Applications of Electrically Conductive Epoxy Adhesives

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Abstract Electrically conductive adhesives (ECAs) mainly comprise the resin matrix, conductive particles, dispersion additives, and other additives. ECAs can effectively bond various materials and have conductive properties. The conductive mechanism of ECAs is considered to be the contact between conductive particles to form an electrical path. ECAs are widely used for microelectronic assembly, including the connection of thin wires with printed circuits, electroplating bottom plates, metal layers of ceramic adhere and metal chassis, bonding wire and tube base, bonding elements, and plane hole passing through printed circuits, bonding waveguide tuning, and hole repair. At present, much research has been done in epoxy-based conductive adhesives, including categories, conduction mechanisms, fillers, and applications.

Keywords Epoxy resin · Conductive adhesives · Conductive mechanism · Conductive fillers

1 Introduction

Electronic products continue to develop to the direction of miniature, flat, high sensitivity, and high reliability. With electric current conductivity and excellent bonding performance, electrically conductive adhesives (ECAs) are used in many electronics fields. As an alternative to tin/lead-based solders, ECAs have many excellent properties and are conductive composites applications owing to their environmental friendliness, low processing temperature, and high flexibility [1]. Normally, ECAs can be prepared by dispersing conductive fillers in an insulating polymer matrix or by physically blending conductive polymers with the matrix. Specifically, conductive fillers mostly include metals/metal-coated materials, carbons, and ceramic materials. Moreover, intrinsic conductive polymers mainly include polypyrrole, polyaniline,

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polythiophene, and polyacetylene, which can be blended with an insulating matrix to achieve conductivity.

Depending on the morphology, filling rate, and performance, conductive adhesives can be roughly divided into isotropic conductive adhesives (ICAs) and anisotropic conductive adhesives (ACAs). The two categories conduct current equally in all directions and only in the Z-direction based on packing arrangement, respectively [2]. The conductive mechanism of conductive adhesives is that the contact between conductive particles forms an electrical pathway (a three-dimensional conducting network), which endows the conductive adhesives with electrical conductivity. Conductive adhesives contain solvents, and conductive particles are separated in the adhesives before curing or drying, so the particles do not continuously contact with each other and are insulating. After conductive adhesive curing or drying, due to the volatilization of solvent and adhesive curing caused by adhesive volume shrinkage, conductive particles stably and continuously contact with each other, showing electrical conductivity.

The electron tunneling effect can also produce a certain current path between conductive particles in the conductive adhesive. When the conductive particles do not contact each other, an isolation layer exists between the particles, which hinders the directional motion of free electrons in the conductive particles. According to the concept of quantum mechanics, for a microscopic particle, even if its energy is lower than the barrier energy, penetration in addition to reflection may occur, which is known as the tunneling effect. Electrons, which are microscopic particles, can pass through the barrier of conductive particle separation. The former mechanism and the latter concept are based on and relating to electrical conductivity, respectively [3]. Generally, applications of ICAs include electrical interconnections for connecting substrates (e.g., ceramics and plastics) and replacement solders for thermal-sensitive elements [4]. ACAs are applied into flat panel display, glass flip-chips, smart cards, and flip boards [5].

Epoxy resin-based ECAs are widely used in the field of electronics, such as die connection and weldless interconnection because they possess outstanding chemical, thermal and mechanical properties, adhesiveness, compatibility with diverse additives and substrates, and availability of solvent-free formulations [1]. However, epoxy resins have low electrical conductivity (10^{-7} to 10^{-14} S m^{-1}), which limits the use of ECAs. Because of this question, this chapter discusses the basic principles and limitations of various ECAs, and the main conductive mechanisms that contribute to conductivity of ECAs based on epoxy resins. Various conductive fillers in ECAs are discussed: metals, carbons, ceramics, metal coatings, polypyrrole, polyaniline, and polythiophene.

2 Electrically Conductive Adhesives

ECAs are generally deemed as conductive composite materials with an essentially clean and straightforward alternative to electronic applications. ECAs can provide an intrinsic adhesion when the polymer substrate is cured. When the concentration of the conductive filler exceeds the critical level (the percolation limit), the composite conductivity rises suddenly. Namely, the conductive filler constitutes a conductive network by linking within the substrate, which provides a path for electron transport. In applications such as integrated circuits, conductive adhesives are a prospective alternative to lead-free tin–lead solders with six merits:

(1) lead-free;
(2) low environmental pollution;
(3) lower curing temperature than that of the solder;
(4) high dimensional stability;
(5) processability;
(6) adhesive ability for multi-material applications.

Conductive adhesives have many advantages for integrated circuits and various electronic applications, but still have some disadvantages, such as low conductivity, poor mechanical properties, easy migration, and unstable contact resistance between the adhesive and the component [6].

Diverse blends of conductive substrates and non-conductive substances were studied in the early twentieth century. A patent (1926) for electromechanical applications of conductive adhesives, a conducting varnish (1933), an electrically conductive composite comprising metal powder or graphite-reinforced Bakelite resin (1933), and a patent with electrically conductive adhesive were registered [1]. U.S. patent in 1956 proposed an application of conductive cement that uses a thermosetting polymer as a binding agent to fix semiconductor crystals to a metal substrate, which was regarded an early use of ECAs in electronics. Then, publications on experimental and theoretical research of conductive adhesives are increasing. ECAs are applied extensively in electronics because of low processing temperature and various low-cost fillers and are significantly superior over the existing interconnection technology. The adhesives have an apparent coefficient of thermal expansion owing to their high flexibility and advantages over solder alloy when bonding large chips on any substrate. In addition, MacDiarmid, Heeger, and Shirakawa won the Nobel Prize in 2000 for their discovery of inherently conductive polymers.

2.1 Types of ECAs

ECAs can be divided by the substrates into thermoplastic ECAs and thermosetting ECAs. The thermosetting substrates of ECAs are originally monomers and prepolymers undergoing polymerization reaction in solidification, forming a three-dimensional crosslinked structure in the polymer chain connection form with high-temperature stability. The substrates of thermoplastic ECAs are composed of very long polymer chains that contain a few branched chains, which and flow easily at high temperature and do not easily form a crosslinked three-dimensional network. At present, the substrates of most of commercial ECAs are thermosetting resins, of which epoxy resin is widely used owing to its excellent comprehensive performance.

Thermoplastic resins can also be added at appropriate temperature to improve the toughness and reprocessing performance of the system.

Depending on the curing system, ECAs can be separated into room-temperature-curing ECAs, medium-temperature-curing ECAs, high-temperature-curing ECAs, and UV-curing ECAs. Room-temperature-curing ECAs are unstable, and the volume resistivity easily changes when stored at room temperature. The metal particles easily oxidize during high-temperature curing of ECAs, and the curing time must be shorter to meet the requirements of ECAs. Medium-temperature-curing ECAs (below 150 °C) are used worldwide, and the temperature resistance of electronic components, the use of temperature matching, and mechanical properties are also better. UV-curable conductive adhesives combine the UV-curable technology with ECAs, which gives ECAs new properties and expands their application range. They can be used in the electronic display technology, such as electroluminescence of liquid crystal display.

Depending on the types of conductive fillers, conductive adhesives can also be divided into metal-filled ECAs, non-metal-filled ECAs, and other-filled ECAs. Metal-filled ECAs can also be separated into precious-metal-filled ECAs. The conductive fillers used are mainly gold, silver, and base metals. Conductive fillers include aluminum, copper, nickel, iron, and other metal powder, sheet, fiber. Nonmetallic conductive fillers mainly include carbon black, graphite, and carbon fiber. Other types of conductive fillers are mainly silver-coated glass fiber, silver-coated carbon powder, and metal oxides. Metal-filled ECAs, especially precious-metal-filled ECAs, have excellent conductive performance and high stability, but are limited by high costs. They are generally used for precise connection or connection in a more demanding environment. Non-metal-filled ECAs have poor conductivity and are mostly used for printing resistors, electromagnetic shielding, and switching contacts. Other-filled ECAs have good comprehensive properties and are one of the important research and development directions in the future.

According to the application fields, ECAs can be classified into ECAs for filling holes, ECAs for printing lines, and ECAs for connecting. The application of ECAs for plugging holes is mainly reflected in high-density interconnect multilayer boards. ECAs are used to fill the micro-holes, formed by photoimaging or laser, and play the role of conductive interconnection between layers. ECAs are used in printed circuits, mainly printed circuit boards, because the ECAs before solidification are commonly liquids or creams, and have a certain fluidity under the action of external force. Hence, the conductive adhesives can be put directly on the insulation layer with a net printing to draw the line. Consequently, circuit boards can be reasonably made to eliminate the chemical plating, plating, and etching, but do not produce pollution, which is good for the environment. ECAs are connected mainly in the manufacturing and assembly process of parts or parts and substrate conductives.

ECAs can also be classified by the conduction direction into isotropic conductive adhesives (ICAs) and anisotropic conductive adhesives (ACAs). The main difference is that ICAs are conductive in all directions, while ACAs are conductive in a direction-dependent way. ICAs are lead-free substitutes for solders because of their environmental friendliness, short assembly time, low cost effective, processing temperature, and thermomechanical fatigue. ICAs can be widely used in non-solderable substrates and finer pitches. However, ICAs have some shortcomings, such as air trap, hygroscopicity, non-self-alignment, and ease of silver migration, which lead to low conductivity, low impact strength and instable contact resistance. ACAs become a research hotspot for fine pitch components thanks to their low cost and processing temperature, no cleaning, and lead-free formulations. However, ACAs rely on complicated methods and special bonding equipment, which limit the applications of ECAs.

2.1.1 Isotropic Conductive Adhesives (ICAs)

The ICA systems require a higher concentration of a filler to quickly meet the permeability percolation threshold, which can form a conductive network and conduct in all directions over this threshold. The matrix acting as the binder for the base material may be thermoplastic (e.g., polyvinyl acetate, polyvinyl chloride, polyvinyl alcohol ethers) or thermosetting (e.g., epoxy, cyanate ester, silicone, polyurethane) and may form mechanical or electric bonds with the base material. Especially, thermoplastic ICAs can be recycled or repaired and are more widely used in ECAs. However, ICAs have certain limitations, including the deterioration at high temperatures and poor strength. Polymer matrix resins mainly include epoxy resins, phenolic resins, polyimide, polyurethane, and thermoplastic plastics. The mechanical properties of epoxy resin include good thermal performance, low curing shrinkage rate, adhesive ability, and strong mechanical/thermal shock resistance. It can be used in various complex conditions (e.g., hot and humid, chemical corrosion) with strong resistance. Epoxy resin can also be cured at a lower temperature, and the formulation can be designed strongly. At present, thus, epoxy resin-based conductive adhesives are dominant in the conductive adhesive market.

In ICAs, conductive fillers as the main formulation component mainly consist of carbon, metal, and metal oxides, which are uniformly distributed in the resin matrix in spherical, sheet, or fibrous form and form conductive paths after curing. Different from the point-to-point contact of spherical metal particles in the conductive adhesives, sheet metal particles have better electrical conductivity because of their high horizontal to vertical ratio, which makes them have both point-to-point contact and face-to-face contact. Table 1 shows the conductivity of various conductive fillers, including Ag, Au, Ni, Cu, and C. Ag is widely used owing to its high conductivity, simple processing, and largest contact with flakes [7].

ICAs have been used for electrical interconnection of non-weldable substrates and welding replacement of thermal sensors with the help of ceramic and plastic properties. In these fields, they are usually called “polymer solders.” Some studies on epoxy-based conductive adhesives focus on obtaining high conductivity of ICAs under different conditions. For example, Sachdev et al. prepared ICAs using epoxy siloxane hybrid composites with excellent bonding strength, durability, low resistivity, and low tensile modulus. Wu et al. (2006) found the volume resistivity of epoxy-based ICAs filled with silver nanowires was remarkably lower at low filler loading (1.2×10^{-6} Ω m at 56 wt% Ag nanowire) [8].

Table 1 Electrical resistivity of common conductive fillers

Conductive filler	Resistivity (Ω cm)	Equivalent to the conductivity of mercury
Au	2.40×10^{-6}	39.6
Ag	1.62×10^{-6}	59.1
Cu	1.69×10^{-6}	56.7
Al	2.62×10^{-6}	36.1
Zn	5.92×10^{-6}	16.0
Fe	9.78×10^{-6}	9.8
Ni	7.23×10^{-6}	13.8
Sn	1.14×10^{-5}	8.3
Pb	2.06×10^{-5}	4.6
Bi	1.06×10^{-4}	0.8
C (graphite)	10^{-3}–1	0.000095–0.095

2.1.2 Anisotropic Conductive Adhesives (ACAs)

ACAs are composed of polymer resins, conductive particles, and other additives. Polymer resins provide conductive adhesives with the bonding ability and mechanical properties. Polymer resins include thermoplastic resins, thermosetting resins, and their mixtures. Thermosetting resins include acrylic resins, epoxy resins, and vinyl acetate copolymers, while thermoplastic resins include polyurethane. Conductive particles provide ACAs with Z-axis conductivity, including gold-plated-type polymer microspheres on the surface of core-shell structures, gold-plated-type metal particles, or solid metal particles. Curing agents react with thermosetting resins to form three-dimensional crosslinking structures and correspond to different thermosetting resins, but thermoplastic resins do not need a curing agent. Compared with ACAs based on thermoplastic resins, ACAs based on thermosetting resins have higher bonding strength and can work stably at higher temperature.

ACAs do not have a complete conductive network system because the conductive filler concentration (about 5–20 vol%) is below the percolation threshold. Thus, ACAs lead to current flow in one direction (Z-axis, unidirectional ACAs) or two directions (bidirectional ACAs) by exerting external forces. ACAs, as the main bonding materials for electronic packaging, are usually connected between the substrate and chip by hot pressing. The bonding process mainly includes three steps: preloading, bonding, and post-treatment. In preloading, the lower protective film of ACAs is removed and placed on the substrate to be bonded to soften ACAs at lower temperature and pressure than required for curing. The purpose of preloading is to make ACAs fully contact with the substrate and rearrange some conductive particles in preparation for bonding. The preloading process usually takes tens of seconds. In the bonding process, the upper protective film of ACAs is discarded, and conductive bumps and substrate circuit chip circuit are aligned. Then, after raising to the curing temperature, a part of the conductive particles under the action of external pressure are sandwiched between the substrate and chip circuit in two conductive bumps, and an insulation layer of conductive particles is crushed. Then, the adhesive and curing agent of ACAs undergoes curing reactions, which achieve the connection between the chip circuit and the substrate circuit. In other directions, conductive particles do not form a conductive path with each other, thus achieving the anisotropic structure of insulation in other directions and conductivity in a single direction. Post-treatment can reduce the stress concentration and internal stress in the solidified colloid. Post-treatment can also prevent colloid solidification and improve the bonding stability in the hot-pressing process.

ACAs can also be divided into film anisotropic conductive pastes (ACFs) and gel anisotropic conductive pastes (ACPs). ACFs and ACPs work in the same principle, but the devices that can be bonded are different. ACFs are supplied in rolls and separated from each other by a protective film to avoid adhesion. ACPs are paste liquids. The biggest difference between ACFs and ACPs is that ACPs are used by dropping or brushing, while ACFs are used by hot pressing. ACFs can connect components in short time with simple hot-pressing equipment. ACPs cannot be easily stored, and gas discharge in large area hot pressing is hard. Even printing thickness and the distribution of conductive particles are uncontrollable. Therefore, ACPs have not been rapidly developed. ACFs can be used for flip-chip packaging, circuit board connection, and LCD connection. Although ACAs provide much convenience for modern bonding and basically meet the requirements, there are still many problems: (1) long-term stable storage problems; (2) low impact resistance of epoxy resin; (3) low stability at high temperature or high humidity.

2.2 Conduction Mechanisms in ECAs

Basically, ECAs comprise conductive fillers distributed in an insulation polymer. The conductive mechanism theories of ECAs are mainly divided into the percolation theory and the tunneling effect theory from macroscopic and microscopic perspectives. The former holds that the shrinkage of ECAs makes the conductive particles form a stable continuous contact and then induces conductivity. With an increase in the content of conductive particles, the resistance of the cured conductive adhesive is weakened first slowly and then sharply when the particle concentration reaches a critical level, which is called the percolation threshold. Initially, the composites are non-conductive until reaching the critical level. With a rise in filler concentration, conductive particle clusters are enlarged in size, forming conductive channels. The conductive filler is spread in the polymer matrix, and the conductivity of the conductive adhesive depends on the particle volume fraction. When the critical filling volume concentration is reached, the resistivity of the electrode suddenly decreases to a low order of magnitude.

The characterization of conductive channels is mainly based on two mechanisms: interparticle contact and electron tunneling. ECAs form a conductive network through physical contact or tunneling between conductive particles during the packing. At the percolation threshold, an uninterrupted particle conductive chain exists in the adhesive formula, which leads to a significant reduction in resistivity. When the filler concentration exceeds the critical level, the particle volume fraction in the system rises, promoting the conduction. As the current carriers intensify the drift of polarized particles, they further combine, and the contact between particles becomes the dominant conduction mechanism of electron tunneling.

As for the conductive mechanism of ECAs, three situations are feasible: The conductive filler is separated, and the intrinsic conductivity of the filler plays a role; the conductive filler is in direct contact, and the electron tunneling between conductive particles is predominant. First, conductive fillers are mutually divided in the polymer; the internal conduction of the conductive fillers takes effect, and the conductivity of the ECAs increases. However, this increase is lower because the internal conductive fillers cannot wholly overcome the polymer barrier and blockage. Second, the conductive fillers of ECAs are in direct contact to constitute a continuous conductive network in the polymer matrix, which transmits electrons via the particle network through the conductance mechanism of metal particles. Last, electrons can be transferred between the conductive fillers by passing through the narrow gap (<10 nm) between the fillers when a thin insulating polymer matrix closely separates the fillers (electron tunneling effect). The alternating current/direct current (AC/DC) behavior of composites can distinguish between interparticle or band conduction and electron tunneling conduction. Moreover, band conduction and tunneling are associated with DC and AC conductivity, respectively.

2.3 Epoxy Resin-Based ECAs

Welding is generally considered a convenient way to connect two matrices, such as metals. Welding offers strong bonding and high conductivity along or across the matrix, but these methods have many troubles, such as the existence of harmful substances (e.g., lead), high processing temperature, the need for a cleaning solvent, and the inability to connect some materials (e.g., glass). To overcome the problems related to solders, many research groups have carried out much research. The first type of conductive cement is based on an epoxy resin composed of silver particles, which connect semiconductor crystals to metal substrates or supports. This material can be regarded as the first ECAs use in electronic technology. For example, the effect of the silver sheet lubricating layer on composite conductivity was studied to remove the lubricating layer with an ordinary solvent. Alternatively, an inherently conductive polymer is introduced to the epoxy matrix to improve electrical performances.

There are many studies on the preparation of conductive adhesives (conductive filler mixed with insulating matrix, and conductive polymer mixed with insulating polymer). For example, Jia et al. (2003) investigated a conductive epoxy-anhydride system involving polyaniline (PANI)-dodecylbenzenesulfonic acid (DBSA) and revealed the percolation threshold of PANI-DBSA filler-reinforced epoxy composites [9]. Choi et al. (2005) characterized the electrics of epoxy composites modified by vapor-grown carbon nanofibers, and results show the electrical resistivity decreased with the filler content [10]. The mechanical and electrical properties of low-viscosity epoxy composites outperformed those of high-viscosity composites.

The conductive fillers integrated into the epoxy insulating substrate include metal, carbon, ceramic, and metal coatings. Ma et al. (2008) provide a simple way to decorate carbon nanotubes (CNTs) with silver nanoparticles (Ag–NPs) to strengthen conductivity [11]. Conductive polymer composites were prepared by adding Ag@CNTs as a conductive filler into epoxy resin. The conductivity of composites with 0.10 wt% Ag@CNTs was over four orders-of-magnitude higher than those with the same content of pristine or functionalized CNTs, which verifies the superiority of Ag@CNTs. Zhang et al. (2010) reported highly reliable, cheap ICAs—silver-coated Cu flakes—for electronic packaging and found the resistivity of ICAs ($2.4 \times 10^{-4}\ \Omega$ cm) was identical to that of commercial Ag-filled ICAs [12]. Yim et al. (2010) reported a new type of ICAs with CNTs and low-melting-point alloys as fillers and found the CNT-filled ICAs had lower electrical resistance than those of common ICAs [13]. The effect of ceramic fillers on the electrical behaviors of epoxy resin-based adhesives was also studied. Zhao et al. (2014) used face-centered cubic (FCC) TiB ceramic powder as a conductive filler to prepare epoxy-based ceramic ECAs with the polymer matrix [14].

When the epoxy monomer of ECAs is mixed with an appropriate curing agent, the viscous liquid monomer or prepolymer is transformed into an insoluble three-dimensional (3D) network. The curing kinetics is mainly affected by the reaction activity and the migrability or flexibility of functional groups. The crosslinking reaction of epoxy resin is mainly affected by curing time, curing temperature, curing agent structure, and filler dosage. Therefore, in epoxy-based ECAs, the conductive filler can be used to catalyze the curing reaction, changing the curing rate, and finally affecting the properties of ECAs (e.g., crosslinking density, strength, bending modulus, hardness, conductivity, heating conductivity).

2.4 Conductive Fillers

ECAs are composed of a non-conductive polymer and a conductive filler. When the filler content exceeds its percolation threshold, a 3D conductive network is formed, which strengthens the conductivity of the polymer. Table 2 shows various conductive fillers.

2.4.1 Metal Fillers

Generally, a wide versus narrow particle size distribution calls for a lower filler concentration to surpass the percolation threshold in imbuing conductivity. The importance of particle size distribution is associated with the particle size and average particle size. Compared with any other metal, silver particles are unique with high

Table 2 Types of conductive fillers

Conductive fillers	Metal fillers	Ag
		Au
		Ni
		C
	Carbon fillers	Carbon nanotube
		Carbon nanofiber
		Carbon black
		Graphene
	Ceramic fillers	BN, TiC, SiC, TiB_2, TiN, TiB, BF
	Metal-coated fillers	Metal core
		Non-metal core

conductivity and thermal conductivity, and silver oxides also have higher conductivity than other metals. When the polymer matrix level is 15–30 vol%, the filler load of silver sheets is usually used to prepare ICAs. In addition to low cost and easy formation, they can be made into diverse shapes and sizes and be composed of silver sheets, particles, wires, and nanorods.

Lu et al. (1999) studied the conductivity of epoxy adhesive after removing the lubricating layer on the silver sheet, and successfully removed some solvents, resulting in higher conductivity of the composites [15]. Johnsen et al. (2012) probed into the conductivity (by current arrangement) of Ag-reinforced epoxy composites [16]. Due to the electronic arrangement, the volume conductivity of epoxy material rose by five orders of magnitude. The conductivity of isolated silver wires increased by 9–10 orders of magnitude as the particle alignment led to a transition from polymer- to silver-dominated conductivity [16]. Despite the high conductivity of silver particles, electrochemical composites made from silver-reinforced materials are limited in practical application by the disadvantages in conductivity, thermal conductivity, silver migration, and impact strength.

Nanosilver particles (e.g., Ag nanoparticles, nanowires, and nanorods) have superior conductivity. Cheng et al. (2007) prepared a UV-curable epoxy adhesive with nanosilver particles without a polymeric protector [17]. With a photosensitive mixture of $AgNO_3$ in ethylene glycol as example, the surface electrical resistivity of photocurable conductive adhesives may be decreased to 8.803×10^6 Ω m^{-1} under 900 mJ cm^{-2} irradiation. Tee et al. (2007) used Ag-NPs as a conductive metal filler to prepare Ag-NPs-filled epoxy resin composites [18]. Electrical characterization showed the insulator transited to the conductor when the Ag content was 5% (vol/vol) because of the effective treatment with a silane coupling agent. As for the morphology, the filler dispersion of the composite system was significantly improved after the treatment. Xiong et al. (2014) prepared a typical epoxy resin-based conductive adhesive and studied the effects of curing processes on the conductivity of adhesives [19]. It was found the curing temperature dramatically influenced the loading of 55% silver, and the volume resistivity of ICAs dropped from 1.0 × 10^{-3} at 180 °C to 4.7 × 10^{-3} at 250 °C. In addition, they discussed why the volume resistivity changed with temperature from the perspective of silver sheet dispersion in ICAs.

Gold particles are usually used as thin-layer coatings for electrical connectors in the electronic industry. They perform well in conductivity, corrosion resistance, oxidation resistance, non-chlorinated acid resistance, non-toxicity, and ductility. However, they also are easily affected by free chlorine and have high costs. Nickel, an essential component of various alloys, is a low-cost filler with high oxidation resistance in the atmosphere. It can maintain high corrosion resistance in a wide range of pH, but its conductivity is worse than that of silver and copper, so it is the preferred filler for electromagnetic shielding materials. Nickel is usually used for spherical particles in ACAs because it has a resistivity two orders-of-magnitude higher than that of Ag-filled adhesives, limiting its application in ICAs. The main reason for the high resistivity of nickel is its high hardness and difficulty in transforming into thin sheets with the best shape and size. Nickel has a wide size range, including spherical and narrow size distribution. Nickel can be plated with chemical gold to improve oxidation resistance.

Copper, a soft and changeable ductile metal, is widely applied as a conductive filler in the electronic industry thanks to its high conductivity, thermal conductivity, good electromigration properties, and economic benefits. Copper has higher electrical conductivity and lower cost than silver, but its oxidation resistance is weak, and it easily oxidized into non-conductive copper oxide, thus affecting the conductivity of the coating. Therefore, as a conductive metal filler, copper shall be modified to enhance its oxidation resistance. The main difficulty of using Cu-based electrochemical composites is to control copper oxidation and gradually reduce the electrical properties of adhesives. Generally, this problem can be solved via organic or inorganic coating of copper, N-based processing of copper, and incorporation of solder powder to the adhesive system. In addition, surface modification (plating conductive silver) of copper improves its stability, and the treatment (nitrobenzotriazole and imidazole) of copper can produce stable oxidation-controlled complexes.

2.4.2 Carbon Fillers

Carbon particles, mainly including carbon black (CB), CNTs, carbon nanofibers (CNFs), and graphene (GR), are a type of conductive fillers with more extensive application. They have abnormally high conductivity because of large surface volume ratio or aspect ratio. Some nanofillers have one- and two-dimensional structures, which are significantly recognized and used because of unique optical, chemical, electrical, thermal, mechanical, and properties.

CNTs featured with high strength, modulus, surface, thermal conductivity, current density, and thermal stability are considered excellent nanofillers to enhance the properties of polymers, adhesives, and composites. However, large specific surface areas and the inherently strong van der Waals force in structures lead to the agglomeration or aggregation of CNTs, limiting the ability of CNTs to strengthen the properties of polymers. To address this problem, CNTs aggregates must be decomposed and completely dispersed in the substrates, which often results in an increase in the properties of adhesives or composites. Therefore, various methods have been proposed to enhance the dispersion of CNTs in the matrix, including high-shear mixing, ultrasound, surfactant, acid oxidation of CNTs, and other chemical approaches. Due to the high aspect ratio, CNTs can form an efficient conducting network with a low percolation threshold so as to make many polymers conductive. CNTs obtain a percolation threshold when the filler load is minimal, which provides high conductivity for the polymer matrix because the aspect ratio is proportional inversely to the volume fraction of the filler.

Material researchers have studied CNTs to improve the conductivity of various polymers. Jakubinek et al. (2015) added low load (nearly 1%, w/w) SWCNTs to raw aerospace-level epoxy resins to transfer conductivity while keeping structural adhesion, and thus developed structural and conductive adhesives [20]. It was found the composites' peel strength and lap shear strength did not vary with the introduction of 0.5 wt% SWCNTs, but increased by 30% and decreased by 10%–15%, respectively, after the addition of 1 wt% SWCNTs. For SWCNTs adhesive with 1 wt% addition, the conductivity of the composite was up to 10^{-1} S m^{-1}. High conductivity and uniform dispersion after the addition of 8 wt% MWCNTs were achieved by three-roll milling. Reportedly, the aspect ratio is among the critical parameters determining the conductivity and seepage behavior of composites, and when the aspect ratio rises by 5.5 times, the conductivity increases by nearly ten times [21]. Moreover, three-roll milling can induce the extended arrangement of MWCNTs with a high aspect ratio under medium load (2–4 wt%). The arrangement of CNTs greatly influences the conductivity of epoxy adhesives. Felisberto et al. (2012) reported the electrical properties of CNTs/epoxy composites filled with aligned and randomly oriented nanotubes [22]. It was found the percolation threshold of the composites with ordered CNTs was one order-of-magnitude smaller compared with those under random orientation (0.06–0.5 wt%). At the percolation threshold, the conductivity was 1.4×10^{-5} S/m.

CNFs or VGCNFs are cheap, hollow, discontinuous cylinders/filaments in diameter of 50–500 nm and length of several microns, providing a high-aspect ratio stacked cones (length/diameter > 100) and nanographene layers arranged in parallel along the axis. This arrangement is about 100 times smaller than standard carbon fibers [23]. CNFs or VGCNFs, featured with outstanding mechanical properties, physical properties, thermal conductivity, and conductivity, have interested researchers as ideal candidates for carbon-filled materials to prepare polymer matrix composites/nanocomposites. For example, the conductivity of nanocomposites is about 10^6 S m^{-1}, and the thermal conductivity is about 1900 Wm^{-1} K^{-1}. However, the performances of VGCNFs are better than CNTs because of their mass production from natural gases or coals and high cost-effectiveness compared with CNTs. VGCNFs are more widely used and easier-to-obtain, making them excellent substitutes for CNTs [23]. Due to the interaction of van der Waals forces between carbon fibers, VGCNFs tend to agglomerate, resulting in poor properties of composites. Therefore, improving the ultimate performance of reinforced composites/nanocomposites is the only goal [23]. Smrutisikha et al. (2010) prepared CNF/epoxy composites with different CNF contents (up to 1 wt%) under different curing conditions and studied the electrical properties [24]. The conductivity of the insulating epoxy resin was improved by 3–6 orders of magnitude after the injection of CNF. In addition, the samples cured at room temperature had high conductivity, which was due to the network formed by nanofiber aggregation along the fiber arrangement direction.

CB is an amorphous carbon and pure para-crystalline carbon material as clusters. This light, loose, and fine black powder has a large surface area of 10–3000 m^2 g^{-1}. CB results from incomplete burning or thermal degradation of carbonaceous materials (e.g., heavy oil, coal, fuel oil, and natural gas) under deficient air. According to records, China is one of the earliest countries to produce CB. The structure of CB is expressed by the degree of chain or grape-like aggregation between CB particles. CB comprises agglomerates in size and morphology, and the particle number in each agglomerate is named high-structure CB. The oil absorption value is indicative of structure, and a larger means a higher structure of CB, which easily forms a spatial network channel that is hard to destroy. High-structure CB has fine particles, dense mesh chains, large specific surface area, and many particles per unit mass, which contribute to the formation of a conductive chain structure in polymers. Among many CB varieties, acetylene CB is the best. CB particles with broad versus narrow particle size distribution can give more conductivity to the polymer, which can be explained by statistical methods.

The larger CB filling amount leads to the higher density and more conductive paths of dispersed CB particles or CB particle aggregates, the smaller average distance between particles, and the higher probability of mutual contact. A more polar blend system composed of polymers with different polarities, and CB contains a larger critical volume fraction of CB, meaning that the system conductivity decreases. Because the surface of CB contains strong polar groups, the polarity of the matrix is significant, and the effect is enhanced. At this time, the strength increases, but this hinders the aggregation of conductive particles, resulting in poor conductivity. However, in the blend system composed of a multi-component resin matrix and CB, the filled CB will produce segregation due to the varying polarities of different matrices. The conductivity relies on the concentration and layout of CB particles and the proportion of polymers both in the segregation phase.

In the example of CB, the dominant mechanism of electron tunneling is current driven because it involves the current between flowing particles that are closely located in the polymer matrix by the interlayer. The net increase in conductivity is due to electrons jumping easily within the whole matrix. Gonza’lez et al. (2005) tested the conductivity of commercial CB under compression and found the conductivity of carbon with small compressed volume rose with the decline of sample volume [25]. The increase of total conductivity is more significant for the densest carbon and less for the lightest carbon. The conductivity and its change under compression are positively correlated with carbon density. Tantawy et al. (2002) showed that epoxy composites were electrically and thermally stable at high CB content, giving them a broad application prospect in heating devices and conductive composites [26]. In addition, the conductivity of the insulating epoxy resin matrix rose with the increase of CB content, and the conductivity (3.4×10^{-5} S m^{-1}) was above 7 wt% CB.

Studies show that CB will significantly impact the curing kinetics and conductivity of epoxy formulations. Trihotri et al. (2015) explored the impacts of curing conditions on the activation energy and dielectric properties of CB-epoxy (CB-EP) composites at varying temperatures and frequencies, and reported that room-temperature-cured CB-EP had higher activation energy and lower dielectric constant compared with heat-cured CB-EP [27]. In addition, with an increment of CB concentration in the composites, the activation energy of the curing system decreases, which may be ascribed to the higher polarization energy or charge carrier density.

GR with outstanding electrical, mechanical, and optical properties is formed by closely packing carbon atoms into a single-layer two-dimensional honeycomb lattice structure. GR is among the materials with the highest strength known. Graphene outperforms other nanofillers in terms of specific surface area and aspect ratio and can build an uninterrupted conductive network in the polymer matrix. However, due to the high aspect ratio, hydrophobicity, and π-π interaction of graphene layers, graphene is unevenly dispersed in the composite matrix, resulting in a reduction and deterioration of material properties. Therefore, researchers use different technologies (e.g., covalent/non-covalent functionalization, microwave stripping, surface modification) to evenly disperse graphene layers into polymers.

The conductivity of different graphene epoxy composite derivatives has already been studied with structural results. Liu et al. (2013) carried out marginal functionalization by Friedel Crafts acylation reaction between original graphite and 4-aminobenzoic acid to obtain 4-aminobenzoic acid-based functional fossil ink [28]. Functionalization mainly occurred in the edges of graphite, and the original graphene structure on the inner substrate was retained. Functional graphene sheets were used as nanoscale reinforcing materials to produce epoxy-based conductive composites for electrical interconnection. The conductivity of the composites increased by 31.3%, and the shear strength rose from 8.7 to 15.2 MPa after adding 0.6 wt% functional graphene. Bindu et al. (2014) prepared microwave stripping reduced graphene oxide (MERGO) was from natural graphite and synthesized epoxy nanocomposites from in-situ polymerization with triethylenetetramine (TETA) as a curing agent [29]. The AC conductivity of the nanocomposites was 10^{-5} S m^{-1}, and the dielectric constant was significantly improved. Preparing epoxy/MERGO nanocomposites from graphene is economical and straightforward and can be applied to the production of other MERGO-based polymer nanocomposites.

2.4.3 Ceramic Fillers

Ceramic materials are inorganic non-metal substances resulting from the forming and high-temperature sintering of natural or synthetic compounds. They have high melting point, hardness, and high wear and oxidation resistance. Ceramic materials are often used as fillers in ECAs owing to their large dielectric constant, low dielectric loss, and high thermal stability. Common ceramic materials include barium titanate

($BaTiO_3$), calcium cupric titanate (CCTO), calcium titanate ($CaTiO_3$), and titanium dioxide (TiO_2). Ceramics have a lower linear expansion index than metals do and have high dimensional stability upon temperature variation. Functional ceramics such as BN, TiC, SiC, TiB_2, TiN, and TiB usually have remarkable physical properties and are applied in many fields, including fillers for epoxy-based conductive adhesives.

Ceramic ECAs were prepared using face-centered cubic (FCC) TiB ceramic powder as a conductive filler and the polymer as a matrix. Also, the conductivity of the ceramic electrolytic capacitor was studied [30]. A percolation threshold was obtained at 60% FCC-TiB with the lowest resistivity of $1 \times 10^{-3}\ \Omega$ m at 75% loading. Some ceramics including BaFe, BN, TiB_2, TiN, and SiC have semiconductor properties. These materials are also considered secondary fillers of ECAs, which are usually used to enhance the conductivity and thermal conductivity of composites. Saad et al. (2015) prepared barium ferrite/polyaniline composites (Ba Ferrite/PANI) by in-situ polymerization, which were dispersed in a diglycidyl ether bisphenol A/carboxyl polyester hybrid powder coating system [14]. The filling amount of Ba ferrite/PANI was directly proportional to the conductivity of epoxy composites. Cui et al. (2013) prepared conductive adhesive (ECAs) by adding microsilver sheet and hexagonal boron nitride (BN) nanoparticles to the matrix resin [31]. The hexagonal BN nanoparticles well affected the reliability of electrochemical ceramics and improved the properties of the ceramics.

Some researchers synthesized ceramic nanomaterials for epoxy-based adhesives. Bouzidi et al. (2015) prepared indium tin oxide (ITO) nanopowders using the sol–gel method and prepared the ITO nanoparticles (ITO-EP-NCs) in the epoxy resin matrix [32]. The UV absorption performance of ITO-EP-NCs was enhanced under 2 wt% ITO load, and the absorption bandwidth reached 400 nm. The addition of ITO nanoparticles improved the UV and IR shielding properties of epoxy resin. Abenojar et al. (2009) probed into the curing and mechanical properties of an epoxy adhesive filled with boron carbide (B4C) [33]. The B4C-reinforced epoxy resin had high wear resistance and specific wear resistance against alumina. With the increase of B4C content, the reinforced epoxy resin showed good mechanical properties and fine particles. T_g decreased slightly after addition of B4C. Singh et al. (2017) reported the synergistic impact of hybrid BN and graphene on the thermal conductivity of epoxy adhesives [34]. The thermal conductivity increased to 1.65 W m^{-1} K^{-1} by about nine folds from the original epoxy resin. The activation energy declined with the incorporation of BN particles into the epoxy/graphene framework. Also, the curing speed of the epoxy/graphene/BN adhesive system surpassed that of the epoxy/graphene adhesive system.

Ceramic fillers are often used in ECAs because of their low dielectric loss and large dielectric constant and heating stability. Achieving a higher dielectric constant at a lower filling amount is difficult. In general, at above 50 wt%, although ceramic/polymer matrix composites have high dielectric constant, the ceramic packing is prone to reunition, leading to the formation of numerous holes and defects in the composite. Hence, the wear performance of the composite material will decline, leading to a conductance loss. The main reason is that the dielectric properties at the interface between the high-dielectric ceramic filler and the low-dielectric polymer matrix are too different, resulting in the distortion of the electric field. Therefore, how to improve the interface compatibility between ceramic fillers and polymer substrates becomes a research focus in recent years. There are two main research directions: to form a core–shell structure on the filler surface and to graft organic polymers on the ceramic surface.

2.4.4 Metal-Coated Fillers

Compared with carbon-based fillers and ceramic fillers, some metal fillers have high conductivity and thermal conductivity. Among them, silver (Ag) is used in ECAs because of its easy processing, high conductivity, thermal conductivity, and chemical stability. However, its high cost hinders its wide application in many electronic fields. Therefore, Ag is usually mixed with other fillers to make coating fillers, which promotes high conductivity, and has a low cost. Copper with low electrical impedance, good electromigration, and low cost is widely used as an epoxy-based conductive filler. However, the main disadvantage of the copper filler is copper oxidation or corrosion, reducing the electrical performance of the electrolytic capacitor. Therefore, the copper filler needs surface modification to control oxidation, which can be achieved by coating other metals (e.g., silver) on the copper surface. On this basis, Nishikawa et al. (2010) coated a silver layer on the surface of copper particles to solve the problems due to high resistance and oxidation [35]. Curing and reliability tests showed the epoxy-based ECAs of the Ag-plated Cu filler were much lower and more stable than the pure Cu filler because the Ag coating over Cu prevented Cu oxidation. Zhao et al. [36] prepared sheet silver-plated copper-filled ICAs with epoxy resin as the matrix and tetraethylpentamine as a curing agent. The Ag content on the copper surface of the coating was up to 96.32%, and the flake Cu–Ag powder with high-content silver had high oxidation resistance. In addition, the percolation threshold of ICAS filled with flake Cu–Ag powder was only 40%.

The non-metal core of metal-coated epoxy conductive fillers mainly includes carbon filler, various polymers, or glasses with lower conductivity than metal particles. Carbon-based materials such as graphite or graphene, CNTs, and CFs have high aspect ratios and provide epoxy-based adhesives with mechanical strength and high thermal stability, but their conductivity is lower than metal fillers. Therefore, with the help of the high conductivity of some metal particles based on Ag and Au, conductive metal particles are coated on carbon-based fillers to improve their conductivity and save costs of ECAs. Wei et al. (2009) prepared nano-graphite from expanded graphite and silver-plated nano-graphite [37]. The Ag-plated nano-graphite conductive adhesive comprised an epoxy resin, a silver-plated nano-graphite conductive filler, triethanolamine, and other additives. The percolation thresholds of the conductive adhesive were 7 wt% and 17 wt%, respectively. When the conductive filler concentration was 20 wt%, the epoxy conductive adhesive had lower resistivity of 1.50×10^{-3} Ω cm and high thermal stability. Gallego et al. (2015) tested gold-functionalized graphene (Au-GNP) as a conductive filler in epoxy adhesives to study the conductivity of ECAs [38]. The Au-GNP nanofiller was distributed into UV-curable epoxy resin. The addition of Au-GNP nanofiller significantly improved the conductivity by about four orders of magnitude relative to the epoxy nanocomposites with the same dose of bare graphene. Kim et al. (2014) showed that MWCNTs can enhance the conductivity by electroless nickel plating (Ni) and improve the electromagnetic interference shielding rate of Ni-MWCNTs-reinforced epoxy nanocomposites, suggesting a high Ni content raises surface conductivity [39]. The insulator was transformed into a conductor by coating metal particles on the surface of the polymer. It can control the overall cost of ECAS and improve the strength and elastic modulus of composites. Zeng et al. (2006) prepared conductive composites with epoxy resin (EP) as a matrix and nickel-plated polyethylene terephthalate (PET) fiber as a filler [40]. Compared with conventional nickel-plated PET/EP composites, ultrasonic electroless nickel-plated PET/EP composites contained more nickel and less phosphorus, showing higher electrical conductivity and better electromagnetic shielding effect.

2.5 Inherent Conductive Polymers

ICPs are organic materials with conductive properties owing to their unique structure, but they are fragile and cannot withstand any significant external load. ICPs show high conductivity (101 S m^{-1}, close to that of copper, 10^3 S m^{-1}) and low specific mass (1.2–1.7). In recent years, ICPs are regarded as promising conductive fillers because of their metal electronic and semiconductor optical properties, flexible mechanics, and processability of traditional polymers. Conductive polymers can be prepared by doping conjugated polymers, which becomes a trend. Generally, the conductivity of conductive materials formed by conjugated polymers is between 10^{-11} and 10^{-8} S m^{-1}, and can be increased by 6–9 orders of magnitude to 10^{-5} to 10^1 S m^{-1} after doping. ICPs are filling materials to provide conductivity for adhesive formulation. However, compared with traditional conductive fillers (e.g., metal and carbon fillers), the conductivity of adhesive formulations prepared from conductive polymers is lower, while traditional conductive fillers-enhanced adhesive systems are usually sufficient to meet some applications. ICPs-reinforced conductive adhesives can be achieved by mixing two polymers (adhesive matrix and ICPs) or building an interpenetrating polymer network. When the adhesive matrix is mixed with ICPs, conductive polymer particles are added to the liquid polymer matrix and cured under thermal conditions. Another method of preparing conductive adhesive is to polymerize and compressed-mold a conductive polymer in an insulating matrix.

3 Prospects of ECAs

According to literature and policy reports, ECAs have an outstanding market prospect and opportunities in various industries. To meet the further requirements of ECAs, high conductivity can be achieved by several methods. New trends may include the integration of different conductive fillers (mainly nanofillers) to generate mixed fillers. Adding hybrid fillers into the insulating matrix can improve the conductivity and show the synergistic effect of the two fillers. The mixed filler promotes electron transport in the 3D electronic network because the secondary filler will be used as the primary filler between the bridges. In addition, the development of ICP fillers based on metal particle coatings may beneficially impact ECAs. The evolution of ICPs-coated carbon-based nanofillers can remarkably improve conductivity. Coating metal conductive particles into carbon-based nanofillers and changing the carbon fillers to strengthen the conductivity of epoxy composites is a sustainable and reliable method to prepare ECAs.

4 Summary

This chapter mainly introduces all aspects of epoxy-based conductive adhesive (ECAs) as economical substitutes of welding connection in many electronic packaging industries. It covers the basic principle of ECAs, especially categories (e.g., ICAs and ACAs) and the conduction mechanism. The mixing of a conductive filler and an epoxy resin matrix to transform an insulating material into a conductive one is elaborated. The conductive fillers introduced into the epoxy matrix include metal fillers, carbon fillers, ceramic fillers, and metal-coated fillers. Several inherently conducting polymers mixed with epoxy include polypyrroles, polyanilines, and polythiophene.

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