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# EPOXY CURING INHIBITION BY RESIDUAL FLUX ON A FLEXIBLE PRINTED CIRCUIT IN THE FLIP-CHIP PACKAGING PROCESS

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A Thesis Submitted in Partial Fulfillment of the Requirements
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| Field of Study | Chemical Engineering |
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ดวงกมล เจตนาไทกุล : การยับยั้งการแข็งตัวของอีพอกซีโดยคราบฟลักซ์ตกค้างบนแผงวงจรไฟฟ้าแบบยืดหยุ่นในกระบวนการประกอบแบบฟลิบชิบ. (EPOXY CURING INHIBITION BY RESIDUAL FLUX ON A FLEXIBLE PRINTED CIRCUIT IN THE FLIP-CHIP PACKAGING PROCESS)
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งานวิจัยนี้ศึกษาหาสาเหตุการแข็งตัวไม่สมบูรณ์ของอีพอกซีโดยคราบฟลักซ์ตกค้างบนแผงวงจรไฟฟ้าแบบยืดหยุ่นในกระบวนการประกอบแบบฟลิบชิบ ในกระบวนการประกอบแผงวงจรไฟฟ้าแบบยืดหยุ่นนั้นประกอบไปด้วยกระบวนการพิมพ์ตัวประสานชนิดไร้สารตะกั่วลงบนบริเวณที่เป็นทองแดง จากนั้นทำการฉีดอีพอกซีบริเวณด้านข้างอุปกรณ์อิเล็กทรอนิกส์ (วงจรเบ็ดเสร็จ) และปล่อยให้ไหลเข้าไปในช่องว่างใต้วงจรเบ็ดเสร็จ ปัจจุบันขนาดอุปกรณ์อิเล็กทรอนิกส์มีแนวโน้มเล็กลงเรื่อยๆ ดังนั้นระยะระหว่างบริเวณที่มีตัวประสานและบริเวณที่มีอีพอกซีจะใกล้กันมากขึ้น การสัมผัสระหว่างคราบฟลักซ์ตกค้างหลังจากผ่านกระบวนการให้ความร้อนและอีพอกซีนั้น เป็นผลให้เกิดการแข็งตัวไม่สมบูรณ์ของอีพอกซีเมื่อผ่านกระบวนการอบให้ความร้อน การศึกษาเริ่มด้วยการหาเครื่องมือ และวิธีการวิเคราะห์คุณสมบัติการแข็งตัวของอีพอกซี ในการศึกษานี้ ใช้เครื่องมือวัดการเปลี่ยนแปลงปริมาณพลังงานความร้อนของตัวอย่างกับตัวอ้างอิง เครื่องมือวิเคราะห์สมบัติเชิงกลความร้อน เครื่องมือวิเคราะห์สมบัติเชิงกลพลวัต เครื่องมืออินฟราเรดฟูเรียทรานสฟอร์ม พบว่าเครื่องมือวิเคราะห์สมบัติเชิงกลความร้อนสามารถบอกความแตกต่างของการแข็งตัวของอีพอกซีได้ชัดเจนกว่าวิธีการอื่นๆ และเครื่องมืออินฟราเรดฟูเรียทรานสฟอร์มแสดงให้เห็นว่าความเข้ากันไม่ได้ของคราบฟลักซ์ตกค้างและอีพอกซีนั้นเป็นตัวยับยั้งการแข็งตัวของอีพอกซี การศึกษาต่อไปยังแสดงให้เห็นว่าพอลิเอทิลีนไกลคอลเป็นองค์ประกอบในฟลักซ์ที่ส่งผลให้เกิดปัญหาการแข็งตัวไม่สมบูรณ์ของอีพอกซี และการศึกษากระบวนการเพื่อหาวิธีการลดคราบฟลักซ์ตกค้างโดยการปรับเปลี่ยนตัวแปรต่างๆ ในกระบวนการให้ความร้อนกับตัวประสาน พบว่าไม่สามารถกำจัดคราบฟลักซ์ตกค้างบนแผงวงจรไฟฟ้าแบบยืดหยุ่นได้ และวิธีการที่ดีที่สุดในการแก้ไขปัญหาการแข็งตัวไม่สมบูรณ์ของอีพอกซี คือการล้างคราบฟลักซ์ตกค้างด้วยน้ำที่ได้รับการกำจัดไอออนออกก่อนเข้าสู่กระบวนการฉีดอีพอกซี

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This study investigates the root cause for epoxy uncuring problem from residual flux on the flexible printed circuits (FPCs) in the flip-chip packaging process. In the FPC assembly, lead-free solder paste is printed on a copper pad. Then, epoxy is filled underneath the IC die by dispensing from the side of the die. Nevertheless, since the product size in the present day is so small that the distance between solder pad and the underfill area becomes very close. The contact between flux residue generated after the heat treatment of the solder (i.e. reflow process) and the underfill epoxy results in uncuring problem of the epoxy. In this study, epoxy curing was also studied by using Differential Scanning Calorimetry (DSC), Thermo Mechanical Analysis (TMA), Dynamic Mechanical Analysis (DMA), and Fourier Transform Infrared Spectroscopy (FT-IR). The results showed that TMA can identify epoxy curing clearer than other methods. FT-IR analysis show that incompatibility between the flux residue and epoxy inhibited the cross linking of the epoxy. Further analysis also suggested that polyethylene glycol is the composition in flux that is responsible for the uncuring problem. Then attempts were made to reduce the flux residue by adjusting the reflow profile (both temperature and time) and finding the appropriate process for the industries. Moreover, the change in reflow conditions could not completely eliminate the flux. The best way to solve this problem is the cleaning of the residual flux by de-ionized water before the underfill process.

Department : …..Chemical Engineering….. Student's Signature ………………………………
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# CHAPTER I

# INTRODUCTION

## 1.1 Introduction and Rational

Flexible printed circuit (FPC) assembly technology is increasingly used to replace hard board so called Printed Circuit Board (PCB) in many applications such as hard-disk drive (HDD), automotive, communication and consumer electronics (CE). The reasons are thinner, lighter and curveable so that it can fit into compact, dense and complex design of current products. Moreover, it delivers same reliability as PCB does. Microelectronic devices (FPC assembly) contain many electrical circuit components, including transistors assembled in integrated circuit chips, resistors, and capacitors. These electronic components are interconnected to form circuits, which are eventually connected to and supported on a substrate [1]. The connections are made between electrical terminations on the electronic components and corresponding electrical terminations on the substrate. In general, in term of process flow shown in Figure 1.1, it starts with printing the solder paste onto FPC then placing the components (passive components and connectors) onto the printed pads. Next step is picking the die which is an integrated circuit (IC) without packaging and dipping it into tacky flux and placing on the FPC. This specific die pick-and-place process is originally called “Flip-Chip”. Then, the FPC is passed through reflow to melt solder and interconnect components to substrate. As die is small and can crack easily, bump interconnection alone is not strong enough to stand the whole lifetime. Therefore, underfilling or a process to dispense epoxy to cover die is applied. After curing, this epoxy will increase strength of interconnection as well as reliability of the product.

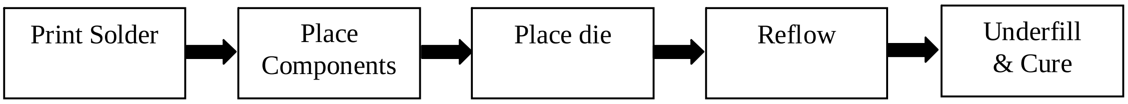


**Figure 1.1** Flow diagram of general assembly process.

As mentioned earlier, key reasons to change from PCB to FPC are smaller, lighter, and thinner products. So, most of the components are also changed to smaller size. However, there is one more factor which comes together with these said changes, namely “performance”. All electronic devices aim to increase the performance by increasing the operation speed and/or frequency. To allow the devices to reach high performance by running at higher speed and higher frequency, all components are needed to be placed as close as possible to each other to reduce the traveling time and to get quick response to signal.

Since the trend of products in the market follows this direction, it is a homework for all manufacturers to find appropriate technology and process to fit in this change and still competitive in term of price. The best solution is simply relying on current processes and fine-tuning only if necessary.

For the change from PCB to FPC, each step of the processing process is considered. It is found that there is no problem with the stencil used in the solder printing process. Instead, the problem should come from solder paste. There are several types of solder paste that are available in the market to choose and fit to our requirement of both metal beads and flux paste. For metal beads, we can choose “Lead alloys” or “Lead-free alloys”. We can also choose from wide range of melting point depending on our applications. Flux paste also has several choices such as no-clean type or water-soluble type. For pick-and- place machine to service both Surface Mount Devices (SMD) and Flip-Chip, there are many choices available, just consider suitable accuracy from $\underline{+}9$ to $\underline{+}75$ μm @3σ ($\underline{+}9$ μm with distribution of three standard deviations). Reflow equipment also has many variations such as 4 zones, 8-9 zones and 12 zones, depending on a speed of reflow conveyor. We can also choose the reflow process with or without nitrogen feature.  Underfill process needs a dispenser to dispense “underfill encapsulant” or simply called “epoxy”. Nowadays, there are several technologies of pump such as piston or jetting-type to improve dispensing performance and fit into different applications. Epoxy is a very important material as it helps strengthen the Flip-Chip packaging and improves reliability by reducing the strain on the solder bumps during thermal cycling imposed by difference in the coefficient of thermal expansion (CTE) between the die and the substrate [2].

After careful consideration, no problem is found on each process, e.g. solder printing, component pick-and-place, flip-chip, reflow, and underfill process. However, a big problem is found when the subsequent process is considered. This problem is the interflow of epoxy and flux residue that causes “Uncured Epoxy”.

As the space between components is limited, the area for printed solder paste becomes close to the flip-chip area. Moreover, post reflow will leave flux residue in certain amount. When epoxy is dispensed, interflow of these two materials will occur. It has been found that this flux disturbs to cross linking process of epoxy during curing.

## 1.2 Purposes of This Study

1) To investigate the root cause of uncured underfill encapsulant problem on the flexible printed circuits (FPCs) in the flip-chip packaging process.

2) To find the appropriate method and process to solve the uncured behavior.

This present thesis is organized as follows. The background and scopes of the study are described in Chapter I. The theory of this research, studies about background and historical overviews of the solder paste, underfill material, flip-chip process, reflow process, and underfill process are presented in Chapter II. Chapter III reviews research works on the chemical and physical properties of underfill material, curing behavior by using thermal analysis techniques, effects of materials on the epoxy properties, and the solder paste composition. Chapter IV describes details of the experimental studies including sample preparation and evaluation method. The experimental results, including an expanded discussion, are described in Chapter V. Chapter VI contains the overall conclusions drawn from this work and some recommendations for future work. Finally, the data of the experiments from this study are summarized in Appendices at the end of this thesis.

# CHAPTER II

# THEORY

## 2.1 Solder Paste

Solder paste, which is widely used in the Surface-Mount Technology (SMT) assembly process as the joining material, is a cream-like mixture of solder powder and flux/vehicle system [3]. Solder is a metallic alloy. The most well known alloy is Sn/Pb (63/37), which is a cost-competitive mature alloy for all electronic applications. However, once the environmental legislation on hazardous materials is strictly applied and controlled by international organizations, Pb is one of the restrict materials. This drives the whole electronic industry to change. The new alloys have been introduced as “lead-free solder”. Lead-free solder is an alloy which has no composition of Pb. Examples of lead-free alloys are Sn/Cu, Sn/Ag/Cu, Sn/Ag/Bi, and Sn/Bi/Zn [4]. Key considerations for selection of the solder are cost, availability of material, melting point, and reliability. The first factor to be considered by engineering prospect is the melting temperature because the substrate and components have a limitation in term of level of temperature and duration that they can endure. The simplest way is finding the new alloy which has melting point as close as possible to the existing solder to minimize the changes. According to the study of solder paste manufacturers, new possible alloy has melting point in the range of 200-240?C (Figure 2.1). This number is acceptable for most assembly house because there is no need to change machines such as reflow and the temperature does not cause damages to substrate and components.

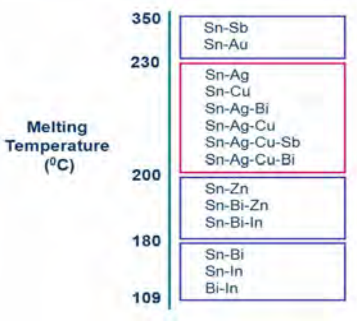
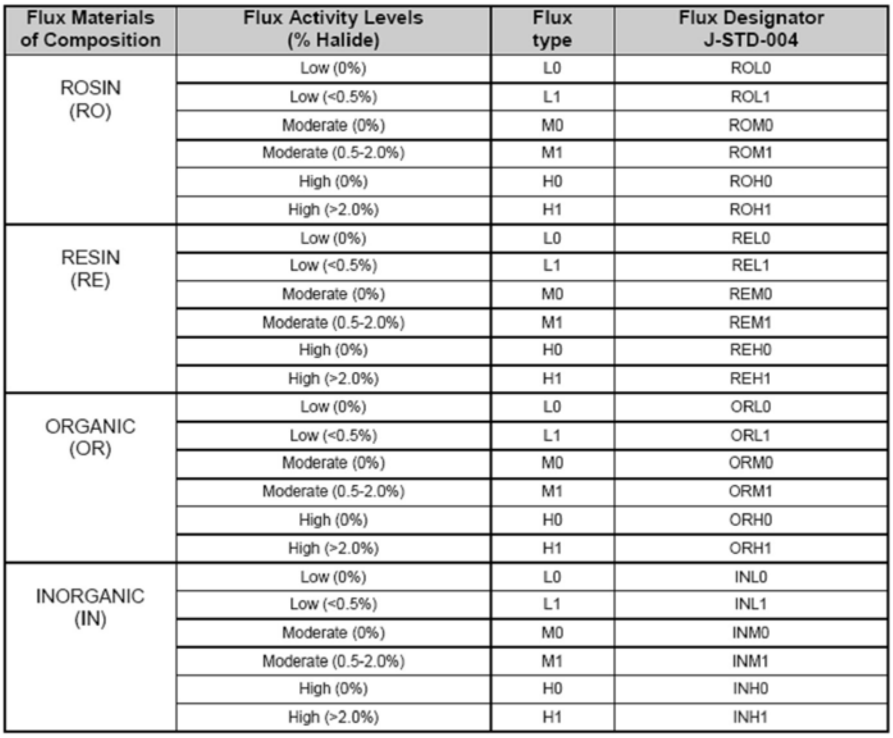


**Figure 2.1** Melting temperature of lead-free solder paste ranged by alloy type [4, 5].

Aside from serving as the source of solder material that forms the mechanical and electrical connections between the Surface Mount Devices (SMD's) and the board, the solder paste also serves the following functions: keeping the components in place on the board prior to the reflow process, cleaning the solder landing sites on the board as well as the external interconnections of the components, and preventing these solder pads and device interconnections from oxidizing until the soldering process is completed. There are several things to consider regarding the choice of the right solder paste. These solder paste selection criteria include: the size of the solder alloy particles in the solder paste, the properties of the flux medium, the design of the stencil to be used, the paste printing parameters to be used, and the tendency to form voids and other defects. Nevertheless, reliability tests must confirm that the solder paste is reliable [6].

Flux is a chemical agent which works with solder in order to prepare surface of soldering by promoting solderability and wetability. Flux is indeed a mixture of flux vehicle and activator. Flux vehicle functions as a carrier and the function of activator is to remove oxide and other contamination on the surface to be soldered and to promote solderability. For soldering flux, it is common practice to use same standard of flux, i.e., ANSI/J-STD-004. There are four categories of flux by material composition, Rosin (RO), Resin (RE), Organic (OR) and Inorganic (IN). Additional consideration is the level of flux activity, which is also classified in the standard. Both are shown in Table 2.1 [7].

**Table 2.1** Classification of fluxes according their activation and halide level [7].



| Flux Materials of Composition | Flux Activity Levels (% Halide) | Flux type | Flux Designator J-STD-004 |
|---|---|---|---|
| ROSIN (RO) | Low (0%) | L0 | ROL0 |
| | Low (<0.5%) | L1 | ROL1 |
| | Moderate (0%) | M0 | ROM0 |
| | Moderate (0.5-2.0%) | M1 | ROM1 |
| | High (0%) | H0 | ROH0 |
| | High (>2.0%) | H1 | ROH1 |
| RESIN (RE) | Low (0%) | L0 | REL0 |
| | Low (<0.5%) | L1 | REL1 |
| | Moderate (0%) | M0 | REM0 |
| | Moderate (0.5-2.0%) | M1 | REM1 |
| | High (0%) | H0 | REH0 |
| | High (>2.0%) | H1 | REH1 |
| ORGANIC (OR) | Low (0%) | L0 | ORL0 |
| | Low (<0.5%) | L1 | ORL1 |
| | Moderate (0%) | M0 | ORM0 |
| | Moderate (0.5-2.0%) | M1 | ORM1 |
| | High (0%) | H0 | ORH0 |
| | High (>2.0%) | H1 | ORH1 |
| INORGANIC (IN) | Low (0%) | L0 | INL0 |
| | Low (<0.5%) | L1 | INL1 |
| | Moderate (0%) | M0 | INM0 |
| | Moderate (0.5-2.0%) | M1 | INM1 |
| | High (0%) | H0 | INH0 |
| | High (>2.0%) | H1 | INH1 |

In addition to liquid or paste form, fluxes come in three primary types of formulations, i.e., rosin based, water-soluble, and no-clean fluxes, each of which has different requirements for post-solder cleaning [8].

Rosin-based fluxes use rosin, a naturally occurring resin found in pine tree sap. Traditional rosin-based fluxes leave residues on the circuit board that is often removed with a cleaning solvent such as Freon or trichloroethylene. Semi-aqueous and saponified aqueous cleaners can also be used to remove residues left by many rosin-based fluxes. Prior to when the Montreal Protocol was signed and concerns over health issues relating to the use of chlorinated solvents became prevalent, rosin-based fluxes were the most commonly used type of flux in the electronics manufacturing industry.

Water-soluble fluxes have been available for decades. They leave a residue behind that must be removed by water. Water-soluble fluxes are among the most active fluxes available today. They are good at removing oxidation and providing a clean surface that will promote solder flow. Issues such as corrosion and other failures relating to higher humidity must be addressed when these fluxes are used. In addition, because of their high activity, which is a result from high halide content in some cases, residue from the water-soluble flux can cause sustained corrosion and electrical problems if it is not adequately cleaned. Water-soluble flux is an organic by standard.

No-clean fluxes have been available for almost a decade but they have become more widely available, with dozens of products available from vendors, in the 1990s. These fluxes are based on a wide range of chemistries and composition, but all share the characteristics of leaving a minimal and theoretically benign residue on electronic assemblies that does not have to be removed with any post-solder cleaning process. Many of these products contain much lower solids content than traditional fluxes — 2-3% by weight as opposed to 25-35% by weight from the traditional fluxes. No-clean fluxes are sometimes used in conjunction with an inert atmosphere such as nitrogen to further reduce the potential for oxidation during soldering. However, no-clean fluxes can be difficult to implement because the "process window" of acceptable operating parameters becomes smaller due to the lower activity of the no-clean fluxes.

Selection of fluxes depends upon applications and requirements. For example, consumer products with low level of cleanliness and reliability can employ “No-clean flux”. On the other hand, products, for in a chamber of hard disk drive (HDD) which requires high level of cleanliness and reliability, we should select cleaning type, e.g. either water-soluble or chemical clean fluxes.

The flux of the solder paste must have rheological properties that allow high-yield printing at very fine pitches. The flux must also exhibit excellent chemical activity for removing the thin oxide films and other contaminants from the surfaces of the metals being soldered.  The flux must be easy to activate thermally, but should not decompose easily. It must also form benign residues that are quickly removed by washing.

Once the electronic industries change to lead-free solder alloy, flux also need to be considered accordingly. For the change in the melting point of solder, it is not big consideration for fluxes because there is only small change so that the current flux still works well. The most impact is “solderability”, which is ability of solder to flow or wet on the substrate. Lead-free solder does not flow well comparing to Sn/Pb alloy. So, flux manufacturers have to adjust chemical formula to improve solderability and wettability of the lead-free soldering.

## 2.2 Epoxy

Epoxy or polyepoxide is a thermosetting epoxide polymer that cures (polymerizes and crosslinks) when mixed with a hardener. Most common epoxy resins are produced from a reaction between epichlorohydrin and bisphenol-A. The first commercial attempt to prepare resins from epichlorohydrin was made in 1927 in the United States. Credit for the first synthesis of bisphenol-A based epoxy resins is shared by Dr. Pierre Castan of Switzerland and Dr. S.O. Greenlee in the United States in 1936. These materials were characterized by terminal epoxide groups and were the germination of the epoxy family of plastics. The commercial production and introduction of this family occurred in 1947 [9]. Epoxy resins are used as adhesives, high performance coatings and potting and encapsulating materials. These resins have excellent electrical properties, low shrinkage, good adhesion to many metals and resistance to moisture, thermal and mechanical shock.

### *2.2.1 Epoxy Composition*

Epoxy consists of three components that react to form a hard and inert material. Three components are epoxy resin, curing agents, and filler. Epoxy resin is a molecule containing more than one epoxide group. Figure 2.2 shows molecular structure of epoxide group. Epoxy resin may be present in an amount 25-100 wt% based on the organic components presented. Suitable resins include epoxy resin such as cycloaliphatic epoxy resins, bisphenol-A type epoxy resins, bisphenol-F type epoxy resins, novolac epoxy resins, biphenyl type epoxy resins, naphthalene type epoxy resins, dicyclopentadiene-phenol type epoxy resins, and mixtures thereof.

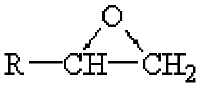


**Figure 2.2** Epoxide group structure [10].

Curing agents or hardeners are substances that are added to a polymer composition to promote or control the curing reaction. A wide variety of curing agent for epoxy resins are available depending on the required process and properties. The commonly used curing agents for epoxies include amines, polyamides, phenolic resins, anhydrides, isocyanates and polymercaptans. The curing kinetics and the glass transition temperature ($T_g$) of cured system are dependent of the molecular structure of the hardener. The choice of resin and hardeners depends on the application, the process selected, and the properties desired. The stoichiometry of the epoxy-hardener system also affects the properties of the cured material. Employing different types and amounts of hardener could control cross-link density, which varies the structure of the cured resin.

Filler is used to adjust the coefficient of thermal expansion (CTE) of the epoxy. Suitable fillers include silica, graphite, aluminum nitride, silicon nitride, silicon carbide, boron nitride, diamond dust, and clays. For epoxy used as underfill in electronics packaging, the fillers may typically be present in the amount of about 20-80 wt% of the total epoxy composition.

### *2.2.2 Type of Epoxy Resin*

There are two main categories of epoxy resins, namely glycidyl epoxy, and non-glycidyl epoxy resins. Glycidyl epoxy resins are prepared via a condensation reaction of appropriate dihydroxy compound, dibasic acid or a diamine and epichlorohydrin. The non-glycidyl epoxy resins are either aliphatic or cycloaliphatic epoxy resins. Non-glycidyl epoxy resins are formed by peroxidation of olefinic double bond.

The glycidyl epoxy resins are further classified into glycidyl-ether, glycidyl-ester and glycidyl-amine. Glycidyl-ether epoxy resins such as, diglycidyl ether of bisphenol-A (DGEBA) shown in Figure 2.3 and novolac epoxy resins shown in Figure 2.4 are most commonly used.

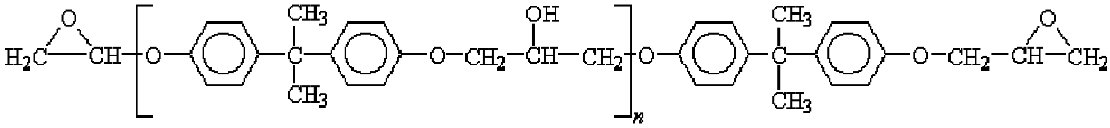


**Figure 2.3** Diglycidyl ether of bisphenol-A (DGEBA) structure [10].

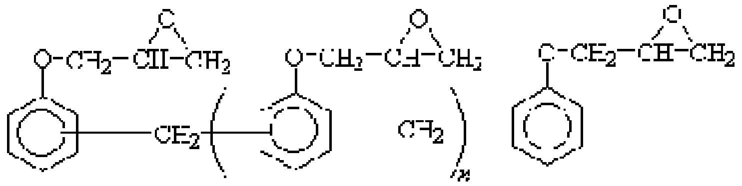


**Figure 2.4** Novolac epoxy resin structure [10].

Diglycidyl ether of bisphenol-A (DGEBA) is a typical commercial epoxy resin synthesized by the reaction between bisphenol-A and epichlorohydrin in a presence of a basic catalyst.

Novolac epoxy resins are glycidyl ethers of phenolic novolac resins. Phenols are reacted in excess, with formaldehyde in a presence of an acidic catalyst to produce phenolic novolac resin. Then, novolac epoxy resins are synthesized by reacting phenolic novolac resin with epichlorohydrin in a presence of sodium hydroxide as a catalyst. Novolac epoxy resins are widely used to formulate the moulding compounds for microelectronics packaging because of their superior performance at elevated temperature, excellent mould ability, mechanical properties, superior electrical properties, and heat and humidity resistance.

### *2.2.3 Epoxy Resin Formation*

There are two steps to make epoxy resins. First step is making diepoxy and then crosslinking it with diamine.

### 2.2.3.1 Making a diepoxy

This step is a type of step-growth polymerization or condensation polymerization as shown in Figure 2.5. Prepolymer was made from bisphenol A and epichlorohydrin.

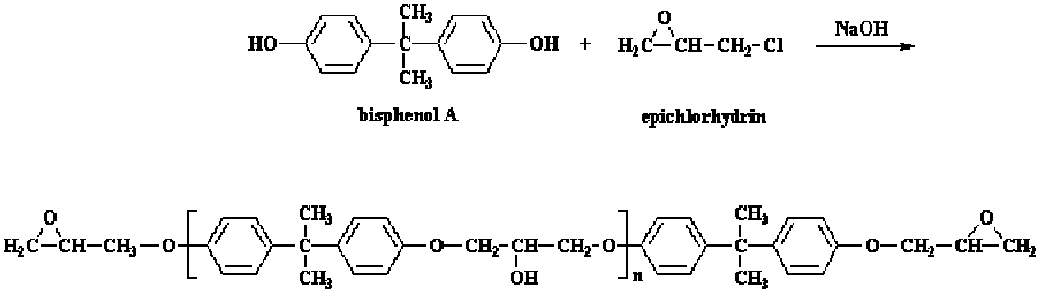


**Figure 2.5** Step-growth polymerization reaction of bisphenol A and epichlorohydrin [11].

The first thing that happens is that sodium hydroxide (NaOH) interacts with bisphenol A, to give bisphenol A sodium salt as shown in Figure 2.6.

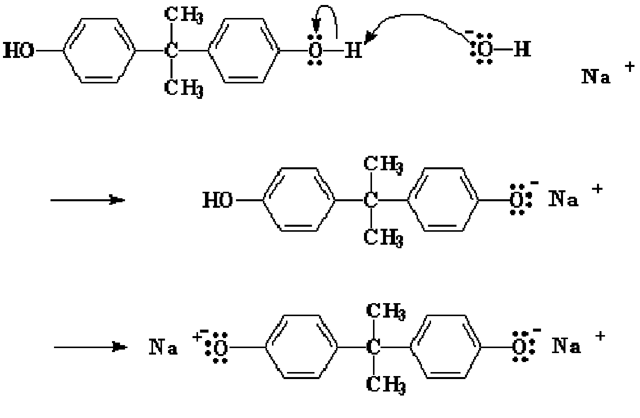


**Figure 2.6** Formaiton of bisphenol A sodium salt [11].

Bisphenol A sodium salt has oxygen with three lone pairs of electrons. Once, oxygen atom shares one electron pair to carbon atom of epichlorohydrin, the carbon atom transfers one electron pair to chlorine in order to take electron pair from oxygen atom. Therefore, chlorine atom separates from epichlorohydrin molecule. The connection between bisphenol A and epichlorohydrin is called “Prepolymer”. As the result, prepolymer with one epoxide group in the molecule as well as sodium chloride (NaCl) are obtained. All steps are shown in Figure 2.7. The degree of polymerization of prepolymer depends on the ratio of bisphenol A and epichlorohydrin in the reaction.

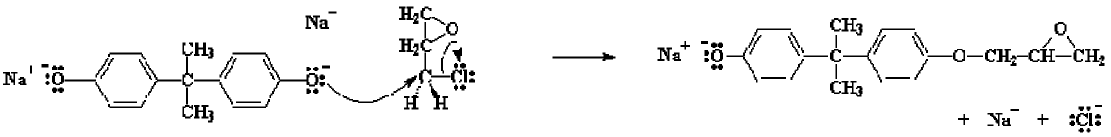


**Figure 2.7** Formation of prepolymer [11].

### 2.2.3.2 Curing the Diepoxy with a Diamine

For prepolymer with two epoxide groups, it is called “Diepoxy prepolymer”. Diepoxy prepolymers will react with diamine, since nitrogen atom in diamine can share its electron pair to carbon atom of epoxide group at the end of diepoxy prepolymer. Then, the bond between one carbon atom and oxygen atom in the prepolymer is broken because of unequal electron sharing between two carbon atoms and one oxygen atom. Next, a new bond between carbon atom and nitrogen atom is occurred. This reaction leaves a negative charge on oxygen atom and a positive charge on nitrogen atom (Figure 2.8).

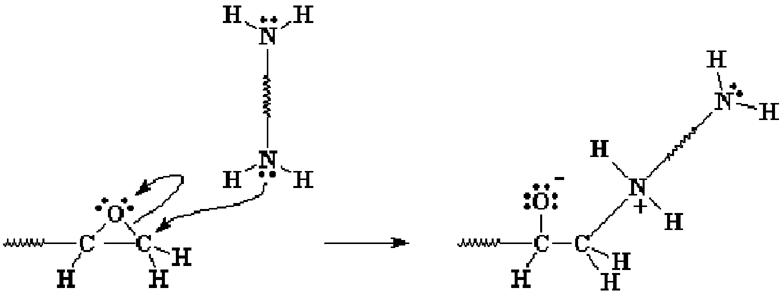


**Figure 2.8** The end of the prepolymer and diamine [11].

Oxygen atom has three electron pairs so that one of the non-bonding electrons can react with hydrogen atom of diamine. As the result, hydrogen atom separates from nitrogen and leaves electron to nitrogen. The step of hydrogen atom separation and bonding between oxygen and hydrogen is called "Oxygen neutralization" as shown in Figure 2.9.

Finally the amine group which still has hydrogen left on it, can further react with other epoxy groups (Figure 2.10), in the exact same manner as mentioned earlier.

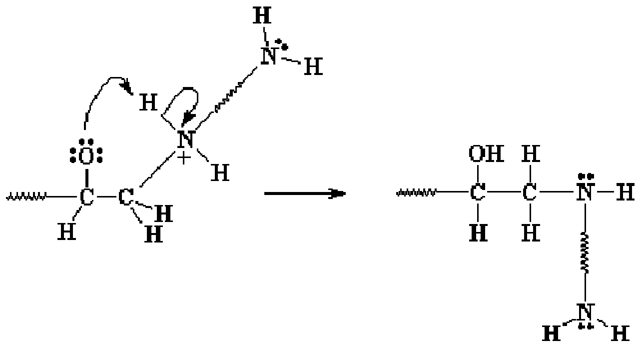


**Figure 2.9** Oxygen neutralization [11].

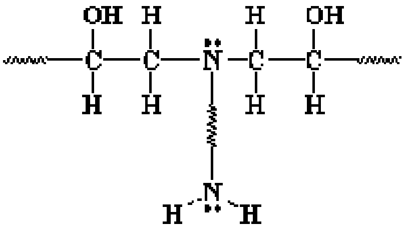


**Figure 2.10** Reaction with other epoxy groups [11].

## 2.3 Flip-Chip Technology

Flip-chip packaging is a first-level interconnect technology. It was first developed about 40 years ago. Since then, great efforts have been devoted to the research and development of this packaging technology. One of the most successful flip-chip packaging processes is the controlled collapse chip connection (C4) invented by IBM in 1960s, in which solder bumps are used to electrically couple the silicon ICs to the substrate [12]. The electronic components are interconnected to form the circuits, and are eventually connected to and supported on a substrate. The connections are made between electrical terminations on the electronic component and corresponding electrical terminations on the substrate. One method for making these connections includes a flip-chip mounting technique is shown in Figure 2.11. Flip-chips are made by positioning the silicon die ("the chip") with the active side ("the face") down on the substrate. Bond pads on the face of the chip are connected by solder bumps or other interconnects to the substrate. Tacky flux is applied to the solder contact areas either by dipping the chip into a flux reservoir or by dispensing flux onto the substrate. During reflow, the solder bumps complete the electrical connections from the active circuitry of the die to the substrate.

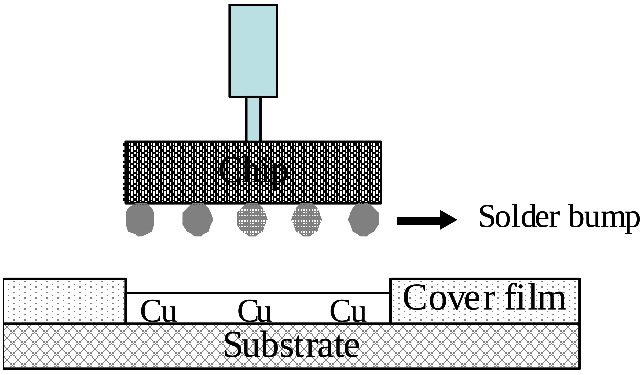


**Figure 2.11** Flip-chip mounting technique.

Therefore, flip-chip package has advantages of high I/O density capability, improved electrical performance due to the short interconnect from the chip to the substrate, reduced size and weight, and improved thermal performance since the top surface of the chip can be used for an efficient cooling component to deal with the increasing power density required by the trend toward the devices using higher packaging densities.

## 2.4 Reflow Process

Reflow soldering is a process in which a solder paste is used to temporarily hold the components to their attachment pads, after which the assembly is carefully heated in order to solder the joint. The assembly may be heated by an infrared lamp, or by passing it through a carefully-controlled oven, or soldering with a hot air pencil. Reflow soldering is the most common method of attaching surface mount components to a circuit board. The goal of the reflow process is to melt the solder alloy particles within the solder paste, without overheating and damaging the electrical components. The purpose of soldering is to form a strong, long-lasting metallurgical bond between the surfaces being joined, both for structural integrity of the assembly and electrical conductivity of the electronic circuits.

In the conventional reflow soldering process, there are usually four stages called "zones", each having a distinct thermal profile. These zones are: preheat, thermal soak (often shortened to just soak), reflow and cooling zones.

## 2.5 Underfill Process

During subsequent manufacturing steps, an electronic assembly is subjected to cycles of elevated and lowered temperatures. Most materials expand when heated because increased thermal energy causes atomic or molecular distances to increase. The parameter used to quantify the dimensional–temperature relationship is the coefficient of thermal expansion (CTE). The difference in CTE between the silicon chip and the organic substrate can cause significant thermal stresses on interconnects during temperature cycling and ultimately results in fatigue cracking and electrical failure. To solve the CTE mismatch problem resulting from assembling the flip-chip with a polymer-based organic substrate, the simplest and most cost-effective approach is to fill the gap between the chip and the organic substrate with an appropriate composite to transfer the thermal–mechanical stress away from the fragile bump zone to a more strain-tolerant region. The underfill is an encapsulant, which is coated over the active area of the die and the interconnect structure. The underfill serves at least two purposes: performance enhancement, and chip/joint protection. It should be noted that the underfill movement is constrained by the very rigid and low expansion chip in its plane. The underfill will expand in the vertical direction with its own CTE. Therefore, underfill should have a CTE value that approximates the value of the solder bump to avoid the mismatch of the CTE between underfill and the solder joint in the vertical direction.

Underfilling may occur after the reflow of the metallic or polymeric interconnect, or it may occur simultaneously with the reflow. If underfilling occurs after reflow of the interconnect, a predetermined amount of the underfill material may be dispensed at one or more sides of the gap between the chip and the substrate. The material will flow by capillary action into the gap, thereby contacting the solder bumps (Figure 2.12). Some of the defects that can originate during the flow of fluid underfill include delaminations, where the underfill fails to wet and adhere to a surface, and voids, where contamination causes local variations in the speed of flow and causes bubbles to be trapped. Reducing the viscosity of underfill material, however, enables the material to flow more easily into the small gaps between the silicon die and the substrate. The underfill material is subsequently cured to reach its optimized final properties. If underfilling occurs simultaneously with reflow of the solder or polymeric interconnects, the underfill material first is applied to either the substrate or the chip. Then terminals on the chip and substrate are aligned and contacted and the assembly is heated to reflow the metallic or polymeric interconnect material. During this heating process, curing of the underfill material occurs simultaneously with reflow of the metallic or polymeric interconnect material.

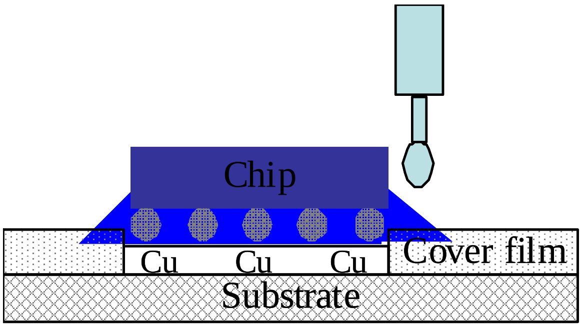


**Figure 2.12** Dispensing underfill process.

In flip-chip applications, precision control is a key concern because the dispensing needle has to move extremely close to the chip throughout the process. The needle must be positioned far enough from the chip to avoid backside contamination but close enough to promote capillary flow of the fluid under the chip. Accurate volumetric control of underfill fluids can only be achieved through the use of a linear positive displacement (LPD) pump that uses a piston to displace the exact volumes required, whether in large or small shots. Unlike older rotary or auger pump technologies, which work adequately for stable viscosity fluids like solder paste, the short pot-life fluids used as underfill encapsulant demand more precise pumping action, such as LPD, where the flow-rate never varies with changes in the viscosity and needle diameter. Even before the actual dispensing process begins, process control above the substrate temperature can help to prepare it for optimal encapsulant flow-out. The dispensing system should also incorporate needle-heating to further optimize the flow characteristics of the encapsulant formulation before it is even dispensed into the part. Finally, maintaining a precise post-dispensing profile over the parts can be used to effectively complete the flow-out after dispensing. The post-heating step can actually improve overall dispensing throughput because the dispensed parts can be moved to the post-heat area to complete their flow-out, while the next set of parts is simultaneously cycled into the dispensing work envelope. By treating the dispensing and curing operations as a single, integrated "process module," it is now becoming possible to optimize overall production throughput while simultaneously improving the quality and consistency of results.

# CHAPTER III

# LITERATURE REVIEWS

Many previous researches on the chemical and physical properties of underfill materials, the epoxy curing behavior, effects of materials on the epoxy properties, and the solder paste composition are presented in this section.

## 3.1. The Chemical and Physical Properties of Underfill Materials

Gilleo examined the chemistry of underfills and the physical properties that are important to their successful use. Most common hardeners for epoxy-based encapsulants and underfills are anhydrides. Low viscosity anhydrides react with the epoxide rings of the resins to form the highly stable polyester group. Each anhydride ring is opened to provide two reactive sites for epoxides. The epoxy resins are selected with two or more reactive sites so that long repeating chains of anhydride and epoxy components are produced. It also results in linkages between adjacent polymer chains. These cross-linking produces excellent materials with mechanical and thermal stability. It rigidizes the entire structure into permanently-shaped super-molecule (essentially one giant 3-dimensional molecule made up of millions of atoms). Figure 3.1 shows the polymerization reaction and Figure 3.2 is a graphical representation of a thermoset structure [13].

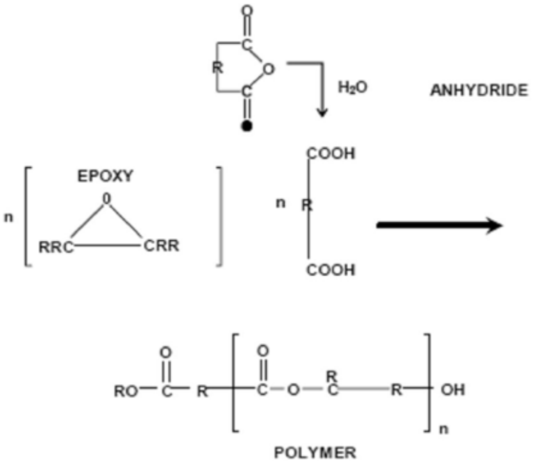


**Figure 3.1** Epoxy-anhydride reaction [13].

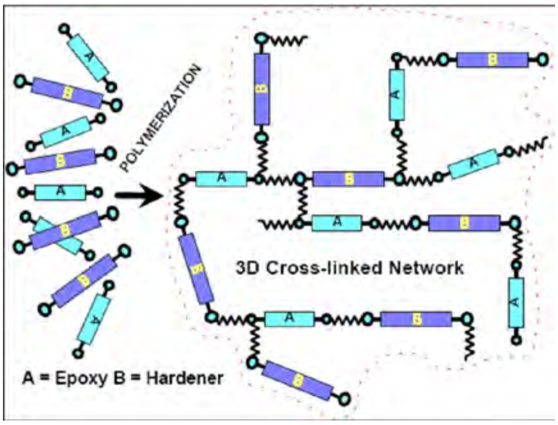


**Figure 3.2** Molecular structure of thermoset polymer [13].

## 3.2 Investigation of Curing Behavior by Various Techniques

He reported that isothermal and non-isothermal differential scanning calorimetry (DSC) and dielectric analysis (DEA) techniques were used to study the curing kinetics of an epoxy-based underfill material used in electronic packaging. The curing reaction was determined from the peak and shoulder on DSC curves at various heating rates, i.e. DSC curves show the main exothermic peak and a smaller shoulder. Thus, it was determined that this curing reaction has at least two stages. The gelation of the underfill epoxy where the viscosity increases sharply was obtained from the peak position in the loss factor curves (DEA) and viscosity curve [14].

Zhang *et al.* studied the curing mechanism of epoxy/phenolic system for underfill applications by using the differential scanning calorimeter and temperature controlled Fourier transform infrared spectrometer. The effect of hardener and catalyst type and the catalyst concentration on the curing mechanism was investigated from the exothermal peak temperature on DSC curing profile and the epoxide concentration obtained from dividing the peak area of absorption at 915 $cm^{-1}$ (epoxy ring structure) by the peak area of absorption at 3000 $cm^{-1}$ (the stretching of aliphatic C-H) of FTIR spectra [15].

Rocks *et al.* studied the low temperature curing behavior of the same epoxy/co-anhydride mixture by means of FT-Raman spectroscopy under isothermal conditions. The detailed changes in a portion of the Raman spectrum during the curing of N,N,N’,N’-tetraglycidyl-4,4’-diaminodiphenylmethane (TGDDM) with maleic anhydride MA/ hexahydrophthalic anhydride HHPA at 75?C included the change in intensity of bands at 1850 cm$^{-1}$ (anhydride), 1590 cm$^{-1}$ (MA double bond), 1260 cm$^{-1}$ (epoxy) and 1734 cm$^{-1}$ (ester from anhydride-epoxy reaction) among others. The ratio of anhydride-to-epoxy was 0.8 and the mixing ratio was 100/48/32 TGDDM/MA/HHPA. The presence of the point at 1760 cm$^{-1}$, the similarity in the rate of disappearance of the bands at 1850, 1590 and 1260 cm$^{-1}$ and the appearance of the bands at 1640 cm$^{-1}$ and 1730 cm$^{-1}$ were used to suggest the dominant reaction for the curing [16].

Wang *et al.* studied the synthesis and characterization of hyperbranched polyester (HBP) with different molecular weight and mainly discussed on the effect of HBP on the modification of epoxy resins cured with anhydride. The reactions between epoxy resin, HBP and anhydride can be confirmed by FTIR spectra. The peak of epoxy group (912 cm$^{-1}$) did not vary after curing in HBP-epoxy system, which indicated that HBP could not react with epoxy resin. While in HBP-tetrahydrophthalic anhydride (THPA) system, the peaks of anhydride group (1776 cm$^{-1}$, 1856 cm$^{-1}$) disappeared after curing, which illustrated that the reaction between HBP and THPA was occurred. So in epoxy-HBP-anhydride cured system, it is supposed that anhydride reacted with epoxy resin and HBP to form copolymer networks, which can also be confirmed by differential scanning calorimetry (DSC) analysis [17].

Liu *et al.* investigated the curing behavior and thermal properties of bisphenol-A type novolac epoxy resin (bisANER) with methylhexahydrophthalic anhydride (MHHPA) at an anhydride/epoxy group ratio of 0.85. The study was conducted with Fourier-transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC), and thermogravimetry. The results showed that the FTIR absorption intensity of anhydride and epoxide decreased during the curing reaction, and the absorption peak of ester appeared at 2963 and 1734 cm$^{-1}$ [18].

## 3.3. Effects of Materials on Properties of Epoxy

Todd investigated organic flux residues deposited onto the surfaces of flip-chip assemblies during reflow soldering operations that have been shown in some cases to affect the thermal and mechanical properties of underfill materials. Flux removal techniques are used in many electronics manufacturing and assembly processes as means of assuring consistent materials properties and improving product reliability. These test assemblies were used to evaluate the effects of various no-clean flux residues on the properties of the epoxy underfill material and on the electrical and mechanical performance of experimental flip-chip components [19].

Grimes tested the curing behaviors, glass transition temperatures, moisture absorption, and density of nano and micron sized silica epoxy composites using amine and anhydride hardeners. Results showed that composites with the amine hardener had generally higher glass transition temperatures, lower moisture absorption, and similar densities to that of the composites with the anhydride hardener. In contrast, the composites with the anhydride hardener showed lower Tg's and higher moisture absorption [20].

Loos *et al.* studied the influence of the presence of residual solvent, namely acetone, on the characteristics of an epoxy resin. It may be concluded that care must be exercised in order to ensure that all solvent is removed before curing, otherwise the cross-linking process is altered, leading to significant changes in physical and mechanical properties, for instance the Young's modulus, even if only a small amount of solvent is left on the matrix. The molecular structure of the cured resin has also been affected, as detected by FTIR analyses. SEM micrographs showed a less brittle-like fracture for the material to which acetone had been added. Thermal degradation has also been affected by the acetone [21].

## 3.4. The Solder Paste Composition

Taguchi *et al*. reported the invention of the paste that is comprised of a water-soluble flux (which includes a glycol vehicle and activator), a solder powder, a hydrophobic surfactant which is preferentially absorbed by the surface of the substrate over the glycol in the flux, and a solvent for carrying the flux and the surfactant to the circuit board along with the solder powder. Additionally, one or more rheology-modifying agents (thixotropes) may also be added to the paste. The water-soluble flux within the paste is comprised of polyethylene glycol (or a mixture thereof) together with one or more activators, such as amine, an organic acid (e.g., citric, tartaric, glycolic etc.) or an aminehydrohalide such as diethanolamine hydrochloride [22].

Bristol *et al*. presented a low residue soldering flux containing a non-subliming dibasic acid mixture about 15-30% by weight of succinic acid, 40-63% glutaric acid and 10-30% adipic acid, e.g., in a volatilizable organic solvent, formed as a rosin-containing or rosin-free flux. The dibasic acid mixture is capable of volatilizing during heating and leaving a soldered product (e.g., an electronic circuit board) essentially free from corrosion-promoting ionic residue. This eliminates the need for a residue-removing washing step [23].

Turner *et al*. presented the invention of the soldering paste comprising of particulate solder alloy and a thixotropic flux base. The thixotropic flux base comprises of (a) a botanical oil, (b) an aqueous emulsion of a thickening agent, and (c) a water-soluble organic acid having at least two carboxylic acid groups. Examples of suitable organic acids included citric acid, malic acid, tartaric acid, glutamic acid, phthalic acid, succinic acid, and the like [24].

Frazier *et al*. presented the water-soluble soldering flux contains 1 - 5 wt% (based on the weight of the water-soluble soldering flux) of an inorganic acid in solution, which forms anions of the acid having a low propensity for forming metal complexes. The flux contains 30 - 70 wt% (based on the total weight of the water-soluble soldering flux) of an anionic surfactant, which serves as a flux vehicle and acts to dissolve reaction products. The anionic surfactant is thermally stable at soldering temperatures in the range about 120-300?C. The flux contains 30 - 70 wt%, (based on the total weight of the water-soluble soldering flux) of a low molecular weight alcohol diluent and contains 5-40 wt% (based on the total weight of the water-soluble soldering flux) of a viscosity modifier selected from the group consisting of glycerol and dipropylene glycol [25].

Sabarese *et al*. presented a soldering paste flux for use in soldering copper and copper alloy piping and the like formed from 40–70% nonylphenol ethoxylate, 10–30% glyceryl monostearate, 3–10% acid activator, 3–10% water, and 4–15% mineral salt. The acid activator is preferably a mineral acid and, most preferably, hydrobromic acid. The mineral salt is preferably zinc bromide [26].

Wada *et al*. carried out intensive study to develop a solder paste which prevents the skinning phenomenon and the viscosity change by aging of solder paste and, can preserve good coating and printing ability for long term in actual use. The paste also has a good resistance to preheating under a high temperature. It was found out that the object can be obtained by containing at least one dicarboxylic acid of carbon number 3 to 5 and at least one dicarboxylic acid of carbon number 15 to 20 as an activator in a flux. The amount of the dicarboxylic acid of carbon number 3 to 5 is 0.05-5 wt%. The amount of dicarboxylic acid of carbon number 15 to 20 is 6-30 wt% [27].

# CHAPTER IV

# EXPERIMENTAL

## 4.1 Materials

Lead-free solder paste employed in this study contains 10.5% flux content of water-soluble type flux called ORM0, which is an organic substance with moderate flux activity levels (0% Halide). Underfill material employed (Hysol) is composed of epoxy resin, silica, and methylhexahydrophthalic anhydride (MHHPA) which is a harderner for hot cured epoxy resins. Epoxy resin is epichlorohydrin-4,4'-isopropylidene diphenol resin. 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexane carboxylate and 1,4-butanediol digycidyl ether are epoxide monomer. This underfill material was purchased from Henkel Loctite Corporation. The chemical structures of the epoxy composition were illustrated in Figure 4.1-4.4.

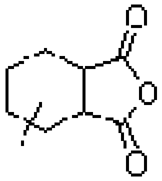


**Figure 4.1** Methylhexahydrophthalic anhydride (MHHPA) [28].

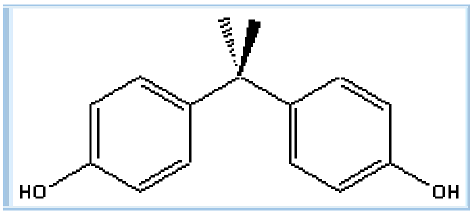


**Figure 4.2** Epichlorohydrin-4, 4'-isopropylidene diphenol resin [28].

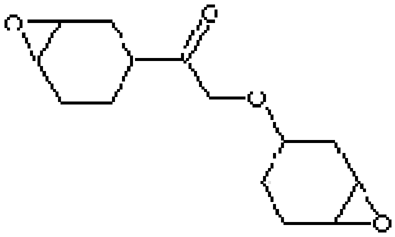


**Figure 4.3** 3, 4-Epoxycyclohexylmethyl 3, 4-epoxycyclohexane carboxylate [28].

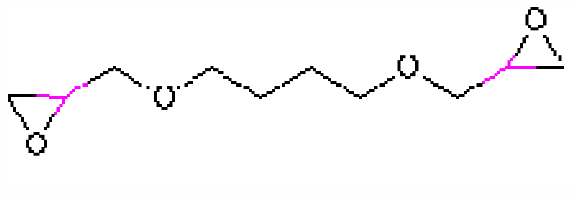


**Figure 4.4** 1, 4-Butanediol diglycidyl ether [28].

Polyethylene glycol 300 ($H(OCH_2CH_2)$) and boric acid ($H_3BO_3$) 99.99% were obtained from Sigma Aldrich. Tartaric acid ($(CHOH.COOH)_2$), sulfuric acid ($H_2SO_4$) 98%, and citric acid ($HOC(COOH)(CH_2COOH)_2.H2O$) were obtained from Analytical UNIVAR REAGENT. Acetic acid glacial grade AR ($CH_3COOH$) and formic acid (HCOOH) 85% were obtained from QRec$^{TM}$. Hydrochloric acid (HCl) 36.5-38% was obtained from J.T. Baker. Phosphoric acid ($H_3PO_4$) 85% was obtained from Merck company.

## 4.2 Flux Residue Preparation

Flux residue was prepared by applying the lead-free solder paste onto the copper foil and passing through the reflow process with the following condition: ramp up rate of 2.6?C/s, preheat (25-150?C) time of 75 second, thermal soak (150-217?C) time of 50 second, and reflow (>217?C) time of 90 second. After the reflow process, the flux residue was manually separated from melted solder paste.

## 4.3 Epoxy and Their Blends Preparation

Epoxy curing was tested by injecting epoxy raw material onto the Teflon substrate and curing in three different conditions, i.e. in an oven at temperature of 165?C for 30 min, at temperature of 145?C for 15 min, and left in ambient temperature for 5 hours. It should be noted that the curing at 165?C for 30 min is the condition which has been known to produce fully cured epoxy in the actual manufacturing process, while the curing at 145?C for 15 min and leaving in ambient temperature for 5 hours have been known to produce partially cured epoxy.

Epoxy curing inhibition was tested by blending epoxy raw material with flux residue on the Teflon substrate and cured it in an oven at temperature of 165?C for 30 min. The inhibition effect was further investigated by using tartaric acid, citric acid, boric acid, formic acid, acetic acid, sulfuric acid, hydrochloric acid, phosphoric acid or polyethylene glycol instead of flux residue. These chemical were chosen because they have been reported as common composition in water-soluble flux. For tartaric acid, citric acid, and boric acid, which are in solid phase, they were prepared by dissolving 15 mg of the acid in 10 ml of water and stirring until obtaining homogeneous solution. For polyethylene glycol, formic acid, acetic acid, sulfuric acid, hydrochloric acid, and phosphoric acid, they were used as received without any further dilution.

## 4.4 Characterization Methods

### *4.4.1 Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR)*

Attenuated total reflectance (ATR) techniques are well established in FT-IR spectroscopy for the direct measurement of solid and liquid samples without sample preparation. The technique requires good contact between the sample and a crystal made from a material which transmits IR radiation and has a high refractive index. When the IR beam enters the crystal at the critical angle, internal reflection occurs.

Infrared spectrum of the air-side and the glass-side surface, of epoxy and their blends were measured using a Perkin Elmer Spectrum GX FT-IR spectrophotometer. Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy was acquired using ZnSe as a prism. The spectral resolution was set at 4 $cm^{-1}$.

### *4.4.2 Differential Scanning Calorimetry (DSC)*

Thermal events and thermal transitions of solder paste, flux, epoxy and their blends were determined using a Differential Scanning Calorimeter model DSC-Q100 from TA Instruments. The measurement was performed using a sample mass of 5-15 mg. The sample was placed in a sealed aluminum pan and was tested using a temperature ramp rate of 10?C/min from room temperature to 280?C under nitrogen atmosphere. The glass transition temperature were taken as the mid point temperature of the change in specific heat in the transition region.

### *4.4.3 Thermo-Mechanical Analysis (TMA)*

TMA has been classified as a method of the thermomechanometry (TM) technique. Thermomechanometry is the measurement of a change of dimension or a mechanical property of the sample while it is subjected to temperature change. Thermo-mechanical properties of epoxy blends were determined using a Perkin Elmer Pyris Diamond TMA instrument. The specimen dimension was 5 mm in length, 5 mm in width, and 2 mm in thickness. The specimen was heated using a temperature ramp rate of 5?C/min from room temperature to 250?C.

### *4.4.4 Dynamic Mechanical Analysis (DMA)*

Dynamic mechanical properties of the epoxy blends were tested using a Perkin Elmer Pyris Diamond DMA instrument. The experiment was done in a tension mode using the dimension of the specimen of approximately 50 x 10 x 1.5 mm. The specimen was heated using a temperature ramp rate of 1?C/min from room temperature to 250?C with the frequency of 1 Hz.

# CHAPTER V

# RESULTS AND DISCUSSION

## 5.1 Characteristic of Uncured Epoxy

In the actual manufacturing process, flux residue is often found around the solder pads. Moreover, after the curing process for the underfill epoxy, incomplete curing is usually observed in the vicinity of the solder pad, as shown in Figure 5.1-5.2

**Figure 5.1** Flux residue and incompletely cured epoxy.

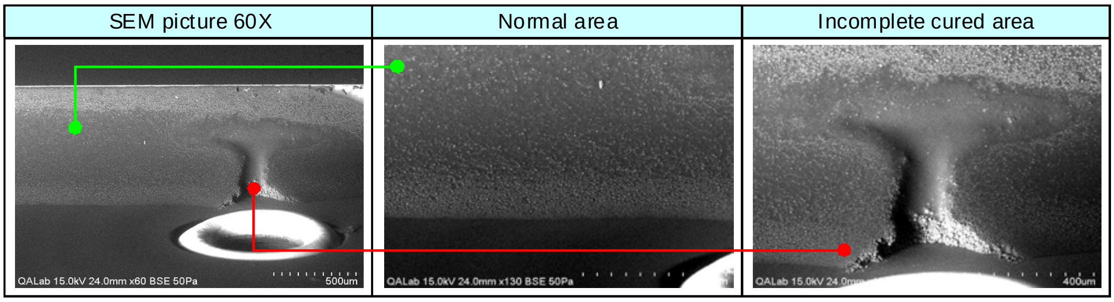
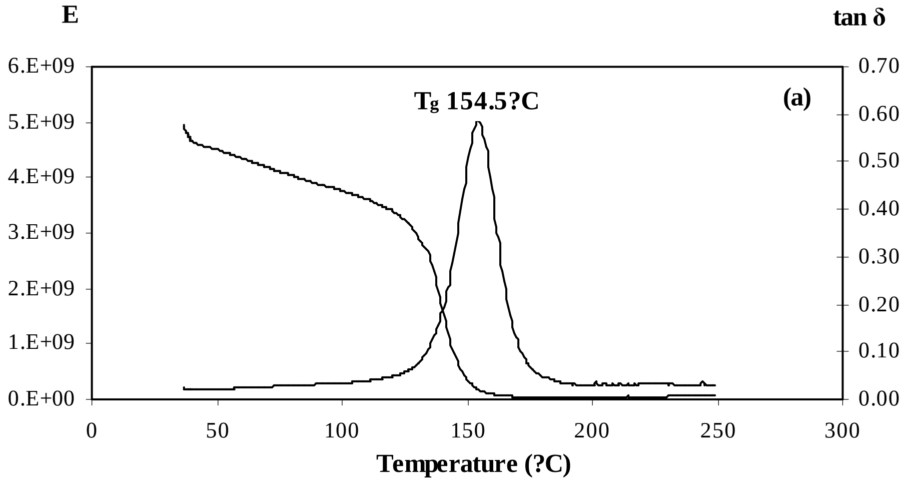


**Figure 5.2** Scanning electron microscope of incompletely cured epoxy.

The evaluation of the epoxy curing usually relies on thermal analysis techniques such as DSC and DMA [29, 30]. In this study, however, the results from DSC, DMA and TMA were evaluated, in order to check the difference between cured and uncured epoxy. Figure 5.3 shows damping factor (tan $\delta$) and storage modulus obtained from DMA analyses of epoxy which was fully cured at 165?C for 30 min and those of epoxy partially cured at 145?C for 15 min. It can be seen that although shape of both damping factor and storage modulus of the fully cured and the partially cured epoxy are slightly different, the difference is not quantitatively significant. The difference in the glass transition temperature ($T_g$) identified from both samples is only about 5?C. The similar result was also observed from DSC analysis, as shown in Figure 5.4, in which the glass transition temperature for the fully cured and the partially cured epoxy were identified as 129.3 and 118?C, respectively. On the other hand, the difference as much as 28?C in the glass transition temperature between the fully cured and partially cured epoxy was identified via TMA, as shown in Figure 5.5. Therefore, this technique is better than DMA and DSC regarding the ability to distinguish the difference in curing of the specimen. However, TMA is limited to homogeneous specimen, but the sample in this work may consist of more than 2 phases due to incompatibility between residual flux and the underfill epoxy.



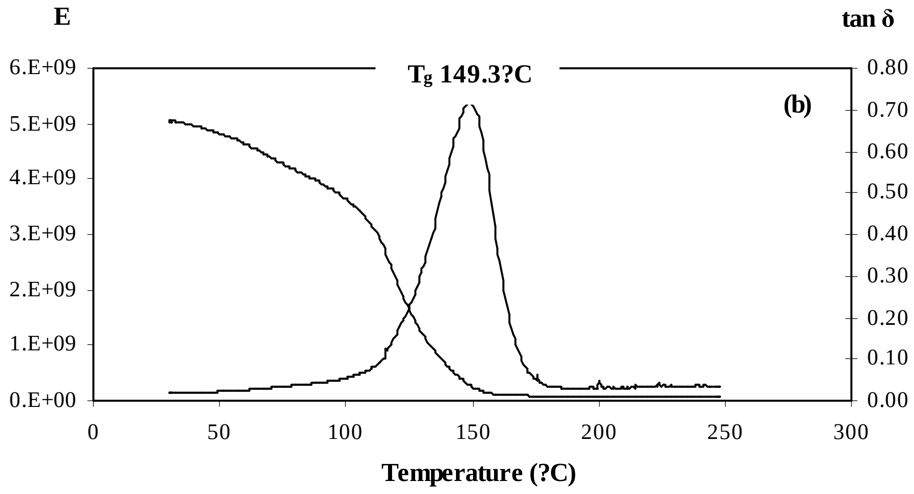
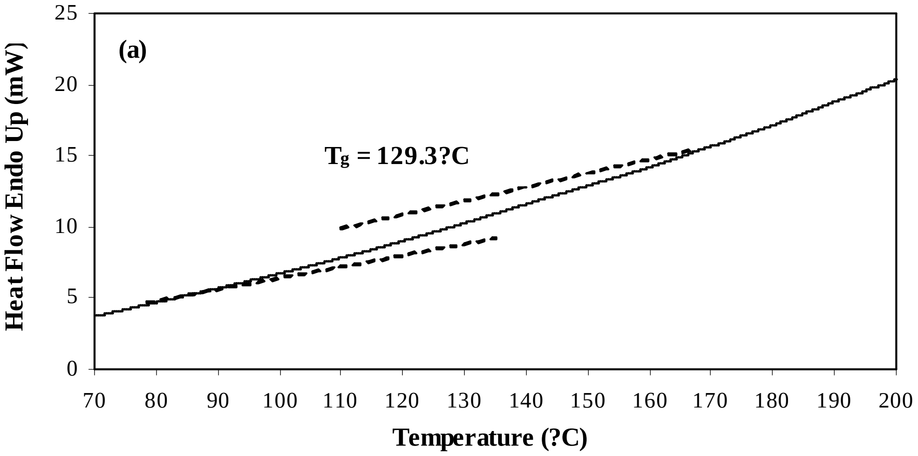


**Figure 5.3** DMA curves of epoxy cured at: a) 165?C for 30 min (fully cured) and b) 145?C for 15 min (partially cured).



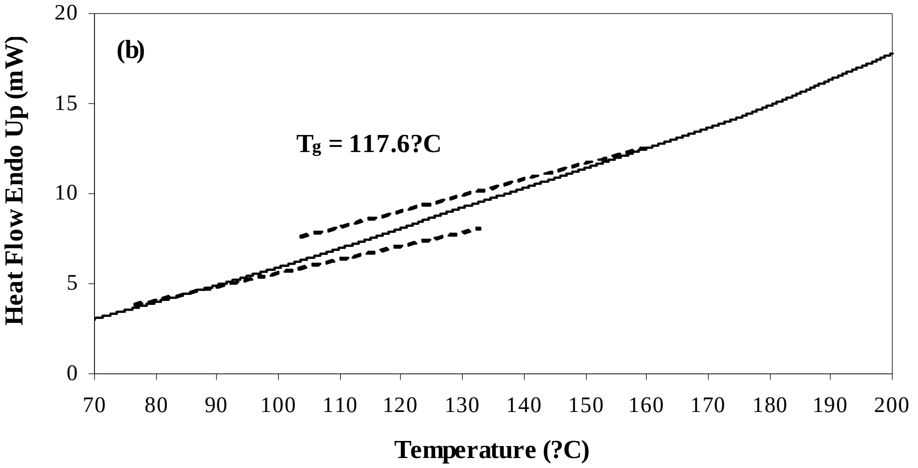
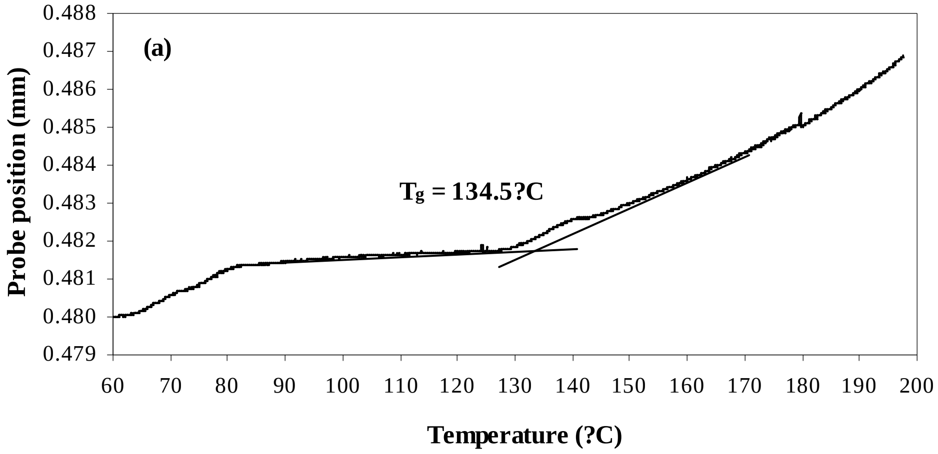


**Figure 5.4** DSC curves of epoxy cured at: a) 165?C for 30 min (fully cured) and b) 145?C for 15 min (partially cured).



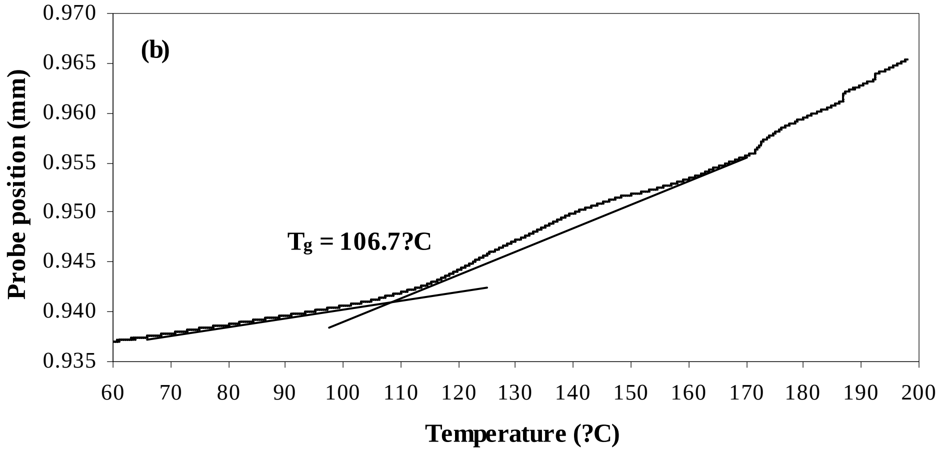


**Figure 5.5** TMA curves of epoxy cured at: a) 165?C for 30 min (fully cured) and b) 145?C for 15 min (partially cured).

FTIR spectroscopy was also adopted to examine the change in intermolecular bonding in the curing of epoxy. This technique has been used to monitor hydrogen bonding of epoxy resin as well as intermolecular bonding within the polymer matrix [31]. Figure 5.6-5.7 show the comparison of FTIR analysis results from epoxy cured at different conditions. According to Park *et al*., when an epoxy sample of Hysol FP4511 was aged for 20 h at 23?C in 78% RH, the absorption bands at 1783 and 1857 $cm^{-1}$ corresponding to anhydride disappeared while an acid peak at 1705 $cm^{-1}$ was formed [32]. This result together with the FTIR data indicated that the anhydride hardener absorbs and reacts with water, resulting in acid that apparently alters the interaction between the hardener and epoxy and lowers the cross-link density as well as the $T_g$ value of the epoxy/anhydride system. To confirm this concept, the FTIR analysis was used to examine the difference among fully cured epoxy, epoxy left in air for 5 hrs, and raw epoxy. The results are shown in Figure 5.6. It can be seen that absorption bands corresponding to anhydride disappear after curing. However, since the type of epoxy used in this work is different than that employed in the previous work, no acid peak at 1705 $cm^{-1}$ was observed. Similar result has been reported by Liu *et al*. investigated the curing behavior and thermal properties of bisphenol-A type novolac epoxy resin (bisANER) with methyl-hexahydrophthalic anhydride (MHHPA) at an anhydride/epoxy group ratio of 0.85. The results showed that the FTIR absorption intensity of anhydride and epoxide decreased during the curing reaction, and the absorption peak of ester appeared [18]. In the present study, the FTIR spectra of the fully cured epoxy and uncured epoxy were also compared to those of the epoxy raw material and flux, as shown in Figure 5.7. Comparing between fully cured epoxy and unsuccessfully cured epoxy, it can be seen that the absorption bands at 1472, 1360, and 1338 $cm^{-1}$ are missing when the epoxy is uncured. These bands should associate with cross-linking bonds formed during the curing process. It should also be noted that some signals from the epoxy raw material, such as the band at 1608 and 1505 $cm^{-1}$, are still observed even after the curing is completed. These bands are also observable in the uncured sample. Therefore, this curing problem should be the result from the chemical alteration of the epoxy by the residual flux, which prohibits formation of the cross-linking bonds.

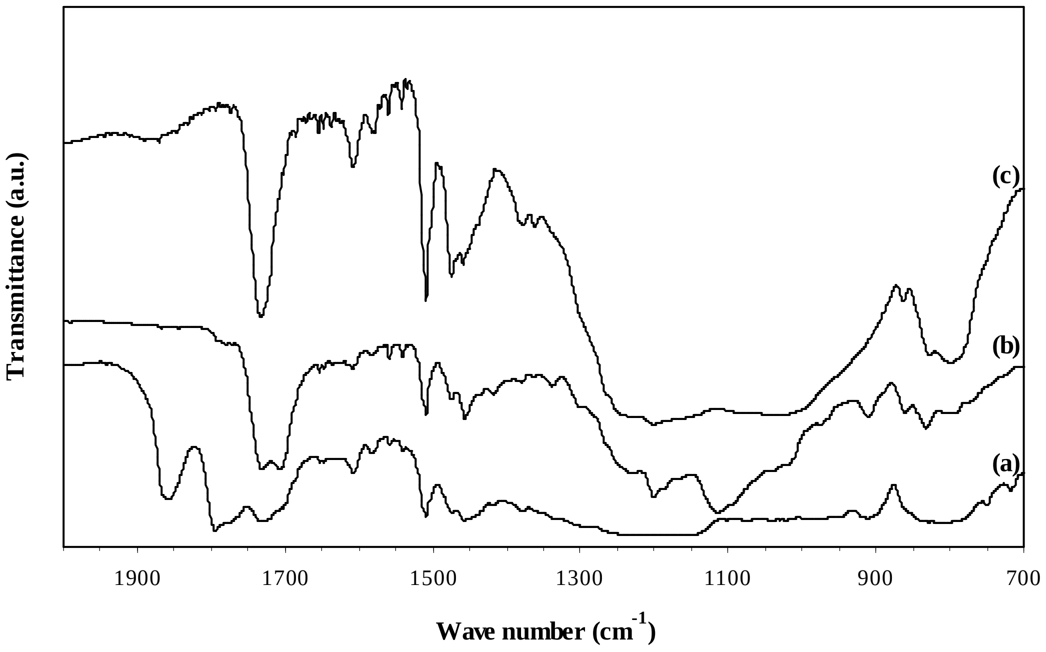


**Figure 5.6** FTIR spectra of: a) epoxy raw material, b) epoxy left in air for 5 hours, and c) epoxy fully cured at 165?C for 30 min.

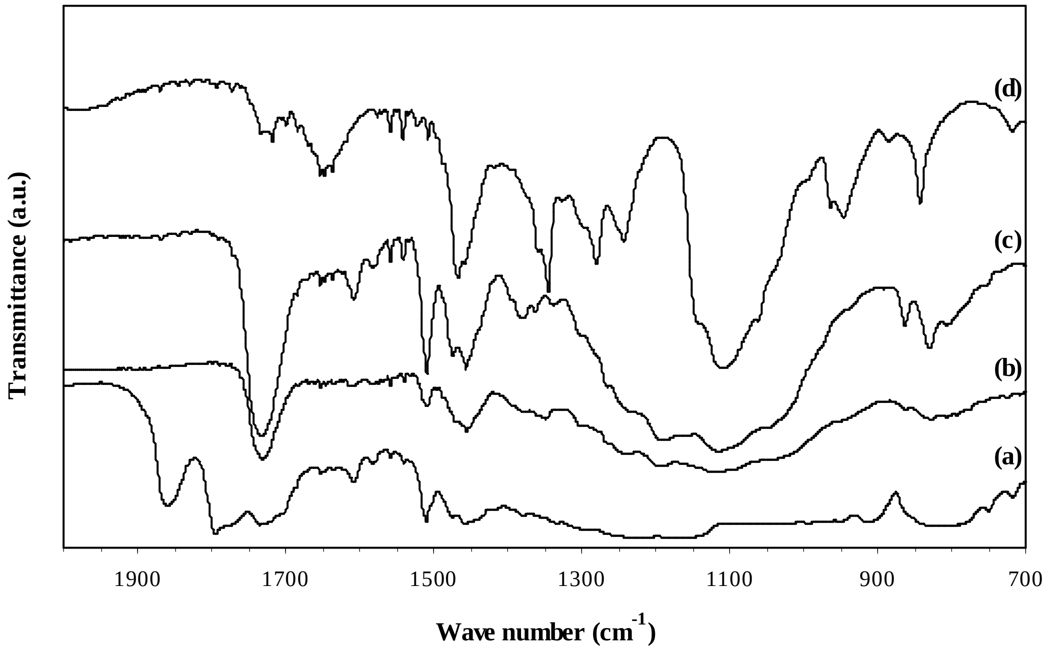


**Figure 5.7** FTIR spectra of: a) epoxy raw material, b) uncured epoxy, c) fully cured epoxy, and d) flux from solder paste.

## 5.2 Evaluation of Reflow Profile

In the conventional reflow soldering process, the key is “temperature profile” which is usually devided into four stages or zones, each having a distinct thermal profile, i.e. preheat, thermal soak, reflow and cooling zones. In term of the thermal profile, there are 2 factors to be considered, i.e., temperature and time. The preheat zone is where the solvent in the solder paste begins to evaporate. However, if either the heating rate or temperature level is too low, evaporation of the volatiles may be incomplete. On the contrary, if the rate exceeds the maximum value, potential damage to electrical components from thermal shock or cracking can occur. The typical ramp-up rate is usually taken at 1-3?C/s. In the thermal soak zone, which is typically set at 60-120 seconds to remove volatiles in the solder paste together with the activation of the fluxes, the components in flux begin to reduce oxides formed on component leads and pads. Too high or too low a temperature can lead to solder spattering or balling as well as oxidation of the paste, the attachment pads and the component terminations. Similarly, fluxes may not fully activate if the temperature is too low.

The reflow zone, which is also referred to as the “time above reflow” or “time above liquidus” (TAL), is the part of the process where the maximum temperature is reached. An important consideration is peak temperature, which is the maximum allowable temperature of the entire process that ensures complete melt of the solder. This limitation is determined by the components and substrate temperature endurance. Additionally, high temperatures (beyond 260?C) may cause damage to the internal die of SMT components as well as foster intermetallic compounds (IMC) growth. Conversely, peak temperature that is not high enough may prevent the paste from reflowing adequately or may cause cold solder and/or incomplete solder joint. The flux reduces surface tension at the junction of the metals to accomplish metallurgical bonding, allowing the individual solder powder spheres to combine. If the profile time exceeds the manufacturer’s specification, the result may be premature flux activation or consumption, effectively “drying” the paste before formation of the solder joint. An insufficient time or temperature relationship causes a decrease in the flux’s cleaning action, resulting in poor wetting, inadequate removal of the solvent and flux, and possibly defective solder joints. Experts usually recommend the shortest TAL possible. However, most pastes specify a minimum TAL of 30 seconds. Too little time above liquidus may trap solvents and flux and create the potential for cold or dull joints as well as solder voids.

The last zone is a cooling zone, which is used to gradually cool the processed board and solidify the solder joints. Proper cooling inhibits excess intermetallic formation or thermal shock to the components. Typical temperature in the cooling zone ranges from 30 to 100?C. Unlike the maximum ramp-up rate, the ramp–down rate is often ignored [33]. Figure 5.8 shows the range of temperature profiles compliant to the JEDEC standard J-STD-020 revision C. The recommendation profile for lead-free solder paste is shown in Table 5.1.

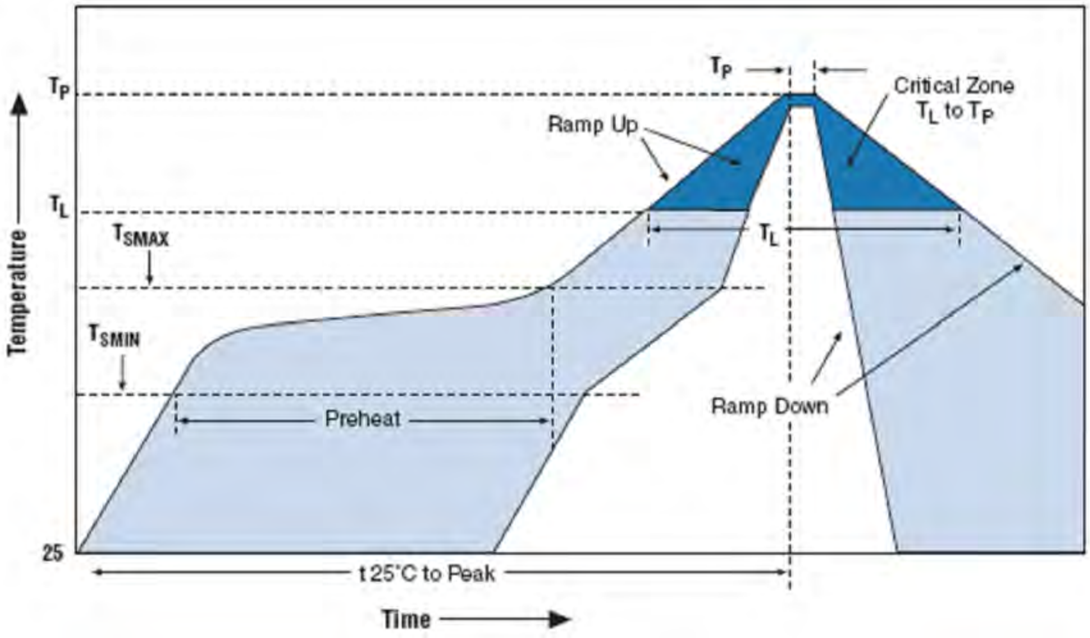


**Figure 5.8** IR/Convection reflow profile (IPC/JEDEC J-STD-020C) [34].

**Table 5.1** IPC/JDEC J-STD-020C for lead-free reflow profile recommendation [34].

| Reflow parameter | Recommendation for lead-free assembly |
|---|---|
| Minimum preheat temperature ($T_{smin}$) | 150?C |
| Maximum preheat temperature ($T_{smax}$) | 200?C |
| Preheat time | 60-180 sec |
| $T_{smax}$ to $T_L$ ramp up rate | 3?C/s max |
| Time above temperature $T_L$ | 217?C 60-120 sec |
| Peak temperature $T_P$ | 260?C |
| Time from 25?C to $T_P$ | 6 minutes max |
| Time within 5?C of peak | 10-20 sec |
| Ramp down rate | 4?C/s max |

In this work, in order to avoid the epoxy uncuring problem caused by the residual flux, the reflow process was adjusted to investigate optimum conditions to eliminate the flux. It should be noted that the experiments were conducted in a SRS-1 reflow simulator. The factors investigated were heating rate in the preheat zone (1.5, 2.0, 2.5 and 3.0?C/s), preheating time (60, 90, 120 and 150 s), reflow time (30, 60, 90 and 120 s) and oxygen content (250, 1500, 3000 ppm and 21%). Unfortunately, the results from all experiments indicated that the flux residues still remained on the solder pad, regardless of the heating time, temperature and oxygen content. These results confirm that the water soluble solder paste will result in flux residue after the reflow. Therefore, the cleaning process after reflow (i.e. before the underfilling process) is needed in order to avoid the epoxy uncuring problem.

## 5.3 Characteristic of Flux in Solder Paste after Reflow Process

The solder paste in this study has melting point of 220?C, determined from DSC curve shown in Figure 5.9. Normally, when a sample was printed with solder paste, it will separate to two phases after passing the reflow process, i.e. solid phase obtained from solidification of melted solder and flux which not completely evaporate in liquid phase. DSC result of the flux in solder paste after passing the reflow process is exhibited in Figure 5.10. From the DSC curve, an apparently endothermic peak at temperature of 30?C and broad peak at 90?C are observed. Next, the heat was applied to the flux residue by using the soldering iron with temperature from 50 to 400?C and hold at each temperature for 1 minute. Results showed that the flux residue did not undergo decomposition and still remained on the solder pad. These results were confirmed by mixing the flux residue obtained from each condition with epoxy. After curing, it was found that uncuring problem took place on all samples.

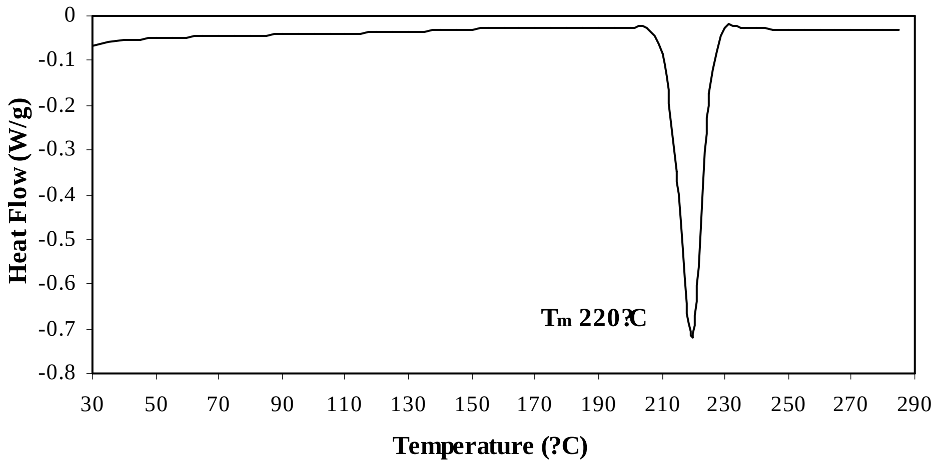


**Figure 5.9** DSC curve of lead-free solder paste.

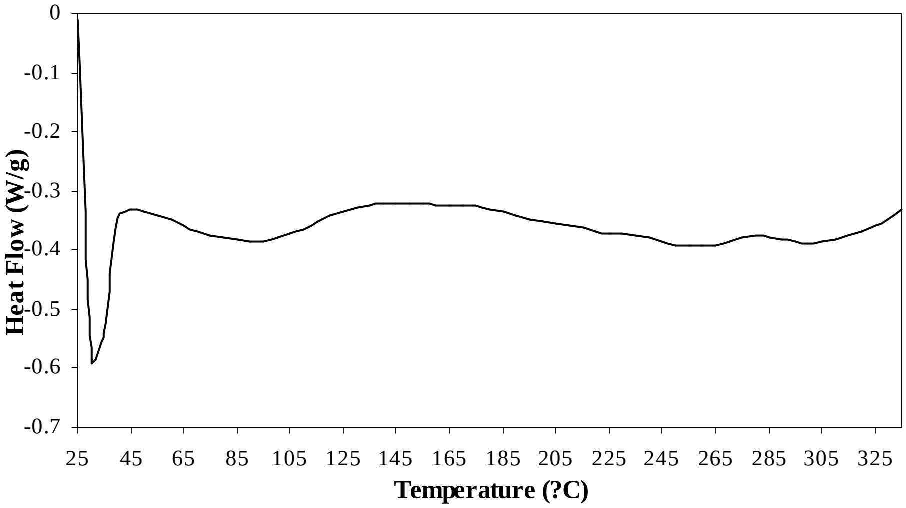
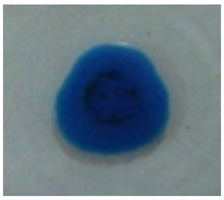
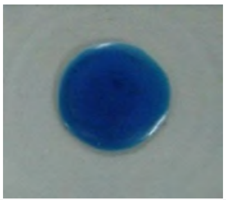
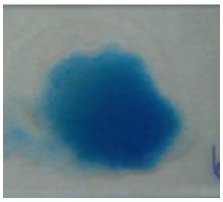
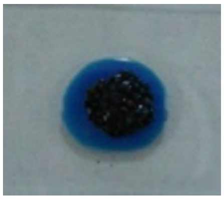
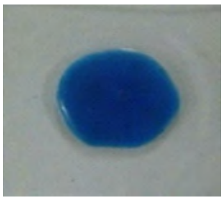
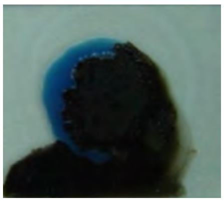


**Figure 5.10** DSC curve of flux residue obtained after passing the reflow process.

## 5.4 Determination of Flux Composition that Affect Epoxy Curing

Extensive survey on patents relating to flux has shown that many types of organic and inorganic acid were used as ingredient in flux. Tartaric acid, citric acid, formic acid, and acetic acid are the representatives of organic acid while sulfuric acid, phosphoric acid, hydrochloric acid, and boric acid represent inorganic acid. Moreover, glycols are also used as a base carrier, diluents or viscosity modifier in flux. Polyethylene glycol is the type of glycol that has been used in many flux formulas. In order to find material that is the cause of uncured epoxy and does not compatible with epoxy, various acids that is the composition of flux in the solder paste was mixed to epoxy on the substrate. The composition between epoxy and each type of acid as well as the sample appearances after curing are shown in Table 5.2. Although all samples are not homogeneous mixture, the epoxy seem to be cured and dried especially for the sample of epoxy with inorganic acid such as sulfuric, hydrochloric, phosphoric, and boric acid have black color on the surface. On the contrary, the samples of epoxy mixed with organic acid have yellow or white color on the surface. Their thermal properties were therefore confirmed by DSC. DSC results of epoxy with each organic acid are exhibited in Figure 5.11. The glass transition temperature ($T_g$) of the epoxy with acetic acid, formic acid, tartaric acid, and citric acid were determined to be 90, 100, 103, and 129?C, respectively. According to the $T_g$ results, all samples were cured. Therefore, the acid in the flux is not the cause of the uncured epoxy.

**Table 5.2** The composition and the appearance of samples formed from epoxy mixed with acid.

| Sample no. | Materials | Appearance |
|---|---|---|
| 1 | Mass ratio of<br>Epoxy : Tartaric acid<br>2.3:1 |  |
| 2 | Mass ratio of<br>Epoxy : Citric acid<br>1.8:1 |  |
| 3 | Mass ratio of<br>Epoxy : Formic acid<br>2.9:1 |  |
| 4 | Mass ratio of<br>Epoxy : Acetic acid<br>6.3:1 |  |
| 5 | Mass ratio of<br>Epoxy : Sulfuric acid<br>2.0:1 |  |
| 6 | Mass ratio of<br>Epoxy : Hydrochloric acid<br>3.1:1 |  |
| 7 | Mass ratio of<br>Epoxy : Phosphoric acid<br>1.7:1 |  |
| 8 | Mass ratio of<br>Epoxy : Boric acid<br>2.1:1 |  |

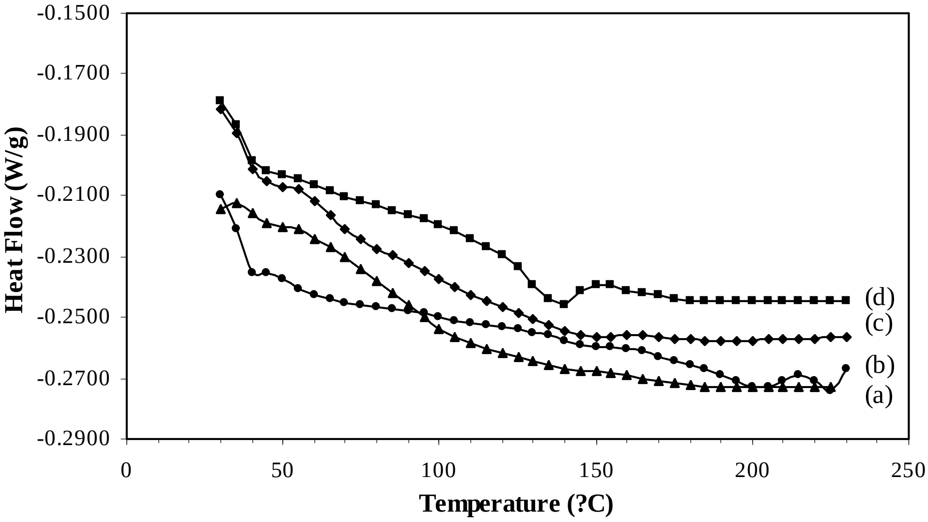


**Figure 5.11** DSC curves of epoxy mixed with: a) acetic acid, b) formic acid, c) tartaric acid, and d) citric acid.

On the other hand, the results of samples that were obtained from epoxy mixed with polyethylene glycol in several ratios (4:1, 10:1, 30:1, 50:1, and 80:1) show uncuring problem as shown in Table 5.3. The uncured appearance of each sample appears only on the surface of the sample, which was exposed to polyethylene glycol, while the unexposed area is cured.

Moreover, blending of epoxy with polyethylene glycol together with the acid investigated earlier was also conducted according to compositional ratio shown in Table 5.4. All samples that contain polyethylene glycol are not cured, as shown in Table 5.4. That means that the interaction between acid and polyethylene glycol, can not prevent the curing inhibition effect from polyethylene glycol. Therefore, it can be concluded that polyethylene glycol is the major cause of the uncuring problem and it does not compatible with epoxy.

**Table 5.3** The composition and the appearance of samples formed from epoxy mixed with polyethylene glycol at various contents.

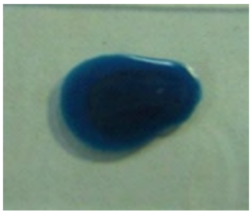
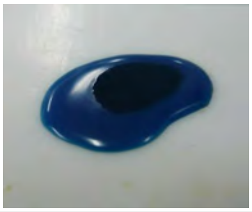
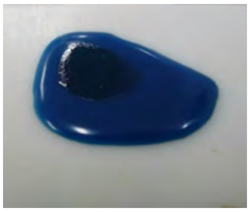
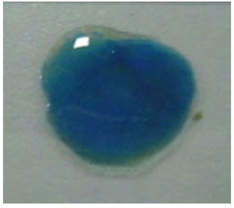
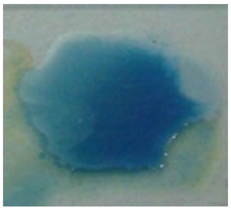
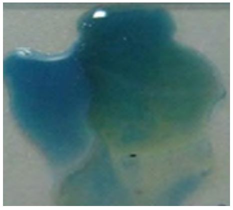
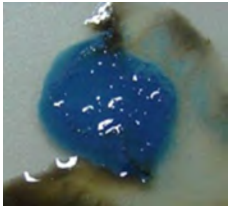
| **Sample no.** | **Mass ratio of Epoxy:polyethylene glycol** | **Appearance** |
|---|---|---|
| 1 | 4:1 |  |
| 2 | 10:1 |  |
| 3 | 30:1 |  |
| 4 | 50:1 |  |
| 5 | 80:1 |  |

**Table 5.4** The appearances of samples formed from epoxy mixed with polyethylene glycol and acid.

| Sample no. | Materials | Appearance |
|---|---|---|
| 1 | Mass ratio of<br>Epoxy : Polyethylene glycol : Citric acid<br>1.9:0.9:1 |  |
| 2 | Mass ratio of<br>Epoxy : Polyethylene glycol : Formic acid<br>3.2:1.6:1 |  |
| 3 | Mass ratio of<br>Epoxy : Polyethylene glycol : Acetic acid<br>3.4:1.8:1 |  |
| 4 | Mass ratio of<br>Epoxy : Polyethylene glycol : Phosphoric acid<br>2.0:0.9:1 |  |
| 5 | Mass ratio of<br>Epoxy : Polyethylene glycol : Boric acid<br>3.1:1.0:1 |  |

Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) technique was used to confirm the uncuring of the sample, i.e. epoxy mixed with polyethylene glycol. Figure 5.12 shows the spectrum of epoxy mixed with polyethylene glycol and uncured epoxy obtained from actual manufacturing process (epoxy mixed with flux from solder paste). The IR spectra of epoxy mixed with polyethylene glycol shows characteristic peaks at 2152, 2002, and 1963 $cm^{-1}$, which are not presented in the spectra of the uncured epoxy. Therefore, these bands should be the result from interaction between epoxy and polyethylene glycol.

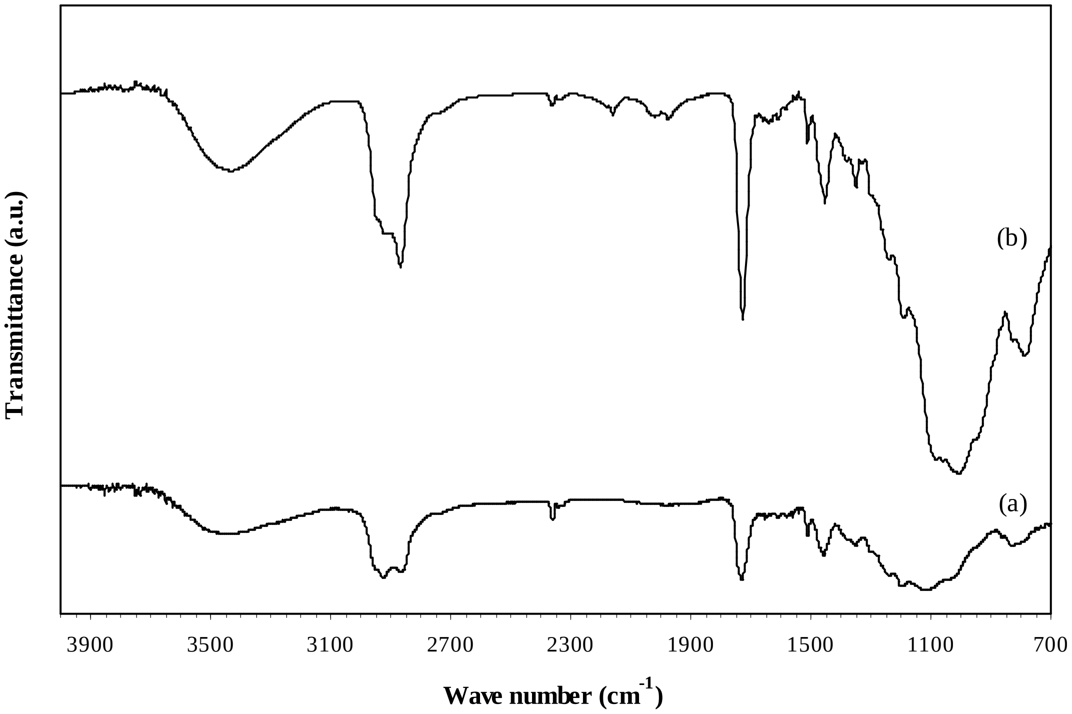


**Figure 5.12** IR spectra of: a) uncured epoxy obtained from actual manufacturing process and b) epoxy mixed with polyethylene glycol.

Figure 5.13 compares FTIR spectra of raw epoxy, polyethylene glycol, and uncured epoxy, which was prepared from epoxy mixed with polyethylene glycol. It is found that the uncured epoxy does not show absorption bands of raw epoxy at 1855, 1788, and 904 $cm^{-1}$. It should be noted that the absorption bands at 1855 and 1788 $cm^{-1}$ are corresponding to anhydride, while the band at 904 $cm^{-1}$ represents epoxide group (=C-H and $=CH_2$). On the other hand, the absorption band of polyethylene glycol at 1346 $cm^{-1}$ (O-H bending) is still present in the uncured epoxy. According to Derosa *et al.*, who used diffuse reflection infrared spectroscopy (DRIFT) to determine interfacial interactions between poly(ethylene glycol) (PEG), alumina and silica powders, the interactions are created by grafting in high temperature and low moisture environments due to preferential adsorption between PEG and water. Under these grafting conditions, a shoulder appears on the C–O–C stretching band of the DRIFT spectrum. This behavior is found when PEG is in the presence of a hydrogen donor such as surface hydroxyls on alumina and silica. The shoulder was reported as an interaction band due to hydrogen bonding between the PEG etheric oxygen and the surface hydroxyls of alumina and silica. Specific band positions were measured when the PEG chain is interacting with alumina (1090 $cm^{-1}$), silica (1080 $cm^{-1}$), or water (1085 $cm^{-1}$) [35]. In the present study, the absorption band of PEG in the mixture of epoxy and PEG shifts from 1085 $cm^{-1}$ to 1080 $cm^{-1}$ when the epoxy is uncured. It means that PEG chain which is interacting with water changes to interact with silica, the filler in epoxy.

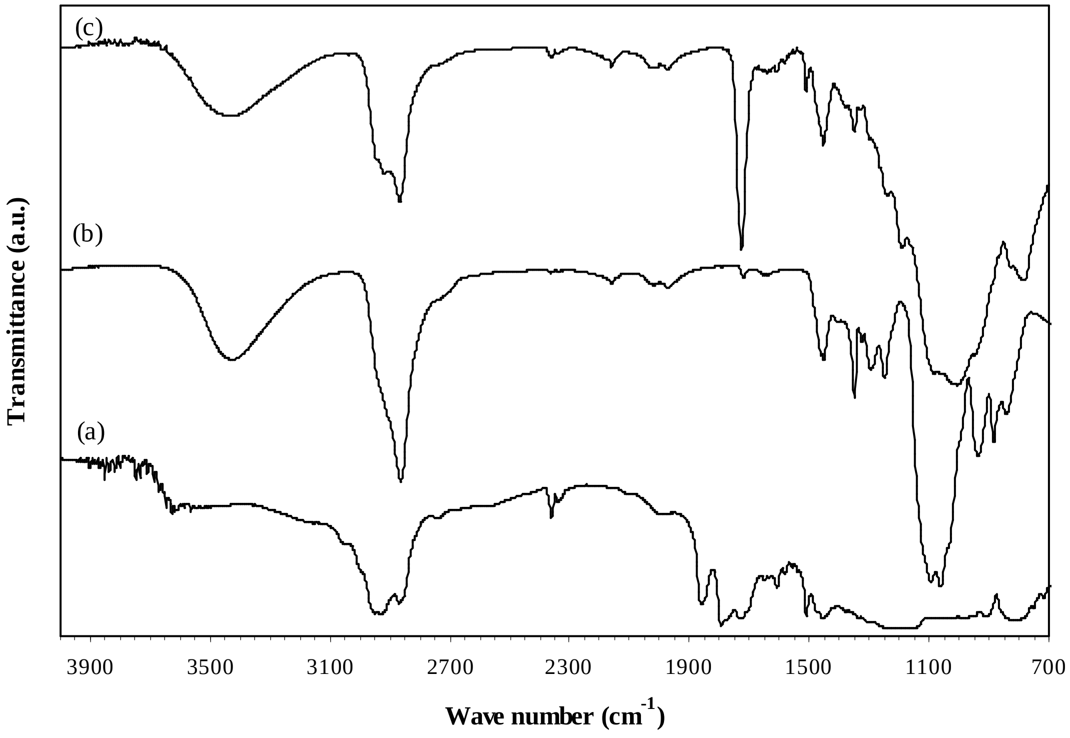


**Figure 5.13** IR spectra of: a) raw epoxy, b) polyethylene glycol, and c) epoxy prepared from raw epoxy mixed with polyethylene glycol.

Figure 5.14 shows the IR spectra of flux in solder paste after passing reflow process comparing to that of polyethylene glycol. The figure shows the characteristic absorption bands for the flux at 1637 $cm^{-1}$ for amino acid group, at 1558 $cm^{-1}$ for ester group, and at 1541 $cm^{-1}$ for nitrite group ($-NO_2$). Beside those bands, the flux also shows all characteristic bands of polyethylene glycol, except an absorption band at 2143 $cm^{-1}$. This means that the solder paste used in this study contains polyethylene glycol in the flux composition which agrees well with description in many patents.

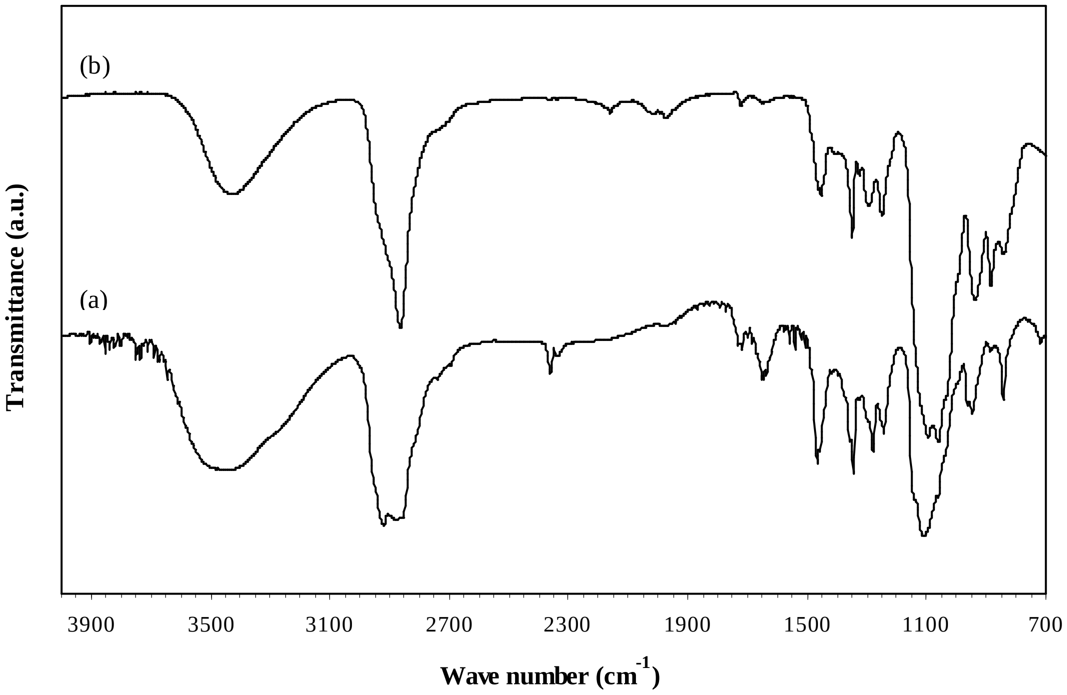


**Figure 5.14** IR spectra of: a) flux and b) polyethylene glycol.

Several solutions are introduced to the uncured epoxy problem. Cleaning the flux residue before underfill process is the best solution as it is appropriate in term of reliability especially when water soluble flux is applied which results in lots of flux residues. However, it is not a good choice in the view of robust production because additional process is required. Moreover, extra care must be provided for product because the product can not withstand much stress at this point of the process. This leads to poor quality and yield loss, such as bump crack and solder-joint damage. The second solution is changing the type of flux in the solder paste from water-soluble to no-clean type. Nowadays this solution is available in the market. There are some solder pastes which are compatible to epoxy, i.e. epoxy still able to be cured completely even after exposed to flux. The limitation of this solution is in case when the product needs high level of cleanliness. The third solution is to keep the solder pad away from underfill area, which may affect the product design product design especially the size and speed. As the product tends to be smaller and smaller and requires faster and faster performances, the space available on the circuit is quite limited. Therefore, alternative is to use smaller underfill needle, which will help limiting the underfill spreading but will affect the production capacity.

# CHAPTER VI

# CONCLUSIONS

Uncured underfill encapsulant on the flexible printed circuits (FPCs) in the flip-chip packaging was investigated by using various analytical techniques such as FT-IR and thermal analysis techniques, i.e. DSC, DMA and TMA to understand its behavior. Polyethylene glycol is found to be the composition of base material in flux used in the solder paste that does not compatible with epoxy and causes “uncured epoxy” problem when they are mixed.

Nowadays the products including hard disk drive (HDD) is getting smaller and smaller so that the space on the FPCs that includes the distance between solder pad and underfill area is limited. Moreover HDD requires high level of cleanliness that dictates the selection of solder paste toward water-soluble type, which is able to easily clean the product at the end of the process. Therefore, the compromised solution considering in term of available technology, quality and cost of FPCA for HDD application is to minimize unnecessary flux from the solder paste and to control the spreading of epoxy to avoid mixing with flux residue.

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# APPENDICES

# APPENDIX A

# MATERIAL SATETY DATASHEET

## Acetic Acid Glacial

### Product Identification

Synonyms: Acetic acid, methane carboxylic acid; ethanoic acid

CAS No.: 64-19-7

Molecular Weight: 60.05

Chemical Formula: $CH_3COOH$

### Physical and Chemical Properties

Appearance: Clear, colorless liquid.

Odor: Strong, vinegar-like.

Solubility: Infinitely soluble.

Density: 1.05

pH: 2.4 (1.0M solution)

% Volatiles by volume @ 21?C (70?F): 100

Boiling Point: 118?C (244?F)

Melting Point: 16.6?C (63?F)

Vapor Density (Air=1): 2.1

Vapor Pressure (mm Hg): 11 @ 20?C (68?F)

Evaporation Rate (BuAc=1): 0.97

### Stability and Reactivity

Stability: Stable under ordinary conditions of use and storage. Heat and sunlight can contribute to instability. Releases heat and toxic, irritating vapors when mixed with water. Acetic acid contracts slightly upon freezing which may cause the container to burst.

Hazardous Decomposition Products: Carbon dioxide and carbon monoxide may form when heated to decomposition. May also release toxic and irritating vapors.

Hazardous Polymerization: Will not occur.

Incompatibilities: Acetic Acid is incompatible with chromic acid, nitric acid, ethylene glycol, perchloric acid, phosphorous trichloride, oxidizers, sodium peroxide, strong caustics, most metals (except aluminum), carbonates, hydroxides, oxides, and phosphates.

Conditions to Avoid: Heat, flame, ignition sources, freezing, incompatibles

### Toxicological Information

Oral rat LD50: 3310 mg/kg; skin rabbit LD50: 1.06 g/kg; inhalation mouse LC50: 5620 ppm/1-hr; investigated as a mutagen, reproductive effector.

## Boric Acid

### Product Identification

Synonyms: ortho-Boric acid; boracic acid; Borofax, boric acid ($H_3BO_3$)

CAS No.: 10043-35-3

Molecular Weight: 61.83

Chemical Formula: $H_3BO_3$

### Physical and Chemical Properties

Appearance: White powder or granules.

Odor: Odorless.

Solubility: 1g/18mL in cold water.

Density: 1.43

pH: 5.1 Aqueous solution: (0.1M)

% Volatiles by volume @ 21?C (70?F): 0

Boiling Point: Decomposes.

Melting Point: 169?C (336?F)

Vapor Density (Air=1): No information found.

Vapor Pressure (mm Hg): 2.6 @ 20?C (68?F)

Evaporation Rate (BuAc=1): No information found.

### Stability and Reactivity

Stability: Stable under ordinary conditions of use and storage. If moisture is present, boric acid can be corrosive to iron.

Hazardous Decomposition Products: Loses chemically combined water upon heating, forming metaboric acid (HBO2) at 212-221F, then pyroboric acid (H2B4O7) at 285-320F, and Boric anhydride at higher temperatures.

Hazardous Polymerization: Will not occur.

Incompatibilities: Potassium, acetic anhydride, alkalis, carbonates, and hydroxides.

Conditions to Avoid: No information found.

### Toxicological Information

Toxicological Data: Oral rat LD50: 2660 mg/kg; oral woman LDLo: 200 mg/kg; investigated as a mutagen, tumorigen, reproductive effector.

Reproductive Toxicity: May impair fertility. May cause harm to the unborn child.

## Citric Acid

### Product Identification

Synonyms: citric acid hydrate, citric acid, 2-hydroxy-1,2,3-propanetricarboxylic acid monohydrate

CAS No: 5949-29-1

Molecular Weight: 210.14

Chemical formula: $C_6H_8O_7$

### Physical and Chemical Properties

Appearance: white crystals or powder

Odor: Not available.

Melting point: 100 ?C

Boiling point: 135-152 ?C

Vapour density: N/A

Vapour pressure: N/A

Density (g cm-3): 1.54

Flash point: 174?C (closed cup)

### Stability and Reactivity

Stability: The product is stable.

Conditions of Instability: Excess heat, incompatible materials, moisture/moisture air. Slightly deliquescent in moist air

Incompatibilities: Reactive with oxidizing agents, reducing agents, metals, alkalis.

Corrosivity: Not available.

Special Remarks on Reactivity: Incompatible with oxidizing agents, potassium tartrate, alkali, alkaline earth carbonates and bicarbonates, acetates, and sulfides, metal nitrates

Polymerization: Will not occur.

### Toxicological Information

Severe eye irritant. Skin and respiratory irritant. Prolonged or repeated exposure may cause allergic reaction in some individuals.

## Formic Acid

### Product Identification

Synonyms: Methanoic acid; hydrogen carboxylic acid; formylic acid

CAS No.: 64-18-6

Molecular Weight: 46.03

Chemical Formula: $HCOOH$

### Physical and Chemical Properties

Appearance: Clear, colorless liquid.

Odor: Characteristic, pungent odor.

Solubility: Infinitely soluble.

Density: 1.2

pH: No information found.

% Volatiles by volume @ 21°C (70°F): 100

Boiling Point: 101°C (214°F)

Melting Point: ca. 8°C (ca. 46°F)

Vapor Density (Air=1): 1.6 @ 19°C (66°F)

Vapor Pressure (mm Hg): 40 @ 24°C (75°F)

Evaporation Rate (BuAc=1): 2.1

### Stability and Reactivity

Stability: Stable under ordinary conditions of use and storage.

Hazardous Decomposition Products: Carbon dioxide and carbon monoxide may form when heated to decomposition. Dehydrated by sulfuric acid to produce carbon monoxide.

Hazardous Polymerization: Will not occur.

Incompatibilities: Sulfuric acid, strong caustics, furfuryl alcohol, hydrogen peroxide, strong oxidizers and bases. Reacts explosively with oxidizing agents.

Conditions to Avoid: Heat, flame, other sources of ignition.

### Toxicological Information

Oral rat LD50: 1100 mg/kg; inhalation rat LC50: 15 gm/m3/15M; investigated as a tumorigen, mutagen.

## Hydrochloric Acid

### Product Identification

Synonyms: Muriatic acid; hydrogen chloride, aqueous

CAS No.: 7647-01-0

Molecular Weight: 36.46

Chemical Formula: $HCl$

### Physical and Chemical Properties

Appearance: Colorless, fuming liquid.

Odor: Pungent odor of hydrogen chloride.

Solubility: Infinite in water with slight evolution of heat.

Density: 1.18

pH: For HCL solutions: 0.1 (1.0 N), 1.1 (0.1 N), 2.02 (0.01 N)

% Volatiles by volume @ 21?C (70?F): 100

Boiling Point: 53?C (127?F) Azeotrope (20.2%) boils at 109?C (228?F)

Melting Point: -74?C (-101?F)

Vapor Density (Air=1): No information found.

Vapor Pressure (mm Hg): 190 @ 25?C (77?F)

Evaporation Rate (BuAc=1): No information found.

### Stability and Reactivity

Stability: Stable under ordinary conditions of use and storage. Containers may burst when heated.

Hazardous Decomposition Products: When heated to decomposition, emits toxic hydrogen chloride fumes and will react with water or steam to produce heat and toxic and corrosive fumes. Thermal oxidative decomposition produces toxic chlorine fumes and explosive hydrogen gas.

Hazardous Polymerization: Will not occur.

Incompatibilities: A strong mineral acid, concentrated hydrochloric acid is incompatible with many substances and highly reactive with strong bases, metals, metal oxides, hydroxides, amines, carbonates and other alkaline materials. Incompatible with materials such as cyanides, sulfides, sulfites, and formaldehyde.

Conditions to Avoid: Heat, direct sunlight.

### Toxicological Information

Inhalation rat LC50: 3124 ppm/1H; oral rabbit LD50: 900 mg/kg (Hydrochloric acid concentrated); investigated as a tumorigen, mutagen, reproductive effector.

## Phosphoric Acid

### Product Identification

Synonyms: Ortho-phosphoric acid; white phosphoric acid

CAS No.: 7664-38-2

Molecular Weight: 98.00

Chemical Formula: $H_3PO_4$ in $H_2O$

### Physical and Chemical Properties

Appearance: Clear, colorless syrupy liquid.

Odor: Odorless.

Solubility: Miscible in all proportions in water.

Specific Gravity: 1.69 @ 25?C

pH: 1.5 (0.1 N aqueous solution)

% Volatiles by volume @ 21?C (70?F): 100

Boiling Point: 158?C (316?F)

Melting Point: 21?C (70?F)

Vapor Density (Air=1): 3.4

Vapor Pressure (mm Hg): 0.03 @ 20?C (68?F)

Evaporation Rate (BuAc=1): No information found.

### Stability and Reactivity

Stability: Stable under ordinary conditions of use and storage. Substance can supercool without crystallizing.

Hazardous Decomposition Products: Phosphorus oxides may form when heated to decomposition.

Hazardous Polymerization: Will not occur.

Incompatibilities: Liberates explosive hydrogen gas when reacting with chlorides and stainless steel. Can react violently with sodium tetrahydroborate. Exothermic reactions with aldehydes, amines, amides, alcohols and glycols, azo-compounds, carbamates, esters, caustics, phenols and cresols, ketones, organophosphates, epoxides, explosives, combustible materials, unsaturated halides, and organic peroxides. phosphoric acid forms flammable gases with sulfides, mercaptans, cyanides and aldehydes. It also forms toxic fumes with cyanides, sulfide, fluorides, organic peroxides, and halogenated organics. Mixtures with nitromethane are explosive.

Conditions to Avoid: Incompatibles.

### Toxicological Information

Oral rat LD50: 1530 mg/kg; investigated as a mutagen.

## Sulfuric Acid

### Product Identification

Synonyms: Oil of vitriol; Babcock acid; sulphuric acid

CAS No.: 7664-93-9

Molecular Weight: 98.07

Chemical Formula: $H_2SO_4$ in $H_2O$

## Physical and Chemical Properties

Appearance: Clear oily liquid.

Odor: Odorless.

Solubility: Miscible with water, liberates much heat.

Specific Gravity: 1.40 (50%), 1.07 (10%)

pH: 1 N solution (ca. 5% w/w) = 0.3; 0.1 N solution (ca. 0.5% w/w) = 1.2; 0.01 N solution (ca. 0.05% w/w) = 2.1.

% Volatiles by volume @ 21?C (70?F): No information found.

Boiling Point: ca. 290?C (ca. 554?F) (decomposes at 340?C)

Melting Point: 3?C (100%), -32?C (93%), -38?C (78%), -64?C (65%).

Vapor Density (Air=1): 3.4

Vapor Pressure (mm Hg): 1 @ 145.8?C (295?F)

Evaporation Rate (BuAc=1): No information found.

## Stability and Reactivity

Stability: Concentrated solutions react violently with water, spattering and liberating heat.

Hazardous Decomposition Products: Toxic fumes of oxides of sulfur when heated to decomposition. Will react with water or steam to produce toxic and corrosive fumes. Reacts with carbonates to generate carbon dioxide gas, and with cyanides and sulfides to form poisonous hydrogen cyanide and hydrogen sulfide respectively.

Hazardous Polymerization: Will not occur.

Incompatibilities: Water, potassium chlorate, potassium perchlorate, potassium permanganate, sodium, lithium, bases, organic material, halogens, metal acetylides, oxides and hydrides, metals (yields hydrogen gas), strong oxidizing and reducing agents and many other reactive substances.

Conditions to Avoid: Heat, moisture, incompatibles.

## Toxicological Information

Oral rat LD50: 2140 mg/kg; inhalation rat LC50: 510 mg/m3/2H; standard Draize, eye rabbit, 250 ug (severe); investigated as a tumorigen, mutagen, reproductive effector.

## Tartaric Acid

### Product Identification

Synonyms: d-tartaric acid; 2,3-dihydroxybutanedioic acid

CAS No.: 87-69-4

Molecular Weight: 150.09

Chemical Formula: $HOOC(CH_2O)_2COOH$

### Physical and Chemical Properties

Appearance: White crystals.

Odor: Odorless.

Solubility: ca. 133 g/100 g of water.

Density: 1.76

pH: No information found.

% Volatiles by volume @ 21?C (70?F): No information found.

Boiling Point: Not applicable.

Melting Point: 206?C (403?F)

Vapor Density (Air=1): No information found.

Vapor Pressure (mm Hg): No information found.

Evaporation Rate (BuAc=1): No information found.

### Stability and Reactivity

Stability: Stable under ordinary conditions of use and storage.

Hazardous Decomposition Products: Carbon dioxide and carbon monoxide may form when heated to decomposition.

Hazardous Polymerization: Will not occur.

Incompatibilities: Silver and silver compounds.

Conditions to Avoid: Incompatibles.

### Toxicological Information

No LD50/LC50 information found relating to normal routes of occupational exposure.

## Polyethylene glycol 300

### Product Identification

Synonyms: PEG; Carbowax; Polyglycol; Polyethylene glycol 200, 300, 400, 600, 1000, 1450, 3350, 4000, 6000, 8000 and 20000.

CAS No.: 25322-68-3

Molecular Weight: Not applicable to mixtures.

Chemical Formula: $(C_2H_4O)$ n.$H_2O$

### Physical and Chemical Properties

Appearance: Clear liquid or white solid.

Odor: Mild odor.

Solubility: Soluble in water.

Density: range: 1.1 to 1.2 (increases as molecular weight increases)

pH: No information found.

% Volatiles by volume @ 21?C (70?F): No information found.

Boiling Point: No information found.

Melting Point: Melting point increases as molecular weight increases: PEG 400 = 4-8?C (39-46?F) PEG 600 = 20-25?C (68-77?F) PEG1500 = 44-48?C (111-118?F) PEG 4000 = 54-58?C (129-136?F) PEG 6000 = 56-63?C (133-145?F)

Vapor Density (Air=1): No information found.

Vapor Pressure (mm Hg): Vapor pressure is very low; as molecular weight increases, vapor pressure decreases.

Evaporation Rate (BuAc=1): No information found.

### Stability and Reactivity

Stability: Stable under ordinary conditions of use and storage.

Hazardous Decomposition Products: Carbon dioxide and carbon monoxide may form when heated to decomposition.

Hazardous Polymerization: Will not occur.

Incompatibilities: Incompatible with polymerization catalysts (peroxides, persulfates) and accelerators, strong oxidizers, strong bases and strong acids.

### Toxicological Information

Oral Rat LD50 for: PEG 200 = 28gm/kg; PEG 300 = 27.5gm/kg; PEG 400 = 30.2gm/kg; PEG 600 = 30gm/kg; PEG 1000 = 32gm/kg; PEG 1450 = > 4gm/kg; PEG 4000 = 50gm/kg; PEG 6000 = > 50gm/kg; PEG 20000 = 31.6gm/kg

Polyethylene glycol has been investigated as a mutagen; PEG 1000 has been investigated as a tumorigen.

# APPENDIX B

# THERMAL PROPERTIES CHARACTERIZATION

**Table B-1** Glass transition temperature of epoxy with different techniques.

| Sample | Technique | Glass Transition Temperature (?C) |
|---|---|---|
| Epoxy cured at 165?C for 30 mins | DSC | 129.3 |
|  | TMA | 134.5 |
|  | DMA | 154.5 |
| Epoxy cured at 145?C for 15 mins | DSC | 117.6 |
|  | TMA | 106.7 |
|  | DMA | 149.3 |

# APPENDIX C

# REFLOW EVALUATION

**Table C-1** Experiment list of Reflow evaluation

| Experiment | Ramp up rate (?C/sec) | Preheat time (sec) | Reflow time (sec) | Oxygen content (ppm) |
|---|---|---|---|---|
| 1 | 1.5 | 60 | 30 | 250 |
| 2 | 1.5 | 90 | 30 | 250 |
| 3 | 1.5 | 120 | 30 | 250 |
| 4 | 1.5 | 150 | 30 | 250 |
| 5 | 1.5 | 90 | 30 | 250 |
| 6 | 1.5 | 90 | 60 | 250 |
| 7 | 1.5 | 90 | 90 | 250 |
| 8 | 1.5 | 90 | 120 | 250 |
| 9 | 1.5 | 90 | 30 | 250 |
| 10 | 1.5 | 90 | 30 | 1500 |
| 11 | 1.5 | 90 | 30 | 3000 |
| 12 | 1.5 | 90 | 30 | 210000 |
| 13 | 2.0 | 60 | 60 | 250 |
| 14 | 2.5 | 60 | 60 | 250 |
| 15 | 3.0 | 60 | 60 | 250 |

# APPENDIX D

# LIST OF PUBLICATION

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# Epoxy curing inhibition by residual flux in flip-chip packaging process

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**Abstract** This study investigates the root cause of uncured underfill encapsulant (epoxy) problem of the flip-chip packaging on flexible printed circuits (FPCs). In the FPC assembly, lead-free solder paste (water soluble type with flux ORM0) is printed on a copper pad. Then, epoxy is filled underneath the IC die by dispensing from the side of the die. Nevertheless, since the product size in the present day is so small that the distance between solder pad and the underfill area becomes very close. The contact between flux residues generated after the heat treatment of the solder (i.e. reflow process) and the epoxy results in uncuring problem of the epoxy. In this study, attempts were made to reduce the flux residue by adjusting the reflow profile (both temperature and time) and finding the appropriate process for the industries. Epoxy curing was also studied by using Fourier Transform Infrared Spectroscopy (FTIR), Differential Scanning Calorimetry (DSC), Thermo-mechanical Analysis (TMA) and Dynamic Mechanical Analysis (DMA). The results showed that the incompatibility between the flux residue and epoxy inhibited the cross linking of the epoxy. Moreover, the change in reflow conditions could not completely eliminate the flux. The best way to solve this problem is the cleaning of the residual flux by de-ionized water before the underfill process or changing the flux type.

## 1. Introduction

FPC assembly technology is increasingly used in many applications such as hard-disk drive (HDD), automotive, and communication and consumer electronics (CE). Solder paste, which is one of materials used in the Surface-Mount Technology (SMT) assembly process, is a combination of spherical alloyed solder particles and paste medium (flux and binding agents) blended together to form a paste. Flux is a chemical cleaning agent, which facilitates soldering by removing oxides from the metals to be joined. Flux is a substance which is nearly inert at room temperature, but becomes strong reducing agent at elevated temperature and prevents the formation of metal oxides. On the other hand, epoxy is also used in the FPC assembly, especially in flip-chip area. Epoxy is a thermosetting epoxide polymer that is cured (i.e. cross-linking) when it is mixed with a curing agent or "hardener". Most common epoxy resins are produced from a reaction between epichlorohydrin and bisphenol-A, and hardened with anhydrides [1]. In this study, a root cause of uncured epoxy problem, when the solder paste printing location is close to the underfill encapsulate area for epoxy, is investigated. This problem particularly takes place in the process where there is no cleaning step prior to the epoxy underfilling.

## 2. Materials and Method

### 2.1 *Materials*

Lead-free solder paste employed in this work contains 10.5% flux content, while the major compositions of the epoxy (Hysol) are resin, silica and methylhexahydrophthalic anhydride (MHHPA), which is a hardener for hot-cured epoxy resins employed as insulators in the electric industry [2]. The remaining compositions of the epoxy are additives such as epichlorohydrin-4,4'-isopropylidene diphenol resin, 3,4-epoxycyclohexyl 3,4-epoxycyclohexane carboxylate and 1,4-butanediol diglycidyl ether.

### 2.2 *Experimental procedures*

The curing of the epoxy was examined by Differential Scanning Calorimetry (DSC, Perkin Elmer Pyris Diamond) in the range of 50-220°C by at the heating rate of 10°C/min, Thermo-mechanical Analysis (TMA, Perkin Elmer Pyris Diamond) in the range of 25-220°C at the heating rate of 5°C/min, and Dynamic Mechanical Analysis (DMA, Perkin Elmer Pyris Diamond) in the range of 30-250°C at the heating rate of 1°C/min with frequency of 1 Hz. For such measurements, epoxy samples were cured in a conventional oven with recommended cure profile at 165°C for 30 min and at 145°C for 15 min.

In order to monitor the changes in molecular structure of the epoxy after curing process, Infrared spectroscopy (FTIR, Perkin Elmer Spectrum 2000) was employed. The specimens were prepared from the actual assembly process in Mektec

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Manufacturing Corporation (Thailand), starting from printing solder paste on copper pad, component and IC placement, thermal treatment in reflow process, dispensing and curing the epoxy.

## 3. Results and Discussion

### *3.1 Characteristic of uncured epoxy*

In the actual manufacturing process, flux residue is often found around the solder pads. Moreover, after the curing process for the epoxy, incomplete curing is usually observed in the vicinity of the solder pad, as shown in Figure 1.

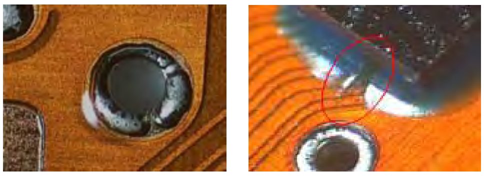

**Figure 1** Flux residue and incompletely cured epoxy

The evaluation of the epoxy curing usually relies on thermal analysis techniques such as DSC and DMA [3, 4]. In this study, however, the results from DSC, DMA and TMA were evaluated, in order to check the difference between cured and uncured epoxy. Figure 2 shows damping factor (tanδ) and storage modulus obtained from DMA analyses of epoxy which was fully cured at 165°C for 30 min and those of epoxy partially cured at 145°C for 15 min. It can be seen that although shape of both damping factor and storage modulus of the fully cured and the partially cured epoxy are slightly different, the difference is not quantitatively significant. The difference in Tg identified from both samples is only about 5°C. The similar result was also observed from DSC analysis, as shown in Figure 3, in which the glass transition temperature for the fully cured and the partially cured epoxy were identified as 129.3 and 118°C, respectively.

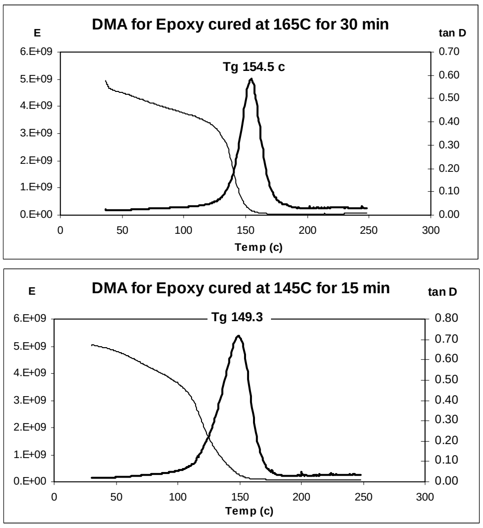

**Figure 2** DMA curves for epoxy cured at 100-165°C for 30 min and cured at 100-145°C for 15 min.

On the other hand, the difference as much as 28°C in the glass transition temperature between the fully cured and partially cured epoxy was identified via TMA, as shown in Figure 4. Therefore, this technique is better than DMA and DSC regarding the ability to distinguish the difference in curing of the specimen. However, TMA is limited to homogeneous specimen, but the sample in this work may consist of more than 2 phases due to incompatibility between residual flux and the epoxy.

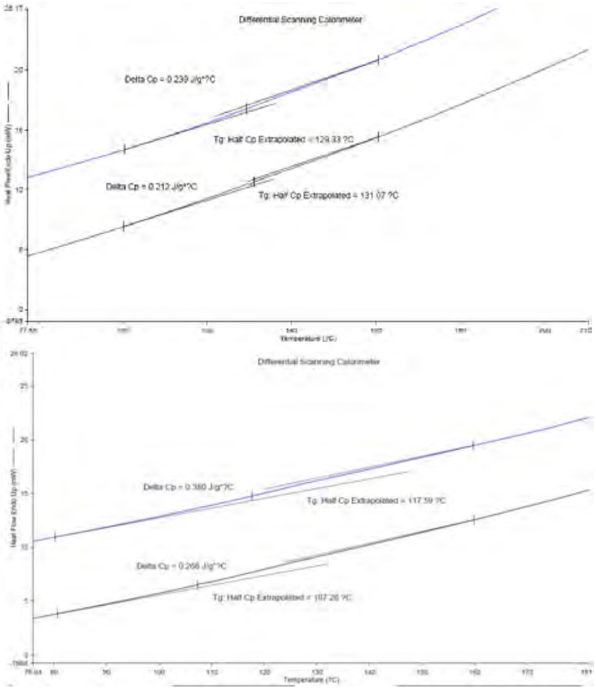

**Figure 3** DSC curves for epoxy cured at 165°C for 30 min and cured at 145°C for 15 min.

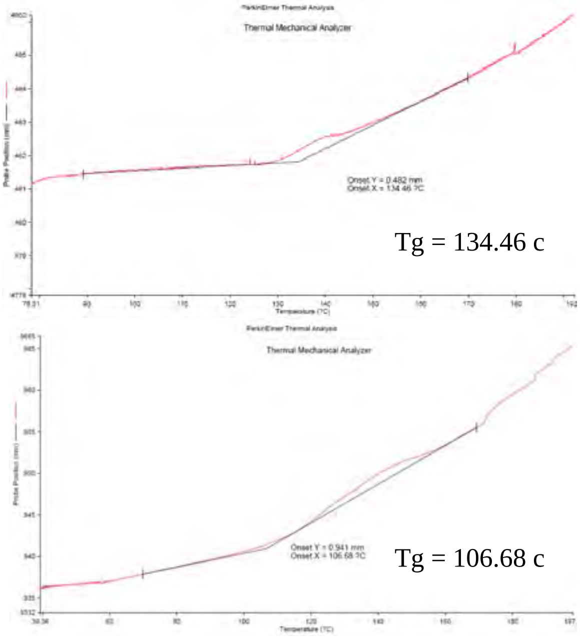

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**Figure 4** TMA curves for epoxy cured at 165°C for 30 min and cured at 145°C for 15 min.

FTIR spectroscopy was also adopted to examine the change in intermolecular bonding in the curing of epoxy. This technique has been used to monitor hydrogen bonding of epoxy resin as well as intermolecular bonding within the polymer matrix [5]. Figure 5-6 show the comparison of FTIR analysis results from epoxy cured at different conditions. According to Park et al., when an epoxy sample of Hysol FP4511 was aged for 20 h at 23°C in 78% RH, the absorption bands at 1783 and 1857 cm$^{-1}$ corresponding to anhydride disappeared while an acid peak at 1705 cm$^{-1}$ was formed [1]. This result together with the FTIR data indicated that the anhydride hardener absorbs and reacts with water, resulting in acid that apparently alters the interaction between the hardener and epoxy and lowers the cross-link density as well as the Tg value of the epoxy/anhydride system. To confirm this concept, the FTIR analysis was used to examine the difference among fully cured epoxy, epoxy left in air for 5 hrs, and raw epoxy. The results are shown in Figure 5. It can be seen that absorption bands corresponding to anhydride disappear after curing. However, since the type of epoxy used in this work is different than that employed in the previous work, no acid peak at 1705 cm$^{-1}$ was observed. Similar result has been reported by Liu et al. whereas the curing behavior as well as thermal properties of bisphenol A type novolac epoxy resin (bisANER) by methyl-hexahydrophthalic anhydride (MHHPA) at an anhydride/epoxy group ratio of 0.85 was studied with Fourier-transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC), and thermogravimetry [6]. The results showed that the FTIR absorption intensity of anhydride and epoxide decreased during the curing reaction, and the absorption peak of ester appeared.

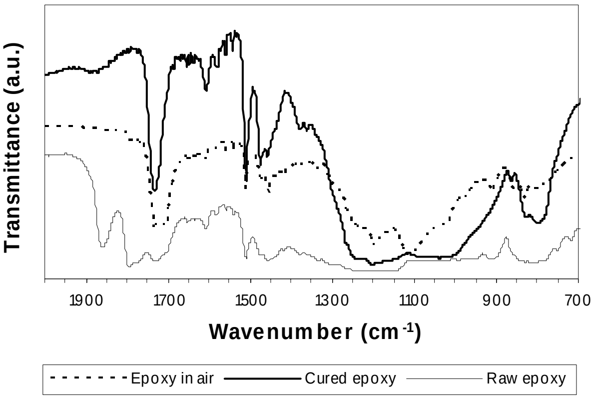

**Figure 5** FTIR spectra of epoxy fully cured at 100-165°C for 30 min, epoxy left in air for 5 hrs, and epoxy raw material.

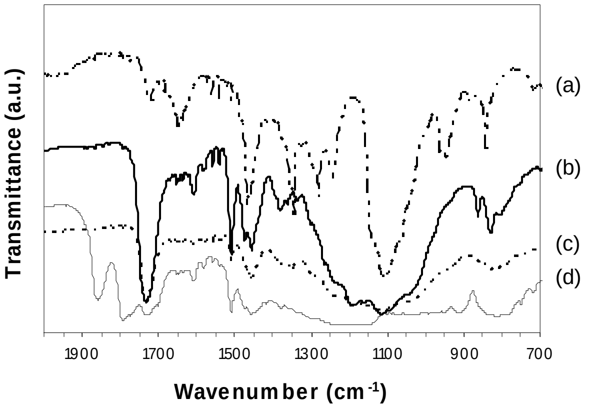

**Figure 6** FTIR spectra of: a) flux, b) fully cured epoxy, c) uncured epoxy, and d) epoxy raw material.

Then, the FTIR spectra of the fully cured epoxy and uncured epoxy were compared to those of the epoxy raw material and flux, as shown in Figure 6. Comparing between fully cured epoxy and unsuccessfully cured epoxy, it can be seen that the absorption bands at 1608, 1380, 863 and 829 cm$^{-1}$ are missing when the epoxy is uncured. These bands should associate with cross-linking bonds formed during the curing process. It should also be noted that some signals from the epoxy raw material, such as the band at 1608 and 1505 cm$^{-1}$, are still observed even after the curing is completed. These bands are longer observable in the uncured sample. Therefore, this curing problem should be the result from the chemical alteration of the epoxy by the residual flux, which prohibits formation of the cross-linking bonds.

### *3.2 Evaluation of reflow profile*

In the conventional reflow soldering process, there are usually four stages called "zones", each having a distinct thermal profile, i.e. preheat, thermal soak, reflow and cooling zones. The preheat zone is where the solvent in the solder paste begins to evaporate. However, if either the heating rate or temperature level is too low, evaporation of the volatiles may be incomplete. On the contrary, if the rate exceeds the maximum value, potential damage to electrical components from thermal shock or cracking can occur. The typical ramp-up rate is usually taken at 1-3°C/s. In the thermal soak zone, which is typically set at 60-120 seconds to remove volatiles in the solder paste together with the activation of the fluxes, the

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components in flux begin to reduce oxides formed on component leads and pads. Too high or too low a temperature can lead to solder spattering or balling as well as oxidation of the paste, the attachment pads and the component terminations. Similarly, fluxes may not fully activate if the temperature is too low.

The reflow zone, which is also referred to as the "time above reflow" or "time above liquidus" (TAL), is the part of the process where the maximum temperature is reached. An important consideration is peak temperature, which is the maximum allowable temperature of the entire process. This limit is determined by the component on the assembly with the lowest tolerance for high temperatures. Additionally, high temperatures (beyond 260°C) may cause damage to the internal die of SMT components as well as foster intermetalic growth. Conversely, temperature that is not high enough may prevent the paste from reflowing adequately. The flux reduces surface tension at the juncture of the metals to accomplish metallurgical bonding, allowing the individual solder powder spheres to combine. If the profile time exceeds the manufacturer's specification, the result may be premature flux activation or consumption, effectively "drying" the paste before formation of the solder joint. An insufficient time/temperature relationship causes a decrease in the flux's cleaning action, resulting in poor wetting, inadequate removal of the solvent and flux, and possibly defective solder joints. Experts usually recommend the shortest TAL possible; however, most pastes specify a minimum TAL of 30 seconds. Too little time above liquidus may trap solvents and flux and create the potential for cold or dull joints as well as solder voids.

The last zone is a cooling zone, which is used to gradually cool the processed board and solidify the solder joints. Proper cooling inhibits excess intermetallic formation or thermal shock to the components. Typical temperatures in the cooling zone range from 30 to 100°C. Unlike the maximum ramp-up rate, the ramp–down rate is often ignored [7].

**Table 1** IPC/JDEC J-STD-020C for lead-free reflow profile recommendation [8]

| Reflow parameter | Lead-free assembly |
|---|---|
| Minimum preheat temperature ($T_{smin}$) | 150°C |
| Maximum preheat temperature ($T_{smax}$) | 200°C |
| Preheat time | 60-180 sec |
| $T_{smax}$ to $T_L$ ramp up rate | 3°C/s max |
| Time above temperature $T_L$ | 217°C 60-120 sec |
| Peak temperature $T_P$ | 260°C |
| Time from 25°C to $T_P$ | 6 minutes max |
| Time within 5°C of peak | 10-20 sec |
| Ramp down rate | 4°C/s max |

In order to avoid the epoxy uncuring from the residual flux, the reflow process was adjusted to investigate optimum conditions to eliminate the flux. It should be noted that the experiments were conducted in a SRS-1 reflow simulator, according the recommended reflow profile. The factors investigated were heating rate in the preheat zone (1.5, 2.0, 2.5 and 3.0°C/s), preheating time (60, 90, 120 and 150 s), reflow time (30, 60, 90 and 120 s) and oxygen content (250, 1500, 3000 ppm and 21%). Unfortunately, the results from the experiments indicated that the flux residues still remained on the solder pad, regardless of the heating time, temperature and oxygen content. These results suggest that the water soluble solder paste will result in flux residue after the reflow. Therefore, the cleaning process after reflow (i.e. before the underfilling process) is needed in order to avoid the epoxy uncuring problem. If industries are not necessary stay with water soluble flux, some no-clean flux is compatibility with epoxy.

## 4. Conclusions

The incompatibility between flux residue and epoxy resin in confirmed to inhibit the cross-linking of the epoxy, i.e. curing of the epoxy. The change in reflow condition could not completely eliminate flux residue. Therefore, the best way to solve this problem is the cleaning of the flux residue by de-ionized water before the underfill process or if space is available, increase distance between the printing pad and underfill area.

## 5. Acknowledgements

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