Chapter C: Conductive Polymers
LEVEL 1: INTRODUCTION

1.1 INTRODUCTION TO POLYMER BONDING

Electrically conductive adhesives have been used for many years for i.c. die mounting and terminal bonding of components in some types of hybrid circuits. There applications are not particularly demanding on either the properties of the conductive adhesive or on the mounting technology. The advent of Surface Mount Technology (SMT) as applied to large area Printed Circuit Boards (PCB) amounted to a major revolution in Printed Circuit Technology which had seen great progress but few revolutionary developments in a period of over four decades. SMT has certainly included some revolutionary concepts and major changes in the design and construction of components to be assembled. This has mainly related to the replacement of leads by solderable pads. This clearly implied the expectation that solder would be used as the bonding agent in the mounting operation.

It was perhaps inevitable that in due course conductive adhesives should be considered for surface mounting on PCBs. The incentive to consider this development received strong support from environmental considerations relating to the growing awareness of the undesirable aspects of solder technology including the use of cleaning agents for removing the flux and the presence of lead and other heavy metals in the solder itself.

However, the apparently simple step of replacing solder with conductive adhesives has proven to be a complex problem where considerable and growing attention has not as yet solved all of the issues.

The challenges to be faced were the shift to large boards, which were not encapsulated as was the case with i.c. die in their various packages or hybrid circuits, which usually had some form of protection for the added devices. Then there was the variety of components to be bonded, all requiring to be placed with considerable precision and some having a large (and as time went by a rapidly increasing) number of small and closely positioned terminal pads.

Many other relevant parameters have now come under scrutiny such as the flexibility of the joint, which together with such items as expansion coefficient can affect stress levels in the bond and its shear strength. Reliability of the many bonds involved in a surface mounted PCB has become a matter of prime concern. Reworkability is attracting considerable attention and the whole question of recovering residues is now regarded as a matter of crucial importance.

When we now carry out an information retrieval study on the subject, we find that those early papers that are most relevant to the subject at the present time came from technologists and manufacturing companies engaged in adhesive mounting techniques. The pioneering work of Estes and Kulesza
And the papers from Emerson and Cuming and from other manufacturers of conductive adhesives are now reinforced with unfortunately only a few number of papers from major companies in the electronics industry describing their experiences and aspirations in the application of conductive adhesives to their main assembly processes. But still there is a lot of secretiveness in the adhesive world.

After a decade of encouraging development the subject of conductive adhesives has now reached a critical stage. This is no passing phase or a minor fashion in experimental assembly techniques. If current progress continues this technology will become a major factor in electronics manufacture affection all of the many branches of the electronics industry. If the quality and reliability of the process meet the required standard a major reinvestment programme will have to be faced. New manufacturing techniques will involve new test procedures and a new quality and standard structure will be required. Reliability levels at least as high as those that can be achieved today with the best soldering techniques will be established.

The focus is on the use of adhesives as solder alternatives. The process discussion attempts to stay within the bounds of the existing solder assembly infrastructure as much as possible. Both major types of adhesives, isotropic (conduction equally in all directions) and anisotropy (unidirectional conductivity), are covered. The two major divisions of polymer adhesives, thermoses and thermoplastics, are described.

Polymers are long-chain molecules, such as epoxies acrylics and urethanes that are widely used to produce structural products such as films, coatings and adhesives. Although polymers occur naturally, most are now synthesised. Their properties can be tailored to meet thousands of different applications. Polymer-based adhesives are used in virtually every industry because of this capability to customise performance. Polymers have excellent dielectric properties and, for this reason, are used extensively as electrical insulators. Most wire insulation is made from polymers. Although a narrow class of conductive polymers, called Intrinsically Conductive Polymers (ICPs), does exist, their other properties do not lend themselves for use as conductive adhesives. Therefore, adding conductive fillers to non-conductive polymer binders makes virtually all-conductive adhesives.

1.2 ADHESIVE OPTIONS

To realise conductive joints with adhesives, three basic options exist, i.e. the use of isotropic conductive adhesives (ICAs), anisotropy systems (or Z-axis adhesives), either film or paste (ACA(F)), and even non-conductive adhesives (NCA). Several applications already exist for all three areas.
For all three options quite some research and development work is going on and many new possibilities are becoming available.
In the area of isotropic conductive adhesives the preferred systems are the silver files epoxy adhesives. Typical curing times are in the order of 3-10 minutes at 120-150°C. Acrylic and polyamide type adhesives and silicones are also known but have either lower electrical performance or more difficult processing (polyamide). New developments have been reported using thermoplastic materials consisting of high melting plastics (e.g. PES type).
Another interesting development is the use of nanoparticles instead of the present silver flakes in the micrometer range; the electrical performances of these systems, however, needs further improvement.

Anisotropy (or Z-axis) adhesives offer several attractive advantages, e.g. very high resolution potential (pitch down to 50 µm due to the possibility of non-specific application), fast curing, and the possibility of avoiding slow curing underfill in the case of flip chip applications. They have, however, restricted current density and need a pressure contact during curing which makes a broad application for the bonding of SMD components unlikely. Their main strength appears to be for interconnection and flip chip bonding. In this area quite a variety of (new) developments have become available, ranging from Au coated plastic spheres, to Ni particles with oxide breaking power, solder (SnBi) filles systems, ways to increase particle density and reducing the danger of short cuts, by particle orientation or double layer systems. The use of thermohardening resins instead of the formerly used thermoplastic systems also improved electrical behaviour and reliability.
Relatively new developments also are Ag-filled UV-acrylate and UV-initiated epoxy systems making very fast curing at relatively low temperature possible.
Non-conductive adhesives (either UV-curing or thermally curing systems) also have been successfully used for flip chip bonding (on CDs and smart cards) and are under further investigation by several groups.

1.3 GENERAL BENEFITS AND LIMITATIONS OF CONDUCTIVE ADHESIVES

Conductive adhesives are very different from metallurgical solders. These differences produce a large set of benefits that are listed below. Not every adhesive presently has all of the features listed, but conductive adhesives technology has the potential to deliver all of these benefits in a single material.

Benefits:

- Compatibility with a wide range of surfaces including non-solderable ones.
- Low temperature processing; low thermal stress during processing
- Low thermomechanical fatigue; good temperature cycling performance
- Low or no significant VOCs
- No residuals; high surface insulation resistance
- Reduced pre-clean or post-clean requirements; no cleaning agents or washing equipment
- Nolead or other toxic metals.
- Wide processing latitude; easy process control. Finer pitch capability
- Soldermask not required

Limitations:

- Lower mechanical strength
- No component self-alignment
- Some adhesives require special finishes on parts and printed wiring boards
- Higher electrical resistance
- Higher thermal resistance
- More difficult to rework

1.4 CONDUCTIVE ADHESIVES GENERAL

The most common conductive adhesives are silver-filled thermosetting epoxies that are typically provided as thixotropic pastes. They are used to electrically interconnect and mechanically bond components to circuits. Heat is most often used to activate a catalyst or co-reactant hardener that converts the paste to a strong, electrically conductive solid. The products, which conduct equally in all directions, are referred to as isotropic conductive adhesives. These metal-filled thermosetting conductive adhesives have been used as die attach materials for many decades and are still the most popular products for bonding ICs to lead frames. More recently metal-filles thermoses have been formulated as component assembly materials. New polymer-based materials are now being used to replace metallurgical solders, especially for surface mount assembly.

A number of other types of adhesives have also been developed. Silver-filled thermoplastic adhesives are available in both paste and film form. The films have found use primarily as die attach adhesives. Thermoplastic pastes are made by dissolving polymer resins into solvents and then adding conductive fillers. Some of the commercially available thermoplastic conductive pastes can be used for component assembly adhesives, but their properties are typically not as well-suited as the thermosets. This guideline will therefore focus on thermoset systems for isotropic type adhesives. Both thermoset and thermoplastic processing will be covered for anisotropic adhesives since both types and mixed polymer systems are widely available at this time.

Anisotropic conductive adhesives represent the other major division of polymer bonding agents. The anisotropic adhesives can provide uni-directional conductivity which is always in the vertical, or Z-axis. The directional conductivity is achieved by using a relatively low volume loading of conductive filler. The low volume loading, which is insufficient for inter-particle contact, prevents conductivity in the plane of the adhesive. The Z-axis adhesive, in film or paste form, is placed between the surfaces to be connected. Application of heat and pressure to this stack up causes conductive particles to be trapped between opposing conductors on the two adherents. Once electrical continuity is produced, the dielectric polymer binder is hardened by thermally initiated chemical reaction (thermosets) or by cooling (thermoplastics). The hardened dielectric polymer holds the assembly together and helps maintain the electrical contact between conductors and particles. Anisotropic adhesive products are now being used to connect flat panel displays, TAB, flip chips and fine pitch SMDs. Since anisotropic adhesives generate different characteristics and require special equipment and processing, they will be covered seperately in more detail later**.**

1.4.1 Materials - Types of polymers

1.4.1.1 Thermoplastics

The introduction briefly discussed the basic types of polymers, thermoses and thermoplastics. Thermoplastic binders, those polymers that are already polymerised, have not found widespread use for component assembly, as have the thermoses isotropic type conductive adhesives. One problem is that useful thermoplastics are solids that must either be melted or dissolved in solvent to be used. Very limited use of isotropic thermoplastics has occurred in calculators, but the difficulty in application has severely limited them.

Anisotropy conductive adhesives do use thermoplastic binders since they do not require selective application. Most anisotropy products are provided in film form. The material is used by first applying it to the circuit (and sometimes to the component). Since electrical conductivity only occurs in the Z-axis where opposing conductors are forced together, the film can be applied to the entire circuit. Assembly is accomplished by forcing components against the adhesive-coated circuit conductors while adding heat. A thermoplastic binder will soften and bond to the adherents. Thermoplastic materials can also be mixed with thermosetting polymers to allow lower temperature assembly by higher temperature performance. It should be emphasised that thermoplastics can be re-melted. They are not altered during the assembly heating process like thermoses. They also have excellent storage characteristics and do not require refrigeration like the one-part thermoses.

<LINK TO 2.2.5>

1.4.1.2 Thermosets

Thermosetting polymers are true to their name. Heat “sets” them and permanently changes the properties. Most thermosetting systems, especially the pastes used for isotropically conductive adhesives, are polymer precursors (ingredients that will polymerise). Epoxies typically consist of a low weight liquid with reactive epoxy groups and a co-reacting hardener. The addition of heat causes the two ingredients to chemically react forming very high weight, cross-linked polymers. Crosslinks, or chemical bonds between adjacent chains, produce the thermoses characteristic of shape retention on heating. The thermoplastics are made up of polymer chains that are independent (not linked). Heat allows the individual chains to move past one another and to be reshaped. The re-application of heat again softens the thermoplastic making them somewhat analogous to solder. The three-dimensional network of cross-links in the thermoses prevents chain movement.

Thermoses adhesives are provided as both singlecomponent (one-part) and as unmixed two-part is stable almost indefinitely. Prior to use, the ingredients must be mixed, however. This often introduces air, a serious problem, and user may not have the equipment to produce good mixing. Both users and manufacturers prefer one-part systems. The one-part system’s major disadvantage is that the mixed system has a limited storage life unless refrigerated. Recalling that a chemical reaction rate increases for every 10°C, the converse is also true. Refrigeration slows the polymerisation rate to a level where storage can be extended to six months or more. While it is possible to make up systems that are stable at room temperature, higher temperatures over extended times are required for curing. However, improvements in catalysts and hardeners continue and pot life, now up to six days at room temperature for some of the products that cure quickly (3-6 minutes) even as low as 130-150°C, can be expected to continue to improve.

<LINK TO 2.2.4>

1.4.1.3 Fillers

Silver is by far the most popular conductive filler, although gold, nickel, copper and carbon are used. Metal-plated con-conductors are also used, especially for anisotropy adhesives. Silver is unique among all of the cost-effective metals by nature of its conductive oxide. Oxides of most common metals are good electrical insulators and copper powder, for example, becomes a poor conductor after ageing. Nickel and copper-based adhesives do not have good stability. Even with antioxidants, copperbased materials will show and increase in colume resistively and ageing, especially under high humidity conditions. Silver-plated copper has found commercial application in conductive inks and this type of filler should work in adhesives as well. While composites made with pure silver particles often show improved conductivity when heat aged, exposed to heat and humidity or thermal cycled, this is not always the case for silver-plated metals, such as copper flake. Presumably, the application of heat and mechanical energy allows the particles to make more intimate contact, but the silver-plated copper may have coating discontinuities that allow oxidation of the copper.

Fillers for anisotropy conductive adhesives are often very different from those for isotropic adhesives. There is usually only one layer of conductive particles between the two adherents in anisotropy configurations. The conductive particle makes a mechanical contact between the conductors with the polymer binder supplying the tensional force. Although both hard and soft conductors are being used, most systems have moved toward resilient particles that deform and act like small springs. The most common type has a plastic core that is over-coated with a good conductor like gold or silver. The most popular conductive particle is a polymer sphere that has been first plated with nickel and then pure gold.

<LINK TO 2.2.6>

1.5 BASIC TYPES OF CONDUCTIVE ADHESIVES

1.5.1 Intrinsically Conductive Polymers (ICP)

Although polymers are natural electrical insulators, especially molecular structures can impart conductivity. Electron-dense multiple double and triple chemical bonds are typically used in the ICP structure. However, theirs multi-bond structures tend to produce rigid, insoluble polymers that are difficult to use. The multiple bonds and fused ring structures found in all of the common ICPs tend to be sensitive to oxidation. The instability in air, brittleness and difficulty of application, make ICPs mostly a lab curiosity at this stage, but there is hope that new conductive structures may someday lead to useful products. A thermoplastic, highly conductive polymer could become the preferred joining material in the future. But for now, only the conductor-filled adhesives are viable.

1.5.2 Isotropically Conductive Adhesives

The isotropic adhesives have been around for many decades as pastes applied by painting, screen printing, stencilling, needle dispensing, pin transfer, pad printing and other less common approaches. Polymer binders have included natural resins, polyesters, urethanes, polyamides, vinyls, phenolics, acrylics, epoxies and every other polymer that has reasonable properties. Epoxies clearly dominate and re likely to maintain that role because of their balance of good properties, wide availability, moderate cost and relative safety of use.

Isotropic adhesives must be applied only where needed since they conduct in all directions like solders. The need to apply isotropic selectively makes their rheology very important. Most products are thixotropic pastes with viscosity's ranging from about 100,000 to 500,000 CPS and higher. The thixotropic nature of most of these adhesives, the reversible lowering of viscosity when shear force is applied, allows these thick pastes to be cleanly printed without bleed or slumping. The thixotropic indes, the ratio of viscosity at a low and a higher shear rate, is a common measure of thixotropy. All common methods used for solder paste work equally well, or even better, for isotropic adhesives. The isotropic class should be considered as the polymer alternative to solder paste.

<LINK TO 2.2.1>

1.5.3 Anisotropic Conductive Adhesives

1.5.3.1 Patterned Conductive Type

A limited number of vendors are starting to supply patterned conductor products. These materials are more difficult to make and must have dimensional stability not required of the random type products. Conductors are located in a repeat pattern such as 1.5-mm centres. One issue is that of providing standard patterns, unless they are custom. The proliferation of so many surface mount packages made it impractical to provide patterned patterns for all of these packages. The advent of area array packages, such as the Ball Grid Array (BGA), now makes it possible to produce a limited number of standard repeat patterns that match virtually all of the popular BGAs. Today, there are only a few common and proposed pitches: 0.5 (micro BGA), 1.0, 1.5 and 1.75 mm centres. Sheets of patterned conductor anisotropy films with these patterns can be died cut to match any packages. Thermoses, thermoplastic and mixed systems are being offered. Some companies are willing to make custom patterns that match package and bare die footprints. While it is too early to tell if the patterned anisotropy's will deliver the superior performance promised, there are several potential benefits over random type materials. We should expect better electrical performance from the patterned system since all conductors are positioned exactly where the required connection sites are located. The random materials place isolated conductive particles between conductor traces where the can degrade signals. A lower resistance junction should be expected from the patterned materials since more conductors are placed between the mating connections. On the negative side, patterned films must be aligned with the component, thus adding and additional registration step.

1.5.3.2 Random Conductor Type

The majority of anisotropic conductive adhesives are made by randomly dispersing conductive particles in a polymer adhesive. The simplicity of the manufacturing process, essentially just mixing conductive particles in a resin vehicle, accounts for the wide availability of the product. While a large number of different polymer systems are in use, a relatively few types of conductors are employed. Most products use small (0.0032-0.00048 mm) particles of either pure metal or metalled polymer spheres. There are a few variations on the theme such as solder powder, which can fuse to the adherents, and polymer-coated metal that allows higher loading. Most suppliers offer films while only a few sell pastes. The pastes can be catalysed one-part or two-component systems that are mixed prior to use. Films are provided as custom performs, strips of various widths and rolls. The most common form factor is adhesive film on a release liner with a second release liner on top.

<LINK TO 2.2.3>

1.5.4 Non-conductive Adhesives Used for Electrical Connections

Non-conductive adhesives, primarily dielectric liquids, have been used to mechanically mate flip chips to circuitry. The component must have raised bumps so that there is some clearance under the die or package. The adhesive shrinks during curing to pull the component or bare die to the circuit. The electrical contact is directly through the package or die terminations to the circuit lands. The adhesive serves a mechanical and protective function only.

<LINK TO 2.2.2>

1.6 WHY LOOK FOR ALTERNATIVES TO SOLDER?

Solder has been used for making electrical joints for many years, but in spite of the long period of experience with this material there are still some problems not fully overcome. Some of the most **relevant problems due to** soldering SMDs onto rigid PCBs are:

* Solder joint stress cracking
* Thermal mismatch problems
* Leaching
* Environmental aspects

1.6.1 Solder joint stress cracking

Stress cracking of solder joints can occur due to mechanical stress. This means that flexing of a rigid board after the assembling process can cause solder joint stress cracking. Furthermore, continuing thermal cycling in such a way that the joint becomes brittle can effect the microstructure of the joint. Also the different values of the coefficient of thermal expansion (CTE) of solder, substrate and component can be the cause of solder joint stress cracking as described below.

1.6.2 Thermal mismatch problems

Thermal mismatch can cause damage to an encapsulated die as well as cracks in the encapsulation material. During the soldering process the components are exposed to high temperatures. A component is a composition of different materials each characterised by a specific value of the coefficient of thermal expansion. This more or less leads to a build-up of stress in the component and/or the joint when soldered or exposed of thermal shocks/cycling resulting in the risk of cracks, sharp pointed filler particle degradations etc.

1.6.3 Leaching

The terminations of some types of passive components contain silver. This is for example the case for several ceramic multilayer chip capacitors. Hot solder has the ability of dissolving this silver leading to a porous metallization or simple demetallization and thereby a poor connection.

1.6.4 Environmental aspects

Today the soldering technique involves the use of fluxes containing different kinds of chemicals, e.g. organic solvents, colophon or a synthetic resin, amino-ethyl ethanolamine or fluoride and alkaline substances, solder, containing lead, and CFCs for cleaning remaining flux after soldering.

1.6.4.1 Flux

With regard to flux the internal environment is of greatest concern. It is known that vapours containing colophon can cause asthma and allergy [C54].

1.6.4.2 Lead

Lead as a heavy metal is of concern when exposed to the environment. When modern SMT soldering techniques are used the amount of solder waste is more or less related to contaminated solder baths (wave soldering) and a minor amount as residuals in the containers in which the solder is delivered. However, to consider the isolated assembling process is not sufficient if any statement should be given about the environmental aspects related to **the use** of lead containing solder. It is important to take into consideration the pollution caused by the production of the raw materials, the consumers' use of the product and finally from recycling or disposal of the discarded product. It is this last part of the product's life cycle that is of special concern in relation to the use of lead containing solder - every time an assembly is discarded the lead will end in the environment in one form or another. Furthermore, the lead is of concern in relation to the working environment.