is the failure location in many adhesive joints. Studies have suggested that a boundary layer of adhesive exists adjacent to the substrate surface and this boundary possesses a different physical and chemical structure such as lower crosslink density [90] or a lower concentration of filler particles [91]. Brockmann *et al* [92] proposed that the mechanism of environmental attack through hydrolysis of this boundary layer of the adhesive might be important for aluminium alloy joints, though most researchers currently suggest that water attack on the metal oxide layer is a more likely failure mechanism of adhesive joints. In some circumstances, substrate corrosion may occur in adhesive joints and act as a factor that weakens the performance of the adhesive joint. Examples for gross corrosion have been reported for rubber/steel joints exposed to seawater or salt-spray [93] when an electrochemical potential is present and also in electrically conductive adhesive joints where the conductive adhesive is bonded to the non-noble metal surface [18, 29].

2.4 Fracture Testing

Mechanical testing of an adhesively bonded system is very important in assessing mechanical performance of adhesives and adhesively bonded joints. Generally, two types of mechanical testing are applicable for studying the failure phenomenon of adhesive joints. The first approach considers the nature and maginitude of the stresses found in certain type of joint designs and test methods. This approach has proven to be particularly useful in initial joint design studies and for interpreting the effects of geometric parameters such as the effect of overlap length in lap joints [43]. The second approach is based on fracture mechanics and has has received considerable attention. The basic tenet of the fracture mechanics approach is

that adhesive joints fail by the initiation and propagation of flaws, which may be voids, cracks, and dirt particles in the adhesive, *etc*. Fracture mechanics has proven to be of particular value in characterizing the toughness of adhesives, identifying mechanisms of failure and estimating the service life of "flawed" structures [43]. The basic aim of test techniques related to fracture mechanics is to provide a parameter for characterizing crack growth which is independent of test geometry. In the present study, a fracture mechanics approach (joint design, testing, and analysis) is utilized to study the mechanical behavior of conductive adhesive joints.

2.4.1 Development of Fracture Mechanics

Basically, there are two alternative approaches to fracture analysis: the stress intensity factor approach and the energy criterion. These two approaches are interrelated and equivalent in certain circumstances. The stress intensity factor approach, based on the work of Irwin [94], states that the stress field around a sharp crack in a linear-elastic material is identical in form and can be uniquely described by a parameter called the stress intensity factor, K. Furthermore, fracture occurs when the value of K exceeds a critical value, K_c, where K_c, referred to as the fracture toughness, is a material property. The energy criterion is based on the research of Griffith [95], and states that fracture occurs when energy released by the growth of the crack is sufficient to supply the energy required to produce new surfaces. This energy criterion is a measure of the energy required to create a unit new surface area, and the critical energy parameter is usually referred to as the fracture energy or the critical strain energy release rate (SERR), G_c,

For a sharp crack in a uniformly stressed, infinite, homogeneous material, in which Hookean behavior and infinitesimal strains are assumed, Irwin [94] gave the following stress function solutions for regions close to the crack tip:

$$\sigma_{ij} = \frac{K}{(2\pi r)^{1/2}} f_{ij}(\theta) \qquad (10)$$

where σ_{ij} are the components of the stress tensor at a point, and r and θ are the polar coordinates of the point with respect to the crack tip, and K is the stress intensity factor, which is a measure of the magnitude of the stress intensity near the crack and is a function of the applied load and geometry of the structure in which crack is located.

In general, cracks may be stressed in three different modes: mode I, the cleavage or tensile-opening mode; mode II, the in-plane shear mode; and mode III, the antiplane shear or tearing mode. For a crack stressed under Mode I loading, the stresses near the crack tip may be expressed as follows, which was developed from Equation 10:

$$\begin{Bmatrix} \sigma_{11} \\ \tau_{12} \\ \sigma_{22} \end{Bmatrix} = \frac{K_I}{(2\pi r)^{1/2}} Cos(\theta/2) \begin{Bmatrix} 1 + Sin(\theta/2)Sin(3\theta/2) \\ Sin(\theta/2)Cos(3\theta/2) \\ 1 - Sin(\theta/2)Sin(3\theta/2) \end{Bmatrix} \quad (11)$$

and

$$\sigma_{33} = 0 \text{ (plane stress)} \quad (12$$

$$\sigma_{33} = \upsilon\,(\sigma_{11} + \sigma_{22}) \text{ (plane strain)} \quad (13)$$

$$\tau_{23} = \tau_{13} = 0 \quad (14)$$

Analogous equations have been developed to characterize the stresses near a crack tip which is under mode II or shear mode, and mode III or tearing mode loading.

It is clear from the above equation that the stress component, σ_{ij}, tends to infinity as r goes to zero. Therefore, it is inappropriate to use stress as a parameter for local fracture criterion. Considering that the stress intensity factor, K, uniquely defines the stress field around the crack, Irwin [70] suggested the following fracture criterion for mode I loading:

$$K_I = K_{Ic} \quad (15)$$

where the mode I stress intensity factor K_I and the critical stress intensity factor K_{Ic} are expressed as follows, respectively:

$$K_I = Q\sigma_0 a^{1/2} \quad (16)$$

and

$$K_{Ic} = Q\sigma_c a^{1/2} \quad (17)$$

where σ_c is the applied stress at the onset of crack growth and Q is a geometric constant, which may be determined either experimentally or theoretically.

In the above, the aspect of cracks located in a bulk material was reviewed. For adhesively bonded joints, cracks may propagate close to or at the bimaterial interfaces, or

within the adhesive layer. When cracks are located at or near an interface and propagate along the bondline length direction, the stress field ahead of a crack in the adhesive joints has been found to be very different from that in the bulk adhesive material due to the presence of the interface between dissimilar materials. An interfacial crack, loaded in pure mode I or mode II, usually results in both tensile and shear stresses around the crack tip. Therefore, both mode I and mode II terms of the stress intensity factor are needed to describe the stress field around the interfacial crack. Rice and Sih [96] and Williams [97] have shown the local stresses ahead of the crack tip at a bimaterial interface are proportional to

$$\frac{f(K_{Ii}, K_{IIi})}{(2\pi r)^{1/2}} \begin{Bmatrix} Sin \\ Cos \end{Bmatrix} (\varepsilon \ln r) \tag{18}$$

where ε is a bimaterial constant [96], which is a function of the moduli and Poisson's ratio of the two materials which form the interface, K_{Ii} and K_{IIi} are the stress intensity factors for mode I and mode II loading, respectively and the subscript i represents the interface where the crack is located.

For an interfacial crack of length $2a$ in an infinite bonded sheet under a tensile applied stress, σ_o, Rice and Sih [96] gave the following expressions to calculate the stress intensity factors in mode I and II:

$$K_{Ii} = \sigma_0 \frac{\{(2\pi)^{1/2}[\cos(\varepsilon \ln 2a) + 2\varepsilon \sin(\varepsilon \ln 2a)]\}}{\cosh(\pi\varepsilon)} a^{1/2} \tag{19}$$

or

$$K_{Ii} = \sigma_0 Q_{Ii} a^{1/2} \tag{20}$$

and

$$K_{IIi} = \sigma_0 \frac{\{-(2\pi)^{1/2}[\sin(\varepsilon \ln 2a) - 2\varepsilon \cos(\varepsilon \ln 2a)]\}}{\cosh(\pi\varepsilon)} a^{1/2} \tag{21}$$

or

$$K_{IIi} = \sigma_0 Q_{IIi} a^{1/2} \tag{22}$$

In the above equations, Q_{Ii} and Q_{IIi}, are geometric factors. As can be noticed in the above equations, the units of a are involved in the expression of Q and hence K, which makes

the evaluation of the mode I and mode II contributions difficult. Several researchers such as Sawuer and Anderson [98] and Piva and Viola [99] have suggested that for cracks at or near the interface, a combined interfacial stress intensity factor can be defined such that:

$$K_{ic} = (K_{Iic}^2 + K_{IIic}^2)^{1/2} \quad (23)$$

The advantage of the above expression/approach is that it combines mode I and mode II contributions into a usable fracture criterion. Meanwhile, the new fracture criterion parameter, K_{ic}, becomes independent of the length term, a.

Wang *et al* [100] have used a finite element analysis to investigate the stress field for a crack in the center of an adhesive layer in an adhesively bonded joints. Wang *et al* have found that, the stress field near a crack located in the center of the adhesive layer, except very close to the crack tip, is very different from that predicted by Equation 11 for a crack in a bulk material or Equation 18 for an interfacial crack, due to the presence of the interface. It is evident from the above discussions that many problems arise and need to be fully resolved when applying the stress intensity factor approach to cracks in adhesive joints. Therefore, many researchers have chosen to adopt the energy criterion when studying crack growth in adhesive joints.

The energy criterion, which is simply an extension of Griffith's hypothesis [68] that describes quasi-static crack propagation in terms of the work done by external forces, W_d, the elastic stored energy in the bulk specimen, U, and the surface free energy, $\boldsymbol{g}_m$, may be written as

$$\frac{\partial(W_d - U)}{\partial a} \geq \boldsymbol{g}_m \frac{\partial A}{\partial a} \quad (24)$$

In the above equation, ∂A is the increase in surface area associated with an increment of crack growth of ∂a. For a crack propagating in a lamina of thickness, b, the energy criterion becomes

$$\frac{1}{b}\frac{\partial(W_d - U)}{\partial a} \geq 2\boldsymbol{g}_m \quad (25)$$

However, Orowan [101] and Berry [102] have found that the energy required for crack propagation was far greater than twice the surface free energy. This discrepancy is due to two

facts. First, the surface energy term γ_m only reflects the energy required for secondary bond rupture, while in some cases, stronger forces such as primary bonds may have formed across the joint interfaces and significant energy is required to break the primary bonds, when cracks propagate along the material interfaces. Second, localized viscoelastic and/or plastic energy dissipation may occur in regions where high strains are involved. Therefore, to make it true for the assumption that energy dissipation around the crack tip occurs in a manner independent of applied forces and test geometry, it has been suggested that the 2 γ_m term may be replaced by G_c, the critical strain energy release rate [43]:

$$\frac{1}{b}\frac{\partial(W_d - U)}{\partial a} \geq G_c \tag{26}$$

Here, G_c encompasses all the energy losses incurred around the crack tip and can be expressed as

$$G_c = G_0 + \boldsymbol{y} \tag{27}$$

where G_0 is the energy required for rupturing intrinsic bonding forces, such as secondary and primary bonds, and $\boldsymbol{y}$ is the energy dissipated in viscoelastic and plastic deformation at the crack tip.

For bonded joints exhibiting bulk linear-elastic behavior away from the crack tip regions and showing linear behavior in the load vs. displacement curve, Equation 26 may be expressed as [43]

$$G_c = \frac{F_c^{\,2}}{2b}\frac{\partial C}{\partial a} \tag{28}$$

where F_c is the load at the onset of crack propagation, and C, the compliance of the bonded joint, is given by the load over displacement. The above equation is the foundation of G_c calculations for several bonded configurations, such as double cantilever beam (DCB) tests, end notch flexure tests (ENF) and wedge tests *etc*. The compliance C is usually determined as a function of a, either experimentally or theoretically by the analytical or numerical technique.

2.4.2 Double Cantilever Beam (DCB) Test

The double cantilever beam (DCB) test is particularly useful for determining the mode-I toughness of an adhesive joint and has been incorporated into ASTM standards [103]. This test geometry was first introduced for fracture toughness testing by Ripling and Mostovoy [104] and has been used extensively to study the effects of static, fatigue and environmental loads on adhesive bonds and thereby the durability of the bonded joints [105-109]. Based on simple beam theory, the value of the interlaminar fracture energy G_I can be expressed by

$$G_I = \frac{12P^2a^2}{B^2h^3E} \tag{29}$$

where B is the width, h is the substrate thickness, *a* is the crack length, *P* is the load at the loading point, and *E* is the elastic modulus of the substrates.

However, in actual DCB tests, several effects that are not accounted for in the simple beam theory may arise and need to be taken into account in the calculation of the fracture energy. Such effects include (1) shear deformation of the adherends and deflection at the crack tip, (2) stiffening the substrates due to the attachment of the end blocks to the substrates, and (3) large deflections of the arm.

When the crack length *a* is much greater than the substrate thickness *h*, the effect of shear deformation and deflection at the crack tip may generally be neglected. However, when the ratio *a*/*h* is sufficiently low, the fracture energy needs to be corrected for the effect of the shear deformation and deflection. ASTM standards [103] considered the effect of the shear deformation based on approximate analytical analysis and gave the expression of the fracture energy of adhesive bonds as follows

$$G_I = \frac{12P^2(a^2+0.33h^2)}{B^2h^3E} \tag{30}$$

Suo *et al* [110] conducted numerical analysis on the fracture of the adhesive joint and showed that Equation 30 underestimated the energy-release rate for the double-cantilever beam geometry. They gave the following equation to analyze experimental DCB results when the shear effect has to be considered

$$G_I = \frac{12P^2(a+0.677h)^2}{B^2h^3E} \tag{31}$$

In some DCB tests, the combination of high toughness and slender beams leads to large displacements in the substrates. In addition, due to the presence of end blocks, the substrates are stiffened, which could affect the accurate determination of the compliance *C*, of the substrates. Hashemi *et al* [105] used the following two correction factors *N* and *F* to account for the large displacements and the stiffening effect in some practical cases:

$$F = 1 - \frac{3}{10}\left(\frac{\boldsymbol{d}}{a}\right)^2 - \frac{3}{2}\left(\frac{\boldsymbol{d}t}{a^2}\right) \tag{32}$$

and

$$N = 1 - \left(\frac{L}{a}\right)^3 - \frac{9}{8}\left[1 - \left(\frac{L}{a}\right)^2\right]\frac{\boldsymbol{d}t}{a^2} - \frac{9}{35}\left(\frac{\boldsymbol{d}}{a}\right)^2 \tag{33}$$

where $\boldsymbol{d}$ is the opening displacement at the loading points, t is the distance from the center of the loading pin to the mid-plane of the arm of the substrate beam, *L* is the distance from the loading pin center to the edge of the block as illustrated in Figure 2. 2.

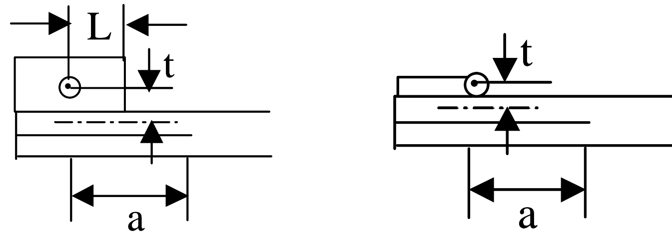


Figure 2. 2 DCB specimens with (a) load-blocks and (b) piano hinges.

By considering the effects of large displacements, stiffening of the substrates, and the end-rotation and deflection of the crack tip, Blackman [108] gave the following expression to calculate the fracture energy of an adhesive joint:

$$G_I = \frac{3P\boldsymbol{d}}{2B(a+x)}\frac{F}{N} \tag{34}$$

where x was introduced for end-rotation and deflection of the crack tip and could be found experimentally by plotting the cube root of the compliance $C^{1/3}$ as a function of crack length a, where the intercept yields the value of the correction factor x.

Hashemi et al [105], Rakestraw [106], and Parvatareddy [109] calculated the fracture energy of DCB specimens by Equation 35 (given below), which was derived using the compliance method with corrections for crack tip deflections and rotations and adherend stiffness, as well as adhesive properties, bond thickness, etc.

$$G_I = \frac{9\boldsymbol{d}^2 (EI_{eff})}{4B(a+x)^4} \quad (35)$$

where B is substrate width, a is crack length, x is crack length offset, EI_{eff} is effective flexural rigidity and $\boldsymbol{d}$ is specimen's opening displacement at loading points. The effective flexural rigidity EI_{eff} and the crack length offset a are determined experimentally by plotting the cube root of the compliance $C^{1/3}$ as a function of the measured crack length a,

$$EI_{eff} = \frac{2}{3m^3}, x = \frac{b}{m} \quad (36)$$

where the experimental coefficients m and b are the slope and y-intercept, respectively, of the cube root of the measured compliance , when plotted as a linear function of the measured crack length. The compliance C is obtained by dividing the specimen's crack opening displacement, $\boldsymbol{d}$ by the corresponding load, P, where $\boldsymbol{d}$ and P are experimentally measured.

The discussion of the previous sections is based on an assumption that the adhesive layer is very thin and the deformation of the adhesive layer is minimal. However, if the compliance of the adhesive layer is large relative to that of the adherends, the deformation of the adhesive may contribute substantially to the overall deformation and needs to be considered in the calculation of the fracture energy. Krenk [111] and Williams [112] used beam on elastic foundation models to analyze the adhesive effects. According to the approach of Williams, the deformation of the adhesive layer was viewed as providing an effective increase in the crack length in calculating the fracture energy.

2.5 High Loading Rate Test

As adhesively bonded joints have been increasingly used in demanding engineering applications, interest has arisen in the failure behavior of such materials and bonded joints under high rates of test including impact loading conditions. ASTM D950-94 [113] describes a test method to study the impact behavior of adhesives, in which a pendulum-type impact machine is used to impact a block shear joint. The difference of the potential energy before and after the impact is assumed to be the energy required to break the adhesive joint. The ASTM block impact test has been shown to only give a qualitative comparison of the ability of different adhesives to withstand impact loading. This test technique is "machine" sensitive and the actual stress condition experienced by the adhesive layer may be significantly affected by the way the loading is applied to the specimen [114]. In addition, only one data point can be obtained in each impact test. Bezemer *et al* [115] developed a rod-cylinder specimen for the impact test in pure shear. They claimed that with a drop tower or an air gun to impact the specimen, the load rate could reach up to $100ms^{-1}$. However, in the actual test condition, this rod-cylinder specimen does not give the desired pure shear as a consequence of lateral contraction. As this test method is very similar to the above pendulum-type impact test, the problems found in the pendulum-type impact test also exist in this test method. Thouless, *et al*. [116] developed a dynamic wedge test to measure the fracture toughness of an adhesively bonded double-cantilever beam (DCB) that fails with extensive plastic deformation of the adherends. The basic procedure is that the test sample is placed over a steel wedge and a weight would impact the sample from above and force the wedge through the specimen, causing the arms of the specimen to bend and the adhesive to fracture. This technique would be very useful for thin adherends which may undergo extensive plastic deformation during testing. However, there are several disadvantages for this test method. First, as significant plastic deformation would occur in the adherends, it would complicate exact calculations of the fracture energy of the adhesive. In addition, as a weight impacts the sample from above, adherend buckling and yielding in the dynamic wedge samples is of concern in utilizing this technique. Blackman, *et al.* [117] proposed the impact wedge-peel (IWP) test to measure the resistance to cleavage fracture of structural adhesives at a relatively high test rate. This test method gives information on the fracture behavior of the adhesive/adherend combination with thin sheet adherends. However, similar to the dynamic wedge test, the IWP test also involves

extensive plastic deformation of the adherends and thus the mechanical properties of the adherends can greatly influence the results recorded from such a test. Therefore, both the impact wedge-peel (IWP) test and the impact wedge test have actually reflected the fracture behavior of the adhesive joint "system", instead of the behavior of the adhesive itself. Blackman *et al* [108] in a different study carried out in-depth studies on the failure of adhesive joints under high rate testing. In their study, a specialized, high-speed tensile testing machine was utilized to complete the experimental work. The tensile testing machine was utilized to load double cantilever beam specimens. The specimens were tested within the range of linear-elastic fracture mechanics (LEFM) and no plastic deformation was expected to occur in the substrates. Blackman *et al* [108] found that at high rates of test, the load signal oscillated violently due to dynamic effects, precluding sensible and reliable values. Therefore, significant errors must be produced if an equation requiring load information is used to calculate the fracture energy at high loading rates. Instead, Blackman *et al* suggested using displacement based equations (e.g. Equation 35), which do not rely upon values of the measured loads to calculate the fracture energy.

In the present study, a novel falling wedge fracture test [118] is adopted to characterize the impact behavior of electrically conductive adhesives. This test technique is able to quantitatively characterize the impact performance of conductive adhesives at the material level and thus could be pursued as a material test for characterization of the impact behavior of newly formulated conductive adhesives.

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