CONDUCTIVE POLYMER COMPOSITES

Introduction to Electrically Conductive Adhesives

Electrically conductive adhesives (ECAs) are composites of polymeric matrices and electrically conductive fillers. Polymeric matrices have excellent dielectric properties and thus are electrical insulators. The conductive fillers provide the electrical properties and the polymeric matrix provides mechanical properties. Therefore, electrical and mechanical properties are provided by different components, which is different from metallic solders that provide both electrical and mechanical properties. ECAs have been with us for some time. Metal-filled thermoset polymers were first patented as ECAs in the 1950s (1–3). Recently, ECA materials have been identified as one of the major alternatives for lead-containing solders for microelectronics packaging applications. There are two types of conductive adhesives: anisotropically conductive adhesives (ACAs) and isotropically conductive adhesives (ICAs). Utilization of both types of conductive adhesives as lead-free alternatives for flip chip, surface mount technology (SMT), chip scale package (CSP), and ball grid array (BGA) applications are reviewed here.

Anisotropically Conductive Adhesives

Anisotropically conductive adhesives (ACAs) represent the first major division of polymer bonding agents. The anisotropic class of adhesives provides unidirectional electrical conductivity in the vertical or z-axis. This directional conductivity is achieved by using a relatively low volume loading of conductive filler (5–20 vol%) (4–6). The low volume loading is insufficient for interparticle contact.
and prevents conductivity in the $x$–$y$ plane of the adhesive. The $z$-axis adhesive, in film or paste form, is interposed between the surfaces to be connected. Application of heat and pressure to this stack-up causes conductive particles to be trapped between opposing conductor surfaces on the two components. Once electrical continuity is achieved, the dielectric polymer matrix is hardened by chemical reaction (thermosets) or by cooling (thermoplastics). The hardened dielectric polymer matrix holds the two components together and helps maintain the pressure contact between component surfaces and conductive particles. A series of sketches in Figure 1 illustrates the attachment steps in achieving ACA joints.

Broadly ACAs fall into two categories: those that are anisotropically conductive before processing and those whose anisotropy arises as a result of processing. Their characteristics can be summarized as follows:

1. Preprocessing anisotropy results from materials characterized by an ordered system of conductor elements interspersed in an adhesive matrix film. They are always in the form of tape or sheet and are evidently complicated to manufacture, requiring an adhesive film to be laser-drilled or etched then filled with conducting materials. They provide predictable contacts and are typically applied to a substrate as preforms.
(2) Postprocessing anisotropy results from materials that are a homogeneous mix of conductive fillers and adhesive matrix and that have no internal structure or order prior to processing. All adhesive pastes and some tapes fall into this category.

**Adhesive Matrix.** The adhesive matrix is used to form a mechanical bond at an interconnection. Both thermosetting and thermoplastic materials are used. Thermoplastic adhesives are rigid materials at temperatures below the glass-transition temperature ($T_g$) of a polymer. Above the $T_g$, polymers exhibit flow characteristics. Thus, the $T_g$ must be sufficiently high to avoid polymer flow during the application conditions, but the $T_g$ must be low enough to prevent thermal damage associated with chip carrier and devices during assembly. The principal advantage of thermoplastic adhesives is the relative ease with which interconnections can be disassembled for repair operations (7,8). However, thermoplastic ACAs suffer from many disadvantages. One of the most serious issues is that adhesion is not sufficient to hold the conductive particles in position, causing the contact resistance to increase after thermal shocks (7,8). Moreover, a phenomenon called spring back increases the contact resistance while the adhesive layer recovers from the stress caused by pressing of an ACA onto the components during bonding. This phenomenon, a creep characteristic exhibited by thermoplastic elastomers, occurs much after an ACA film has been heated to create the electrical joints. The contact resistance sometimes increases to more than three times the initial resistance during spring back (ie unloading) (7).

Thermosetting adhesives, such as epoxies and silicones, form a three-dimensional cross-linked structure when cured under specific conditions. Cure techniques include heat, UV light, and added catalysts. As a result of the cure reaction which is irreversible, the initial uncross-linked material is transformed into a rigid solid. The thermosetting ACAs are stable at high temperatures and, more importantly, provides a low contact resistance. This results from a compressive force that maintains the conductive particles in intimate contact after the cure. That is, the shrinking caused by the cure reaction achieves a low contact resistance with long time stability. The ability to maintain strength at high temperature and robust adhesive bonds are the principal advantages of these materials. However, because the cure reaction is not reversible, rework or repair of interconnections is not an option (7,8). The choice of adhesive matrix and its formulation is critical to the long-term life properties of a composite. In practice, many options exist for the adhesive matrix. Acrylics can be used in low temperature applications (under 100°C), while epoxies are more robust and can be used at higher temperatures (up to 200°C). Polyimide is used in the harshest environments where the temperature approaches 300°C (6).

**Conductive Fillers.** Conductive fillers are used to provide the adhesive with electrical conductivity. The simplest fillers are metal particles such as gold, silver, nickel, indium, copper, chromium, and lead-free solders (SbBi) (6,7,9–11). The particles are usually spherical and range 3–15 µm in size for ACA applications (12). Needles or whiskers are also quoted in some patents (6).

Some ACA systems employ nonconductive particles with a thin metal coat. The core material is either plastic or glass with a metal coating consisting of gold, silver, nickel, aluminum, or chromium. The basic particle shape of these systems is
also spherical. Plastic-cored particles deform when compressed between opposing contact surfaces, and thus provide a large contact area. Polystyrene (PS) is often selected as the core material because the coefficient of thermal expansion (CTE) of metal-coated PS beads is very close thermoset adhesives. The combination of epoxy resin and metal-plated PS beads results in a large improvement in thermal stability (7). In addition, glass can also be selected as the core material. Glass-cored particles coated with metal lead to a controlled bond-line thickness because the glass core is not deformable. Since the conductive particle size is known, the conductivity of the joint can be predicted.

To achieve fine pitch connections, a metal sphere or metal-coated plastic sphere coated with an insulating resin fillers were developed. The insulating resin layer is broken only under pressure to expose the underlying conductive surfaces, referred to as a microcapsule filler (MCF). A higher filler loading can be achieved with MCFs for fine pitch applications, which avoid creating electrical short circuit conditions between printed circuit features (7,12). A typical cross section of an ACA interconnection with MCF material is illustrated in Figure 2.

**Flip Chip Applications Using ACAs**

In traditional flip chip packages, solder bumps provide electrical connections between a chip and chip carrier. To achieve high reliability, organic underfill materials are usually required to fill the gap between the chip and chip carrier. The cured underfills create a monolithic structure that evenly distributes the stress over all the material in the gap, not just on the solder connections. In the past several years, much research has been conducted to develop flip chip packages, using ACAs in place of solder bumps. The primary advantages of ACA over lead-bearing solder for flip chips include ACAs’ fine pitch capability, lead-free, low processing temperature, absence of flux residue, and generally lower cost. Also, ACA flip chip technology does not require an additional underfilling process because the ACA resin acts as an underfill.

ACA flip chip technology has been employed in many applications where flip chips are bonded to rigid chip carriers (13). This includes bare chip assembly of ASICs in transistor radios, personal digital assistants (PDAs), sensor chip in digital cameras, and memory chip in lap-top computers. In all the applications, the common feature is that ACA flip chip technology is used to assemble bare chips where the pitch is extremely fine, normally less than 120 µm. For these fine applications, it is apparently the use of ACA flip chip instead of soldering which is more cost effective.
ACA flip chip bonding exhibits better reliability on flexible chip carriers because the ability of flex provides compliance to relieve stresses. For example, the internal stress generated during resin curing can be absorbed by the deformation of the chip carrier. ACA joint stress analysis conducted by Wu and co-workers indicated that the residual stress is larger on rigid substrates than on flexible substrates after bonding (14).

**ACA Flip Chip for Bumped Dies.**

*Comparison of ACAs with Hard and Soft Fillers.* Kishimoto and co-workers reported (15) ACA pastes using two different fillers: Au-coated rubber particles (soft) and nickel particles (hard). The ACAs were used to bond a flip chip with Au plated bumps to a board with copper metallization. With the application of pressure, the soft particles were brought into contact with surface pads and were deformed, which lowered this contact resistance. The hard particles, however, deformed the bumps and pads, and thus were also in intimate contact with the surfaces to help reduce this contact resistance. Their study showed that their choice of both hard and soft fillers in ACA materials had similar voltage–current behavior, and both exhibited stable contact resistance values after 1000 cycles of thermal cycling and 1200 h of 85°C/85% RH aging conditions (15).

*Coated Plastic Filler.* Casio developed an advanced ACA film called the Microconnector (Fig. 3) (16–18). This adhesive contains conductive particles made by coating plastic spheres with a thin layer of metal, followed by an additional 10-nm-thick layer of insulating polymeric material. The insulating layer consists of a large number of insulating micropowder particles which electrically insulate the outer surface of the spheres. The thin insulation layer is formed by causing insulating micropowder particles to adhere to the surface of the metal layer via electrostatic attraction. The base adhesive resin is thermoplastic or thermosetting.

**Fig. 3.** Schematic depicting Casio’s ACF technology – Microconnector.
producing compressive force when cured. When heat and pressure are applied during bonding, the insulating layer, which is in contact with the bump surface of an IC, is broken. However, the insulating layer remains intact on conductive particles not crushed by the bonding pads, thereby producing only Z-axis electrical interconnections and preventing lateral short circuit conditions. With an additional insulating layer, a fine pitch and low contact resistance can be achieved without the risk of lateral short circuiting by increasing the filler percentage (ie amount of particles per unit volume base adhesive resin or film). Casio is manufacturing pocket TVs with a liquid crystal using this material (18).

**Solder Filler Systems.** Unlike most commercial ACAs, where the electrical conductivity is based on the degree of mechanical contact achieved by pressing conductive particles to contact pads on board and chip bumps, solder-filled ACAs establish microscopic metallurgical interconnections. The advantage of these joints is that the metallurgical bonds that are established prevent electrical discontinuities from occurring should the adhesive polymeric matrix undergo relaxation during the operational lifetime. Therefore, solder-filled ACAs combine the benefits of both soldering and adhesive joining resulting in more reliable ACA joints. Furthermore, better electrical performance is achieved as a result of lower contact resistance established through metallurgical bonds (19).

Joints made with SnBi- and Bi-filled ACAs experience brittle intermetallic compound formation and have problems with typical conductor and coating materials such as copper, nickel, gold, and palladium (20). But Bi and BiSn are compatible with tin, lead, zinc, and aluminum. However, Zn and Al are easily oxidized, and so in practice only Sn and Pb are suitable surface finish materials for SnBi- and Bi-filled ACA applications (Fig. 4). Vuorela demonstrated that high quality interconnections were formed by metallurgical bonding SnPb-bumped chips on SnPb-coated substrates at relatively low temperature and pressure utilizing a

![Fig. 4. Schematic illustration of the formation of electrical interconnects between a bumped chip and a mating carrier using a Bi-filled ACA. (a) The chip is aligned and placed on a chip carrier. (b) The Bi particle is deformed between a chip bump and a carrier pad when a bonding pressure is applied. (c) The Bi particle dissolves into the liquid lentil upon exposure of heat. (d) Bi diffuses into the Sn–Pb matrix and forms fine solid precipitates.](image-url)
ACA bonds flip chips exhibit the same transmission coefficient, $S_{21}$, as solder-bonded flip chips from 1 to 21 GHz. —— Transmission: ACA; ---- Transmission: solder.

Bi-particle-filled ACA. The ACA joints exhibited a stable resistance after 2000-h 85°C/85% RH aging or after 1000-h temperature cycle testing (−40 to 125°C). Even though this work was still preliminary, it demonstrated an interesting idea and concept. For lead-free applications, different materials such as pure Sn can be used for chip bumps and surface finish on the substrate (21).

ACA Bumped Flip Chips for High Frequency Applications. The high frequency behavior of ACA interconnections has attracted much attention in the past several years. Sihlbom and co-workers demonstrated that ACA-bonded flip chips can provide performance equivalent to solder flip chips in the frequency range of 45 MHz to 2 GHz on FR4 chip carriers and 1 to 21 GHz on a high frequency Teflon-based chip carrier (Fig. 5). The different particle sizes and materials in the conductive adhesives gave little difference in high frequency behavior of ACA joints (22,23).

Yim and co-workers developed a microwave frequency model for ACF-based flip chip joints based on microwave network analysis and S-parameter measurements. By using this model, high frequency behavior of ACF flip chip interconnections with two filler particles, Ni and Au-coated polymer particles, was simulated. It was predicted that Au-coated polymer-particle-filled ACF flip chip interconnections exhibited comparable transfer and loss characteristics to solder bumped flip chips up to about 13 GHz and thus they can be used for up to 13 GHz, but Ni-filled ACF joints can only be used for up to 8 GHz because the Ni particle has a higher inductance compared to the Au-coated particle. Polymeric resins with a low dielectric constant and conductive particles with low inductance are desirable for high resonance frequency applications (24).

ACA for Unbumped Flip Chips. Although ACAs are typically utilized with flip chip bumped dice, they are also used for unbumped flip chips in some cases. For unbumped flip chips, a pressure-engaged contact must be established by bringing the particles to the aluminum chip pads rather than a bump. The
pressure must be sufficient to break the oxide on the aluminum pads. A sufficient quantity of particles must be trapped in the contact pad area and remain in place during bonding and curing to achieve a reliable interconnection. In addition to maximizing the number of particles in the contact area the number of particles located between adjacent pads must be minimized so as to prevent electrical shorts. An additional factor that must be in the case of unbumped flip chips is adhesive flow during bonding and curing. It is essential to control the temperature heating to be sufficiently slow when the polymeric resin is curing so that the conductive filler particles can migrate from the chip carrier side to the chip side pad (25).

**Ni/Au Coated Silver Bumps.** A flip chip technology developed by Toshiba Corp. utilized an anisotropic conductive film (ACF) to attach bare unbumped chips (with Al pads) onto a printed circuit board (PCB) with bumps formed from a silver paste screen printed on the PCB (26). After curing, Ag bumps were formed (70-µm diameter, 20-µm height), which were subsequently overplated with Ni/Au. It was determined that ACF with a low CTE (28 ppm/°C), low water absorption rate (1.3%), and that utilized a Au-plated plastic ball worked best. It was also found that Ni/Au plated Ag-paste formed bumps exhibited a smaller initial connection resistance (22 and 48 Ω for Ag bumps with and without Ni/Au overplating, respectively) and a smaller connection resistance increase compared to Ag-paste formed bumps which were not overplated with Ni/Au after 1000-h accelerated thermal cycling (ATC) testing (ie the final connection resistances after aging are 294 and 717 Ω for Ag bumps with and without Ni/Au overplating, respectively).

**Conductive Columns.** Nitto Denko Corp. developed an ACF for fine pitch flip chip applications (27). The features of this ACF were (1) connectability between bumpless chips and fine pitch PCB; (2) high electrical conductivity; (3) repairability (easy to peel off chips from a printed circuit board at elevated temperatures); (4) high reliability; and (5) potential storage at room temperature. There are other notable features too: (1) ACF is usable at pitches down to 25 µm, (2) the conductive elements are micrometallic columns as opposed to random-shaped particles, and (3) this adhesive matrix consists of a thermoplastic polymer resin, conductive columns coated with an insulator, and a high T_g polymer, which completely separates the columns from the adhesive (Fig. 6).

It is easy to change the diameter of the conductive columns in order to make the film compatible with a variety of pitches. Sn/Pb or other solder materials are plated on both the top and bottom of the conductive columns (usually copper). The plated solder on the both ends of the conductive columns melts and forms metallurgical connections between the conductive columns and metal pads on a chip and the mating chip carrier, which ensure a good connection. Figure 6a illustrates the cross section of the film structure. A rough surface, a result of plating, has the advantage of providing a good connection with the terminal pads it is in contact with. A typical terminal pad structure of a chip without bumps is shown in Figure 6b. To achieve a good connection, the height of the conductive columns must be larger than the thickness of the passivation layer (t_p). Since t_b (the distance from a Cu pad surface of the chip carrier to the passivation layer surface of the chip) is usually smaller than t_p (the distance from solder mask surface of the chip carrier to the passivation layer surface of the chip), the conductive columns will assume an inclined position during bonding if the thickness of the conductive columns
is larger than the ACF thickness ($t_{ACF}$). It is important to adjust the thickness of board or chip carrier pads and ACF thickness to achieve good connection and adhesion. Reliability results indicated that the ACF possessing an adhesive matrix with a high $T_g$ ($282^\circ$C) exhibited high reliability and the contact resistance remained unchanged after 1000 cycles of ATC testing ($-25$ to $125^\circ$C). Figure 6c is a photography of a cross section of a joint formed between an unbumped die and a chip carrier using this ACF flip chip interconnection method.
ACAs for CSP and BGA Applications

**Area Bonding Conductive Adhesives.** Aiming at the CSP application market, Merix Corp. and Auburn University collaborated to develop an ACA called area bonding conductive (ABC) adhesives. ABC adhesive is a two-region thermoset adhesive with ECA pads surrounded by a continuous oxide-filled dielectric adhesive to form a total area bond. Both regions are solvent-free, B-staged, nontacky epoxies supplied on a Mylar carrier release film. In contrast to conventional ACAs, conductive areas of ABC adhesive are only at bond pad locations. The assembly process for using ABC adhesives is shown in Figure 7. The ABC adhesives potentially can provide a reliable, low cost, low temperature, low pressure process for flip chip and CSP applications (28).

**Au-Stud vs Electroless Ni/Au Bumps.** As the demand for miniaturization has increased dramatically, concentrated efforts have been made to find cheaper alternatives to established technologies of area array solder bumps.

![Diagram of flip chip assembly processing utilizing ABC adhesive](image)

**Fig. 7.** Schematic depicting a flip chip assembly processing utilizing ABC adhesive. (a) A chip is aligned to the ABC preform which is on a carrier film. (b) The ABC preform is tacked to the die at 100°C and under a pressure of 150 g for 30 s, and then the carrier film is removed after the chip is cooled down. (c) The chip with ABC preform is aligned to a mating chip carrier (FR4 board). (d) The chip/ABC preform is attached to the chip carrier at 100°C and under a pressure of 150 g for 30 s, and then the package is cooled down.
ChipPAC, Inc., demonstrated an alternate process/package concept covering both CSP and PBGA package formats whose construction is illustrated in Figure 8. The concept package consisted essentially of three parts: ACF, metallic bumps on the die bond pads, and an organic chip carrier (29).

Although this packaging solution was not entirely unique, reducing it to a high volume assembly and packaging process, where low cost and high reliability were key, was innovative. This configuration provides an appealing package solution, based on several factors. First, the connection can be implemented at a much finer pitch (~100 µm) compared to conventional solder bumps, and so there is a potential for a die-size reduction in flip chip IC designs that are normally implemented as multirow perimeter arrays using conventional solder bumps. Second, the ACF interconnect approach allows the use of inexpensive bumping technologies, thereby greatly reducing the wafer bumping cost portion of the overall package cost.

The combination of cured adhesive interconnection, bumps, and organic substrate provides a reliable, cost-effective flip chip CSP. It was determined that Au-stud bumps were preferable to Ni/Au bumps because of the former's compliant nature. Since the planarity control of organic chip carriers is difficult, given the nature of the material, it was simpler to change the interconnection method, ie, using Au-stud bumps. However, electroless Ni/Au bumps are still an option, if the material properties of the ACF and/or chip carrier are altered to provide compliancy.

**Double-Layered ACF.** Motorola developed a low cost and low profile flip chip on flex (FCOF) CSP package using ACFs (30). The package has the flexibility to utilize the existing wire-bonding pad configuration without adding prohibitive redistribution and wafer solder bumping costs, and eliminated the need for underchip encapsulation. Two types of ACF film were studied: double layer films with the second layer loaded with Ni/Au plated polystyrene–divinylbenzene (PS–DVB) spheres, and solid Ni particles. The film structure, consisting of a nonfilled and a conducting particles-filled adhesive layers, is illustrated in Figure 9. The double-layer design reduces the particle density in x-y spacing of interconnection pads, which serve to enhance the x-y plane insulation characteristics. At the same time, the double-layer film provides more adhesive volume that helps to entrap more particles on the bonding interconnection pads. Both calculated and observed values show that the number of conducting particles trapped is much higher than those in single-layer ACF. This indicate that even though particle density in a
double-layer ACF is low, conducting particles to effect electrical contact with both interconnection pads are trapped more effectively between interconnection pads in the double-layer ACF. The die has Ni/Au plated bonding pads and the chip carrier is flexible polyimide which can provide adequate compensation for the planarity differences. Its compliant nature under compressive bonding operation allows the copper traces at the bonding area to deform and compensate for nonplanarity or irregularity that exists. The ACF adhesive system provided the system with stable contact resistance after 500 cycles of liquid–liquid temperature shock (LLTS) aging (−55 to 125°C).

Ceramic Chip Carriers vs Organic Chip Carriers. A ceramic chip carrier and an organic chip carrier, whose configuration is equivalent to that of microball grid array (µBGA) style CSP and broadly representative of BGA and flip chip devices, were evaluated using ACAs with conducting particles of various sizes (31). The ceramic chip carrier has AgPd thick-film bonding pads and the organic chip carrier is a conventional PCB (1 oz Cu clad FR5 laminate) with submicron Au-coated Cu pads. It was determined that uniform conductivity and high yield were more readily achieved with organic chip carrier rather than ceramic chip carriers. This is because bonding pads on the FR5 chip carrier have better coplanarity compared to the thick-film ceramic chip carrier. ACAs with finer particles exhibited worse overall performance on both chip carriers, while ACAs with larger and polymer-cored particles exhibited better performance because the deformable polymer-cored particles compensated the gap variations between the chip bumps and the chip carriers.

SMT Applications

ACAs have been investigated as replacement for SnPb solder in surface mount (SM) attachment for fine pitch applications. The key attractive advantage is the cost effectiveness of using ACA to bond fine pitch SM components. A limitation of ACAs is the need to cure under a contact pressure. The concept of using an ACA as a solder replacement on rigid chip carriers utilizing conventional SMT
has been demonstrated by Liu and co-workers (32). Fine pitch SM components were bonded to FR4 boards with ACAs using a fine pitch bonder and then components with larger pitches were bonded with ICAs using standard SM equipment. The study demonstrated that standard surface-mounting tools could be used to assemble conductive adhesives. The connection resistance of solder-plated, plastic components (0.65 mm pitch) with ACAs bonded did not change after an accelerated temperature cycling (ATC) test conducted at $-40$ to $85^\circ$C. However, similar parts failed under conditions of $-55$ to $125^\circ$C for 1000 cycles (33). The mechanical stability problem may have been the result of an improper joint geometry, ie not optimized for ACA bonding.

**Failure Mechanism**

Since the adhesive matrix is a nonconductive material, interconnection joints rely to some extent on pressure to assure contact for conventional ACAs. Adhesive interconnections therefore exhibit different failure mechanisms compared to soldered connections, where the formation of intermetallic compounds and coarsening of grains are associated with the main mechanisms. Basically there are two main failure mechanisms that can affect the contacts. The first is the formation of an insulating film on either the contact areas or conductive particle surfaces. The second is the loss of mechanical contact between the conductive elements due to either a loss of adherence or relaxation of the compressive force.

**Oxidation of Nonnoble Metals.** Electrochemical corrosion of nonnoble metal bumps, pads, and conductive particles results in the formation of insulating metal oxides and significant increase in contact resistance. Electrochemical corrosion only occurs in the presence of moisture and metals that possess different electrochemical potentials. Humidity generally accelerates oxide formation and so too the increase in contact resistance. Reliability test results for FCOF using gold bumps and ACFs filled with Ni particles indicated that the connection resistance increased with time under elevated temperature and humidity storage conditions (34). In this case, the gold bump acts as cathode and the Ni particle as an anode. A nickel oxide, which is electrically insulating, eventually forms on the surface of the Ni particles.

**Loss of Compressive Force.** The compressive forces acting to maintain contact among the conductive components are partly achieved because of curing shrinkage achieved when curing the polymeric matrix of ACAs. Both the cohesive strength of the adhesive matrix and the interfacial adhesion strength between the adhesive matrix and the chip and chip carrier must be sufficient to maintain the compressive force. However, the thermal expansion of adhesives, their swelling due to moisture adsorption, and mechanical stresses due to applied loads tend to diminish this compressive force created as a result of curing. Moreover, water not only diffuses into the adhesive layer but also penetrates to the interface between adhesive and chip/chip carrier, causing a reduction in adhesion strength. As a result, the contact resistance increases and can even result in a complete loss of electrical contact (35).
Isotropic Conductive Adhesives

Percolation Theory of Conduction. Isotropic conductive adhesives (ICAs), also called as polymer solder, are composites of polymer resin and conductive fillers. The conductive fillers provide the composite with electrical conductivity through contact between the conductive particles. With increasing filler concentrations, the electrical properties of ICAs transform from an insulator to a conductor. Percolation theory has been used to explain the electrical properties of ICA composites. At low filler concentrations, the resistivities of ICAs decrease gradually with increasing filler concentration. However, the resistivity drops dramatically above a critical filler concentration, $V_c$, called the percolation threshold. It is believed that at this concentration, all the conductive particles contact each other and form a three-dimensional network. The resistivity decreases only slightly with further increases in the filler concentrations (36–38). A schematic explanation of resistivity change of ICAs based on percolation theory is shown in Figure 10. In order to achieve conductivity, the volume fraction of a conductive filler in an ICA must be equal to or slightly higher than the critical volume fraction. Similar to solders, ICAs provide the dual functions of electrical connection and mechanical bond in an interconnection joint. In an ICA joint (Fig. 11), the polymer resin provides mechanical stability and the conductive filler provides electrical conductivity. Filler loading levels which are too high cause mechanical integrity of adhesive joints to deteriorate. Therefore, the challenge in formulating an ICA is to maximize conductive filler content to achieve a high electrical conductivity without adversely affecting the mechanical properties. In a typical ICA formulation, the volume fraction of the conductive filler is about 25–30% (4,5).

Adhesive Matrix. Polymer matrices of ICAs are similar to ACAs. An ideal matrix for ICAs should exhibit a long shelf life (good room temperature latency), fast cure, relatively high glass-transition temperature ($T_g$), low moisture pickup, and good adhesion (39). Both thermoplastic and thermoset resins can be used for ICA formulations. The main thermoplastic resin used for ICA formulations is polyimide resin. An attractive advantage of thermoplastic ICAs is that they are reworkable, eg, can

![Fig. 10. Effect of filler volume fraction on the resistivity of ICA systems.](image-url)
A major drawback of thermoplastic ICAs, however, is the degradation of adhesion at high temperature. Another drawback of polyimide-based ICAs is that they generally contain solvents. During heating, voids are formed when the solvent evaporates. Most of commercial ICAs are based on thermosetting resins. Epoxy resins are the most commonly used in thermoset ICA formulations because they possess superior balanced properties. Silicones, cyanate esters, and cyanoacrylates are also employed in ICA formulations (40–44).

Conductive Fillers. Because polymer matrices are dielectric materials, conductive fillers in ICA formulations provide the material with electrical conductivity. In order to achieve high conductivity, the filler concentration must be at least equal to or greater than the critical concentration predicted by percolation theory.

Pure Silver vs Ag-Coated Fillers. Silver (Ag) is by far the most popular conductive filler, although gold (Au), nickel (Ni), copper (Cu), and carbon (C) are also used in ICA formulations. Nickel and copper-based conductive adhesives generally do not have good conductivity stability because they are easily oxidized. Even with antioxidants, copper-based conductive adhesives show an increase in volume resistivity on aging, especially under high temperature and humidity conditions. Silver-plated copper has been utilized commercially in conductive inks, and should also be appreciable as a filler in adhesives. While composites filled with pure silver particles often show improved electrical conductivity when exposed to elevated temperature and humidity or thermal cycling, this is not always the case with silver-plated metals, such as copper flake. Presumably, the application of heat and mechanical energy allows the particles to make more intimate contact in the case of pure silver, but silver-plated copper may have coating discontinuities that allow oxidation/corrosion of the underlying copper and thus reduce electrical paths (4).
Particle Shape and Size. The most common morphology of conductive fillers used for ICAs is flake because flakes tend to have a large surface area, and more contact spots and thus more electrical paths than spherical fillers. The particle size of ICA fillers generally ranges from 1 to 20 µm. Larger particles tend to provide the material with a higher electrical conductivity and lower viscosity (45). A new class of silver particles, porous nano-sized silver particles, has been introduced in ICA formulations (46,47). ICAs made with this type of particles exhibited improved mechanical properties, but the electrical conductivity is less than ICAs filled with silver flakes. In addition, short carbon fibers have been used as conductive fillers in conductive adhesive formulations (36,48). However, carbon-based conductive adhesives show much lower electrical conductivity than silver-filled ones.

Silver-Copper Fillers. In 1992, a powder with a specific structure was introduced as a filler for conductive adhesives (49). A powder particle consists of two metallic components, copper and silver. Silver is highly concentrated on the particle surface and concentration gradually decreases from the surface to the inner of the particle, but always contains a small amount of silver. Conductive adhesive paste filled with this powder exhibits excellent oxidation resistance, i.e., can be exposed to oxygen content about 100 ppm in a nitrogen atmosphere. It also exhibits higher solderability than commercially available copper pastes, sufficient adhesion strength even after heating and/or cooling test, and least migration, almost same degree to pure copper paste (49).

Low-Melt Fillers. In order to improve electrical and mechanical properties, low-melting-point alloy fillers have been used in ICA formulations. A conductive filler powder is coated with a low-melting-point metal. The conductive powder is selected from the group consisting of Au, Cu, Ag, Al, Pd, and Pt. The low-melting-point metal is selected from the group of fusible metals, such as Bi, In, Sn, Sb, and Zn. The filler particles are coated with the low-melting-point metal which can be fused to achieve metallurgical bonding between adjacent particles, and between the particles and the bond pads that are joined using the adhesive material (50,51).

Flip Chip Applications Using ICAs

A key factor in achieving a low cost, flip chip technology is the use of ICAs. In comparison to the classical flip chip technologies, the use of ICAs for the bumping and joining provide numerous advantages:

(1) The simplification of the processing and the reduction of indexing steps by the omission of activation and purification process
(2) The smaller temperature load on elements and wiring carriers
(3) The availability of a large spectrum of possible material pairs and combinations
(4) The broad range of applicable adhesive systems and thus the selection of different processing parameters and joining characteristics
(5) Few requisites for under bump metallization (UBM) since alloy phase formation does not have to be considered
Unbumped Flip Chip Joints.

Polymer Flip Chip. Several flip chip bumping and joining techniques have been reported in the literature. Flip chips using ICAs are often called polymer flip chips (PFCs). The PFC process is a stencil printing technology in which an ICA is printed through a metal stencil to form polymer bumps on bond pads of IC devices subsequent to the UBM deposition on aluminum termination pads. The sequential processes to achieve PFC interconnects are UBM deposition, stencil printing an ICA, bump formation (ICA solidification), flip chip attach to achieve electrical connections, and underfill for enhanced mechanical and environmental integrity (52,53).

Protective Chip Pad Layer. As with virtually all flip chip processes, the Al bond pads must be protected to eliminate the formation of nonconductive aluminum oxide. This ensures a low and stable resistance at bond–bond pad interface. The PFC process utilizes an electroless plating technique, using Ni/Au or Pd, to cover the Al bond pads prior to polymer bumping. The typical metal thickness is 0.5–1.0 µm for Pd and 3.0–5.0 µm for Ni/Au.

The PFC process combines high precision stencil printing techniques with highly conductive ICAs. These polymers can be thermosetting or thermoplastic. First the polymer bumps are formed by deposition of an ICA through the metal mask directly onto the metallized bond pads on a wafer. Printed conductive adhesive bumps can offer an attractive alternative to the other bumping technologies in terms of cost and manufacturability. The printing process typically involves a screen or stencil with openings through which bumps are deposited. A screen consists of an interwoven wire mesh with an emulsion that covers the wire mesh. The emulsion is photolithographically patterned to match the bump sites. Stencils are made of metal foil. Holes for bump deposition are made by etching, electroforming (plating), or laser drilling.

During the printing process, the paste is typically dispensed some distance away from the stencil apertures. A schematic of the printing process is shown in Figure 12. Typically, the stencil is separated from a substrate by the snap-off distance. The squeegee is lowered, resulting in contact of the stencil to the substrate or wafer surface. As the squeegee moves across the stencil surface, a stable flow pattern develops in the form of a paste roll. The consequent hydrodynamic pressure developed by the squeegee pushes the paste into the patterned stencil openings. The stencil lifts away from the substrate surface with the paste remaining on the substrate.

Curing. The polymer bumps are then either fully cured or partially cured to the so-called B-stage for thermosetting polymer bumps. For thermoplastic polymer bumps, after stencil printing the solvent is removed to form solid bumps. Bump heights are typically 50–75 µm and process can accommodate pitches down to 5 mil. Bump densities of up to 80,000 bumps/wafer have been formed with excellent coplanarity.

Once the bumped wafers are diced, chips are picked from the wafers, flipped over, and then placed on and bonded to chip carriers. Different process procedures are utilized to bond thermosetting polymer bumps to similar thermoplastic bumps, as noted in Figure 13. Final processing involves a heat cure for thermosetting bumps, while thermoplastic bump connections only require in a few seconds under heat and pressure to melt the thermoplastic.
Underfill. An underfill is then injected into the gap between the chip and chip carrier and then cured to complete the flip chip process. The function of the underfill or encapsulation as it is sometimes referred to is to provide mechanical integrity and environmental protection to a flip chip assembly. Studies have demonstrated that both thermoset and thermoplastic ICAs can offer low initial joint resistances of less than 5 mΩ and stable joint resistances (Au-to-Au flip chip bonding) during all the accelerated reliability testing listed in Table 1. The reliability results have indicated that there is no substantial difference in the performance of thermoset and thermoplastic bumps and both types of polymers apparently offer reliable flip chip electrical interconnections (53).

Micromachined Bumping. A PFC bumping process is known as micromachined bumping (54,55). The bumping procedure is illustrated in Figure 14. Initially Cr/Au contact metal pads for conductive polymer bumps are deposited on Si wafers, followed by patterning a thick photoresist to create bump holes. A high aspect ratio and straight side-wall patterns are very important in shaping the conductive polymer bumps. After the lithography, thermoplastic conductive polymer material, usually thermoplastic paste filled with Ag flake, is applied by either dispensing or screen printing the paste into the bump-hole patterns. The wafer

<table>
<thead>
<tr>
<th>Test</th>
<th>Condition</th>
<th>Time</th>
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<tr>
<td>Temperature cycle</td>
<td>−55 to 150 °C</td>
<td>1000 cycle</td>
</tr>
<tr>
<td>Thermal shock</td>
<td>−55 to 125 °C</td>
<td>500 cycle</td>
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<tr>
<td>Elevated temperature and humidity</td>
<td>85 °C/85% RH</td>
<td>1000 h</td>
</tr>
<tr>
<td>Pressure cooker</td>
<td>121 °C/15 psi</td>
<td>168 h</td>
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</table>
is heated in a convection oven to remove the solvent. Because of the difference in curing conditions between the thick photoresist and conductive polymer, the photoresist can be carefully stripped to expose the dried polymer bumps. Finally, the wafer is diced into individual chips.

Chips with thermoplastic bumps are placed on chip carriers and preheated to approximately 20°C above the melting point of the polymer, causing the bumps to melt onto the matching chip carrier pads. Mechanical and electrical bonds are
established as the chip carrier cools below the polymer melting temperature. To enhance the mechanical bonding strength, a small amount of pressure can be applied by placing a weight on the chip.

This flip chip bonding technique has high potential to replace conventional solder flip chip techniques for sensor and actuator systems, optical microelectromechanical systems, optoelectronic multichip modules, and electronic system applications (55).

**Metal-Bumped Flip Chip Joints.** ICAs can also be used to form electrical interconnections with chips that have metal bumps. ICA materials utilize much high filler loading than ACAs to provide electrical conduction isotropically (ie in all directions) throughout the material. In order for these materials to be used for flip chip applications, they must be selectively applied to only those areas that are to be electrically interconnected. Also, the materials are not to spread during placement or curing to avoid creating electrical shorts between circuit features. Screen or stencil printing is most commonly used to precisely deposit the ICA pastes. However, to satisfy the scale and accuracy required for flip chip
bonding very accurate pattern alignment is required. To overcome this difficult requirement, Matsushita developed the transfer method (56).

Raised studs or pillars are required on either the die or the chip carrier. Matsushita uses a conventional ball bonder to form Au-stud bumps. Bumping is significantly faster than creating a complete wire bonds. A ball bumping process eliminates the need for traditional sputtering and plating processes used for standard bump formation. To prevent the bond area from becoming too large, the bumps are formed in a conical shape. The stud-bump bonding process is illustrated in Figures 15–18. The bumps are pressed level by a flat surface which adjusts both height and planarity. The ICA is selectively transferred on the bump tips by contacting the face of the die to a flat thin film of the ICA which is produced by screen printing and whose transfer thickness is controlled by changing the printed film thickness. Then the die is picked, aligned, and placed on a chip carrier. The whole assembly is exposed to heat to cure the ICA and form connections between the

Fig. 15. Schematic of the process flow of forming joints with stud-bumped flip-chips using ICAs. (a) Planarize the tips of the gold-stud bumps formed with a wire bond tool. (b) Dip the planarized bumps into a thin layer of ICA. (c) Withdraw the chip leaving the bumps coated with ICA. (d) The chip is placed on mating pads of a chip carrier with pressure required during curing. (e) An underfill (an insulating adhesive) is dispensed and cured.
Fig. 16. Schematic of a joint formed using transient liquid phase sintering conductive adhesives. (a) Initial state after chip attachment and before temperature reach the melting point of the low-melting-alloy filler. (b) The low-melting-alloy fillers start to melt and dissolve the high-melting-alloy filler. (c) After the high-melting-alloy fillers are completely dissolved, the liquid metal phase solidifies and forms a three-dimensional network in the joint.

die and chip carrier. Finally, an underfill (an insulating adhesive) is dispensed between the die and the chip carrier and cured. This method offers the options of oven curing an assembly since bonding pressure is not required. A specially formulated ICA is used to avoid silver migration, containing 20% palladium in a silver–palladium alloy. This is done to avoid silver migration. A schematic of the process flow of forming joints with stud-bumped flip chips using ICAs is shown in Figure 15.

Another process for bonding a flip chip with metal bumps consists of screen printing an ICA on a chip carrier, aligning and placing the chip, curing the ICA to form bonds, and underfilling. By using this approach, SINTEF Electronics conducted a comparison study between an ICA-bonded and solder-bonded flip chips on FR4 chip carrier with Ni/Au metallization. The number of thermal cycles (−55 to 125°C) to failure for both solder and ICA flip chip circuits was compared. The study showed that stable contacts could be maintained for at least 1000–2000
Fig. 17. Schematic depicting the effect of galvanic corrosion of a nonnoble metal pad on electrical conduction of a silver-filled ICA. (a) Good electrical conduction before corrosion. (b) Poor electrical conduction due to the formation of a metal hydroxide or oxide formation as a result of galvanic corrosion.

Fig. 18. Effect of a corrosion inhibitor on contact resistance between an ICA and a Sn–Pb surface with time. Aging condition: 85°C/85% RH.

cycles for ICA flip chip joints. This is comparable to the lifetime for solder flip chip joints. However, the variation among ICA samples was very high and optimization of assembly processes is needed in order to achieve more reproducible joint resistance (57).
Other Applications of ICAs

**Surface Mount Applications.** Tin–lead solders (Sn–Pb) are the standard materials used to interconnect electronic components on PCBs. The most common reflow soldering process is SMT which uses tin–lead solder pastes (58–61). The pressure to reduce the industrial use of lead is growing, particularly in Europe, since it poses as a hazard to human health (62).

Thus, the use of tin–lead solder paste in SMT processes must be reduced or eliminated to both satisfy legislative actions and market-driven pressures as well. Lead-free and environmentally sound interconnect bonding processes are urgently needed. Among the possibilities are ECAs and lead-free solders (63–65). Compared to soldering technology, ECA technology can offer numerous advantages such as fewer processing steps which reduces processing cost, lower processing temperature which makes the use of heat-sensitive and low cost chip carriers possible, and fine pitch capability (64).

However, conductive adhesive technology is still in its infancy, and concerns and limitations do exist. The main limitations of commercial ICAs include lower conductivity than that of solder materials, an unstable contact resistance with nonnoble metal finished components, and poor impact performance. The electrical conductivity (∼10^4 Ω \(^{-1}\)·cm\(^{-1}\)) of an ICA is lower than Sn–Pb solders (∼10^5 Ω \(^{-1}\)·cm\(^{-1}\)). Although generally adequate for most electronics applications, the electrical conductivity of ICAs must be improved. Contact resistance between an ICA and nonnoble metal (such as Sn/Pb, Sn, and Ni) finished components is noted to dramatically increase with time especially under elevated temperature and humidity aging conditions (66–69). In addition, PCB assemblies are often subject to significant mechanical shock during assembly, handling, and throughout their product life. Packages cannot survive without adequate impact resistance. However, most microelectronic commercial ICAs exhibit poor impact performance. Components assembled using ICAs tend to separate from the substrate when the package experiences a sudden shock (68,70). For conductive adhesive technology to provide an acceptable solution as a solder replacement, new conductive adhesives with the desired overall properties must be developed (68). There has been a considerable effort to improve the properties of ICAs and to make them more reliable materials. These improvements are described in the following sections.

**CSP Applications.** Matsushita Electric Industrial Co., Ltd., developed solderless joining technologies using nickel-filled ICAs to mount a ceramic chip scale package (CSP-C) onto a FR4 board (71). Nickel was selected instead of Ag because, unlike Ag, nickel does not migrate. A significant CTE mismatch existed between the CSP-C ceramic chip carrier (CTE = 7 ppm) and the FR4 organic chip carrier (CTE = 16 ppm). This CTE mismatch resulted in large stress to be generated within the solder joints during ATC testing which resulted in early failure due to solder fatigue. ICAs usually exhibit better thermomechanical properties than solders. Also, metal-migration between joints is a great concern because the joints in a CSP area array package are arranged with a close pitch (ie in close proximity).

The packaging procedure was as follows: (1) the ICA was screen-printed on the area array lands of the FR4 motherboard; (2) the CSP-C was mounted; (3) and the ICA was cured to form bonds. The Ni-filled conductive adhesive demonstrated
a much higher resistance to metal migration compared to Ag-filled IACs, and equivalent to solder joints. However, the thermal fatigue life of the Ni-filled ICA joints was five times greater than comparable solder joints.

Performance of ICAs

High Frequency Performance of ICA Joints. Only very limited work has been conducted to investigate the high frequency behaviors of ICA joints. Felba and co-workers (72) investigated a formulation of ICA that performed well as a solder replacement in microwave applications. The study involved in various different adhesive base materials and several types of main (silver flakes, nickel, and graphite) and additional (soot and silver semiflake powder) filler materials. In order to assess the usefulness of a given adhesive formulation, an additional gap in the gold strip of a standard microstrip bandpass filter was made and bridged by an adhesive bonded silver jumper. Both the quality factor ($Q$) and loss factor ($L$) of the filter with the bonded jumper were measured at a frequency of 3.5 GHz in a preliminary experiment and at 3.5 and 14 GHz in a final experiment. It was determined that silver flake powders are the best filler materials for ICA for microwave applications because ICAs filled with the silver flake powders exhibit the highest $Q$-factor and lowest $L$-factor. Also, addition of soot should be avoided since it decreases the quality factor (72).

A study was made at Georgia Tech, of a flip chip test vehicle mounted on a FR4 chip carrier with a gold-plated copper transmission lines (73). The performance of eutectic Sn–Pb and ICAs were evaluated and compared using this test device. Both ICAs and eutectic Sn–Pb solder were determined to exhibit almost the same behavior at a frequency range of 45 MHz to 2 GHz and the measured transmission losses for both materials were minimal. It was also found that the $S_{11}$ characteristics of both Sn–Pb and ICAs after exposure to 85°C/85% RH aging for 150 h did not vary from the previous signals prior to aging, but $S_{12}$ value of the Sn–Pb joints deviated more than that of ICA joints after the aging.

Fatigue Life of ICA Joints. There have been several studies investigating the fatigue life of ICA joints. Aiming to understand the performance of ICA interconnects under fracture and fatigue loading, Constable and co-workers (74) investigated performance of ICA interconnects under fracture and fatigue loading by monitoring resistance changes (microohm sensitivity) of ICA joints during pull and fatigue testing (cyclic loading up to 1000 cycles). Observation of the fracture surface suggested that the ICA joint life depended upon the adhesive failure of the bond to the metal surface. It was observed that fracture strains for the ICAs were in the range of 20–38%, and resistance remained approximately constant in the elastic region, but the resistance started to increase rapidly as soon as the pull-force departed from linear elastic behavior. For fatigue tests, linear displacement was ramped up the preprogrammed maximum displacement and ramp back to the starting position. It was observed that the shear strain for ICA joints surviving 1000 cyclic loading was typically 10%, which is about an order of magnitude greater than solders. This suggests that using conductive adhesives may be advantageous for some flip chip. It is believed that since silver filler particles of
ICAs cannot accommodate this large strain, the silver filler particles must move relative to one another as the epoxy matrix is strained. The most common pattern of resistance change was only increased to a point corresponding to about a 70% loss in interface contact resistance before sudden failure. This was an indication that the interface crack slightly propagated into the adhesive (74).

In an effort to gain a fundamental understanding of the fatigue degradation of ICAs, Gomatam and co-workers (75) studied the behavior of ICA joints under temperature and humidity conditions. The fatigue life decreased at elevated temperature and high humidity conditions. It was also observed that the fatigue life of the ICA joints decreased considerably as the temperature cycle frequency was decreased. This effect was attributed to the fact that as the frequency was decreased, the propagating crack was exposed to higher loads for longer periods of time, effectively resulting in high creep loading (75).

**Improvement of Electrical Conductivity of ICAs**

Electrical conductivity of ICAs is inferior to solders (76). Even though the conductivity of ICAs is adequate for most applications, a higher electrical conductivity of ICAs is still needed. To develop a novel ICA for modern electronic interconnect applications, a thorough understanding of the materials is required.

**Eliminate Lubrication Layer.** An ICA is generally composed of a polymer binder and Ag-flake filler material. A thin layer of organic lubricant is present on the surface of the Ag flakes. This lubricant layer plays an important role in the performance of ICAs, including the dispersion of Ag flakes in adhesives, and the rheology of the adhesive formulations (45, 76–78). The organic layer consist of a Ag salt formed between the Ag surface and the lubricant, which typically is a fatty acid such as stearic acid (78, 79). This lubricant layer affects the conductivity of an ICA because it is electrically insulating (78, 79). To improve conductivity, the organic lubricant layer must be partially or fully removed through the use of chemical substances that can dissolve the organic lubricant layer (78–80). However, the viscosity of an ICA paste may increase if the lubricant layer is removed. An ideal chemical substance (or lubricant remover) should be latent (does not remove the lubricant layer) at room temperature, but be active (capable of removing the lubricant layer) at a temperature slightly below the cure temperature of the polymer binder. The lubricant remover can be a solid short-chain acid, a high-boiling-point ether such as diethylene glycol monobutyl ether or diethylene glycol monoethanol ether acetate, and a polyethylene glycol with a low molecular weight (78–80). These chemical substances can improve electrical conductivity of ICAs by removing the lubricant layer on the Ag-flake surfaces and providing an intimate flake–flake contact (78, 79).

**Increase Shrinkage.** In general, ICA pastes exhibit low electrical conductivity before cure, but the conductivity increases dramatically after they are cured. ICAs achieve electrical conductivity during the cure process, mainly through a more intimate contact between Ag flakes caused by the shrinkage of polymer binder (81). Accordingly, ICAs with a high cure shrinkage generally exhibit the best conductivity. Therefore, increasing the cure shrinkage of a polymer binder is another method for improving electrical conductivity. For ICAs based on epoxy
resins, a small amount of a multifunctional epoxy resin can be added into an ICA formulation to increase cross-linking density, shrinkage, and thus increase conductivity (81).

**Apply Electric Field.** The electrical conductivity of ICAs can be improved significantly by applying an electrical field before or while curing them. However, the exact reasons for this improvement are not yet clear (82).

**Transient Liquid Phase Fillers.** Another approach for improving electrical conductivity is to incorporate transient liquid-phase sintering metallic fillers in ICA formulations. The filler used is a mixture of a high-melting-point metal powder (such as Cu) and a low-melting-point alloy powder (such as Sn–Pb). The low-melting-alloy filler melts when its melting point temperature is achieved. The liquid phase dissolves the high-melting-point particles. The liquid exists only for a short period of time and then forms an alloy and solidifies. The electrical conduction is established through a plurality of metallurgical connections formed *in situ* from these two powders in a polymer binder. The polymer binder fluxes both the metal powders and the metals to be joined and facilitates the transient liquid bonding of the powders to form a stable metallurgical network for electrical conduction, and also forms an interpenetrating polymer network providing adhesion (Fig. 16). High electrical conductivity can be achieved using this method (83–85). The ICA joints formed include metallurgical alloying to the junctions as well as within the adhesive itself. This provides a stable electrical connection during elevated temperature and humidity aging. In addition, the ICA joints showed good impact strength due to the metallurgical interconnection between the conductive adhesive and the components. One critical limitation of this technology is that the numbers of combinations of low melt and high melt fillers are limited. Only certain combinations of two metallic fillers which are mutually soluble exist to form this type of metallurgical interconnections.

**Improvement of Contact Resistance Stability**

Contact resistance between an ICA (generally a Ag-flake-filled epoxy) and non-noble metal finished components increases dramatically during an elevated temperature and humidity aging, especially at 85°C/85% RH. The National Center of Manufacturing and Science (NCMS) defined the stability criterion for solder replacement conductive adhesives as a contact resistance shift of less than 20% after aging at 85°C/85% RH conditions for 500 h (67).

**Causes for Resistance Increase.** Two main mechanisms, simple oxidation and corrosion of the nonnoble metal surfaces, have been proposed in the literature as the possible causes for the increase in contact resistance of ICA joints during elevated temperature and humidity aging. Simple oxidation of the nonnoble metal surfaces is claimed to be the main reason for the observed increased resistance. Corrosion is claimed to be the possible mechanism for resistance increase only by several investigators (65,66,68,86,87). One study strongly indicates that galvanic corrosion rather than simple oxidation of the nonnoble metal at the interface between an ICA and nonnoble metal is the main reason for the shift in contact resistance of ICAs (Fig. 17) (88,89). The nonnoble acts as the anode, and is reduced to a metal ion \( \text{M}^{-n} \rightarrow \text{M}^{n+} \) because of the loss of electrons. The
noble metal acts as a cathode, and its reaction generally is \( 2 \text{H}_2\text{O} + \text{O}_2 + 4 \text{e}^- = 4 \text{OH}^- \). Then \( \text{M}^{a+} \) combines with \( \text{OH}^- \) to form a metal hydroxide or metal oxide. As a result of this electrochemical (corrosion) process, a layer of metal hydroxide or metal oxide is formed at the interface which is electrically insulating, causing the contact resistance to increase dramatically (88,89).

**Prevention.** Galvanic corrosion requires the presence of moisture. An electrolyte solution must be formed at the interface before galvanic corrosion can occur. Therefore, one way to prevent galvanic corrosion at the interface between an ICA and the nonnoble metal surface is to lower the moisture pickup of the ICA. ICAs that have a low moisture absorption generally exhibit more stable contact resistance on nonnoble surfaces compared with those with high moisture absorption (90,91). Without the electrolyte, galvanic corrosion rate is very low. The electrolyte in this case is mainly from the impurity of the polymer binder (generally epoxy resins). Therefore, ICAs formulated with high purity resins should perform better.

**Use of Corrosion Inhibitors.** Another method of preventing galvanic corrosion is to introduce organic corrosion inhibitors into ICA formulations (89–92). In general, organic corrosion inhibitors act as a barrier layer between the metal and environment, forming a film over the metal surfaces (93–96). Some chelating compounds are especially effective in preventing metal corrosion (95). Most organic corrosion inhibitors react with the epoxy resin at a specific temperature. Therefore, if an ICA is epoxy-based, the corrosion inhibitors must not react with the epoxy resin during curing, which would cause them to be consumed and lose their effect. Organic corrosion inhibitors are thoroughly discussed in the literature (94,96). Figure 18 shows the effect of a chelating corrosion inhibitor on the contact resistance between an ICA and a Sn–Pb surface. It can be seen that this corrosion inhibitor is very effective in stabilizing the contact resistance.

**Use of Oxygen Scavengers.** Since oxygen accelerates galvanic corrosion, oxygen scavengers can be added into ICA formulations to slow down the corrosion rate (93). When oxygen molecules diffuse through the polymer binder, they react with the oxygen scavenger and are consumed. However, when the oxygen scavenger is completely depleted, then oxygen can again diffuse into the interface and accelerate the corrosion process. Therefore, oxygen scavengers can only delay the galvanic corrosion process. Similar to corrosion inhibitors, the oxygen scavengers used must not react with the epoxy resin at its cure temperature. The common oxygen scavengers utilized are listed below (93,97–100):

1. hydrazine
2. carbohydrazide
3. hydroquinone
4. oximes
5. gallic acid
6. propyl gallate
7. hydroxylamines and related compounds
8. dihydroxyacetone
9. 1,2-dihydro-1,2,4,5-tetrazines
10. erythorbic acid
Sharp-Edge Filler Particles. Another approach of improving contact resistance stability during aging is to incorporate some electrically conductive particles, which have sharp edges and referred as oxide-penetrating fillers, into the ICA formulations. Force must be provided to drive the oxide-penetrating particles through the oxide layer of adjoining particles and metal pads, and keep them in position. This can be accomplished by employing polymer binders that show high shrinkage when cured (Fig. 19) (101). This concept is used in Poly-Solder which has good contact resistance stability with standard surface-mounted devices (SMDs) on both solder-coated and bare circuit boards (101).

Improvement of Impact Performance

The ability to resist a performance degradation when subjected to mechanical shock is a critical property that solder replacement ICAs must possess. There are ongoing efforts to develop ICAs that exhibit acceptable impact strength, ie capable of passing the standard drop test used to evaluate the impact strength of components attached to a PCB. Among the methods are:

1. Decrease in the filler loading to improve the impact strength (102), and reduction in the electrical conductivity of the conductive adhesives. A development was reported where conductive adhesives were formulated using low modulus resins that absorb the impact energy developed during a drop (103), but the electrical properties was not noted.
2. Conformal coating of the SMDs to improve mechanical strength. A study demonstrated that a conformal coating improved the impact strength of conductive adhesives joints (104).
**Fig. 20.** Changes of tan δ and the storage modulus with temperature of an ETPU-based conductive adhesive as measured by a dynamic mechanical analyzer. To convert MPa to Psi, multiply by 145.

**Epoxide-Terminated Polyurethane Systems.** A class of conductive adhesives based on an epoxide-terminated polyurethane (ETPU) has been developed (105,106). This class of conductive adhesives exhibits properties typical of polyurethane materials, such as high toughness and good adhesion. The modulus and glass-transition temperature of an ICA can be adjusted by incorporating epoxy resins such as bisphenol-F epoxy resins. Conductive adhesives based on ETPU exhibit a broad loss factor (tan δ) peak with temperature changes and a high tan δ value at room temperature. The tan δ value of a material is a good indication of the damping property and impact performance of a material. In general, the higher the tan δ value, the better the damping property (impact strength) of the material. As an example, changes in tan δ and storage modulus with temperature of an ETPU-based ICA are shown in Figure 20. ICAs based on ETPU resins also exhibit a much higher loss factor over a wide frequency range compared to ICAs based on bisphenol-F epoxy resins (Fig. 21). This indicates that ICAs based on ETPU resins should exhibit good damping property and improved impact performance in a variety of electronic packages. This class of conductive adhesives has demonstrated superior impact performance and a substantial improvement in contact resistance stability with nonnoble metal surfaces, such as Sn–Pb, Sn, and Cu (105,106).

**Future Challenges**

**Anisotropically Conductive Adhesives.** Significant research has been conducted on ACAs as a potential solder replacement for some electronics packaging applications. However, many aspects of this technology must be better
understood before it can be widely used to replace lead-bearing solders. Some critical issues that must be addressed in the future are discussed below:

**Materials Development.** Develop new ACA materials that have good adhesion, high $T_g$, fast curing, storage stability at ambient, and stable contact resistance after various conditions frequently encountered in the field such as thermal aging and cycling, thermal shock, high temperature/high humidity/bias, etc. Also, ACAs with low CTE are required. Commercially available ACAs typically exhibit very high CTEs because of the low filler loading levels utilized. Some preliminary studies have shown that ACAs with a low CTE created by introducing nonconductive silica fillers have a lower shear strain and better contact resistance stability during thermal cycling test (107).

**High Frequency Compatibility.** The number of high frequency applications and utilizations are increasing rapidly; thus it is important to characterize the cross talk between particles, coupling with semiconductor devices, and other fundamental behavior of ACAs under high frequency conditions. It is also necessary to maximize the current carrying capability of ACAs at high frequency range, and after exposure to various environment tests.

**Reliability.** It is necessary to understand the effect of the chip carrier material on ACA joint reliability. This is a key issue before ACA technology is widely utilized in manufacturing (ie in high volume and low cost applications). It is also necessary to establish failure rate prediction models for ACA joints for a wide variety of field conditions. It is essential to gain full understanding on effects of high current and high power on ACA joints, degradation, and stress relaxation of polymeric matrices; and the effects of temperature, humidity, and other environments on matrix materials and the effects of fillers.

**Isotropically Conductive Adhesives.** There have also been a significant number of studies to improve ICA technology. However, several critical issues associated with this technology must also be addressed before it can be used as a replacement for soldering technology:
**Electrical Characteristics.** The electrical conductivity of ICAs must be vastly improved since their electrical conductivity is typically 1 or 2 orders of magnitudes lower than that of solders. Silver-filled ICAs achieve their electrical conductivity through a physical contact among the Ag flakes. Because of the high particle–particle contact resistance, ICAs exhibit a high bulk resistivity. Although some preliminary work has been done to improve electrical conductivity by introducing low-melting-point alloys which form metallurgical interconnections with the Ag flakes, additional work is necessary to achieve the desired electrical conductivity. Also, the behavior of ICA joints under high current or high power conditions, and high temperature/humidity/bias is not clear.

**High Frequency Performance.** The high frequency behavior of ICAs over a wide frequency range must be investigated and compared to that of solders.

**Reliability.** Silver-filled ICAs have a potential for silver migration, which cause electrical shorts especially in fine pitch applications. A palladium-treated silver filler exhibited a much improved antimigration characteristics compared to standard silver-filled ICAs. However, the preparation of the Pd-coated silver particles is expensive. Some low cost approaches must be developed. More comprehensive understanding of the fatigue resistance of ICA joints is required. Activities in this area have been limited and nonconclusive.

**Manufacturability and Yields.** Since most commercial ICAs are epoxy based, they are thermosetting materials and thus not reworkable. ICAs with reworkability must be developed by using thermoplastic or thermally degradable resins. Because of their high surface tension, SnPb solders have a self-alignment capability during solder reflow operations. However, conventional ICAs cannot self-align. Therefore, components that are bonded using ICAs require a high placement accuracy. Some preliminary research has been conducted to improve the self-alignment capability of ICAs (108,109), but much more work needs to be done.

**Conductive Polymer Composites with Large Positive Temperature Coefficient**

Conductive polymer composites (110,111) that contain conductive fillers such as metal powder, carbon black, and other highly conductive particles in a nonconductive polymer matrix have been widely used in electrostatic dissipation (ESD) and electromagnetic interference shielding (EMIS). A special group among electrically conductive polymer composites are conductive polymer composites that have large positive temperature coefficients (PTCs), which in some cases are called positive temperature coefficient resistance. The resistivity of this kind of composite increases several orders of magnitude in a narrow temperature range, as shown in Figure 22. The transition temperature ($T_t$) is defined by intersection between the tangent to the point of inflection of the resistivity versus temperature curve and the horizontal from the resistivity at 25°C ($\rho_{25}$). This kind of smart material can change from a conductive material to an insulating material or vice versa upon heating or cooling, respectively. The smartness of this kind of material not only lies in this large PTC amplitude (defined as the ratio of maximum resistivity at the peak or the resistivity right after the sharp increase to the resistivity at
FIG. 22. Resistivity versus temperature behavior of a conductive polymer composite that has a large PTC.

25°C), but also in its reversibility, its ability to adjust the transition temperature, low temperature resistivity, and high temperature resistivity. PTC behavior in a polymer composite was first discovered by Frydman in 1945 (112), but not much attention was paid to it originally. Because Kohler obtained a much higher PTC amplitude from high density polyethylene filled with carbon black in 1961 (113), this kind of temperature-sensitive materials has aroused wide research interest and also led to many very useful applications. In this review, the general theories of PTC conductive polymer are introduced. Carbon-black-filled conductive polymer composites and their PTC behavior are discussed in more detail, in regard to the effects of fillers, the polymer matrix, processing conditions, and additives. At the end, applications of this kind of smart temperature-sensitive material are presented.

**Basic Theory of Conductive Polymer Composites and PTC Behavior.** The conductivity of polymer composites that contain conductive particles dispersed in a polymer matrix may result from direct contact between conductive particles and electron tunneling. The conductivity of a highly filled conductive adhesive is due to the former mechanism. Matsushige used atomic force microscopy to study the conduction mechanism in a PTC composite on a nanoscale (114). It was proposed that electron tunneling or hopping through the conductive carbon particles in the polymer matrix might be the governing mechanism for organic PTC materials.

There are two very simple mechanisms for small PTC behavior of conductive polymer composites: reduction of the contact area of neighboring conductive particles and an increase in the junction distance in electric tunneling when heated. Although the large PTC phenomenon is well known, its mechanism has not been fully understood. Different theories have been proposed (113,115,116) to explain the large PTC behavior.

Kohler (113) suggested that the PTC is due to the difference in thermal expansion of the materials. His theory was supported by some other researchers...
in percolation theory (110). The conductivity of conductive polymer composites increases as the volume fraction of the conductive filler increases. For a polymer filled with conductive particles, a critical volume fraction of filler may exist, which is called the percolation volume fraction. The resistance of the conductive polymer composite whose filler volume fraction is higher than the percolation volume fraction is several orders of magnitude less than that of the composite whose filler volume fraction is less than the percolation volume fraction. In the region of low filler concentration, the filler particles are distributed homogeneously in the insulating polymer matrix. There is no contact between adjacent filler particles. The resistance decreases slowly as the volume fraction of filler particles increases. As the filler concentration further increases, filler particles begin to contact other particles and agglomerate. At a certain filler concentration, the growing agglomerates form one-, two-, or three-dimensional network of the conducting phase within the insulating polymer matrix. At this range, the resistivity of the mixture shows a deep decrease to the low value of the conductive network. After the formation of the continuous conductive network, the resistivity of the mixture increases slowly because of the slightly improved quality of the conductive network as the filler content increases.

Many models have been proposed (117) to explain the electrical conductivity of mixtures composed of conductive and insulating materials. Percolation concentration is the most interesting of all of these models. Several parameters, such as filler distribution, filler shape, filler/matrix interactions, and processing technique, can influence the percolation concentration. Among these models, the statistical percolation model (118) uses finite regular arrays of points and bonds (between the points) to estimate percolation concentration. The thermodynamic model (119) emphasizes the importance of interfacial interactions at the boundary between individual filler particles and the polymeric host in the network formation. The most promising ones are the structure-oriented models, which explain conductivity on the basis of factors determined from the microlevel structure of the as-produced mixtures (120).

Because the thermal expansion coefficient of a polymer matrix is generally higher than that of the conductive particles, the volume fraction of a conductive filler in conductive polymer composite decreases as temperature increases; thus, the resistivity increases. If a conductive polymer composite is made of semicrystalline polymer as an insulator and a filler of conducting particles, whose concentration is just above the percolation volume fraction, the relatively large change in specific volume of the polymer at its melting temperature may bring the volume fraction of the conductive filler down below the critical volume fraction when the composite is heated beyond the melting temperature of the polymer crystal. Thus, the resistivity increases greatly. Kohler's theory cannot explain the very small rise in resistance exhibited by such filled polymer systems when they are strained to an amount equivalent to that found at the crystalline melting point. And the PTC amplitude should be a direct function of volume change according to Kohler's theory; however, it is not the case in reality.

Ohe proposed a more complex theory (115). He stated that PTC phenomenon could be explained by the increase of the intergrain gap among the carbon black particles caused by thermal expansion. He visualized that the distribution of the intergrain gaps in conductive composite is rather uniform at low temperature,
and the gap is small enough for extensive tunneling to occur, but the distribution at high temperature becomes random due to thermal expansion. Although the average gap distance does not change greatly, the presence of a significant amount of gap distance too large to allow electron tunneling will result in a great increase in resistance.

Meyer’s theory was based on the assumption that a thin (300 Å) crystalline film of polymer is much more conductive than an amorphous film of polymer. It was shown that carbon black particles remain in the amorphous region between crystallites in a conductive composite. The high conductivity at low temperature is due to tunneling through the thin crystallite, and the PTC phenomenon is caused by a preliminary change in state of these crystallites just before the crystalline melting point that leads to a sharp reduction in the ease of tunneling and thus much higher resistivity.

Large thermal expansion during crystal melting surely contributes to a large amplitude of PTC behavior. But it contributes only to a limited level. Ohe’s vision of the change from uniform distribution of carbon particle to random distribution is groundless and cannot be justified. Actually, as is shown later, cross-linking can eliminate the redistribution of carbon black after melting and stabilizes PTC behavior. PTC behavior takes place at the same time as melting, rather than before crystalline melting, as stated by Meyer. It probably is true that tunneling is easier in a crystalline region than in an amorphous region. The difference is probably due to polymer chain mobility. The work function of the conductive particle at the interface between the conductive particle and polymer matrix may increase after crystal melting due to the high mobility of the polymer chain. The same theory can explain PTC behavior in conductive polymer composites as well as the conductivity phenomenon in an ECA after curing (80). Before conductive adhesive is cured, the resin matrix has high mobility and prohibits tunneling between conductive particles. After curing, the mobility of the polymer chain is greatly reduced and thus allows tunneling between conductive particles.

Effect of Conductive Fillers on PTC Conductive Polymer. Different conductive fillers have been used as in PTC conductive polymers. Metallic powders that are stable at high temperature, such as tin, gold, and silver, were suggested as conductive fillers in PTC materials (121). In addition, ceramic powder such as tungsten carbide was also used as a filler in PTC conductive polymer composites (122). It was found that V$_2$O$_3$ has several phase transitions (110). At 160 K, it is transformed from an antiferromagnetic insulator (AFI) to a paraelectric metallic conductor (PMC), accompanied by a resistivity change from $10^5$ to $10^{-2}$ Ω·cm. At 400 K, it changes from a PMC to a PI (paraelectric insulator) whose resistivity is $10^3 - 10^4$ Ω·cm. Most interestingly, low density polyethylene filled with V$_2$O$_3$ shows a square well in the resistivity versus temperature profile by combining a sharp NTC (negative temperature coefficient) around $-110^\circ$C, and a sharp PTC around 100°C (110,123–125). A PTC transition temperature of conductive polymer composites filled with V$_2$O$_3$ was also reported in other polymer system (121,122). The $T_1$ of a V$_2$O$_3$-filled system changes in the following manner: 100°C (low density polyethylene) < 150°C (polypropylene) < 260°C (polytetrafluoroethylene). However, the fillers mentioned before are expensive. Work has been done to develop alternative less expensive PTC conductive polymer composites. Most
of the conductive polymers for ESD and EMIS applications are thermoplastics filled with carbon black or carbon graphite because of their very low cost. Carbon black is also one of the major fillers used in so-called PTC conductive polymers (126–128).

There are several important parameters of carbon black (129): particle size (surface area), aggregate structure (carbon black particles aggregate to form a grapelike structure), porosity, crystallinity, and surface functionality. Small particle size and high structure lead to more difficult dispersion. The initial grapelike structure of carbon black formed during the manufacturing of carbon black is highly stable and can be destroyed only by very intensive processing such as grinding in a ball mill. For a given loading of carbon black, a smaller particle size would add more particles to the composite than that using carbon black of larger particle size. Thus, carbon blacks of smaller particle size would produce a composite that has a smaller separation between carbon particles (as well as the probability of more carbon particles in contact), resulting in greater conductivity. Small particle size gives a low critical volume for a carbon-black-filled polymer system (110). However, for fiberlike conductive fillers, large filler particles favor the formation of conducting paths at a low percolation concentration. High structure carbon blacks tend to produce a larger number of aggregates in contact, as well as smaller separation distances that result in greater conductivity. For a given carbon black loading, the more porous carbon black generally provides a larger number of aggregates to the composite. This results in a smaller interaggregate distance and higher conductivity. The increase in the degree of carbon black structuring is found more efficient than the increase of the specific surface of carbon black in conductive polymers. Carbon blacks that have higher oxygen content carbon particles have higher resistance. Removal of the surface oxides increases the conductivity of the original carbon black much more than heat treatment to produce graphitization. Higher graphite content in carbon black leads to higher electrical conductivity.

Although carbon black of small particles size and high aggregated structure (such as BP2000 with an average particle diameter of 12 nm manufactured by Cabot Corp.) can give polymer composites that have low resistivity, this kind of composite does not show large PTC amplitude because the aggregated structure cannot be broken down by the thermal expansion of the polymer (Fig. 23). On the contrary, a polymer composite filled with carbon black that has a large particle size and low aggregate structure (such as N660 with an average particle diameter of 70 nm manufactured by Columbia Chemicals) shows high room temperature resistivity, but high PTC amplitude (130). To obtain a PTC conductive polymer composite that has both lower room temperature resistance and high PTC transition amplitude, porous carbon black is much better than nonporous carbon black. Ueno and co-workers reported that etching a carbon black at an elevated temperature to remove the less crystalline portion and therefore to increase the surface area can improve the PTC characteristics of a conductive polymer filled with carbon black, and this material was suitable for use as a resettable fuse (126).

The PTC amplitude depends on the loading of carbon black. It was shown that for different carbon blacks, a different loading exists at which the composite has a maximum PTC amplitude (131). The carbon black concentration that gives the
Fig. 23. Resistivity versus temperature of conductive polymer composite with different carbon blacks (the weight percentage of carbon black is 30). —— Filled with BP2000 carbon black; - - - - filled with N660 carbon black.

optimum PTC intensity can be predicted approximately from room temperature data (132).

**Effect of Polymer Matrix on PTC Behavior.** Polymers used as the matrix in electrically conductive polymer composites can vary from elastomers to thermoplastics and thermosets that have crystallinity varying between 0 and 80%. As mentioned in the previous section, the large PTC anomaly is due to the large thermal expansion of the polymer matrix, especially during melting of a polymer crystal. The PTC transition temperature is determined by the melting point of the polymer matrix. Because polymers that have low and high melting points are available for use in conductive polymer composites, the transition temperature can be controlled by selecting and compounding the matrix polymer for different applications that require different transition temperatures (133). A PTC conductive composite based on high density polyethylene whose melting peak temperature is 129–131°C and whose specific volume increases by approximately 10% due to melting across a narrow temperature range showed a maximum resistivity at 129–131°C (130). The transition temperature can be slightly adjusted by using a copolymer or polymer blend that has more than one homopolymer. A compound of 40 parts weight of carbon black, 60 parts of melted olefin copolymer (ethylene–ethyl acrylate copolymer), and an organic peroxide, had a $T_t$ of 82°C (114). Another reported recipe (134) is a composite of carbon black dispersed in high density polyethylene and poly(ethylene vinyl acetate), whose $T_t$ is 120°C. Ultrahigh molecular weight polyethylene reportedly enhanced the PTC behavior (127). Thermosetting material such as thermosetting polyester resin that was cross-linked by a free-radical reaction, was also reportedly used as a polymer matrix for a PTC conductive polymer composite (135).

The PTC amplitude depends on crystallinity. Meyer (136) showed that crystalline trans-polybutadiene filled with carbon black has low room temperature resistivity and a significant anomaly, whereas the amorphous cis-polybutadiene filled with the same amount of carbon black has much higher resistivity and no
anomaly. Within a polymeric family, a polymer that is more crystalline has higher PTC amplitude. But different classes of polymers that have the same crystallinity do not exhibit identical PTC behavior and no relationship was correlated. PTC amplitude depends on polymer type. PTC amplitude increases in the following order with respect to the polymer matrix: nylon-6,6 < polypropylene < polyethylene oxide < low density polyethylene < high density polyethylene.

As mentioned before, the mechanism for the PTC anomaly in semicrystalline polymer composites is accompanied by a relatively large change in specific volume of the polymer at its melting temperature. The resistivity versus temperature curve can be well matched by the specific volume–temperature curve. Crystallization during cooling of a polymer is the reverse of melting of polymer crystal during heating. The PTC transition of this kind of smart material is reversible. During cooling, the same material shows a sharp decrease in resistivity, as shown by Figure 24. The thermal expansion of a polymer depends on its heating and cooling cycle. Because the melting temperature of a polymer crystal is always higher than the recrystallization temperature, the PTC transition of a conductive polymer composite is always higher in the heating cycle than that during the cooling cycle (110). The difference is about 18°C for polyethylene, 34°C for polyoxymethylene, and 50°C for polypropylene. Actually, all factors that affect the melting and recrystallization behavior, such as pressure and heating and cooling rates, influence the PTC behavior of a conductive polymer composite. Meyer showed that the PTC transition temperature increases and PTC amplitude decreases as the pressure increases (136).

In some conductive polymer composites, the NTC effect follows, for example, the resistivity decreases as the temperature increases further after PTC transition. The NTC effect is probably due to the reorientation, reaggregation, or reassembling of carbon black. Initially dispersed particles may become mobile in the temperature range of polymer melting to repair the broken percolation network. The measurement of resistance versus the temperature behavior of the conductive

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**Fig. 24.** Resistivity versus temperature for a PTC conductive polymer composite during heating and cooling cycles. —— Heating; ---- cooling.
The composite was repeated for the same sample (134, 137). Tang (134) observed that the PTC intensity and the base resistance decrease with thermal cycles. The reason is obviously reorganization of carbon at the high temperature.

Radiation was used to cross-link a carbon-black-filled conductive polymer composite. The NTC effect can be alleviated or reduced by cross-linking, and the PTC amplitude is stabilized (the resistance at lower temperature is stabilized) after cross-linking (110, 134). The organization of carbon black is hampered in a cross-linked polymer network.

**Effect of Processing Conditions and Additives.** The effect of mixing time on the resistivity–temperature behavior was also investigated (134). Both the PTC effect and the reproducibility were improved greatly when the sample was mixed for a long time. It was suggested that the improvement is due to increasing absorption of the polymer on the carbon black surface and this absorption forms a polymer layer outside the carbon black particle. The room temperature resistivity increases with mixing time at constant carbon black concentration. It can also be explained that structures are broken down during mixing; thus, the resistivity increases. If the power consumption during mixing is too high, the composition would have too high resistivity at a temperature below $T_g$ and have unsatisfactory electrical stability on aging at elevated temperature. If the power consumption is too low, it can also result in a composition that has a low PTC amplitude.

Tang (134) studied the effect of the interaction between carbon black and the polymer on electrical behavior. The absorption of polymer on the carbon black surface may be physical or chemical. The latter is caused by free-radical reaction between the polymer and carbon black, and it can occur during radiation or the preparation of the composite. In carbon-black-filled high density polyethylene, the cross-linked network of the polymer restricts the freedom of movement of carbon black. The free-radical reaction enhances the binding force between the polymer and carbon black.

Polymeric materials may be broken down under high voltage. The voltage stability of a cross-linked PTC conductive polymer is improved by incorporating a polymerizable monomer such as triallyl isocyanurate before it is cross-linked (138). Antimony oxide, which does not degrade the PTC characteristics, can be used as a flame-retardant agent (121). A semiconductive inorganic substance such as silicon carbide or boron carbide was used to improve the high voltage stability (139). Alumina trihydrate can be added to a PTC conductive polymer composite to prevent dielectric breakdown, arcing, and carbon tracking under high voltage (138).

**Application of PTC Conductive Polymer Composite.** There are many applications for PTC conductive polymer composites, including thermistors (122), circuit protection devices (140), and self-regulating heaters (141). Because the material both heats and controls the temperature, it can be used to manufacture a self-regulating heating device. As the temperature increases, the resistance increases, and thus the power decreases. This kind of self-regulating heater can be used to prevent freezing of water and pipes used in chemical processing. It has also been used to manufacture a heater for heating a hot-melt adhesive to seal a cable splice case (142) as well as a hair curler (143). Self-regulating heaters can be
manufactured into different forms. The blanket form of PTC conductive polymer composite can allow precise temperature control across larger areas. This kind of device has been used in the repair of thermally complex aircraft structures (141,144).

Another application of PTC conductive polymers is in over-temperature and over-current protection. A device manufactured from a PTC conductive polymer composite has low resistance and much less resistance than the rest of the circuit; thus it has no influence on normal performance. But at high temperature, these devices become highly resistant or insulating; thus they dominate the circuit, reduce the current, and protect the circuit. For large abnormal current, the device can rapidly self-heat to a high resistance state, and thus reduces the current. The smartness lies in the over-temperature and over-current protection and also lies in its resettability. After the current drops and the temperature of the device decreases, the device returns to a low resistance state and allows current to pass. A resettable fuse made from a PTC conductive polymer has been on the market. This kind of resettable fuse has been used in battery chargers to terminate the charging function based on the battery temperature and protect the battery from overheating. It is also used in telecommunication equipment, computers, and power supplies.

Summary. A temperature-sensitive PTC conductive polymer composite is a true smart material. Its property can be tailored by selecting the filler, polymer matrix, and processing conditions. Its transition temperature is determined by the melting point of the polymer matrix. Its room-temperature resistivity, high temperature resistivity, and PTC transition amplitude can be adjusted by the filler and its combination with the polymer matrix. PTC transition behavior can be stabilized by cross-linking of the polymer matrix. This kind of smart material can be used in many temperature-sensitive applications such as thermistors, self-regulating heaters, and circuit protection devices.

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