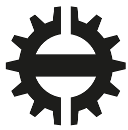

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Sanna Lahokallio

Performance and Reliability of Polymer-based Sensor Packages at High Temperatures

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Abstract

Electronics is increasingly used in many applications. In addition to new consumer electronics, there is a trend to implement electronics and sensors in many industrial applications, which often requires improved reliability in very demanding conditions. This thesis concerns the effect of high temperature on electronics packages. High temperature tends to accelerate chemical reactions, aging of materials and thereby also failures. Properties of polymer materials, which are often used in electronic packaging, are heavily temperature-dependent. They are, however, very versatile and compatible materials which are readily available and easy to manufacture compared to expensive high-temperature speciality materials such as ceramics. Therefore, using polymers at high temperatures would be highly beneficial. However, it is crucial to understand the effects of high temperature on polymer materials before they are used.

This work concentrates on the reliability of polymer-based sensor packages at high temperatures and the changes occurring in their materials at different temperatures. The structures were aged using several high temperature tests including thermal cycling, step stress and thermal storage tests at several temperatures around 200°C. The effects of high temperature on several commercial polymer-based printed circuit boards (PCB) and electrically conductive adhesives (ECA) were analysed from an electrical and mechanical perspective. Moreover, changes in material parameters due to aging were studied to achieve a more profound understanding of the effects of high temperatures.

The temperature of 180°C seemed to be low enough not to cause reliability problems in the polymer-based packages studied. Additionally, a good performance in thermal cycling testing up to 180°C was achieved. At 200°C degradation was seen on the surfaces of the polymer materials and their mechanical properties gradually declined. Good electrical performance was nevertheless achieved with suitable material choices. A temperature of 240°C was shown to be too high for extended exposure of the materials studied. With careful material choices relatively good electrical performance was achieved, but FTIR showed dramatic and rapid degradation with most of the polymer-based materials at this temperature. The degradation was much more severe than at 200°C, and the mechanical properties also showed drastic impairment at 240°C.

Material selection was shown to be absolutely critical for the reliability of the whole polymer-based package. With poor PCB material interconnections failed much earlier than with more stable PCB materials. Additionally, ECA selection was also important. This thesis showed that polymer-based electronic packages can withstand high temperatures, especially for limited exposure times. However, it is crucial that all materials present are able to withstand the selected temperatures.

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Table of Contents

Abstract.. i

Acknowledgements.. ii

List of Symbols and Abbreviations.. vii

List of Publications... ix

Author's Contribution...x

1 INTRODUCTION 1

1.1 Objectives and Scope of the Thesis 3

1.2 Structure of the Thesis 3

2 POLYMER MATERIALS IN ELECTRONICS PACKAGING 5

2.1 Printed Circuit Boards 5

2.2 Electrically Conductive Adhesives 8

2.2.1 Isotropically Conductive Adhesives 9

2.2.2 Anisotropically Conductive Adhesives 10

2.3 Polymer Materials at High Temperatures 13

2.3.1 PCBs at High Temperatures 15

2.3.2 ECAs at High Temperatures 18

3 RELIABILITY TESTING AT HIGH TEMPERATURES 22

3.1 Reliability.. 22

3.1.1 Accelerated Testing 22

3.1.2 Statistical Analysis 23

3.2 High Temperature Reliability Testing.. 25

3.2.1 Thermal Cycling Testing 26

3.2.2 Step Stress Testing 27

3.2.3 Thermal Storage 27

3.3 Test Evaluation Methods and Samples 28

3.3.1 Evaluation with Resistance 28

3.3.2 Test Sample Description 30

4 MATERIAL CHARACTERIZATION 35

4.1 Thermal Analysis 35

4.1.1 Methods and Samples Used 35

4.1.2 Thermal Analysis Results 37

4.2 Fourier Transform Infrared Spectroscopy 40

4.2.1 FTIR Results 40

4.3 Mechanical Analysis 43

4.3.1 Tensile testing 43

4.3.2 Shear testing 45

4.4 Conclusion of Material Characterization 47

5 RELIABILITY OF POLYMER-BASED SENSOR PACKAGES AT HIGH TEMPERATURES 48

5.1 Reliability in Thermal Cycling Tests 48

5.2 Reliability in Step Stress Tests 52

5.3 Reliability in Thermal Storage Tests 54

5.4 Discussion on the Thermal Testing and Reliability of the Polymer-based Sensor Package 71

5.4.1 The Effect of the ECA Material 71

5.4.2 The Effect of PCB Material 72

5.4.3 The Effect of Temperature 73

6 CONCLUSIONS AND FINAL REMARKS 75

REFERENCES 80

List of Symbols and Abbreviations

ACA	Anisotropically conductive adhesive
ACF	Anisotropically conductive film
ACP	Anisotropically conductive paste
AF	Acceleration factor
ALT	Accelerated life tests
ATR	Attenuated total reflection
β	Shape parameter
C	Censored samples
CDF	Cumulative distribution function
COB	Chip-on-board
COF	Chip-on-flex
COG	Chip-on-glass
CTE	Coefficient of thermal expansion
DGEBA	Diglycidyl ether of bisphenol A
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis
ECA	Electrically conductive adhesive
ED	Electro-deposited
η	Characteristic lifetime, scale parameter
ENIG	Electroless nickel immersion gold
F	Failed sample
F(t)	Cumulative distribution function
FTIR	Fourier transform infrared spectroscopy
HTCC	High temperature co-fired ceramics
ICA	Isotropically conductive adhesive
IoT	Internet of things

LCD	Liquid-crystal display
LTCC	Low temperature co-fired ceramics
NCA	Non-conductive adhesive
NEMA	National Electrical Manufacturers Association
OLED	Organic light emitting diode
OSP	Organic solderability preservative
PCB	Printed circuit board
PEN	Polyethylene naphthenate
PET	Polyethylene terephthalate
PI	Polyimide
PTFE	Polytetrafluoroethylene
RA	Rolled annealed
RFID	Radio-frequency identification
SST	Step stress test
STA	Simultaneous thermal analysis
T_g	Glass-transition temperature
TGA	Thermogravimetric analysis
TMA	Thermomechanical analysis
UF	Underfill
UTS	Ultimate tensile strength
γ	Location parameter, minimum life

List of Publications

I. Lahokallio, S., Parviainen, A., Frisk, L. (2013) “Thermal Cycling of Anisotropically Conductive Adhesive Interconnections in Demanding Sensor Applications”, Proceedings of the EMPC Conference, Grenoble France.

II. Lahokallio, S., Frisk, L. (2014) “Performance of Electrically Conductive Adhesive Attached Sensors in High Temperature Cycling”, Proceedings of the EPTC Conference, Singapore.

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IV. Lahokallio, S., Kiilunen, J., Frisk, L. (2014) “High temperature reliability of electrically conductive adhesive attached sensors on flexible polyimide substrates”, Microelectronics Reliability, Vol 54, No 9-10, pp. 2017-2022.

V. Lahokallio, S., Hoikkanen, M., Marttila, T., Vuorinen, J., Kiilunen, J., Frisk, L. (2015) “Performance of a Polymer-Based Sensor Package at Extreme Temperature”, Journal of Electronic Materials, Vol 45, No 2, pp. 1184-1200.

VI. Lahokallio, S., Hoikkanen, M., Vuorinen, J., Frisk, L. (2015) “High-Temperature Storage Testing of ACF Attached Sensor Structures”, Materials, Vol.8, No. 12, pp. 8641-8660.

VII. Lahokallio, S., Frisk, L. (2016) “Performance of Anisotropically Conductive Adhesive Attachments on Adhesiveless Polyimide Substrate during High-Temperature Storage Tests”, MRS Advances, July 2016, pp. 1-6.

Author's contribution

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IV. Publication IV, "High temperature reliability of electrically conductive adhesive attached sensors on flexible polyimide substrates", was accomplished by the present author together with the co-authors as follows: The tests were planned with the help of L. Frisk and J. Kiilunen, the test samples were assembled, the testing carried out and the results analysed by the present author. The SEM analysis was conducted at the Department of Material Science at Tampere University of Technology under the supervision of the present author. The present author wrote the manuscript with the help of the co-authors.

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1 Introduction

Electronics is an important part of everyday life. Electronics can be found in most electrical equipment in the home, from mobile phones to washing machines. In addition to consumer electronics, electronics is increasingly used in other applications such as industrial electronics and automotive applications [Dre08, Jul13, Sha15]. The Internet of things (IoT) will further increase the number of applications. Often these applications have increased reliability needs compared to those of consumer electronics. Moreover, the applications are often exposed to harsh, much more demanding environments [Bec09]. This implies new requirements for the materials used in these applications [Sha15].

Different sensor components are widely implemented in current electronic applications, and are also essential parts of IoT. They are more often used in applications needing to withstand harsh environments. Several kinds of sensor structures are available, the structure depending on the quantity they are sensing. Sensors used to measure temperature or humidity are often based on material parameter change, such as a change in the resistance or capacitance. Consequently their structure must be open to the environment and the sensors often cannot be protected against that environment. Open structure combined with harsh environment of use may cause reliability problems. Furthermore, reliable attachment of these sensor components is crucial for the reliable performance of the sensors: if sensing is based, for example, on the resistance of the sensor, unstable attachment may lead to erroneous sensing data. The structures of these sensor components may differ considerably from traditional components. Moreover, the sensors are often made of materials other than silicon, therefore possibly restricting the use of attachment methods such as soldering. Polymer-based electrically conductive adhesives (ECAs) offer a promising attachment alternative for these kinds of components.

One of the most demanding harsh environments for electronics is high temperature [Esc06, Ohr98]. High temperature is a challenging stress for electronics, because high temperature accelerates chemical reactions, ages and degrades polymer materials and also causes changes in their material

parameters [Esc06, Dre08, Gil95, NRC95, O'Co02, Rus95]. The exposure to high temperature, for example in automotive or industrial electronics, may be constant or cyclic in nature, and these applications should withstand this at least temporarily. In this work, high temperature was determined to be around 200°C, the highest temperature studied being 260°C. Material selections for such temperatures are somewhat problematic. Temperatures around 200°C are lower than the temperatures for which often rather expensive specialty high temperature materials, such as ceramic substrates or high-temperature solders, are typically designed [Wer01, Sha15]. Moreover, materials in electronic packages, such as printed circuit boards (PCBs), component packages and coating materials, are traditionally based on polymers. Polymers, however, tend to be extremely susceptible to temperature.

A temperature of around 200°C is much higher than the recommended temperatures for the majority of the polymers used in electronics. Thus, when used at such temperatures, polymer materials are often near or above their functional limits. This may cause reliability problems for the electronic package. For example, widely used epoxies tend to have quite a low glass transition temperature (T_g), which is easily exceeded at high temperatures [And13, Gal98]. As a consequence, epoxies soften and lose their mechanical and dimensional properties [Cal07]. However, polymers are very versatile and cost-effective materials with good availability and easy processing [Gal98, Gil95]. These are very important factors even for applications outside the scope of consumer electronics. Therefore using polymers at high temperatures would be beneficial. Using polymers at high temperatures has not been widely studied, but due to aging both the short-term and the long-term stability of polymers have been assumed to be restricted. In addition, the changes of material parameters due to high temperature and the effect of such changes on the reliability of electronics package are not fully understood.

The effect of high temperature exposure on a polymer-based electronic package and its materials can be studied using reliability testing and material characterization. With reliability testing the performance of an item in a certain environment can be studied and the data can be used for lifetime prediction. A reliable product has consistently good performance in its environment of use over a required period of time [Suh02]. With material characterization material properties and the possible changes in them can be measured with several techniques. Examples of these techniques are thermal analysis methods such as thermogravimetric analysis (TGA). Such analyses can be used to understand the behaviour of materials in different conditions.

Due to the aforementioned challenges regarding performance and material selections at high temperatures, this thesis experimented whether polymer materials could be used in high-temperature applications, what kinds of reliability problems may arise and what kinds of changes in the materials may occur. These research problems were studied with the help of seven individual publications with the main research questions listed below.

- Publication I: What kind of performance and reliability could be achieved with widely accepted thermal cycling test exceeding T_g of some of the studied polymer materials?
- Publication II: What happens to the performance and reliability when the cycling temperature range widens?
- Publication III: What kinds of high temperatures and exposure times could polymer-based sensor packages withstand?
- Publication IV: What kind of performance and reliability could be achieved for polymer-based sensor package at 200°C?
- Publication V: What kind of performance and reliability could be achieved for polymer-based sensor package at 240°C?
- Publication VI: What kind of performance and reliability could be achieved for polymer-based sensor package with rigid PCBs?
- Publication VII: What kind of performance and reliability could be achieved for polymer-based package with high quality thermally very stable flexible PI PCB?

1.1 Objectives and Scope of the Thesis

The object of this thesis was to study the behaviour and reliability of polymer-based sensor packages at high temperatures. The thesis concentrated on the effect of temperature on the polymer materials, not the functionality of the sensor itself. The aim was to examine how temperature affects the polymer materials and to understand the suitability and limitations of polymers for applications used in harsh environments with high temperatures. Polymer materials are widely used in different parts of electronics, but this thesis concentrated on the reliability and performance of PCB and ECA materials.

High temperature reliability was studied with several thermal tests including cycling tests, step stress tests and thermal storage tests by measuring the electrical behaviour of a sensor package during testing. Material parameter characterization and mechanical testing were conducted to understand the effect of thermal testing on the polymer materials as well as failure mechanisms and to study their long-term stability. Several different commercial ECA and PCB materials as well as sensor components were studied and compared.

1.2 Structure of the Thesis

This thesis consists of an extended summary followed by seven publications. The extended summary is divided into six chapters. These chapters present the background information relevant to the topic as well as the main results. Chapter 1 gives a general introduction to the research problem and objectives of this work. Chapter 2 introduces polymer-based materials used in

electronic packaging concentrating on PCBs and ECAs. Additionally, Chapter 2 discusses the effects of high temperature on these materials. In Chapter 3 basic information about reliability and high temperature reliability test methods are given. The test samples and evaluation methods are likewise discussed. The results of this work are divided into two chapters. Chapter 4 discusses material characterization, whereas the reliability of organic electronic packages is presented in Chapter 5. Chapter 6 gives the final conclusions and summarizes the publications.

2 Polymer Materials in Electronics Packaging

Polymers are widely used in electronics packaging for a variety of purposes due to their combination of good properties and low price. A large selection of different types of polymers is available for different needs. Component packages are commonly made of polymers if hermetic properties are not needed. Moreover, different coating materials, glop tops, fill materials and underfills are made of polymeric materials. This work will concentrate on substrates and adhesives. Therefore printed circuit boards (PCB) and electrically conductive adhesives (ECA) are discussed in more detail in this chapter.

Typical polymers used in PCBs and ECAs include epoxies, polyimides (PI), silicones, acrylics, urethanes, polyethylene terephthalate (PET) and polytetrafluoroethylene (PTFE). Both thermoset and thermoplastic polymers are used in electronics. Thermosets and thermoplastics differ from each other in their molecular structure: Thermosets form a cross-linked, three-dimensional network structure when they cure and the material becomes permanently solid. Thermoplastics, on the other hand, form from linear or branched polymer chains which are bonded together by weak secondary bonds. Therefore they can be re-melted and re-solidified.

Compared to thermoplastics, thermosets generally have better chemical resistance, dimensional stability and strength as well as lower coefficient of thermal expansion (CTE) [Gal98, Her01]. Due to their cross-linked structure, thermosets can also be used at relatively high temperatures, even above their glass transition temperature (T_g). For thermoplastics, the loss of mechanical properties at high temperatures is much more dramatic due to their structure. This will be discussed more in Chapter 2.3. Thermosets such as epoxies are often used as adhesives, coatings and PCBs [Hod01]. As their viscosity tends to be lower than that of thermoplastics, complex moulds and reinforced composites are easy to manufacture due to their good flowing properties [Hod01].

2.1 Printed Circuit Boards

Printed circuit boards are laminate structures consisting of dielectric and conductive materials [Lu09a]. Conductive materials are used to form electrically conducting paths on insulating dielectric materials. PCBs are used as substrates in electronics assembly to electrically connect different components together. In addition, PCBs offer electronics assemblies not only electrical functionality, but also mechanical support. According to their construction, PCBs can be divided into two basic groups: rigid and flexible PCBs.

Rigid PCBs

Traditionally PCBs have been rigid. Rigid PCBs are laminated by first producing a prepreg, which is done by bonding several sheets of fibrous reinforcing material together with a thermosetting resin [Lu09a]. Dielectric resins are mostly thermosets even though thermoplastics can be used [Lu09a]. To form a PCB laminate, several layers of prepreg are laminated with conductive foil acting as circuitry. Rigid PCBs are mostly multilayer boards, but when complexity and miniaturization are not needed, single-layer boards can be used. Interconnections between the layers in multilayer boards can be done using vias. They can penetrate through the whole board, or be buried and blind, meaning that the via connections are either completely or partially inside the structure. An example of a rigid PCB is shown in Figure 1. Protective cover layers can be applied on the top and bottom layers of PCBs to offer protection against moisture, mechanical damage, self-shortening and contamination [Lu09a].

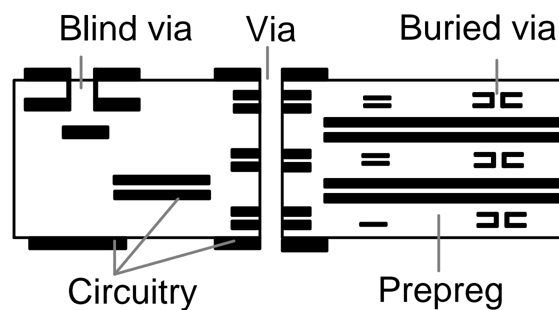


Figure 1. Schematic example of a rigid multilayer PCB with vias.

The most often used resin material in rigid PCBs is epoxy, and diglycidyl ether of bisphenol A (DGEBA) based epoxy is one of the most common. DGEBA is also the most widely used thermoset resin in general [Bro14, Hod01]. Epoxy-based thermosets are very widely used in electronics due to their suitability for different formulating techniques and large possibilities for optimization and modification with several additives [Bro14]. They are stiff and mechanically durable, have good insulation and corrosion properties, are compatible with reinforcing fibres, have good adhesion to many substrate materials and metals and are easy to manufacture [Bro14, Ode11]. Epoxies are formed using polyepoxide resins with hardeners such as polyamines [Ode11].

NEMA (National Electrical Manufacturers Association) grade FR-4 is the most widely used rigid PCB [Coo01]. It is a flame-retardant PCB consisting of woven fibreglass cloths as reinforcement material, impregnated with an epoxy-based resin [Coo01, Goo04]. It has an excellent combination of electrical, thermal and mechanical properties required of PCBs. The epoxy resin of FR-4 is typically based on DGEBA into which curing agent and flame retardant materials are added [Goo04, Lu09a]. The T_g of basic FR-4 is typically around 130°C - 140°C, but high T_g materials with glass transition around 170°C - 180°C are available [Coo01].

Flexible PCBs

Flexible PCBs can offer flexibility, lighter weight and thinner profile than rigid PCBs. They withstand thermomechanical stresses and vibration better. However, they may be dimensionally unstable and are more expensive to manufacture. Flexible substrates consist of base, conductor, and cover layers, which are typically bound together with an adhesive layer (Figure 2). Usually only one dielectric material is used to have matching properties, therefore base and cover layers tend to be made of the same dielectric film [Ste96]. The most often used films are thermoplastics [Lu09a]. The cover layer has openings so that terminals and pads are open for connections. As in rigid PCBs, the cover layer acts as a solder mask and gives the circuitry mechanical strength. The cheapest solutions may be processed without cover layers [Ste96]. Flexible boards are often single-sided without reinforcement materials to maximise flexibility, but other constructions are also possible.

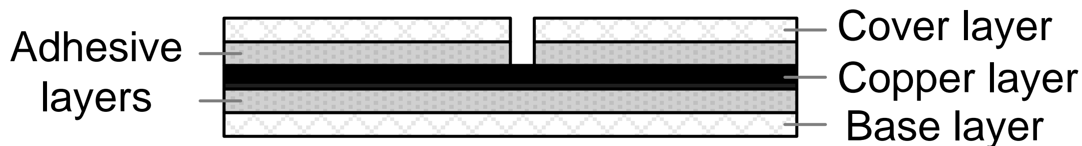


Figure 2. Schematic example of a flexible PCB.

Flexible boards are typically made of polyester or polyimide bases [Coo01]. The most used polyester is PET. This is a low-cost material with excellent mechanical properties, low moisture absorption and good dimensional stability, but its drawback is limited thermal stability at elevated temperatures [Coo01] as its T_g is around 80°C [Goo99, Ste96]. PET also withstands temperatures above its T_g very poorly in humid environments [Lah13, Kii14]. Polyethylene naphthenate (PEN) is similar to PET, but it has approximately 40°C higher T_g [Goo99, Har00]. PEN therefore offers improved thermal performance compared to PET. If even better thermal stability is needed, PI is a popular choice for base materials. It has good mechanical properties and very good thermal stability [Coo01] with T_g above 300°C [Goo99]. The drawbacks of PI are high water absorption [Ste96] and much higher price [Coo01].

As discussed above, different dielectric materials are used with rigid and flexible PCBs, but the conductive materials used are the same for both of these [Lu09a]. The most typical conductive material is copper due to its excellent electrical properties, good processing and low price [Lu09a]. Especially in rigid PCBs the copper used is usually electrodeposited copper (ED) foil. In flex PCBs ED copper is sometimes replaced with rolled annealed copper (RA), which has superior flexing endurance, but is also much more expensive than ED copper [Coo01]. Other conductor materials such as aluminium can be used. Aluminium is often used in radio-frequency identification (RFID) substrates as antenna material due to its low price.

Surface finishes are often applied on top of conductor material, especially copper, to prevent oxidation and corrosion. There are many different options for surface finishes. If the interconnections are going to be soldered onto a PCB, organic solderability preservative (OSP) is the cheapest option. Another widely used option is electroless nickel immersion gold (ENIG) having superior properties. ENIG is often used with adhesives as an interconnection material, if its high price it not a problem for the application.

Reinforcement materials provide most of the mechanical properties such as strength and rigidity to rigid laminates, but also affect the electrical properties of PCBs. Reinforcement materials include fibreglass, cellulose, or synthetic polymers in the form of woven fabric or paper [Goo99]. Woven fibreglass is the most commonly used reinforcement material because it is strong and inexpensive [Lu09a]. Additionally, flame retardants can be added to PCB materials as well as different kinds of additives to enhance their properties or facilitate the production.

2.2 Electrically Conductive Adhesives

The most widely used interconnection method in electronics is soldering. In soldering metallic solder materials are used to form a metallurgical contact between a component and a substrate. Wire bonding is another very widely used metallurgical method to electrically connect a chip to a substrate using thin metallic wires. However, ECAs are gaining more popularity as an attachment material. ECAs are polymer-based interconnection materials, which form a mechanical contact between a component and a substrate. ECAs are very often used in flip chip technology in which a bare chip is attached active side towards the substrate. ECAs consist of a polymer matrix and conductive particles added as fillers. The polymer matrix is inherently an insulator, offering mechanical stability for the interconnection. The matrix determines most of the physical and mechanical properties for the ECA [Li06].

In ECAs the polymer matrix is a mixture of different chemical components. For thermosets such as widely used epoxy matrix, the matrix consists of a resin and a hardener. Additionally, several other components are added to the matrix. Conductive fillers provide electrical conductivity for the material. Non-conductive fillers can also be used. For example, silica fillers are often added to reduce the coefficient of thermal expansion (CTE) value of ECAs, especially below T_g [Hwa08, Yim00]. Moreover, different kinds of additives can be added to ECAs to improve or modify their properties [Lic11]. These may include thixotropy and coupling agents, flame retardants and stabilizers [Lic11].

The concentration of the conductive filler particles determines the type of the ECAs. These are *isotropically conductive adhesives* (ICAs) or *anisotropically conductive adhesives* (ACAs). *Non-conductive adhesives* (NCAs) do not have conductive particles in their matrix, and the electrical

conductivity is formed with mechanical contact between the interconnection areas while the adhesive only gives mechanical support [Li06]. Schematic illustrations of all three are shown in Figure 3.

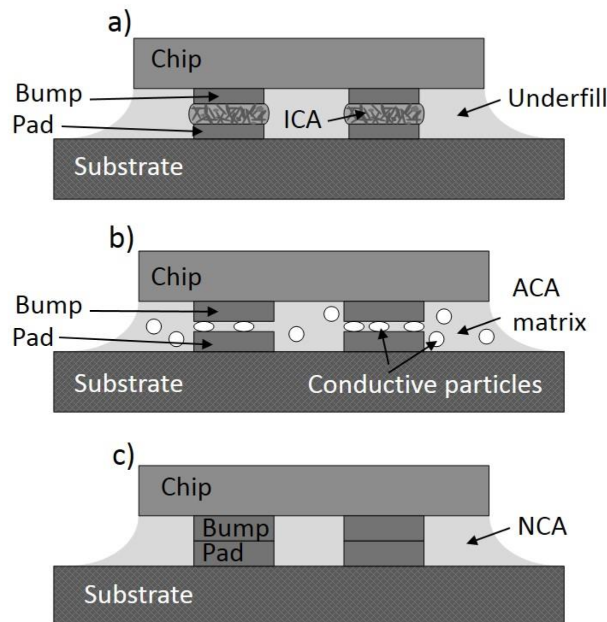


Figure 3. Schematic illustration of a flip chip interconnection with a) ICA b) ACA c) NCA.

Unlike solders, ECAs do not need fluxes and post-cleaning operations. Consequently, fewer processing steps are needed compared to solders [Gil95]. ECAs are lead-free, and usually also free of other harmful metals [Gil95]. ECAs are versatile materials which can be used with a wide variety of different materials, for example with substrates not amenable to soldering [Gil95]. However, ECAs have low surface tension, causing them not to be self-aligning as solders are [Gil95]. Therefore good alignment is needed during assembly. Additionally, as the interconnection in ECAs is not metallurgical, electrical conductivity tends to be somewhat less than with solders [Li06].

2.2.1 Isotropically Conductive Adhesives

The conductivity of ICAs is usually explained through percolation theory [Irf08, Li97, Lu99, Lu09b]. If the filler concentration is low, the material is an insulator having a high resistance. When the filler concentration increases, the resistivity gradually decreases. At the percolation threshold the filler concentration is at a level at which the resistivity drops markedly and the material becomes electrically conductive. After the threshold the conductivity no longer increases with increasing filler concentration. In the case of ICAs the filler concentration is so high that the percolation threshold is exceeded [Li06, Lu09b, Mir08]. The exact percolation threshold limit depends on the filler shape and size, but is approximately 15-20% in volume [Li07]. The filler concentration of ICA should be safely above the threshold limit, but not too much above, as mechanical properties such as impact strength may suffer at high filler concentrations [Lu09b, Liu11]. Hence the filler concentration in ICAs is typically 15-35% [Li06, Liu11].

At the threshold point most of the particles in the ICA matrix are assumed to be in contact, forming a three-dimensional network [Lu09b]. The exact conduction mechanism, however, is unknown. The percolation threshold is the onset point for conductivity [Koh14], but the conductivity is also assumed to be affected by curing kinetics and different filler particle relations including size, distribution, orientation and macroscopic contact effects [Li97] as well as matrix shrinkage due to curing [Lu99b].

Due to high filler concentration, ICAs conduct as a bulk form in x, y and z directions [Li06]. High conductivity for ICA interconnections is nevertheless achieved only after curing [Lu99, Mir08]. Similar to solders, ICA should be dispersed only to the connected areas, and additional underfill is often needed to provide mechanical strength for the interconnection [Li06]. This is illustrated in Figure 3a. Curing is most often conducted at elevated temperature in an oven. Higher curing temperature enables shorter curing time and conversely with lower temperature longer curing time is needed. These factors and the resulting curing degree in the case of thermosets affect the conductivity of the interconnection [Ino07]. Curing degree is discussed in more detail in subchapter 2.2.2.

Polymer matrix can be either thermoplastic or thermoset material. From thermosets, epoxies and silicones are widely used. Otherwise thermoplastics such as PI or acrylics can offer a solution if, for example, reworking is needed [Li06, Lu09b]. The most commonly used fillers in ICAs are silver flakes due to their affordable price [Mir08, Mo02], stability [Mo02] and the high conductivity of both silver and its oxide [Lu09b, Mo02]. Other fillers such as copper and copper-coated iron have been widely studied with a view to cost reduction and more environmentally friendly options. However, there are challenges due to their rapid oxidation in curing, resulting in high resistivity [Ino15, Liu14]. Particle size is mostly in the micrometer range. Sizes as small as nanoparticles have been studied, but the small size causes conductivity problems [Lu09b].

ICAs have traditionally been used in surface mount attachments to replace solders [Li06]. They have been predicted to have potential, for example, in printable electronics [Liu14]. ICAs offer lower curing temperatures than solders, but also have lower conductivity, may have unstable contact resistance with non-noble surface finishes and have poor impact strength [Lu09b]. Adding self-healing silver nanowires into the matrix has been tried to overcome the cracking problem [Tao14a].

2.2.2 Anisotropically Conductive Adhesives

In ACAs the filler concentration is low and thus it does not exceed the percolation threshold. Typical particle concentration is 0.5-5% in volume [Lic11, Riz05]. The ACA interconnection is formed in the bonding process when the conductive particles get trapped between the interconnection areas of the chip and the substrate. Their anisotropic property ensures that ACAs can be deposited under the whole component and not only on the connection pads. The ACA conducts in the z-direction only and the matrix works as an underfill material, providing mechanical support for the connection. This is illustrated in Figure 3b.

The bonding process of ACA always requires curing the matrix under pressure. The curing itself is typically done with heat or UV. The most commonly used bonding process is thermocompression, which combines moderately elevated temperature and pressure. ACAs are typically bonded using a short time of a few to twenty seconds. As with ICAs, bonding time and temperature affect each other. When the adhesive matrix is cured, it shrinks and thus helps to keep the interconnection together with contraction stresses [Kim07]. A high enough curing degree is needed with thermosets to create high enough contraction stresses to maintain the connection with low and stable resistance [Chu10].

ACAs are mostly thermosets such as epoxies, silicones and acrylics [Lu09b]. Epoxies are the most widely used matrix materials [Ebn09]. As a very short curing time is needed for ACAs, the epoxies are so-called snap-cure epoxies and differ somewhat from those used in PCBs. Thermoplastics such as acrylics can also be used in ACAs. They often have problems with adhesion and holding the particles in contact, thus leading to high contact resistances [Lu09b].

Filler particles in ACAs are usually metal particles or metal-coated polymer particles [Lu09b], but glass [Lic11] and solder balls [Ver06, Kim12, Kim15] can also be used. Metal particles are mostly made of nickel, and they can be gold-coated to prevent oxidation and thereby improve the quality of the interconnection. The polymer particle cores are often made of polystyrene [Lu0b9]. Typical coating materials for polymer particles are nickel, gold and silver. The particles may be additionally coated with a thin insulating layer on top of the metal layer to ensure that adjacent particles do not cause lateral short-circuiting, especially in fine-pitch applications [Lu09b].

The selection of filler type depends on the application and the materials involved. Metal particles, especially without coating, are cheap to manufacture and are therefore often used in low-cost products such as radio-frequency identification (RFID) tags. If the bump or pad material easily forms an oxide layer, such as copper without finishing, the rigid nickel particles are able to break the oxide layer during bonding and form a stronger interconnection than polymer-particles [Kok10, Par16]. Polymer particles are more expensive than metal particles. However, they can be manufactured with a fairly uniform size distribution [Liu11, Tao14b], thereby improving the quality of the interconnection [Lai96]. Polymer particles also deform considerably in the bonding process, and can thus even out height differences between the contact areas [Fri16]. Pliable polymer-particles have been shown to have better ability to withstand CTE differences than rigid nickel particles [Sep04]. Therefore polymer particle filled ACAs are used especially often in applications designed for demanding environments with thermal cycling.

Bonding temperature, time and pressure all affect the quality of the ACA interconnection. Temperature and time are directly linked to each other. With high temperature shorter curing time can be used, whereas lower curing temperature requires longer curing time. The temperature should be selected so that the matrix does not solidify too quickly: the matrix must have long enough time to flow [Liu11]. High curing temperature tends to improve resistance [Gom08, Riz05], but may also cause degradation [Tan04, Riz05].

Curing degree refers to the level of cross-link density in thermoset polymers [Riz05]. High curing temperature tends to result in higher cross-link density. Longer curing time with lower temperature has also been reported to result in good curing degree, but the slow process has a negative effect on production [Liu11]. Adequate curing degree is typically around 80-90%. Beyond this, the properties of the adhesive do not further improve with further curing [Chu10, Riz05, Tan04]. Properties such as storage modulus, T_g, shear strength and cohesive strength increase with increasing curing degree, thereby leading to both mechanically and thermally stable structure [Bro14, Cha03, Chu10, Riz05].

Pressure plays a vital role in the quality and the reliability of the ACA interconnection. Good contact requires large contact area for the particles. The number and size of the conductive particles has an effect on the contact area, but the chosen pressure also affects the contact area through particle deformation. If the pressure is too low, the particles will not be able to form a reliable contact. However, too high pressure may deform the polymer particles so much that their metal coating totally breaks, exposing the non-conductive polymer [Cha02]. Usually higher pressure improves the reliability [Li06, Kii15, Sep04]. Bonding pressure has also been reported to affect the failure mode, as with lower pressure non-conductive gap [Kim07] and with high pressure delamination [Kim07, Fri10] has been reported as the main failure mode in thermal cycling. Low bonding pressure tends to cause failures at high temperature extremes, high bonding pressures on the other hand at low temperatures [Fri06b, Fri09].

The optimal bonding pressure depends on the PCB and interconnection materials used. Substrate and chip thicknesses have been reported to affect the level of optimal pressure [Fri06b, Publication I]. The material of the conductive particles also plays a decisive role [Kwo06]. Rigid metal particles deform only slightly when pressed between interconnection areas, and high pressure is needed for their deformation. With high pressure the particles may sink into the pads or bumps if their material is soft, such as gold or copper [Fri12]. Both deformation and sinking will increase the contact area and thus increase conductivity. Soft polymer particles, on the other hand, require less force for deformation than rigid particles [Fri10]. Polymer particles are greatly deformed in the bonding process, forming a large contact area. The possible insulating layer of a filler particle is broken in the bonding process due to deformation.

ACAs are versatile materials with good compatibility and mechanical adhesion [Udd04b] with several metallization, chip and substrate materials [Gil95]. Compared to solders and ICAs, ACA require fewer process steps [Udd04b]: due to its anisotropic characteristic the material can also be dispersed between the contacts and no secondary underfill is needed. Additionally, interconnections with a very fine pitch are also possible [Yim00]. ACAs are available in either paste (ACP) or film (ACF) form. The conductivity of ACAs, however, is inferior to that of solders.

ACAs have been used for decades in display modules such as liquid crystal displays (LCD) [Gil95, Kim13, Li06, Lu09b, Yim06], plasma displays and organic light emitting diode displays (OLED)

[Kim13]. For example, in LCD panels ACAs have been used to directly attach the IC chips onto the glass panels (chip-on-glass, COG), driver/control circuit chips to flex substrate (chip-on-flex, COF) and LCD panels further to PCBs (flex-on-glass, FOG) [Yim06]. Furthermore, they have been generally used in consumer electronics to ensure lighter, smaller and thinner packages, and in applications needing very fine pitch [Gom08]. In recent years they have been used more and more in industrial electronics, sensor attachments and in smart cards and RFID [Cai09] applications.

2.3 Polymer Materials at High Temperatures

High temperature is not a self-explanatory term, as the definition depends on the field and application and the party making the definition. In electronics high temperature may refer, for example, to temperatures of 125°C [Liu16] or 600°C [Sav98] or something in between, depending on the application and materials used. In material science high temperature can mean thousands of degrees Celsius. The widely accepted upper temperature limit for typical electronics structures and materials is 125°C [Dre08, NRC95, Jul13]. The limit of 125°C most likely does not relate to any physical material limitation, but is based on the demands of the industry [O'Co02]. However, 125°C may already exceed the T_g of commonly used thermosets, for example epoxy-based materials. When the temperature increases, the polymer-based materials often used in PCBs and ECAs may experience stability and degradation problems. Due to this, in the literature it is commonly stated that polymer-based packaging and interconnection materials are not suitable for use above temperatures of 150°C because for many polymer materials at these temperatures detrimental losses of important parameters may occur [Dre08, Gil95, NRC95, Rus95]. Another important aspect is long-term stability, because long exposures even at relatively low temperatures may still cause degradation.

There are, however, applications which must withstand much higher temperatures, even above 200°C. These applications are used, for example, in automotive, aerospace, industrial electronics and sensors [Dre08, Gal98, Jul13, Sha15]. For automotive electronics, for example, withstanding a permanent temperature of 150°C is essential [Dre08]. As there is a need to push the limit of 125°C at least to 200°C [Jul13], *in this work the high temperature refers to temperatures around 200°C.* In the experimental part of this work, the constant temperatures used varied between 180°C and 260°C. Additionally, thermal cycling tests were also conducted up to 125°C and 180°C. In subchapters 2.3.1 and 2.3.2 materials designed for even higher temperatures are discussed to provide a broader perspective. Often materials specifically designed for high temperature are not polymer-based.

The Effect of Polymer Structure on Upper Temperature Limit and Thermal Stability

In polymers the atoms are connected by covalent bonds, forming molecules. These primary bonds hold an individual polymer chain together. Polymers also have weaker secondary bonds in their structure. These intermolecular forces are the bonds between different polymer chains. Secondary

bonds determine many of the physical properties of polymers. These secondary bonds are susceptible to heat, thus enormously affecting the thermal stability and thermal use limits of polymers.

The crystalline or amorphous nature of a polymer determines its upper temperature limit [Cal07]. Thermosets are amorphous, because cross-linking will prevent their crystallization. Thermoplastics, on the other hand, can be both amorphous or crystalline in nature. The degree of crystallinity in thermoplastics varies. Full crystallinity is not achievable with long polymer chains with large molecules, therefore amorphous parts always exist in the structure of a crystalline polymer. Thus a term 'semicrystalline polymer' is widely used, referring to polymers with both crystalline and amorphous regions.

Glass transition describes the transition in which the amorphous parts of a polymer will change from rigid to rubbery state due to increased motion of large segments in polymer chains during heating [Cal07]. Therefore, when amorphous polymers are heated up to their glass transition temperature they will soften to a rubbery state. Glass transition is a temperature range, but a single temperature for T_g is given in the data sheet of materials. For thermosets, such as epoxies, T_g is generally considered to be their upper use temperature limit. For structural applications the T_g as a use temperature limit is more critical than for other applications [Her01]. Above T_g the thermoset materials often lose their mechanical properties and CTE rapidly increases [Cal07]. CTE describes the length or volume change corresponding to a unit change in temperature [Sha98]. Despite the changes, due to their cross-linked structure thermosets can still be used above T_g without melting, but such exposure may lead to irreversible changes due to degradation of molecular chains [Pec99]. For amorphous thermoplastics T_g is the upper temperature limit. As the secondary bonds between the chains are much weaker than the cross-linked structure of thermosets, mechanical changes above T_g are much more critical for amorphous thermoplastics.

For semicrystalline thermoplastics, there are two different thermal limits. At T_g their amorphous parts will pass through glass transition and these parts will soften. When the material is heated further, the crystalline regions will melt at melting temperature T_m at which the polymer completely softens [Cal07]. Whether semicrystalline materials can be used above their T_g depends on the polymer and its degree of crystallinity. Often thermoplastics tend to regain their former properties when cooled again below T_g [Pec99].

Discussion on thermal degradation of polymers usually concentrates on the effect of heat on primary bonds. Weakness of these covalent bonds generally makes polymers thermally sensitive [Sha98, Pie05] compared to metals and ceramics. There are, nevertheless, differences between polymers depending on the bonding energies in the molecular structures: higher bonding energy corresponds to thermally more stable material [Cal07]. Therefore, fluorocarbons like PTFE with strong C-F bonds can withstand higher temperatures than hydrocarbons like polyethylene with weaker C-H bonds.

Degradation

Other materials present in electronics application, for example silicon as chip material and metals as wiring materials, may also suffer from high temperatures [Wer01, NRC95, Yeh02]. When metals and ceramics age and lose their properties, the phenomenon is typically called corrosion. For metals this is mostly an electrochemical process starting from the surface [Cal07]. For polymer corrosion the term 'degradation' is typically used. Polymer degradation is physiochemical, meaning that external chemical or physical stresses, such as oxygen or heat, cause polymers to degrade [Pie05, Cal07]. Degradation causes changes in both the chemical structure of the polymer and in its physical properties [Pie05].

Due to the complicated chemical structure of polymers, the degradation mechanisms are not well understood [Cal07]. Thermal degradation can cause chain scission, cross-linking and oxidation, and, depending on the exposure temperature and time, these may occur individually or simultaneously [Cha09b, Dem80]. Chain scission of molecular chains at high temperatures is the most commonly referred type of degradation and is valid for all polymers [Cal07, Pie05]. The scission may occur either at the main chain or at side fragments with volatile and char production [Pie05]. It causes physical and chemical changes such as a decrease of T_g [Cha09b]. The competitive method for chain scission in case of thermosets is additional cross-linking, which causes embrittlement of the polymer material [Dem80, Dre08]. Thermo-oxidation also causes chain scission due to the formation of free radicals, which attack the chains [Pin04]. Oxidation typically starts from the surface [Cha09b]. At the beginning oxidation does not yet cause chain scission, but the formation of free radicals often causes discoloration and minor electrical or mechanical changes [Lic11]. Excessive oxidation leads in chain scission [Lic11].

2.3.1 PCBs at High Temperatures

At high temperatures common polymer materials in PCBs may suffer from stability problems and degradation. Therefore many non-polymeric PCB materials are available, ceramic materials being the most important. These are discussed first, followed by a review of different polymer-based PCB material possibilities and their challenges at high temperatures.

In addition to the thermal stresses of the use environment, the thermal stability of PCBs is also important from manufacturing point of view. During manufacturing processes PCBs may be subjected to processing phases involving high temperatures, such as lamination, or then to several reflow runs with high peak temperatures. Lead-free soldering temperatures are typically quite high, additionally increasing the thermal requirements of PCB materials [Goo04].

Ceramic Substrates

When electronics products for high temperatures are designed, ceramic substrate materials are often chosen due to their excellent thermal stability [Jul13]. Typical ceramic materials used in substrates

include alumina, boron nitride, aluminium nitride, silicon nitrides and carbides as well as diamond [Cha09a, NRC95, Wer01]. Noble metals are typically used with these as wiring materials to form ceramic substrates [NRC95]. Commonly used ceramic substrates are low temperature co-fired ceramics (LTCC) and high temperature co-fired ceramics (HTCC), which differ mainly with regard to metallization materials and co-firing temperatures [Bec09]. Of these two, LTCC substrates are often used in electronics due to their mature production process and good availability [Bec09].

Ceramic substrates are used with microelectronics and sensor packaging in applications which must be extremely reliable in harsh conditions, such as high temperature in the automotive industry [Bec09]. Ceramic substrates are preferred if hermetic packaging is needed [Bec09]. Compared to polymer-based PCBs, ceramic substrates have a much longer life time and lower CTE [Bec09]. However, their material, processing and manufacturing costs are much higher than those of polymer-based PCBs [Bec09, Gal98]. In 2009, the average materials and processing costs for LTCC substrates were 20 to 30 times higher than for traditional polymer-based PCBs due to the more expensive materials and special processing steps and equipment [Bec09]. Ceramics are also characteristically brittle, and therefore do not withstand impact stresses well [Gal98]. Ceramic materials may also have problems with mechanical and electrical integrity as well as resistivity [Wer01]. Additionally, if flexible or thin and lightweight options are needed, ceramics cannot be used.

Polymer-based PCBs

Special high temperature PCBs are often designed for extremely high temperatures. Ceramic substrates, for example, are typically designed for applications needing to withstand temperatures above 300°C or 400°C [NRC95, Sha15, Wer01]. Such temperatures may be used in the automotive and oil industries. Temperatures around 200°C, however, are somewhat complicated. Special high temperature PCBs are often designed for specific use only for even harsher environments and higher temperatures. Temperatures around 200°C are also significantly higher than traditional microelectronic temperatures, and above the T_g of the most commonly used thermosets. Nevertheless, polymer-based PCBs tend to be more attractive in terms of cost, size, weight, performance and mechanical strength than ceramic substrates [Gal98]. Thus using polymer-based PCBs at high temperatures around 200°C would be beneficial. Possible degradation due to temperature must, however, be taken into account and carefully studied. The background of polymer-based PCB materials at high temperatures will therefore be discussed next.

Epoxies have relatively good thermal resistance, but are generally considered to withstand moderate, but not very high temperatures [Her01]. The most commonly used epoxy-based FR-4 PCBs are cheap, easy to manufacture with widely available infrastructure, but their T_g is typically too low for high temperature applications [And13, Gal98]. Even short exposures to high temperature may affect the properties of FR-4. It has been reported that 30h aging at 200°C caused changes both to the surface of the epoxy-based PCB laminate and to the inner structures, for example delamination between the resin and the glass-fibres [Pol09]. For traditional FR-4 the T_g value has been reported

to decrease markedly if the peak temperature of the reflow profile is increased, or if the number of reflow cycles or the overall profile time is increased [Lal12].

Epoxies with a higher number of functional groups per molecule cure with a higher degree of cross-linking, which typically leads to higher T_g [Lu09a, Goo04]. The epoxies may be either di-, tetra- or multifunctional [Lu09a]. In addition to increasing T_g with multifunctional epoxy, it can also be increased using crosslinking agents [Goo04]. Consequently, for high temperature applications, enhanced FR-4 resin systems are available with T_g values of 170°C or more [Lu09a]. The drawback of these high T_g resins is high flexural modulus, which causes the material to be brittle and difficult to process [Goo04, Lu09a]. Furthermore, even high T_g FR-4 PCBs may have stability problems. Changes in T_g due to reflow have also been reported with higher T_g FR-4 (T_g >145°C), and the most dramatic change in this material was caused by increasing the number of reflows [Lal12]. Consequently, even very short high temperature exposures typically decrease T_g values of all kinds of FR-4 boards.

PI [And13, Goo04], fluoropolymers and hydrocarbons [Coo11, Goo04] have much better thermal stability than epoxy. However, their processing is often more challenging compared to epoxy [And13, Goo04]. As the chemical resistance of these materials is typically enhanced, traditional chemistry used in the PCB fabrication process is not as effective as with epoxy materials [Goo04]. Consequently, as both the pure material and their fabrication is more expensive, the cost of these advanced PCBs is higher compared to traditional FR-4 [Goo04]. For high temperature use, PI is the most commonly used polymer material due to its excellent thermal stability [Har00]. PI PCBs are selected especially if thin and flexible PCBs are needed. Fluorocarbon-based and hydrocarbon-based PCBs were originally designed for high frequency telecommunications applications, but they also render a more consistent performance than FR-4 in environments with temperature variations [Coo11]. Fluoropolymers such as PTFE, however, are especially challenging to manufacture [Coo11]. They are also prone to adhesion problems [Har00, Coo11]. Hydrocarbon-based polymer substrates, on the other hand, can usually be processed with the same processes as FR-4 and are also suitable for multi-layer PCB lamination with good dimensional stability [Coo11]. One easily available hydrocarbon-based PCB is a hybrid of ceramic and hydrocarbon, manufactured by Rogers Corporation (Rogers PCB).

Generally regarding the management of thermal stresses, the T_g of the polymer material in a PCB plays a critical role because CTE tends to rapidly increase above T_g. In the case of polymer-based PCBs the increase is especially large in the z-direction [Goo04], which is critical with multilayer PCBs due to the possible loss of via integrity [Goo04, Gal98]. Using PCB material with very high T_g not exceeded in the use environment will reduce the thermal mismatch between polymers, metallization and chip materials [Goo04]. The Rogers PCB, for example, typically has T_g above 280°C, therefore at use temperatures around 200°C the CTE will remain at a lower level [Coo11].

On the other hand, for flexible PCBs their three-layer structure may cause thermal stability problems. As mentioned above, PI PCBs are very widely used at high temperatures due to the excellent thermal stability of polyimide. PI PCB consists of polyimide film and metallization laminated together with an adhesive layer [Lu09a] (adhesive later referred as *PI PCB adhesive*). The curing temperature of this adhesive is selected so that it is lower than the T_m and T_g temperatures of the PI film to make the lamination process easy and to avoid distortion of the PI film [Lu09a]. The properties and thermal stability of the adhesive layer are thus typically inferior to those of the polymer film [Har00, Lu09a, Nak89, Fro91]. Consequently the thermal stability of PI PCB is much lower than the thermal stability of neat PI film, and this should be taken into account at high temperatures. In multilayer PCBs the adhesive layer also causes challenges in via manufacturing [Fro91]. Adhesiveless PI PCBs are not as widely available as conventional PI PCBs. Often PI-based adhesive is used in them to bind the structure together [Lu09a]. It is also possible to attach copper directly to the PI film using, for example, sputtering and plasma treatment [Fro91], forming literally an adhesiveless PI PCB structure.

The choice of PCB material for use at high temperatures is consequently a trade-off between the required properties and costs. Polymer-based materials can offer a good balance of these, but the material should be selected so that degradation of important parameters will not compromise the reliability of the electronics package. In this work the following PCB materials were studied: FR-4, PI and Rogers.

2.3.2 ECAs at High Temperatures

Similar to PCBs, ECAs as polymeric interconnection materials may have stability problems and degrade at high temperatures. This must be taken into account if these materials are used in high temperatures. High temperature solders are first briefly discussed to provide background information. High temperature issues with ECAs are first discussed in general and after that for ICAs and ACAs separately due to their somewhat different nature caused by filler concentration.

Solders

As solders are the most widely used interconnection materials, they are also the natural choice for high temperature applications. Hard solders are often used at high temperatures [Kis09, NRC95]. There are several possible solder alloys such as high-lead solders [Sug07], gold-based Au-Sn, Au-Ge and Au-Si [Kis09, Man11, Sou10], Ag-In [Man11] or glass-based solutions [NRC95]. The melting temperatures of these are typically around 300°C - 400°C [Sou10], which causes high thermomechanical stresses in the structure during the soldering process. These solders may additionally require complicated processing steps [Sou10]. Due to the presence of noble metals, they also tend to be very costly. Therefore, ECAs could offer a competitive alternative for use at elevated temperatures.

ECAs in General

The performance and reliability of ECAs at high temperatures has not been widely studied, but it is mainly assumed that polymer-based interconnection materials are not reliable at high temperatures. It has been reported that ECAs can withstand mechanical stresses at 150°C without detrimental loss of conductivity and adhesion strength [Rus95]. Silver-filled epoxy ICAs have been reported to fail at temperatures near 200°C [Kis09, Man11], but can be modified to withstand temperatures from 200°C to 350°C [Man11].

At high temperatures thermoset-based ECAs are often used due to their cross-linked structure. As most commercial ECAs as well as all the ECAs used in this work are thermosets, thermoplastic ECAs are not discussed here. When adhesives face thermal aging, the changes in properties tend to be positive at the beginning of the process. For example post-curing of thermoset ECAs causes additional cross-linking, thus the properties of partially uncured ECAs tend to improve. For example, post-curing has been observed to decrease the resistivity and thickness [Xia05] as well as shear strength [Riz05] of the interconnection, and to improve the ability of the ECA to withstand thermal cycling [Xia05]. However, if the aging is prolonged, the post-curing may cause degradation of the ECA [Mac00], impairing the properties [Bar11].

One often mentioned drawback of thermosets at high temperatures is their decreased flexibility. Flexibility is an important feature for ECAs, as that can be used to compensate CTE differences between a component and a substrate [Dre08]. Due to flexibility of ECAs, they should also withstand mechanical stresses better than solder joints [Rus95]. Epoxies have, for example, good mechanical strength and fairly good high temperature performance, but high temperature may impair their flexibility [Dre08]. At first the flexibility decreases and following hardening will shrink the volume of the ECAs, thus improving the contact resistance [Bar11]. However, in long-term high temperature exposure the epoxy becomes brittle due to post-curing and additional cross-linking caused by thermally initiated free radicals [Dre08]. If an ECA maintaining its flexibility at high temperature is needed, modified epoxies, or urethanes, silicones and bismaleimides can be used [Dre08]. Silicones are better than epoxies for lowering the CTE differences at high temperatures [Dre08, Kli09], but they also have lower adhesion [Dre08] and deform easily under mechanical stresses.

As temperature typically increases the rate of chemical reactions, the temperature and exposure time play a critical role in degradation. Therefore higher temperature tends to be more detrimental than lower temperature. However, prolonged aging at lower temperatures, such as below T_g, may also cause reliability problems [Ode11]. The effect of temperature depends a lot on the material and structure, therefore aging exceeding T_g may not cause failures even after a prolonged time period [Fri06a, Fri06b, Rus95]. It has nevertheless been claimed that at approximately 50°C above T_g thermosets also begin to behave like melting thermoplastics due to softening [Gil95] and this may cause reliability issues even if the polymer does not degrade.

ICAs

Several commercial ICAs are available for high temperature use. Silver-filled ICAs have often been proposed as substitutes for high temperature solders [Du11, Jul13, Man11, Rus95, Sug07, Sou10]. Epoxy-based ICAs have been reported to function above T_g without necessarily causing any problems for the interconnection performance [Rus95]. Epoxy may still easily degrade at high temperatures, as discussed earlier. However, thermal stability of ICAs can be increased by choosing a matrix material which is more suitable for high temperature. As ICAs do not need to be cured quickly like ACAs, the range of possible matrix materials is wider. PI ICAs, for example, may offer higher stability for the ICA matrix, but cracking problems have been reported to occur very quickly in the interconnection when exposed to thermal cycling [Jul13].

It has been reported that ICAs have poor stability when used in oxidative environments, and silver migration has been seen with ICAs when aged at 250°C for a prolonged time [Sou10]. No migration effect was observed in N_2 environments. Therefore hermetical sealing could offer a solution, but it is expensive [Sou10].

ACAs

It is challenging to find an ACA material which can withstand high temperature environment reliably and at the same time be amenable to snap-curing to meet the production requirements. High temperature ACAs are not currently commercially available, and the behaviour of commercial ACAs at high temperature has not been widely studied. Epoxy-based ACAs have been used above their T_g temperature without reliability problems [Fri06a, Lah14, Lah15a, Lah15b]. A few things must, however, be taken into account for electronics packages with ACA interconnections above T_g.

At elevated temperatures the CTE differences between materials affect the whole package structure. Polymer materials expand more than the chip, causing shear forces [Udd04b]. Different expansion behaviour leads to warping of the structure. It has been reported that below T_g the material deformation causing warpage is mainly elastic [Kwo04].

Contact resistance generally increases faster when the aging temperature increases [Udd04b, Cha01]. When the T_g of the ACA is exceeded, the ACA matrix relaxes and loses its stiffness [Ali05, Cha03]. The ability to maintain compressive forces in the ACA interconnection is reduced or lost, and therefore particle movement in the structure is possible [Ali05, Cha03]. The relaxation in the z direction causes the matrix to swell, thus decreasing the contact area of the particles and increasing resistance [Ali05, Cha01, Udd04b]. This is caused by particles deforming back to their original shape due to the relaxation of the compressive forces [Udd04b]. In the x and y directions the pads and bumps are able to slide against each other, which may break the conductive particles [Ali05, Udd04b]. This movement may also cause fretting, in which the sliding causes constant cracking and oxidation of exposed materials occurs, forming debris material in the contact area [Fri12, Ohr98]. The oxide

materials formed will increase the resistance of the interconnection and finally cause open interconnections [Fri12, Ohr98].

At high temperatures the stresses are highest at corner bumps, whereas much lower stresses have been reported for the middle bumps [Udd04b]. Thermally induced warpage, sliding effect and shear forces are much higher at corners than in the middle of the chip [Ali05, Udd04b]. Thus the resistance increase due to the aforementioned challenges is also much greater at corner joints than in the middle joints. Consequently, the corner bumps are the ones more likely to have cracks or delamination [Udd04b]. The stresses are even worse for rectangular chips than for square chips [Udd04b] and for large chips [Kli09], but can be somewhat reduced by using flexible attachment materials [Kli09].

The eight commercial ECAs studied here were not designed for high temperature use. Two of them were ICAs and six were ACAs with T_g values between 74°C and 165°C according to the datasheets. The ECAs were chosen based on historical information, availability and the attractiveness of the materials. The particles were typical particle materials in commercial ACAs, and the ECAs were not selected according to their particle type. However, the effect of particle type was studied with ACF1 and ACF2, which had the same matrix material, but different particle type.

3 Reliability Testing at High Temperatures

This chapter first addresses reliability testing in general, followed by a more detailed discussion of reliability testing methods at high temperatures, as well as describing the testing and test samples related to this work.

3.1 Reliability

Reliability in engineering is typically defined to be an ability or probability, that in a given environment or operating conditions, a system will perform a required function for a specified period of time without failures [Jen95, Liu11, Ohr98, Suh02]. A reliable product has consistently good performance [Suh02]. Reliability testing is therefore done to study the reliability of an item. The item may be a single component, an entire product or something in between. There are many different reasons for and approaches to reliability testing. Reliability testing may be qualification testing for standardization purposes, studying the most critical product weaknesses to improve the reliability or studying the performance in a certain environment for lifetime purposes. The last mentioned is the approach used in this work. Performance under conditions present in the use environment of a product should be carefully studied and understood to ensure its good reliability.

Failures may occur, for example, due to errors in design, component variation, wear-out or overstress [O'Co02]. Regarding failures, the terms *failure mode* and *failure mechanism* frequently occur. Failure mode can be determined as an electrical symptom by which the failure is observed, such as a short or open circuit, decreased resistance or increased current value [Ohr98]. Failure modes are caused by one or more failure mechanisms. The mechanisms can be determined as specific physical, chemical or environmental phenomena causing the malfunction [Ohr98]. An example might be corrosion or delamination.

In addition to testing, reliability engineering may include many other aspects. One essential part is failure analysis. Reliability testing has no value without proper failure analysis, where the root causes are determined [Liu11]. Other aspects are, for example, statistics of failures or failure modelling. Statistics are briefly discussed in Chapter 3.1.2. Modelling is excluded from this work.

3.1.1 Accelerated Testing

Testing in normal use conditions is typically very uneconomical as it is time-consuming and expensive [Suh02]. Consequently, reliability tests are typically run as accelerated tests [Esc06]. Accelerated testing in laboratory conditions provides reliability data within a reasonable timeframe [Liu11]. With accelerated test methods the life time of the tested parts is shortened [Nel04]. Testing can be accelerated by increasing the frequency of occurrence of stress or the stress level, or by both

simultaneously [Liu11, Suh02]. For example, thermal cycling is an effective way to accelerate aging [Jen95]. When thermal cycling is done in a wide temperature range combined with increased frequency (more cycles in less time), the duration of the test is shortened [Vis98]. In this case both increased frequency and increased severity of conditions are applied [Liu11].

There are different kinds of accelerated tests using harsh environments to accelerate the occurrence of defects and failures [Suh02]. Often used tests include high temperature storage, high humidity, mechanical shocks, power cycling and voltage extremes [Suh02]. Accelerated tests can be divided, for example, into product development tests, qualification tests and accelerated life tests (ALT) [Suh02]. With ALT it is possible to ascertain the useful lifetime of a component and also to study failures and their mechanisms in long-term aging and to collect statistical information [Liu11, Suh02].

When ALT is designed, the use conditions and the failure modes and mechanisms existing in those conditions should be taken into account [Suh02]. It is critical that the mechanisms generated with accelerated testing methods are the same as those generated under normal conditions [Jen95, Liu11]. The test results should therefore be speeded up without distorting the behaviour of the tested items [Ohr98]. Careful planning is needed; otherwise the risk of accelerating the wrong mechanism increases [Liu11, Suh02]. This is especially critical if the acceleration is done by increasing the severity of the conditions [Liu11]. For example, it may be risky to exceed the T_g of a material if the T_g is not exceeded in normal use conditions [Liu11]. However, if the testing temperature used is low enough, the acceleration may be too low for the failures to occur within a reasonable time. The failure mechanisms may also interact with each other [Liu11], causing challenges in analysing the actual root causes.

The results obtained from accelerated testing should be extrapolated to normal operating conditions [Jen95, Esc06]. This, however, is very challenging. The extrapolation can be done with different analytical models. In electronics most of these are designed for solder joints, therefore their use with other structures and materials may yield incorrect results. There are no models specifically for the ECA interconnections available due to their complex nature. The acceleration can be described with an acceleration factor (AF), which is defined as the ratio between lifetime under normal use conditions and the lifetime under accelerated conditions [Ohr98, Suh02]. The AF can be determined only if the failure mechanism does not change between the different tests [Ohr98].

3.1.2 Statistical Analysis

After testing, the failure percentages can be plotted as a function of time to provide a visual representation of reliability. The cumulative distribution function (CDF) shows how failures accumulate with increasing time. In statistics it is defined as the probability that an item operating at time $t_0 = 0$ under stated conditions fails at or before time t [Jen95], therefore describing the probability of a failure occurring.

Statistical information obtained from ALTs can be analysed with several statistical distributions. Of these the Weibull distribution is the most widely used for modelling product life [Jen95, Nel04, O'Co02]. It was originally used to describe the properties of ball-bearings [Jen95]. The Weibull distribution has three parameters: shape or slope parameter β, characteristic lifetime η and location parameter or minimum life γ [Jen95]. The location parameter is typically assumed to be zero, leading to a two-parametric Weibull distribution [Jen95]. The CDF for two-parametric Weibull distribution is shown in Equation 1.

$$F(t) = 1 - \exp\left[-\left(\frac{t}{\eta}\right)^{\beta}\right] \qquad \text{(Equation 1)}$$

Shape parameter β can be understood as wear characteristics, and is associated with different failure mechanisms [Liu11]. Characteristic lifetime η describes the time at which 63.2% of the tested items have failed. Parameters β and η are material related, β characterizing aging effect and η the strength of the material [Liu11]. Greatly diverging β values may indicate different failure mechanisms.

One of the reasons for the popularity of the Weibull distribution is its ability to analyse both increasing and decreasing failure rates. Therefore it can describe the failure rates throughout the lifespan of a population of products. The lifespan and failure rate for a hardware error can de described with a bathtub curve, as shown in Figure 4.

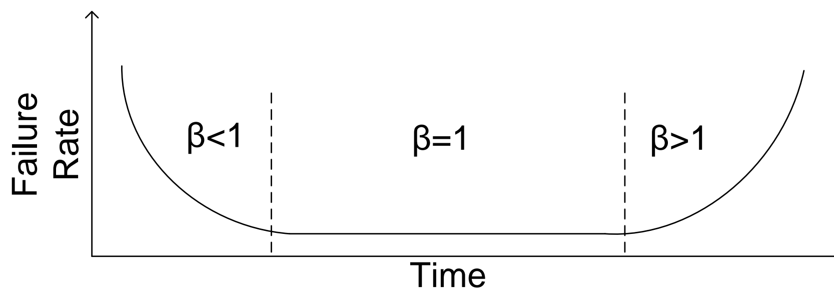


Figure 4. Bathtub curve.

The shape parameter β values can be linked to the various parts of the bathtub curve. With β<1 the hazard rate is high, but decreases with increasing time [Jen95, Ohr98]. This part of the bathtub curve describes the infant failures due to defects in the design, materials and used processes [Jen95, Ohr98]. Some of these may be eliminated by screening by doing burn-in testing [Ohr98]. When β=1, the failure rate is constant. This phase describes the useful life period of a product [Jen95, Ohr98]. The possible failures occurring during this part are random failures [Ohr98]. Furthermore, with β>1, the hazard rate is increasing while components degrade at an accelerated pace. This phase describes the wear-out failures when the number of defects grows over time [Jen95, Ohr98]. In order to study the wear-out failures in a reasonable space of time, ALT is needed [Liu11]. The Weibull

distribution is said to fit to early failure times exceptionally well, while later failure times may have a better fit with other distributions such as with lognormal [Ohr98].

In this work the results were analysed with the Weibull distribution if the number of samples and failures was high enough for statistical analysis. For other samples, CDF was used to plot the failures as a function of their occurrence time.

3.2 High Temperature Reliability Testing

Temperature is one of the most commonly used stresses to test the reliability of electronics [Esc06, Yeh02]. Increased temperature is said to be the most effective way to hasten failures in many cases [Ohr98]. In electronics it is important to understand the behaviour of materials and components at elevated temperatures, because increased temperature is known to accelerate chemical processes [Esc06, O'Co02] as well as degradation, corrosion and oxidation reactions [Wer01]. The acceleration caused by temperature can be expressed with Arrhenius' law [O'Co02]. Arrhenius' law, however, is quite a simplification. It has therefore been criticized for easily leading to erroneous reliability predictions [Bay10], and non-Arrhenius behaviour has been reported, for example, in polymer degradation studies [Cel05].

High temperature testing can be performed either at a constant temperature as thermal storage test or as a cycling test between two different temperatures. Both methods were used in this work. In addition to these, step stress testing was used to study the temperature limits by increasing the testing temperature step by step. Constant temperature causes thermal degradation and mechanical stresses between different materials due to their CTE differences. This also applies to thermal cycling, but adds the effect of cyclic expansion and contraction of materials, which causes fatigue in the structure. Therefore thermal cycling causes much higher stress levels than constant temperature testing. Thermal cycling can also be performed as a shock test in which the temperature change rate is very fast [Liu11]. There is no clear limit between cycling and shock tests. One definition proposed is a temperature change rate for more than 20°C/min for a shock test and less than 20°C/min for a cycling test [Liu11]. The mass of the test samples also affects the distinction between these terms due to thermal gradients. A sample with a small mass can reach the testing temperature faster than a larger and heavier sample, and thus for small samples shock testing may have the same effect as a cycling test. Both terms have been used in this work for the small samples tested.

ALT at high temperature may be challenging, because it is difficult to accelerate the aging phenomenon with higher temperature without causing changes to the failure mechanisms [Jul13]. In this work the aim was to study how the materials and structures could withstand high temperatures. The cycling tests used were ALTs, but step stress tests were used solely to study which levels of high temperature the materials could withstand. The thermal storage tests, on the other hand, were

used to study the actual use temperatures. Therefore these tests were not exclusively ALTs. The increased temperature will hasten the failure occurrence, still giving the tests an accelerated nature. Additionally, the exposure times used in the tests in this work may have been longer than the exposure times in actual use conditions. This may also accelerate the aging of the items tested.

3.2.1 Thermal Cycling Testing

Electronics packages are frequently exposed to some extent to a thermal cycling environment during their use life [Vis98]. As thermal cycling causes repeated expansions, contractions and fatigue, mechanical stresses may be induced in the structure [Esc06, Gao12a]. Thermal strain may also exceed the elastic limit, leading to plastic deformation and failures [Vis98].

Two different thermal cycling tests were used in this work. The first test involved cycling between the extreme temperatures of -40°C and +125°C according to JEDEC standard JESD22-A104D [JED09]. Dwell time at both extreme temperatures was 14 minutes and the transition time between the extreme temperatures was one minute, resulting in a total cycle length of 30 minutes. With such a rapid temperature change rate the test can also be called a shock test. The testing was continued for 10,000 cycles. The second test involved cycling between extreme temperatures of -55°C and +180°C. The temperature change rate was very slow, resulting in approximately 9-hour cycle time. The testing was performed from 100 to 400 cycles depending on the sample. The test was not based on any standard and was done to study the effect of high temperature cycle on the materials and structures.

According to the literature, the -40°C/+125°C test is a very widely used accelerated life test in electronics in general and also with ECAs. However, it may exceed the T_g of polymer materials, and therefore cause reliability issues [Gao12a]. ICA attachments have typically been reported to perform fairly reliably in -40°C/+125°C tests [Kim11, Rus95]. For ACAs, -40°C/+125°C is a very widely used reliability test. The first papers on the reliability of ACAs in chip attachments published in the late 1990s often reported failures, as resistance increases and failures were seen during the 1,000 test cycles [Gus97, Lai96, Liu99]. However, over the years the materials and designs have improved, because excellent reliability has subsequently been reported for ACA attachments. Especially flexible substrates lasting for 10,000 or 20,000 cycles of -40°C/+125°C without failures have been reported [Fri06a, Fri09] or the failures seen have been intermittent [Sep04]. In cycling testing CTE differences play a major role in reliability. Consequently, thinned structures give the best reliability, and thick and rigid PCBs and chips the poorest [Fri06b].

Harsher temperature cycling tests, especially with higher upper temperature extremes, have also been performed for ECAs. Dudek *et al.* studied ICA interconnections in -40°C/+160°C cycling and reported resistance increases with increasing testing time [Dud00]. Additionally, Jullien *et al.* studied PI-based ICA attachments in -55°C/+180°C cycling tests and observed cracks after 3 cycles of testing [Jul13]. The cracks were most likely due to voids in the ICA matrix, leading to strain

accumulation and crack initiation [Jul13]. Ali *et al.* studied ACAs with three cycling tests (-40°C/+140°C, -55°C/+125°C and -65°C/+150°C) [Ali05]. The lower temperature extreme did not affect the failure occurrence. When the upper temperature extreme was below the T_g of the ACA, only small increases in resistance occurred. When T_g was exceeded, more failures were seen [Ali05].

3.2.2 Step Stress Testing

Step stress testing can be used to find critical stress levels causing failures in a system by increasing the stress in steps. It can also be used to find the most critical weaknesses of a product [Liu11]. With this kind of testing the failures do not have to correlate with field failures, because overstressing may and often does occur [Liu11]. In this work the upper temperature limit for the materials was studied with step stress tests by increasing the temperature with certain steps and dwell times. According to the literature, step stress testing is not a common test to study the temperature limits of ECAs, even though it is commonly used with other electronics structures.

In this work three different step stress tests (SST) were used. In SST1 the temperature was increased in 10°C steps from 180°C to 260°C. Dwell time at each step was 15 minutes, and the temperature change between two steps took an additional 10-15 minutes. In SST2 and SST3 the increase was done in 20°C steps from 200°C to 260°C. In SST2 the dwell time was 24h, whereas in SST3 a longer dwell time of 168h was used.

3.2.3 Thermal Storage

Thermal storage testing is done at a constant temperature. Storage tests have been traditionally used to accelerate failure of IC components [Jen95]. Selecting the storage temperature may be challenging. Too high temperature may cause rapid degradation of the materials, but too low temperature may not cause failures within a reasonable timeframe.

The thermal stability of the materials and structures was studied with thermal storage tests at temperatures of 180°C, 200°C and 240°C. Different test durations up to 3,000h were used. Additionally, some of the samples were aged for short periods of time and removed from the test to study the progress of corrosion and degradation.

According to the literature, thermal storage has been widely used to study the thermal reliability of ICAs. The results vary between the test materials and test temperatures. During 200h of testing at 125°C, increased resistances for epoxy-based ICAs were reported [Dud00], whereas in another test resistance was only seen to decrease during 840h due to post-curing [Bar11]. Resistance decrease was also reported at 150°C during a 1,000h test, but the resistance was not measured in real time [Du11]. Additionally, a decrease in flexibility measured with an increase in storage modulus at 125°C, 150°C, 175°C and 200°C during 1,000h for epoxy ICA was seen, but not for silicone-based ICA [Dre08]. The loss of flexibility in epoxy ICAs was seen to occur even at 125°C and 150°C after a few hundred hours of testing, leading to cracking [Dre08]. Furthermore, silver migration may become an

issue at high temperatures, as observed in a test conducted at 250°C [Sou10]. For ACAs thermal storage has been less used. In storage testing at 125°C failures were seen during a 1,000h test [Lai96] and 10-20% resistance increases were reported in a test having a duration of 100h [Liu99]. Resistance increases were also observed at 150°C, but the rate of increase was much higher for samples cured at lower temperatures than those cured at higher temperatures [Riz05].

3.3 Test Evaluation Methods and Samples

Several evaluation methods were used in this work. Resistance of the test samples was the main tool for observing the behaviour of the interconnections during high temperature reliability testing. This is discussed in Chapter 3.3.1. Mechanical testing methods and material characterization were also used. These topics are discussed in Chapter 4. The samples used in this work are discussed in Chapter 3.3.2.

3.3.1 Evaluation with Resistance

The reliability of ECA attachments is often monitored by resistance of the interconnection [Ali05, Bar11, Dud00, Dre08, Gil95, Kii15, Liu99]. Stable resistance is important for the reliable functionality of an interconnection. Temperature sensor attachments were studied in Publications II-VI. For these sensors reliable attachments with stable resistance were crucial, because they sense the temperature through resistance changes. Therefore fluctuation in the resistance may lead to false measurement data.

Resistance can be measured either after certain testing intervals at ambient temperature or *in situ*, in real time during testing. The electrical behaviour of ECAs is sensitive to minor damage, thus resistance is a good indicator of microstructural changes [Kim02]. With ECAs real-time measurements are especially important as the materials tend to have intermittent failures at both low and high temperatures, but often they at least partially attain the original state at room temperature [Kim02, Udd04b]. Real-time measurement of resistance was used in all publications in this thesis, excluding the samples which were removed from thermal storage testing after short time periods and used for failure analysis.

In this work the resistance of the interconnections was measured as daisy-chain resistance, in which the interconnection areas of the chip and the substrate are connected in series (Figure 5). With a four-point measurement method resistance on a single joint could be monitored. This method is preferable for studying variations in interconnection locations [Udd04b] as the corner joints tend to fail first. However, as the four-point method only gives information on a single joint, the need for measurement capacity easily increases if a more comprehensive view of the interconnections in

general is needed. In this work the four-point measurement technique was not used due to limitations in the test structure.

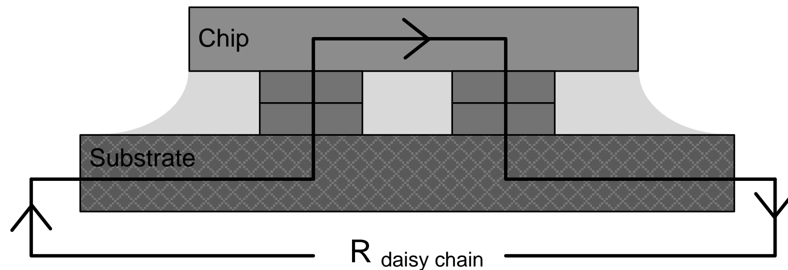
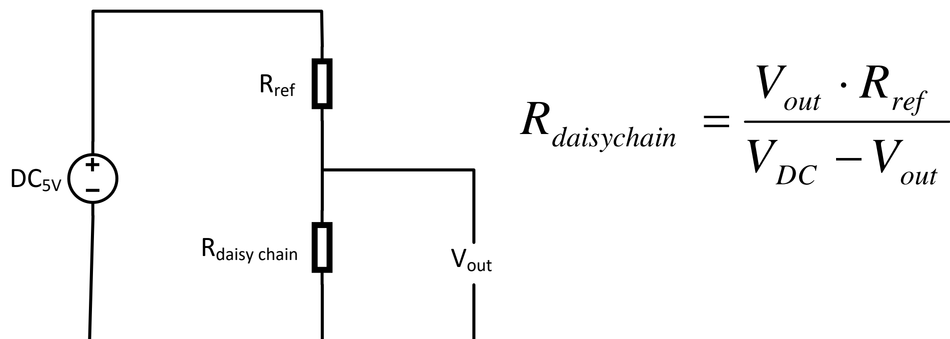


Figure 5. Principle of daisy chain.

The continuous, real-time measurement of resistance values was conducted with a data logger system from National Instruments. The daisy chain resistance consisted of the resistances of the chip, attachments, as well as the wirings on the PCBs and measurement wires. Each daisy chain was measured individually with its own measurement channel using two wires: one for the voltage and another for the ground signal. As shown in Figure 6, a 5V supply voltage in series with a reference resistor (1000 Ω) was used to feed a constant current to the measured channels. The voltage over the daisy chain structure was measured and the voltage was converted to daisy chain resistance (Figure 6). Thus any rise in the measurement voltage indicated an increase in the sample resistance. As open joints were formed on the test samples the measured voltage rose to the supply voltage. The voltage was measured every 10 seconds during all tests.



$$R_{daisychain} = \frac{V_{out} \cdot R_{ref}}{V_{DC} - V_{out}}$$

Figure 6. Real-time measurement setup and conversion between measured voltage and daisy chain resistance.

Failures are usually determined by an increase over a certain, pre-determined failure criterion. Typically it is an increase in the resistance, which is known to have an effect in the functionality of the sample. What kind of change in resistance is counted as a failure therefore depends on the application. In this work several different criteria were used depending on the test chip and test temperature. In Publication I with capacitive humidity sensors the criteria used were quite high, 4Ω, 20Ω and 250Ω, the initial resistance being 0.3Ω. A marked resistance increase was used because

capacitive sensors are not very sensitive to resistance increases. In Publication II the failure criterion was a double resistance value compared to the initial values at testing temperatures. In Publication III the samples were deemed to have failed when the measured voltage across the attachment had exceeded 1V. Publication IV used 210Ω (0.85V across the attachment) and 256Ω (1V across the attachment) as failure criteria, corresponding to 5% and 30% increases at 200°C. Publication V used 215Ω (0.87V) and 256Ω (1V) as failure criteria, corresponding to 5% and 25% increases at 240°C. Publication VI used the same criteria: 206Ω (0.85V, 5% increase) and 256Ω (1V, 30% increase) at 200°C, and 228Ω (0.93V, 5% increase) and 256Ω (1V, 15% increase) at 240°C. Consequently, Publications III - VI used the same principles in determining failure criteria. The lower criterion was always a 5% resistance increase and the upper criterion a 1V excess in voltage, but the actual resistance and voltage values behind the criteria varied due to different test temperatures and the effect of different substrate materials on the resistance. In Publication VII double resistance value compared to the initial values at testing temperatures was used as a failure criterion at all testing temperatures.

It is important to differentiate between errors in the measurement setup and real resistance changes. Single spikes in the resistance may be due to error, therefore one method is to count a high enough number of resistance changes within a certain time limit as an error. In this work such a method was not used. When the failure limit was exceeded and no simultaneous interference in other measurement channels was seen, failure was considered to have occurred. Additionally, ECA failures are often intermittent, but in this work the intermittent failures were also considered as actual failures.

3.3.2 Test Sample Description

The test samples in this work consisted of test chips, attachment materials and PCBs. Different combinations of materials were used in the different tests and publications. The attachments were done with the flip chip method, offering lower costs, finer pitch and better electrical performance and often improved reliability compared to other methods [Kwo04].

Three different test chips, a humidity sensor, a temperature sensor and a dummy test chip, were used in this work. The dummy test chip used in Publication VII was a silicon chip with 180 peripherally located Au bumps which formed a daisy-chain structure. In the tests the daisy chain was divided into two identical chains 90 bumps long. Humidity sensors were used in Publication I and temperature sensors in Publications II-VI. The humidity sensor consisted of a polymer film attached to a glass substrate. One contact area was manufactured directly on top of the glass substrate and the other on top of the polymer film. Both contact areas were coated with a thin Ni/Au coating. The sensor was able to measure the amount of humidity in the environment by monitoring the capacitance changes in the polymer film as a function of humidity. A more detailed description of the humidity sensor is given in Publication I. The temperature sensors used in Publications II-VI had a simple structure. The sensor was manufactured on alumina substrate. The structure consisted of four adjacent Ni/Au-

coated contact pads on one side of the sensor chip. The temperature measurement of the sensor was based on the resistance of the sensor structure, which was measured from the outermost pads. The internal resistance of the structure was more than 100Ω.

The structure of both sensor chips prevented bumping of the contacts. Bumped chips usually provide better reliability than unbumped chips [Gus97], but gold-coated nickel particles in particular have yielded good results with unbumped chips [Lu09b] and the contact can be improved with gold-coated interconnection areas. In general, sensors are challenging components to attach. They are used increasingly in electronics and often in challenging environments. Their structure depends largely on the factor they measure, which maybe humidity or other chemical substances, temperature, pressure or acceleration. While other sensors such as MEMS can be protected from the outside environment with packaging, sensors measuring temperature and humidity must be open to the environment. This may cause reliability problems, as they cannot be sealed to be safe from the harsh environment. Moreover, the materials and structures used in sensors, such as those in this work, may differ from traditional silicon-based electronics, prohibiting the use of soldering. Versatile ECAs, on the other hand, combined with flip chip technology, offer a promising attachment method for sensors.

The various PCBs used in this work are listed in Table 1. All the PCBs were single-sided. The rigid ones were two different FR-4s and Rogers PCB. Two different flexible PI PCBs were also studied. PI PCB processed with adhesive layer having poorer properties than PI itself was used in most of the studies. Adhesiveless PI PCB had a more stable, possibly PI-based adhesive layer. More detailed information of all the PCBs can be found in the publications.

Table 1. PCBs used in this work.

PCB	Publication	Thickness	Other matters
FR-4 traditional	I	120µm, 1mm	
FR-4 “enhanced”	II, VI	1mm	Data sheet T_g 170°C ; Measured T_g traditional
Rogers PCB	VI	0.8mm	
PI PCB	II – V	140µm	Poor adhesive layer
Adhesiveless PI PCB	VII	80µm	Improved adhesive layer

All the combinations of chips and substrates according to each test used in this work are shown in Table 2. Additionally, cross-sectional schematic drawings (not to scale) depicting various materials in test structures are shown in Figure 7, Figure 8 and Figure 9.

Table 2. All combinations of PCBs and chips used according to the tests.

Sample	-40°C /+125°C	-55°C /+180°C	Step stress test	Storage 180°C	Storage 200°C	Storage 240°C
FR-4 + humidity sensor	X					
PI PCB + temperature sensor		X	X		X	X
FR-4 + temperature sensor		X			X	X
Rogers + temperature sensor					X	X
Adhesiveless PI PCB + chip				X	X	X

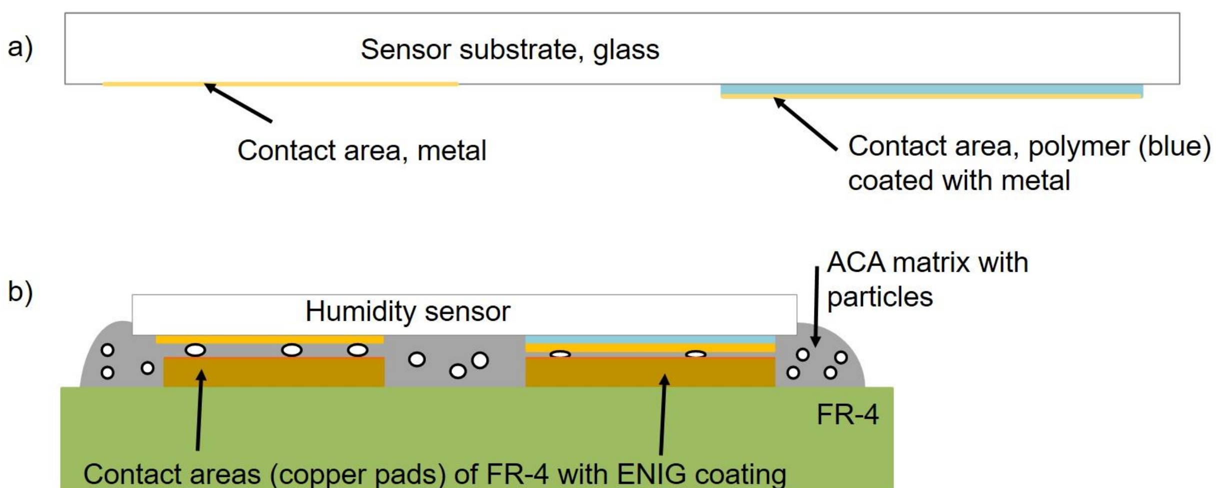


Figure 7. Schematic drawing of a) humidity sensor chip b) humidity sensor attachment on FR-4.

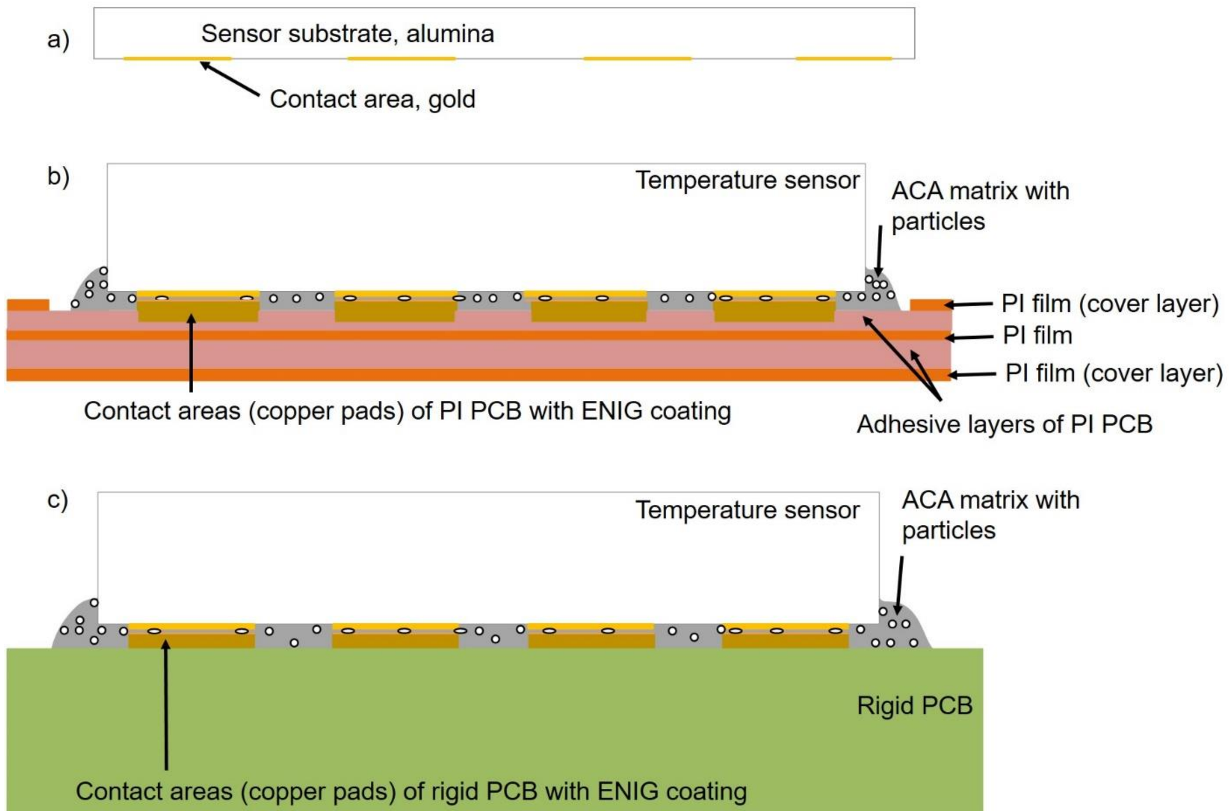


Figure 8. Schematic drawing of a) temperature sensor chip b) temperature sensor attachment on PI PCB c) temperature sensor attachment on rigid PCB.

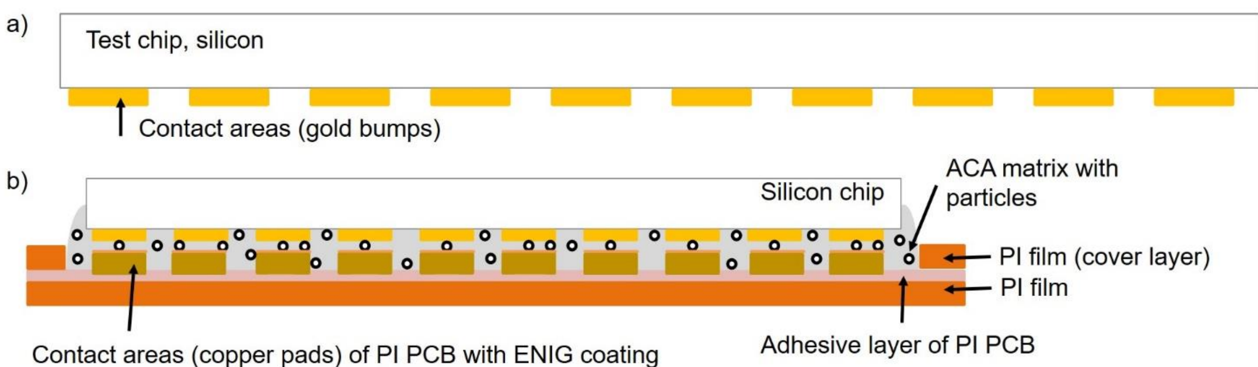


Figure 9. Schematic drawing of a) test chip b) test chip attachment on PI PCB.

A total of eight ECAs were studied, two of these were ICAs and six ACAs. The ICAs were silver-filled and they were studied with and without an underfill (UF). The ACAs were filled with nickel-gold particles or gold plated polymer particles. ACF1 and ACF2 had the same matrix, but different particle type. Three of these were anisotropically conductive films (ACF 1-3) filled with both particle types. Three anisotropically conductive pastes (ACP 1-3) were also studied. They were all filled with nickel-gold particles. All the ECAs were commercial thermosets whose exact chemical composition was

unknown. According to the data sheets the matrices of the ACAs were epoxy-based except for ACP3, which was designed for low temperature attachments and was based on a polycarbaminacid derivative. The matrices of the ICAs were unknown.

Table 3. Characteristic parameters of the ECAs and UF.

ECA	T_g (°C)	T_d (°C)	CTE [ppm]	Particle type (size)	Bonding parameters (°C,s)
ICA1				Ag	100, 60 min
ICA2	120		35/110	Ag	150, 30min
UF	145		33/100	Silica (0.6μm)	150, 60min
ACF1	112	330	40/561	Polymer with Au coating (4μm)	210, 20
ACF2	113	332	39/552	Ni/Au (5-8μm)	210, 20
ACF3	118	320	101/1836	Polymer with Au coating (5μm)	220, 15
ACP1	165		55/180	Ni/Au (5μm)	200, 12
ACP2	135		61/180	Ni/Au (2.5μm)	220, 12 +post-curing 150, 30min
ACP3	74		91/	Ni/Au (2.5μm)	180, 8

Characteristic parameters according to the data sheets are shown in Table 3 for all the ECAs and the UF. Bonding temperature (tool) and bonding time are also given in Table 3. The stage temperature for all the ACAs was 100°C. The actual bonding temperature in the adhesive was approximately 20 - 30°C less than the tool set temperature. The bonding pressure was 100MPa in Publications II – VII. In Publication I three different bonding pressures of 25, 50 and 100MPa were compared. All the ECAs used in this work according to each test are shown in Table 4.

Table 4. All ECAs according to the tests.

ECA	-40°C /+125°C	-55°C /+180°C	Step stress test	Storage 180°C	Storage 200°C	Storage 240°C
ICA1		X	X		X	X
ICA2		X				
ACF1	X	X	X		X	X
ACF2	X	X	X	X	X	X
ACF3		X	X		X	X
ACP1	X	X	X		X	X
ACP2		X	X		X	X
ACP3		X	X		X	X

In Publication I the naming system was different from those used in the other publications, even though the same ACAs were used. ACA A = ACF1, ACA B = ACF3 and ACA C = ACP1. In the publications with only one ICA used, ICA = ICA1.

4 Material Characterization

Material characterization is a broad term covering a wide range of techniques used to analyse material properties and possible changes in them. This chapter is concerned with the thermal, chemical and mechanical analysis methods discussed in Publications V and VI. The PCB materials and the ACF analysed in this chapter include the materials used in Publications II – VII.

4.1 Thermal Analysis

Thermal analysis refers to a set of methods used to analyse the connection between temperature and the physical properties of materials [Men09]. These methods measure the response to different temperatures or changes therein. They are especially widely used with polymer materials [Men09]. Commonly applied techniques include differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), as well as thermomechanical and dynamic mechanical analyses (TMA and DMA respectively). In the field of electronics, DSC has been a very widely used method to study the curing behaviour of ECAs, including determination of curing profile and curing degree, as well as to study curing kinetics [Cao04, Cha03, Chu10, Klo98, Li05, Riz05, Til10, Won01, Wu97, Yim01, Zha08]. It is also commonly used to determine T_g and T_m values and crystallinity for materials such as ECAs and PCBs [Gec14, Lah13, Li05, Saa16, Won01, Yim01]. TGA is typically used for analysing the decomposition behaviour or thermal stability of polymer materials [Du11, Tan04, Wu97, Yim01, Zha08]. With TMA and DMA different moduli values, such as elastic modulus (Young's modulus) and storage modulus, can be determined [Chu10, Dud00, Lah13, Saa16, Yim01, Zha08]. The elastic modulus describes the stiffness of elastic material and storage modulus the stiffness of viscoelastic material. At low frequencies the storage modulus is typically approximately equal to the elastic modulus [Ehr04]. Shrinkage and expansion, such as CTE values and $T_{g,}$ can also be determined with these methods [Chu10, Gec14, Klo98, Lah13, Saa16, Udd04b, Yim01]. Depending on the sample and the parameter of interest, the analysis may be conducted either from the first or second heating run. The first run will give information on the sample and its thermal history, whereas the second run will give information about the characteristic properties of the material itself [Ehr04].

4.1.1 Methods and Samples Used

The thermal properties of the polymer materials used in this work were studied with simultaneous thermal analysis (STA) and DSC methods. STA methods is a combination of TGA and differential thermal analysis (DTA).

TGA is a method in which a sample is exposed to a controlled temperature programme in a controlled atmosphere while the mass of the sample or changes in it are measured [Men09, Ehr04]. The

measurement is done with a sensitive thermobalance. The outcome of TGA is absolute or relative mass plotted as a function of temperature or time. Depending on the material and reactions, there are one or more steps in the mass change. The possible reactions causing changes in mass include chemical reactions, evaporation and decomposition [Ehr04]. Polymers typically undergo mass drop, but oxidation can also cause the mass to increase [Ehr04, Men09].

DTA and DSC have somewhat similar purposes. With both techniques the temperature difference of a sample and an inert reference sample is measured during a controlled temperature programme in a controlled atmosphere [Ehr04, Men09, Mül63]. DTA only makes it possible to determine characteristic temperatures for reactions, whereas calorimetry used in DSC also allows determination of quantitative caloric values, including enthalpy and crystallization. In this work DTA was mainly used as a supportive tool for TGA results, helping to separate the sequential decomposition steps.

DSC is by far the most used thermal analysis technique [Men09]. The outcome of a DSC analysis is heat flow as a function of temperature [Ehr04]. Enthalpy changes between the sample and the reference are either endothermic or exothermic, showing the direction of the heat flow. In endothermic processes the enthalpy increases due to energy absorption [Men09]. This means that the sample is using the heat energy for its internal reaction and the temperature of the samples does not momentarily increase, unlike the temperature of the inactive reference sample. In exothermic processes the enthalpy decreases due to energy release [Men09]. Examples of endothermic processes are glass transition, melting and evaporation, and examples of exothermic reactions are crystallization and degradation [Men09, Ehr04].

Both ECAs and different PCB materials were analysed with STA with a test simulating the degradation conditions in air. The samples were not aged; the ECAs were cured with a thermal profile similar to that of the ECAs used in the attachments, as explained in Publication V, and the PCBs were used as such. All the main mass loss steps up to 930°C were analysed. The residual mass at the temperature of the lowest mass was used to determine the amount of non-oxidising fillers in the materials. Degradation at the testing temperatures used in this work was analysed by determining the weight loss at 240°C and onset temperature, which corresponds to the sample temperature at which 1% organic mass loss occurs.

Aged PCB materials and ACF1, on the other hand, were studied with DSC in nitrogen atmosphere. Before DSC runs they were aged in thermal storage tests. With DSC endo- and exothermic steps formed and possible changes in these were analysed, especially the endothermic step corresponding to glass transition. The thermal analysis samples are listed in Table 5 and Table 6.

Table 5. PCB samples used in thermal analysis.

PCB Material	Thermal analysis method used		Aged (200°C, 240°C) for DSC
	DSC	STA	
Kapton	X		30h, 60h, 120h, 480h, 1920h
PI PCB	X	X	30h, 60h, 120h, 480h, 1920h
Adhesiveless PI PCB		X	
Rogers	X	X	120h, 480h, 1920h
FR-4	X	X	120h, 480h, 1920h

Table 6. ECA samples used in thermal analysis.

ECA Material	Thermal analysis method used		Aged (200°C, 240°C) for DSC
	DSC	STA	
ICA1		X	
ICA2		X	
ACF1	X	X	30h, 60h, 120h, 480h, 1920h
ACF2		X	
ACF3		X	
ACP1		X	
ACP2		X	
ACP3		X	

4.1.2 Thermal Analysis Results

Table 7 shows the TGA results for the ECA materials. The onset temperatures varied rather much between the materials. For some adhesives, the onset temperature was exceeded in all the thermal storage tests used. The weight loss increased somewhat when the testing temperature was increased from 180°C up to 240°C. The weight loss at 240°C, however, was only a few percent. The endothermic reactions seen in DTA at the region of the first step all occurred at much higher temperatures than the testing temperatures [Publication V]. Thus, in testing conditions the materials were quite stable. The small weight losses at the start of the TGA run may be also due to solvent vaporisation and final curing of the ECA material. Generally it can be stated that decomposition degradation occurring at the testing temperatures was not significant. Similar TGA results with thermal stability of ACF up to 300°C[Tan04] and for ICA up to 250°C [Du11] have been reported earlier.

The residual fraction was much higher with ICAs than ACAs, which can be explained by their higher filler concentration. In fact, ICAs had fairly low onset temperatures and high weight losses at 240°C compared to ACAs. It is difficult to draw firm conclusions between different ACAs. ACF1 and ACF3 were the only ACAs with polymer particles. Compared to most of the nickel-filled ACAs, the polymer-

filled ACAs showed greater weight loss at 240°C. Additionally, ACF1 and ACF2 were known to have similar matrices but different particle types. ACF1 with polymer particles had lower onset temperature and higher weight loss. The polymer particles may have been more prone to degradation at lower temperatures than the nickel particles, which would explain the difference. However, ACP3 with nickel particles had low onset temperature and high weight loss value, which may have been due to a thermally poorly stable adhesive matrix.

Table 7. TGA results for ECAs. mi = initial sample mass, mf = residual sample mass at 930°C.

Material	Onset [°C]	Weight loss at 240°C [%]	Step 1		Step 2		Step 3		Residual fraction (m_f/m_i) [%]
			Temp. range [°C]	Δm [%]	Temp. range [°C]	Δm [%]	Temp. range [°C]	Δm [%]	
ICA1	127.8	2.8	60 – 377	6.9	377 – 460	9.1	460 – 529	3.1	80.9
ICA2	111.5	1.7	57 – 410	3.7	410 – 462	5.4	462 – 530	5.1	85.3
ACF1	180.4	1.3	62 – 405	20.1	405 – 461	18.8	461 – 631	35.7	24.4
ACF2	227.9	0.9	60 – 393	16.2	393 – 464	19.9	464 – 660	35.6	28.4
ACF3	134.7	2.7	60 – 393	20.1	393 – 480	30.8	480 – 640	35.8	12.7
ACP1	231.3	0.7	50 – 481	37.1	–	–	481 – 665	29.7	33.4
ACP2	287.9	0.3	100 – 405	11.7	405 – 496	45.4	496 – 664	31.4	11.6
ACP3	136.9	3.0	55 – 388	44.1	388 – 479	20.4	479 – 665	23.4	12.0

Table 8 and Figure 10 show the TGA results for the PCB materials used in this work (excluding Publication I). All PCB materials were very stable at the testing temperatures. The onset temperatures for all the PCB materials were above the testing temperatures. Weight losses at 240°C occurred only for PI PCB having an adhesive layer with poor thermal properties. However, the amount of weight loss for this material is so low that it may also be a measurement error.

Table 8. TGA results for PCBs. mi = initial sample mass, mf = residual sample mass at 930°C.

Material	Onset [°C]	Weight loss at 240°C [%]	Step 1		Step 2		Step 3		Residual fraction (m_f/m_i) [%]
			Temp. range [°C]	Δm [%]	Temp. range [°C]	Δm [%]	Temp. range [°C]	Δm [%]	
Rogers	387.1	0	–	–	382 – 505	18.8	505 – 577	5.5	74.1
FR-4	305.8	0	265 – 379	26.1	379 – 597	12.6	–	–	61.3
PI PCB	277.8	0.3	189 – 346	20.4	346 – 491	14.5	491 – 729	57.8	7.2
PI PCB adhesiveless	269.5	0	207 – 446	9.7	446 – 580	12.3	580 – 760	72.8	5.2

For the Rogers and FR-4 the first decomposition step occurred at temperatures higher than those used in testing. The Rogers was clearly also the most stable material, as shown in Figure 10. With both PI materials, however, the first decomposition step started at lower temperatures, around 200°C (Table 8). The adhesiveless PI PCB was more stable than the PI with an adhesive layer. Compared to FR-4, the decomposition of PI initiated earlier, but the DTA results showed that the endothermic reaction occurred at a lower temperature for FR-4 [Publication VI]. FR-4 decomposition has also been reported earlier to occur around 300°C [Pan15]. Furthermore, for Rogers, FR-4 and

adhesiveless PI PCB the weight increased at the beginning of the TGA run, indicating oxidation. However, the increase was quite small, especially for FR-4.

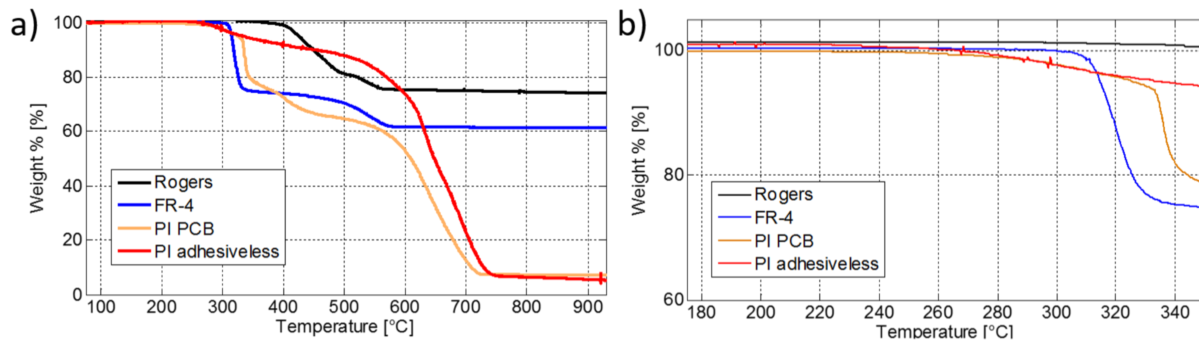


Figure 10. TGA results for PCBs. b) a close-up for testing temperatures.

Aged materials were analysed with DSC. Of all the ECAs, ACF1 was the only analysed material. Due to aging, the T_g value of ACF1 increased. At the same time the step got wider and lower as shown in Publication V. This indicated increased cross-linking of the material. This behaviour also suggested a decrease in elasticity, which could make the material more prone to cracking.

For PI PCB, neat Kapton and Rogers PCB, glass transitions were not seen before or after aging. Additionally, aging did not change the DSC curve of the PI PCB materials. For the Rogers after long aging time and high aging temperature (1,920h at 200°C, 480h and 1,920h at 240°C) an endothermic peak was seen at a low temperature, suggesting increased water immersion of the aged materials. These peaks were, however, small.

With unaged FR-4 the T_g decreased markedly between the first and second DSC runs (midpoint from 133°C to 94°C). The DSC run up to 300°C seemed to be severe enough to cause permanent changes in the FR-4 material. This indicated problems with the thermal stability of FR-4, even if no marked decomposition at this temperature range could be detected with TGA. The decrease in T_g is typically linked to onset of chain scission [Cha09b]. For the aged FR-4 samples no T_g was seen, corresponding to dramatic degradation already after 120h at 200°C. T_g decrease due to thermal aging has been reported earlier, and the rate of decrease was accelerated with higher aging temperature [Pol09, And13]. Short reflows also typically decrease the T_gs of FR-4 [Lal12].

With longer aging and higher aging temperature the FR-4 samples lost their structure and turned into dark powder due to degradation. This degradation seemed to make the FR-4 material more prone to water immersion, as endothermic peaks at low temperatures were seen similar with the Rogers. With FR-4, however, these peaks were marked in range and size, and increased with increasing degradation. However, a sample aged at 240°C for 1,920h showed no water absorption peak, most likely due to loss of the organic part and low water absorption ability of the remaining glass cloth.

4.2 Fourier Transform Infrared Spectroscopy

Chemical analysis was done with Fourier transform infrared spectroscopy (FTIR), which is a method able to determine chemical groups [Moo10]. FTIR can recognise vibrational frequencies caused by the absorption of IR radiation, because the frequencies are characteristic for each chemical group [Moo10]. This results in an absorption spectrum with absorption peaks [Sha98]. With recognition of functional groups and changes and shifts of the absorption peaks, polymers can be identified and changes in the chemical composition can be determined [Moo10, Sha98]. In this work the FTIR used was a reflection-based, diamond Attenuated Total Reflection (ATR) system. In ATR the chemical group analysis can be done at the surface only [Moo10].

In electronics, FTIR has been used, for example, to determine curing degree [Chu10, Lee07a, Ma06, Tan04], to characterize materials and their differences [Li05, Saa16] and to study the changes in chemical structure due to aging or field condition [Lah13, Pol14, Tan04, Zha12]. It has been claimed to be an excellent method for studying the early phases of degradation because it can detect small molecular changes unlike other methods such as TGA [Mus01]. In this work FTIR was used to study degradation and other possible chemical changes in the materials. The samples studied are listed in Table 9.

Table 9. Samples used in FTIR analysis.

Material	Aged (180°C, 200°C, 240°C)
Kapton	30h, 60h, 120h, 480h, 1920h
PI PCB, cover layer	30h, 60h, 120h, 480h, 1920h
PI PCB, adhesive layer	30h, 60h, 120h, 480h, 1920h
Adhesiveless PI PCB, adhesive layer	120h, 480h, 2500h
Rogers	120h, 480h, 1920h
FR-4	120h, 480h, 1920h
ACF1	30h, 60h, 120h, 480h, 1920h

4.2.1 FTIR Results

A detailed chemical analysis of the materials was not feasible because all the materials were commercial, proprietary materials and their chemical compounds were unknown. All the materials, except the Kapton and PI cover layer, were also composites of several different materials. The Kapton and PI PCB cover layer were neat polyimide. The adhesives used in PI PCB and adhesiveless PI PCB were unknown polymer materials. Traditional PI PCB was studied with EDS, indicating that its adhesive layer contained small amounts of sulphur, antimony, potassium and aluminium. The Rogers was a mixture of hydrocarbon and ceramic. FR-4 was most likely bifunctional

DGEBA. Both the Rogers and FR-4 also contained reinforcement materials and curing agents and FR-4 also contained flame retardants. ACF1 was epoxy-based, most likely DGEBA with unknown curing agent and additives. It also contained polymer particles. This subchapter includes the general conclusions of the analysis. A more detailed analysis of the chemical groups is given in Publications V – VI.

No changes in the FTIR spectra were seen for the Kapton and PI PCB cover layer when the non-aged samples were compared to the aged ones. Consequently, neat PI itself seemed to be very stable at the testing temperatures used. The adhesive layer of the traditional PI PCB, however, had stability problems, as the adhesive layer in the PI PCB was seen to degrade rapidly (Figure 11a-b). Clear changes in the spectra were already apparent in samples aged for 30h at 200°C at all areas of the spectrum. When the aging time was increased, the spectrum lost its shape. At 240°C the changes occurred faster: after 30h more degradation was seen than after 1,920h at 200°C, and the shape loss of the spectrum was again seen. It seemed that oxidation and a very dramatic scission of polymer chains occurred at both aging temperatures in the PI PCB adhesive layer. Consequently, even though PI in the PCB was thermally very stable, the adhesive layer was not and thus the PI PCB was not thermally stable at the testing temperatures used.

The FTIR analysis for the thin adhesive layer used in the adhesiveless PI PCB is shown in Figure 12 for all three testing temperatures of 180°C, 200°C and 240°C. Compared to the thick adhesive layer in the traditional PI PCB considerably less degradation occurred at all three temperatures. Oxidation was seen to already occur after the first aging period at all temperatures, but after this no dramatic changes were discernible. Even after long aging of 2,500h the changes were rather small compared to the non-aged samples. The differences between aging temperatures were also very small. According to the spectrum, the adhesive used in the structure remained unknown. It seems not to be pure PI-based adhesive, and was possibly a combination of several polymers.

Stability problems from the chemistry point of view were also seen with Rogers and FR-4. Aging was observed to cause changes in the Rogers PCB spectra (Figure 11c). Several peaks seen in the non-aged samples disappeared or changed their shape due to aging after 120h at 200°C. However, after this very few further changes were seen to occur, and no marked changes were seen between the aging temperatures. Consequently, the behaviour was quite similar to that of adhesiveless PI PCB, in which no changes were seen after the initial oxidation. FR-4, shown in Figure 11d, was also seen to have changes in its spectra after 120h at 200°C. With further aging the spectra were seen to lose shape due to further degradation. At 240°C a marked change was seen to occur after 120h of aging. At this point the spectra had already lost its shape and no further changes appeared with additional aging. The aged Rogers and FR-4 samples formed new wide peaks in the carbonyl area, indicating oxidation. In FR-4 the polymer chains broke, most likely due to degradation. Similar chain scission most likely occurred with the Rogers, but its higher level of inorganic substance made it more stable at high temperatures.

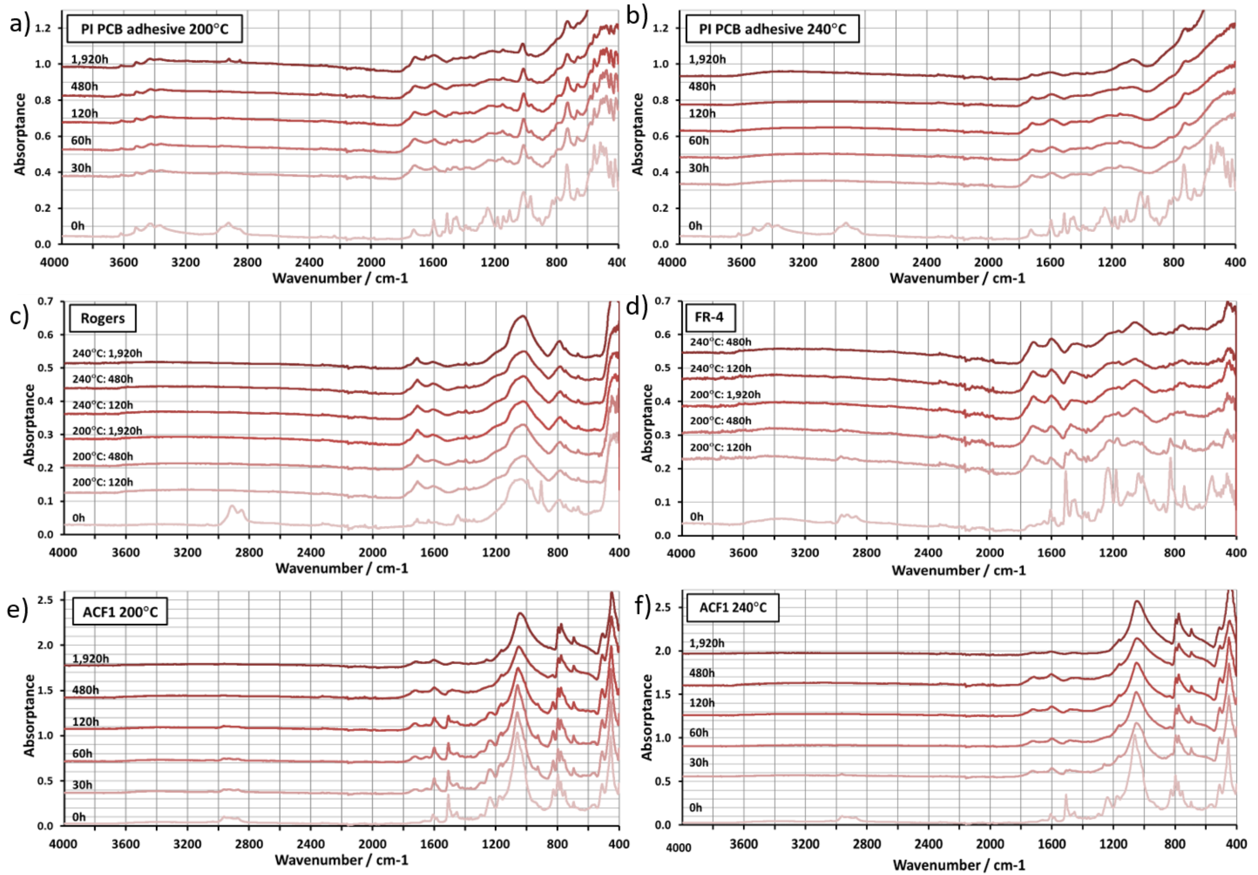


Figure 11. FTIR spectra of) PI PCB adhesive layer aged at 200°C b) PI PCB adhesive layer aged at 240°C c) Rogers PCB aged at 200°C and 240°C d) FR-4 PCB aged at 200°C and 240°C e) ACF1 aged at 200°C f) ACF1 aged at 240°C.

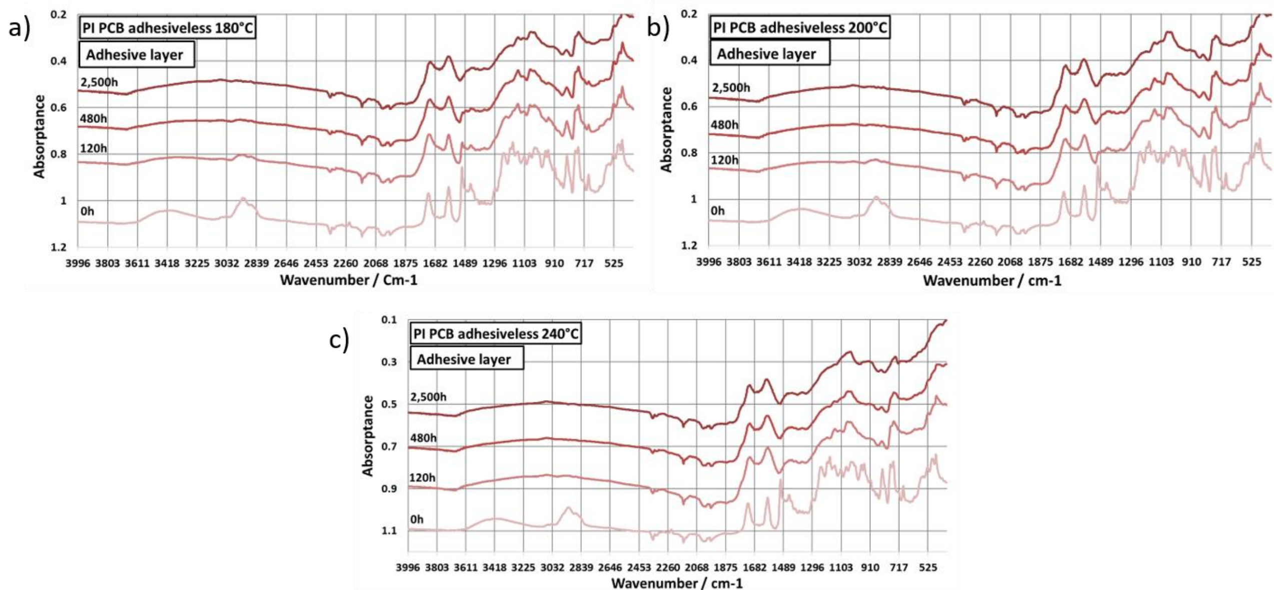


Figure 12. FTIR spectra of) “Adhesiveless PI PCB” adhesive layer aged at 180°C b) “Adhesiveless PI PCB” adhesive layer aged at 200°C c) “Adhesiveless PI PCB” adhesive layer aged at 240°C.

In ACF1 changes in the spectra were already seen after 30h at 200°C, as Figure 11e shows. At 240°C, as shown in Figure 11f, the changes were much faster, as the spectrum of the material aged for 30h at 240°C was similar to that of the sample aged for 1,920h at 200°C. Tan *et al.* reported degradation for epoxy-based ACF occurring during the bonding process with increasing bonding temperature [Tan04]. Some of the same degradation signs seen in this work were reportedly seen when bonding temperature was increased from 160°C to 225°C [Tan04]. Thus it is not surprising that changes occurred during the much longer aging. As ACF1 and FR-4 were both assumed to be based on the same epoxy type of DGEBA, some similarities in their degradation were discernible. The curing agents used were different, which also explains the differences in their spectra.

4.3 Mechanical Analysis

Mechanical analysis methods can be used to study mechanical properties of materials. Mechanical properties are very important, as all applications will likely face some degree of mechanical loading during their lifetime [Sha98]. Important properties, such as tensile, shear and impact strength as well as hardness, creep and fatigue depend on the material and application [Che06, Sha98, Tan03, Udd04a, Wu04]. These properties can be measured with a wide variety of measurement techniques. In this work mechanical properties were studied with tensile testing and shear testing methods, because tensile and shear stresses can be very damaging to interconnections [Xia05]. The samples used with both methods are listed in Table 10.

Table 10. Samples used in mechanical analysis.

Material	Mechanical analysis method used		Aged (200°C, 240°C)
	Shear	Tensile	
Rogers+sensor+ACF1	X		30h, 60h, 120h, 480h, 1920h
ACF1		X	120h, 480h, 1920h

4.3.1 Tensile testing

One of the most used correspondences to understand the mechanical properties is stress-strain dependence. With this relationship tensile properties can be determined, giving information about the ability of a material to withstand pulling forces and to determine to what extent the material elongates before breaking [Sha98]. Thus in tensile testing the sample is subjected to tension, and tensile force as a function of sample elongation is measured and converted to a stress-strain curve [ASM]. Tensile testing can be used to determine a set of parameters, such as elastic modulus during elastic deformation or different stress and strain determinations [ASM]. Chung and Paik used it to study the connection between curing degree of ACF and its ultimate tensile strength values [Chu10].

Tensile testing in this work was done by pulling cured and aged ACF1 film strips with the tensile testing equipment shown in Figure 13. The samples were not according to any standard, nor in the typical dog-bone shape [ASM], but rectangular pieces of adhesive with a size of 0.3 x 12 x 70 mm. The adhesive pieces were attached with thick adhesive tape to the testing equipment and pulled until breaking. The parameters determined included ultimate tensile strength (UTS) corresponding to the highest stress value before the sample broke, and maximal tensile strain at UTS [ASM]. Young's modulus was also analysed.

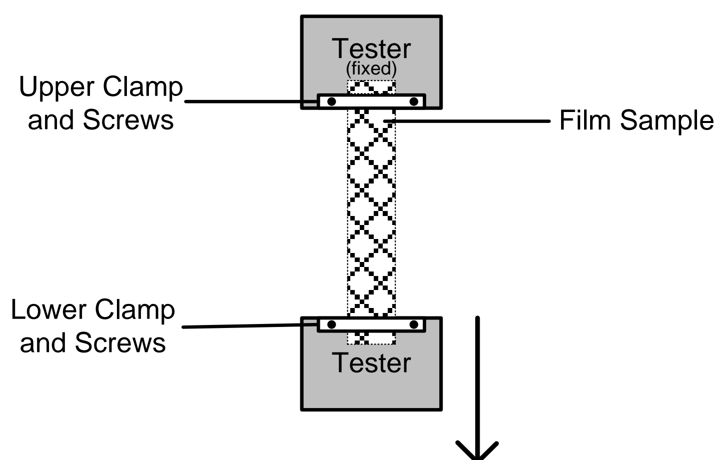
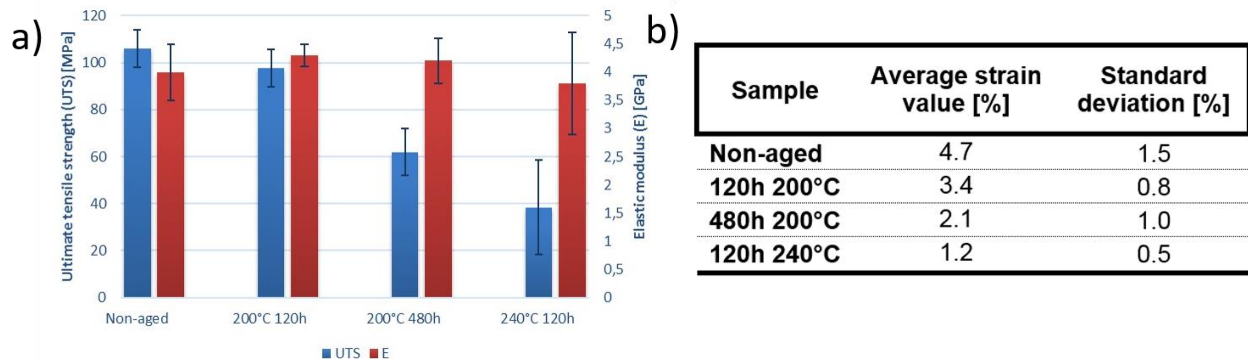


Figure 13. Tensile testing principle.

Figure 14 shows the UTS and Young's moduli values with the standard deviations with error bars as well as the corresponding strain values. With increasing aging temperature and time, the UTS and corresponding strain values were observed to decrease. A clear decrease was seen after 480h at 200°C and at higher temperature of 240°C the decrease was even higher after only 120h. Decrease in the strain value was already apparent after 120h at 200°C, but no clear difference in strength value was seen. However, standard deviation of both values was relatively large. This behaviour indicates increased cross-link density and decreased elasticity similar to the DSC results. However, no clear changes in the elastic moduli were seen. The samples were observed to become brittle; 480h at 240°C and 1,920h at both 200°C caused the samples to become brittle so that tensile testing was not feasible. In other studies the elastic modulus decreased: the storage modulus of a thermosetting resin decreased when aging time increased [Cha09b] and both elastic modulus and tensile strength decreased during a DMA run while the temperature was increased [Gao09]. For ICA with copper and silver fillers a 30% decrease in tensile strength was reported after 30min of aging at 300°C, whereas no decrease was observed at 150°C after 1,000h of aging [Sug07].



Sample	Average strain value [%]	Standard deviation [%]
Non-aged	4.7	1.5
120h 200°C	3.4	0.8
480h 200°C	2.1	1.0
120h 240°C	1.2	0.5

Figure 14. Ultimate tensile strength and elastic modulus values for tensile test samples. b) Strain values corresponding to the UTS values.

4.3.2 Shear testing

Shear properties, on the other hand, have been measured to understand interconnection strength and adhesion between different materials [Che06, Lee07b, Ma06, Tan03]. In this work shear testing was performed as a die shear test to study the adhesion between different materials in the interconnections. In die shear testing, according to MIL-STD-883E, the test is used to study bond strength between a semiconductor die and a substrate when a tool is applied exerting force perpendicular to one edge of the die and parallel to the substrate, causing shearing failure [MIL883]. The principle is illustrated in Figure 15. The test sample consisted of a temperature sensor attached onto Rogers substrate with ACF1. The maximal force needed to separate the sensor chip from the substrate was analysed, likewise the fracture surfaces.

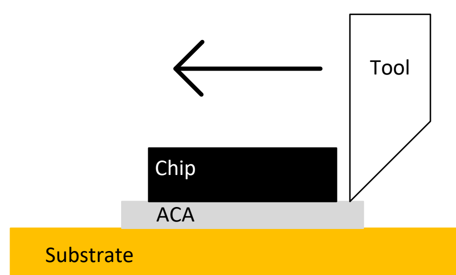


Figure 15. Die shear testing principle.

The shear testing results are shown in Figure 16. Similar to the tensile strength test, aging was seen to decrease the shear force values. The decrease in the shear forces was already apparent after 30h with no clear differences between aging temperatures. After 60h of aging the temperature became more significant. At 200°C the maximal forces gradually decreased. However, at 240°C the decrease occurred much faster. The maximal force after 120h at 240°C was in the same range as after 1,920h at 200°C. In addition, after 480h of testing at 240°C the attachment was too fragile for the shear equipment to record a force value. Large cracks around the chip in the ACF could be seen

in these samples. Earlier cracks and delamination caused by CTE differences has been reported to affect the adhesion strength of ACF attached chips [Riz05]. Shear strength decrease with prolonged aging has also been reported in cycling testing with upper temperature of 150°C [Gao12b] and with thermal storage at 150°C after 1,000h [Du11]. Aging at 250°C has been reported to decrease the shear force markedly after 300h, and after 1,000h the shear force was non-existent [Kli09], a result quite similar to the result in this work.

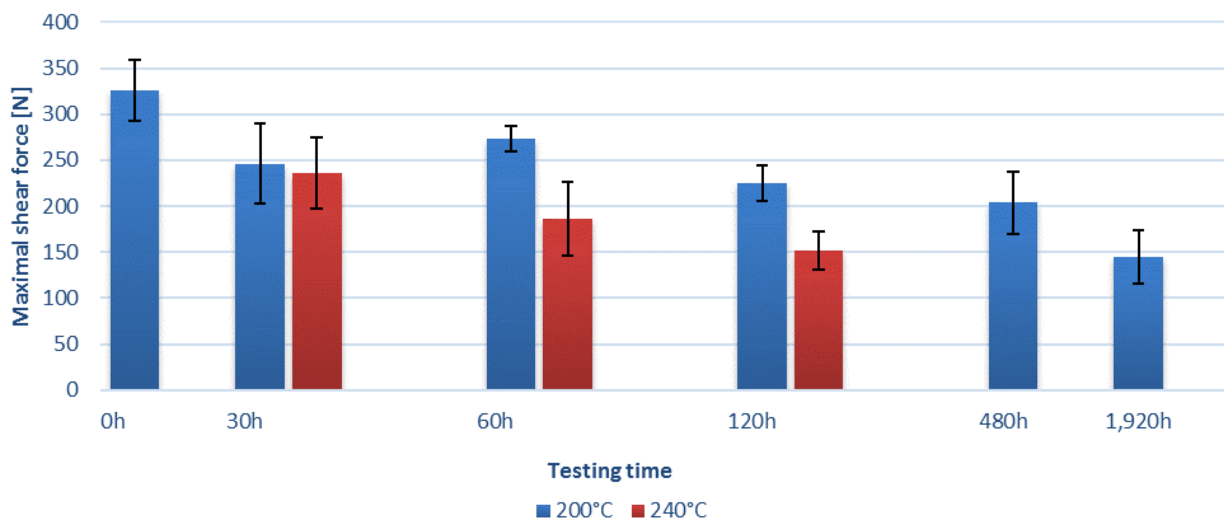


Figure 16. Maximal shear force values.

Adhesion was further studied by analysing the fracture surfaces of the shear tested samples of the Rogers PCB and the sensor chip. For all the samples tested at 200°C the failure was partially cohesion and partially adhesion failure. The interconnection broke partially between ACF and sensor (adhesion), partially in the adhesive (cohesion) and partially on the reinforcement layer of the Rogers PCB (Figure 17a-b). This was also the case for the samples aged for 30h at 240°C. However, for the samples tested at 240°C for 60h and 120h the failure was almost pure adhesion failure between the ACF and the chip (Figure 17c-d).

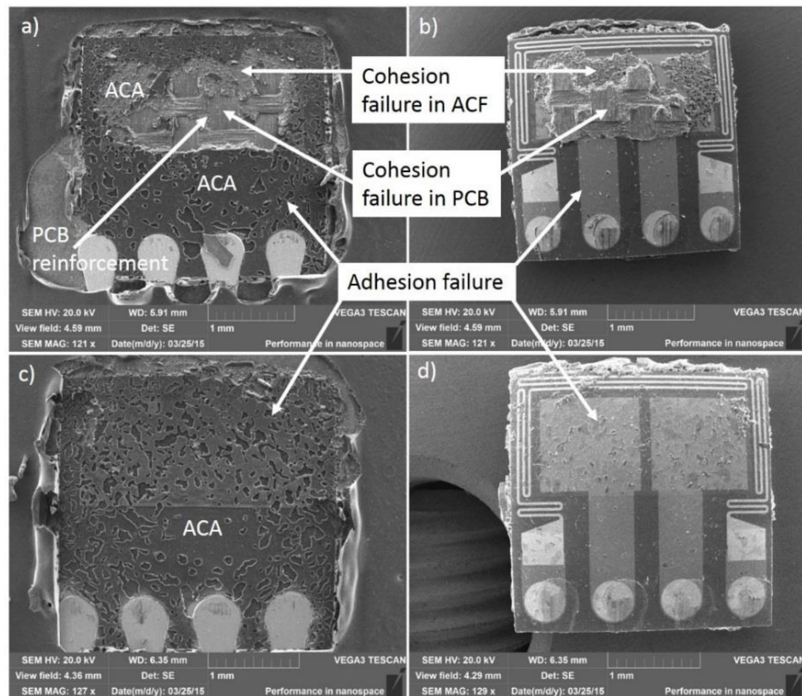


Figure 17. Micrograph of fracture surface of a) Rogers PCB aged for 120h at 200°C b) chip aged for 120h at 200°C c) Rogers PCB aged for 120h at 240°C d) chip aged for 120h at 240°C.

4.4 Conclusion of Material Characterization

According to the TGA runs, short exposures to high temperatures for the ECAs did not cause marked decomposition degradation at testing temperatures. TGA runs, however, already showed additional cross-linking. Moreover, FTIR revealed significant chemical changes and decomposition occurring rapidly in the aged samples, especially at higher aging temperatures. Mechanical strength was seen to decrease due to aging as adhesion impaired quickly at 240°C.

Similar to the ECAs, the TGA runs showed no marked decomposition degradation for any of the PCBs. FTIR, however, showed marked changes due to aging. Neat PI itself was very stable as no changes were seen with any of the analysis methods. However, the PI PCB adhesive degraded markedly at high temperature, thus decreasing the overall thermal stability of PI PCB. With the more stable adhesive layer used in adhesiveless PI PCB as well as with the Rogers a much better performance was seen. Aging rapidly caused oxidation in the PCBs, but when the aging time or temperature was increased, no further degradation was seen. Thus after the oxidation at the beginning of aging these materials were observed to be quite stable at high temperatures. FR-4, on the other hand, underwent major chemical changes, especially at 240°C.

5 Reliability of Polymer-based Sensor Packages at High Temperatures

This chapter considers high temperature environmental tests and the reliability of the polymer-based sensor packages tested in them. First the reliability of sensor packages in thermal cycling tests (Publications I and II) is discussed. After this the thermal limits studied with step stress tests (Publication III) are discussed. The thermal storage tests reported in Publications IV-VII are discussed last.

5.1 Reliability in Thermal Cycling Tests

Thermal performance of polymer-based packages was first studied with two thermal cycling tests.

-40°C/+125°C Thermal Cycling Test

Reliability of the polymer-based sensor packages was first studied with -40°C and +125°C thermal cycling tests with humidity sensors attached with ACF1 on FR-4 (Publication I). Very good reliability was achieved with the thin FR-4 regardless of the bonding pressure used, as no failures were seen during 10,000 cycles. With the thicker FR-4 the selection of optimal bonding pressure was more critical. With very low pressure of 25MPa, only one late failure was seen, and the reliability was very good. This pressure was considerably less than the value recommended by the manufacturer. On the other hand, it has been reported earlier that lower bonding pressure may lead to lower failure percent [Sep04].

With higher pressures (50, 100MPa) more failures were seen with the thick FR-4. The characteristic lifetime for these test samples was between 4,500 and 8,000 cycles depending on the failure criteria used. The results are shown in Figure 18 (lot 5-6). With the thick FR-4 two other ACAs were also studied using the highest bonding pressure. The reliability of these ACAs was markedly lower, the characteristic lifetime being between 900 and 2,000 cycles for ACF3 (Figure 18 lot 7) and only 300 to 500 cycles for ACP1 (Figure 18 lot 8). The selection of ACA therefore clearly played an important role in the reliability.

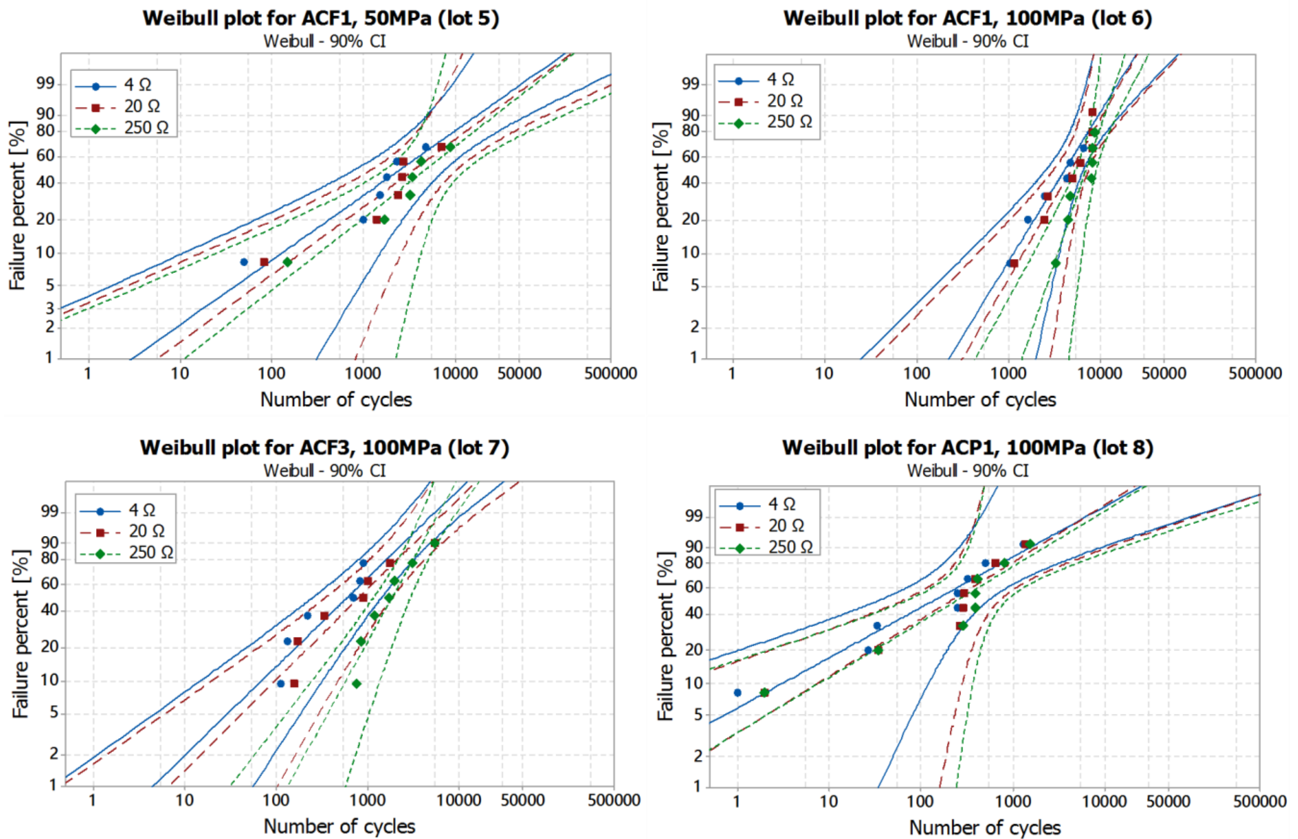


Figure 18. Weibull plots in -40°C and +125°C thermal cycling with 90% confidence intervals.

The upper temperature extreme of 125°C exceeded the T_g (datasheet value) of ACF1 and ACF3, but not the T_g of ACP1. ACP1, however, clearly had the poorest reliability of these three ACAs. Whereas other attachments failed first at low temperature extreme, ACP1 attachments failed at temperature changes. Delamination was observed to be the failure mechanism in all samples, but with ACP1 it was more severe. For ACP1 the location of the delamination also varied, but for other samples the delamination occurred at the interface of the copper pad and the ACA. Example of delamination seen with ACF1 (100MPa) is shown in Figure 19a whereas the delamination seen with ACP1 (100MPa) can be seen in Figure 19b. Non-pliable nickel particles may have caused the difference in the behaviour of the ACAs, as in the ACFs gold-coated polymer particles were used. The high T_g of ACP1 may also have been achieved through modifications causing the material to be fragile.

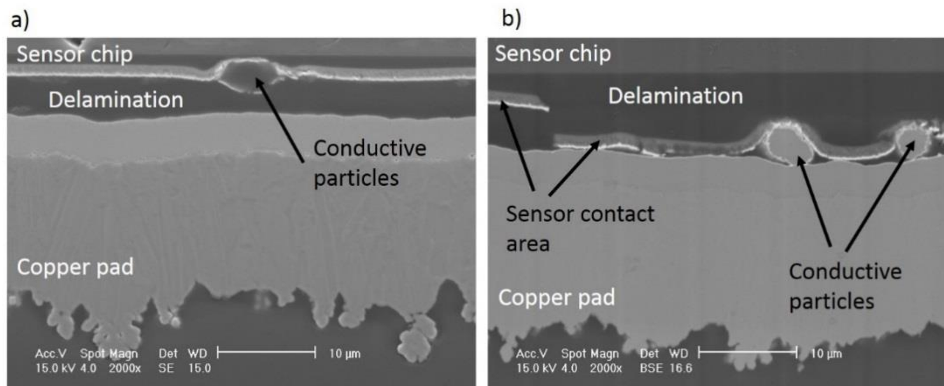
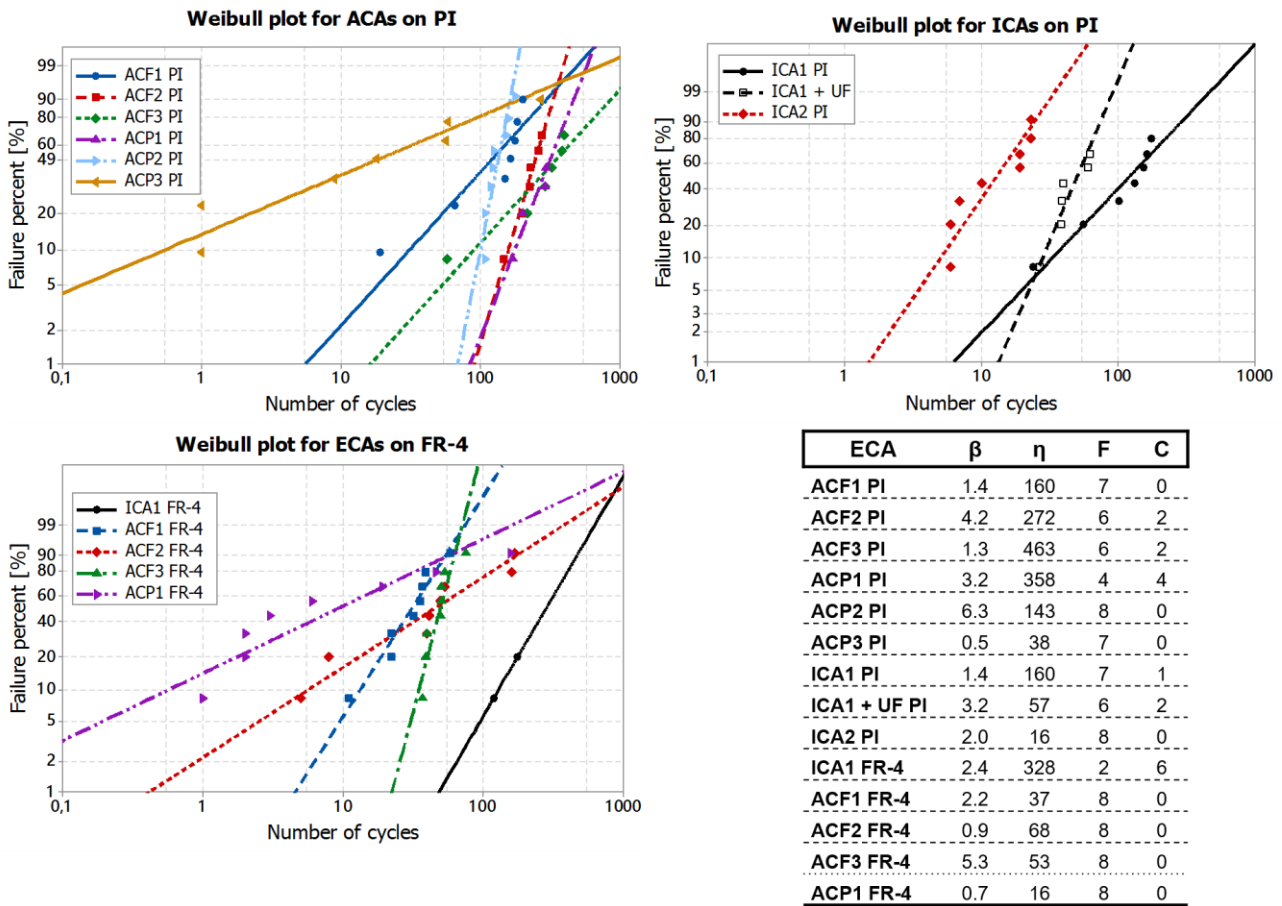


Figure 19. Micrograph of a) ACF1 attachment with thick FR-4 and 100MPa pressure b) ACP1 attachment with thick FR-4 and 100 MPa pressure.

-55°C/+180°C Thermal Cycling Test

High temperature reliability was further studied in Publication II with a slow temperature cycling test between extreme temperatures of -55°C and +180°C. The test structure consisted of a temperature sensor attached with several ECAs onto thick FR-4 or PI PCB. The Weibull distribution of the failures as well as the shape and scale factors and number of failed samples (F) and censored, non-failed samples (C) are shown in Figure 20. The harsher cycling test dramatically decreased the lifetime of the test samples. For all samples the characteristic lifetime was only a few hundred cycles at maximum.

The reliability was much better with flexible PI PCB than with rigid FR-4. The only exception was ICA1, which performed without an underfill much better with a rigid PCB. This was most likely because the rigid PCB provided more mechanical support for the mechanically fragile ICA attachments than flexible PI. Surprisingly, the underfill impaired the reliability of the attachments, even though according to the datasheet its parameters were very good for this kind of use. Most likely the underfill caused mechanical stresses in the structure. The selection of ECA was again proven to be important, as there was a marked difference between the adhesives. In this test the T_g of all ECAs was exceeded. The best reliability was achieved when ACP1 was used with PI PCB. ACP1 seems to be suitable only for flexible substrates, as its reliability with FR-4 in this test as well as in -40°C and +125°C (Publication I) was extremely poor.



ECA	β	η	F	C
ACF1 PI	1.4	160	7	0
ACF2 PI	4.2	272	6	2
ACF3 PI	1.3	463	6	2
ACP1 PI	3.2	358	4	4
ACP2 PI	6.3	143	8	0
ACP3 PI	0.5	38	7	0
ICA1 PI	1.4	160	7	1
ICA1 + UF PI	3.2	57	6	2
ICA2 PI	2.0	16	8	0
ICA1 FR-4	2.4	328	2	6
ACF1 FR-4	2.2	37	8	0
ACF2 FR-4	0.9	68	8	0
ACF3 FR-4	5.3	53	8	0
ACP1 FR-4	0.7	16	8	0

Figure 20. Weibull distribution for -55°C/+180°C thermal cycling. Shape and scale factors and number of failed samples (F) and censored, non-failed samples (C).

The differences between ACFs and ACPs as well as the effect of filler particle were studied using CDFs in Publication II. No clear difference between the ACA types was seen, and the ACA matrix seemed to be a more decisive factor in the performance than the particle type. However, when ACF1 and ACF2 with the same matrix, but different particles were compared, ACF2 with nickel particles was more reliable than ACF1 with polymer particles. Polymer particles are typically more suitable for use in thermal cycling environment compensating the strains and warpage caused by CTE differences [Sep04]. However, it is possible that high temperature impairs the reliability of the polymer particles due to degradation of the polymer more than that of the nickel particles.

As with the -40°C/+125°C cycling tests, delamination as a failure mechanism was seen in the cross-sections of the failed ACA samples tested in the -55°C/+180°C cycling test. Cracking of the ICA joints was seen in the failed ICAs. The reason for cracking is thermomechanical stress between the various materials present in the test structures caused by CTE differences during repeated temperature cycles. In the harsher cycling test the characteristic life of test samples decreased markedly compared to the -40°C/+125°C test. However, the harsher test was very slow with one cycle lasting for nine hours, much of which was spent at relatively high temperature. During one

cycle of the -55°C/+180°C test, the -40°C/+125°C cycling test completed 18 cycles and during 200 cycles of the -55°C/+180°C test, the -40°C/+125°C cycling test had already completed 3,600 cycles. Therefore the total testing time in hours was quite long despite the small number of cycles. On the other hand the long dwell time at high temperatures, especially in the -55°C/+180°C test, exposed the materials to oxidation and degradation. Nevertheless, the results from both cycling tests showed that sensor attachments could withstand a high number of cycles in harsh environment if the ECA and PCB materials and bonding parameters were correctly chosen.

5.2 Reliability in Step Stress Tests

Temperature sensor attachments with several ECAs on PI PCB were used to study the thermal limits of ECA materials with step stress testing (SST) in Publication III. Testing was conducted between 180°C and 260°C. No higher temperature than 260°C was used due to the temperature use limit of the measurement wires of the real-time measurement system. Due to the limited number of test samples in each test series, CDFs were used.

In SST1 with a dwell time of 15 minutes no failures occurred. The resistance of the temperature sensor increased normally with increasing temperature and after testing, when the temperature was decreased to ambient, the sensor chips reverted to their initial resistance values. The failure analysis revealed no changes in the materials of the test structures (Figure 21). Therefore short exposure to high temperatures was found to harm the performance of neither the sensor package nor the materials.

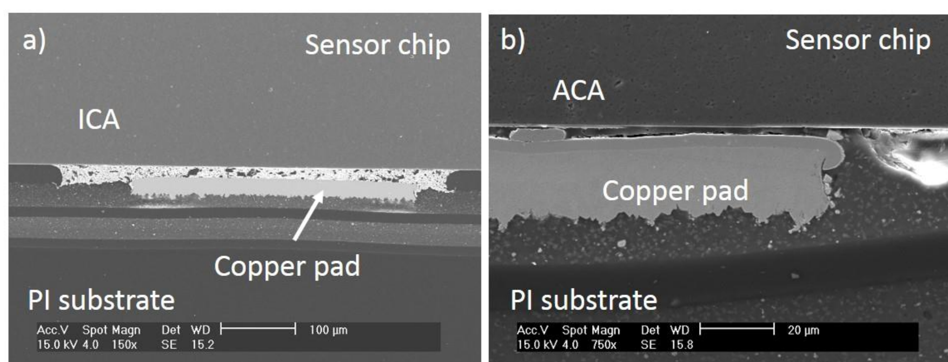


Figure 21. Micrograph of an a) un-tested ICA b) ACF2 after SST1.

Similar results were also obtained when the exposure time was increased to 24h in SST2. No failures were seen during testing. Instead of decreasing the temperature to ambient after the last step at 260°C, the testing was continued further as a thermal storage test at 260°C until failures were seen to occur. The CDFs for this test are shown in Figure 22a. The first failure occurred after 27h (ACP1) and the last sample failed after 63h (ICA) of testing at 260°C (both times including the 24h step).

The differences between the ECAs were small. ACP1 had the poorest reliability, and ACFs and ICA the best. All ACAs having nickel particles started to fail first, but the difference between ACF1 and ACF2, which had different particles but the same matrix, were extremely small. However, the number of samples was quite low. ICA showed very promising behaviour. However, without an underfill it would probably be mechanically too unstable to be used in an actual product.

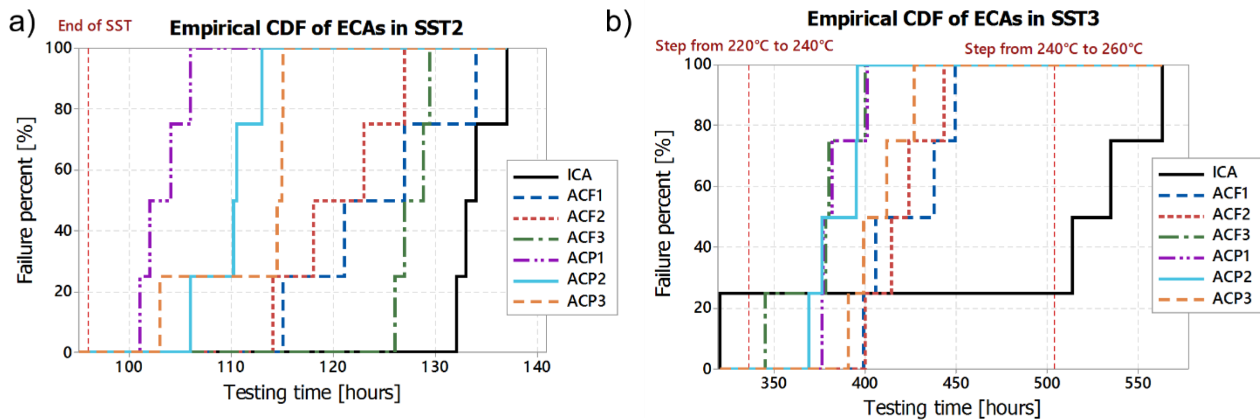


Figure 22. CDF for a) SST2 b) SST3.

SST3 was the only step stress test in which the failures started to occur during the actual testing. The CDFs for this test are shown in Figure 22b. Most of the failures occurred during the step at 240°C; ICA was the only adhesive to have most of its failures at 260°C. The samples were observed to withstand high temperatures for long periods of time, as the first failure occurred after more than 300h of exposure. The first ICA failure occurred long before the other failures, therefore it was assumed to have been caused by poor quality of the sample. Again, the differences between ACAs were small, but ACPs started to fail first. No marked difference between ACF1 and ACF2 with different particle type was seen.

Failure analysis for the samples tested in SST2 and SST3 revealed delamination between the chip and the copper pads in all samples studied. Severe corrosion of the copper pads was seen, and the pads were observed to have oxidized due to long exposure to high temperatures. A greater amount of pure copper was seen to exist after SST2 (tested for 190h) than SST3 (tested for 580h) as shown in Figure 23. Degradation of the PI PCB adhesive layer holding the copper and PI together was also seen. The oxidized copper and degraded PCB adhesive seemed to have reacted with each other, forming a migrating oxide material (Figure 23b). EDS analysis showed the migrating material to consist mainly of copper and aluminium oxides, and therefore be electrically non-conductive. Residuals of other materials were also found, such as antimony most likely used as a fire-retardant in the PCB [Bi11]. The corrosion seen in these samples had not been earlier seen with any of the thermal cycling samples.

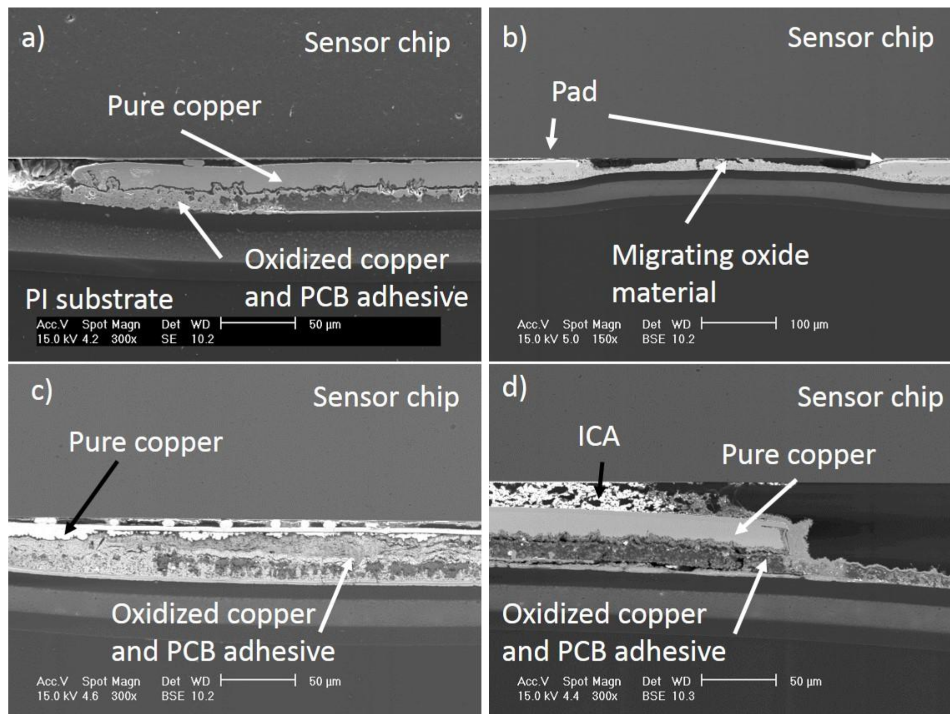


Figure 23. Micrograph of an a) ACF2 interconnection after SST2 with oxidized materials b) ACP3 interconnection after SST2 with migrating oxide material between the pads c) ACP1 interconnection after SST3 with severe oxidation d) ICA interconnection after SST3 with oxidation.

ICA withstood the high temperature better than ACAs. Its bondline was much thicker than that of the ACA attachments, which may have caused the differences seen in the results. It was, however, shown that quite long exposures were required for the failures to occur. From the failure analysis it was difficult to say whether the delamination or corrosion and degradation of the materials occurred first. It seems, however, that the PI PCB was the most critical part of the interconnection and not the ECA material. The thick adhesive layer in PI PCB was seen to degrade fast, causing the PCB to have very poor thermal stability.

5.3 Reliability in Thermal Storage Tests

Thermal performance of polymer-based packages was further studied with several thermal storage tests. PI PCBs with temperature sensors were studied in Publication IV at 200°C and in Publication V at 240°C. Temperature sensors with FR-4 and Rogers PCBs were studied at 200°C and 240°C in Publication VI. In Publication VII better quality PI PCB (Adhesiveless PI PCB) was studied at 180°C, 200°C and 240°C. A test chip larger in size and with a greater number of interconnections compared to sensor chips was used in this study.

Thermal Storage at 200°C for PI PCB

Figure 24 shows the CDFs for sensor attachments with all ECAs on PI at 200°C (Publication IV). Again, CDF was used because of limited number of samples. It can be seen that there was no difference between the two failure criteria used; the interconnections were observed to form open connections quite soon after the resistance started to increase.

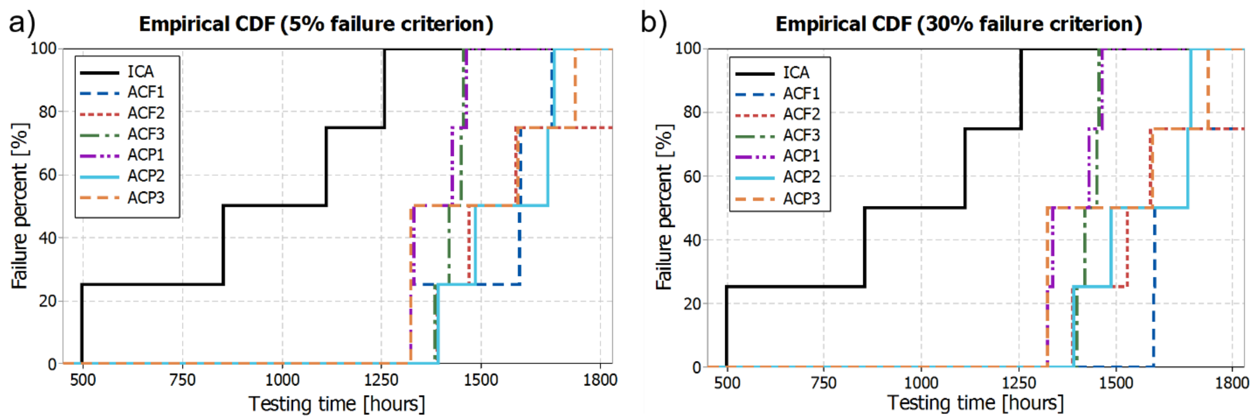
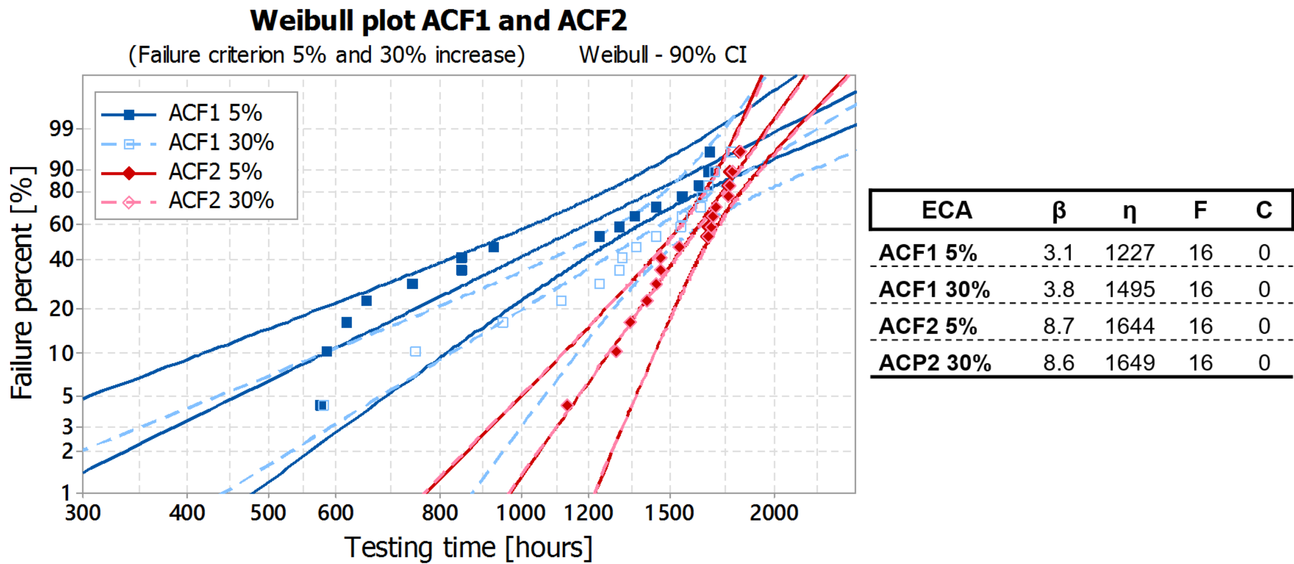


Figure 24. CDF for all ECAs on PI at 200°C with a) 5% failure criterion b) 30% failure criterion.

ICA, which was again studied without an underfill, started to fail quite early, and all ICA samples also failed before any ACA failures were seen. ACAs gave a promising performance as the failures started to occur only after more than 1,200h of testing. No marked differences between ACPs and ACFs could be seen. ACF1 and ACF2 both had one sample which did not fail or failed only on other criteria. After testing at ambient temperature the resistances did not fully recover, therefore the long exposure did indeed have a permanent effect on the materials.

A few ACF1, ACP2 and ICA samples were also observed to fail when their resistance dramatically decreased, indicating the possibility for short-circuiting. The resistance decrease was an intermittent failure before the resistances started to increase and exceed the failure limits. According to the failure analysis oxide materials migrated within the structure, possibly causing the short-circuiting.

ACF1 and ACF2 were further studied using a greater number of test samples. Figure 25 shows the Weibull distribution for these ACFs. It can be seen that ACF1 samples started to fail much earlier than the ACF2 samples. ACF1 also differed between the two failure criteria used. ACF1 had several early failures, and many intermittent failures, which may have caused the difference seen. Two different failure mechanisms are also possible. As ACF1 had polymer particles, they may not have been as reliable at high temperatures as nickel particles. ACF2 had no difference between the failure criteria, and its characteristic lifetime was more than 1,600h. For ACF1 the characteristic lifetime was a few hundred hours less (Figure 25). Again, dramatic resistance decrease before exceeding the failure limits was seen for one sample of each material.



ECA	β	η	F	C
ACF1 5%	3.1	1227	16	0
ACF1 30%	3.8	1495	16	0
ACF2 5%	8.7	1644	16	0
ACP2 30%	8.6	1649	16	0

Figure 25. Weibull distribution for ACF1 and ACF2 on PI at 200°C with 90% confidence intervals. Shape and scale factors and number of failed samples (F) and censored, non-failed samples (C).

In the failure analysis similar issues were seen as in SSTs. The long exposure (~1,800h for all ECAs and ~3,000h for additional test for ACF1 and ACF2) at 200°C had caused the samples to be very fragile. Therefore handling and cross-section moulding may have caused at least some of the delamination seen in the cross-sectioned ACA interconnections (Figure 26b). The adhesion strength had most likely decreased markedly in the ACA interconnections. In shear testing a slow, but consistent decrease in shear force values was seen at 200°C. Most likely this caused the delamination seen in the samples. Cracking in ICA samples was not seen, but voids had formed. As in the step stress tests, oxidation and formation of the migrating oxide material was seen (Figure 26c-d). Almost all the pure copper had corroded from the samples. Cracking of the substrate was also seen, often located at different interfaces, such as between pure copper and oxide material. Clear changes in ICA bondline were also seen. As shown in Figure 26a, in the sides of the thick bondline of ICA the composition had clearly changed due to exposure to high temperature.

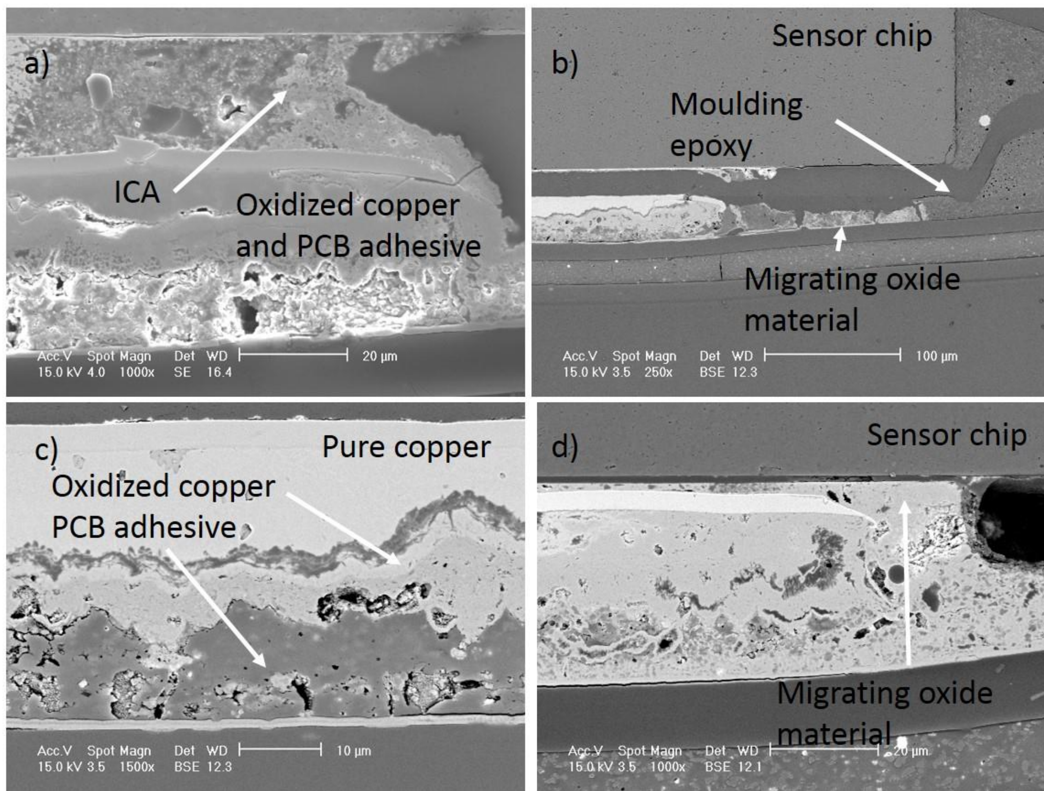


Figure 26. Micrograph of ECA interconnection on PI after thermal storage at 200C. a) ICA interconnection with composition changes b) ACF2 interconnection with oxidation and delamination c) ACF2 with pad changes d) ACF3 interconnection with migrating oxide material.

In all cross-sectioned samples the oxidized copper was seen to migrate to the interface between the PI and the PCB adhesive layer. Similar behaviour was also seen in step stress test samples. The migration stopped when the PI film was reached. An example of this compared to a non-tested sample is shown in Figure 27.

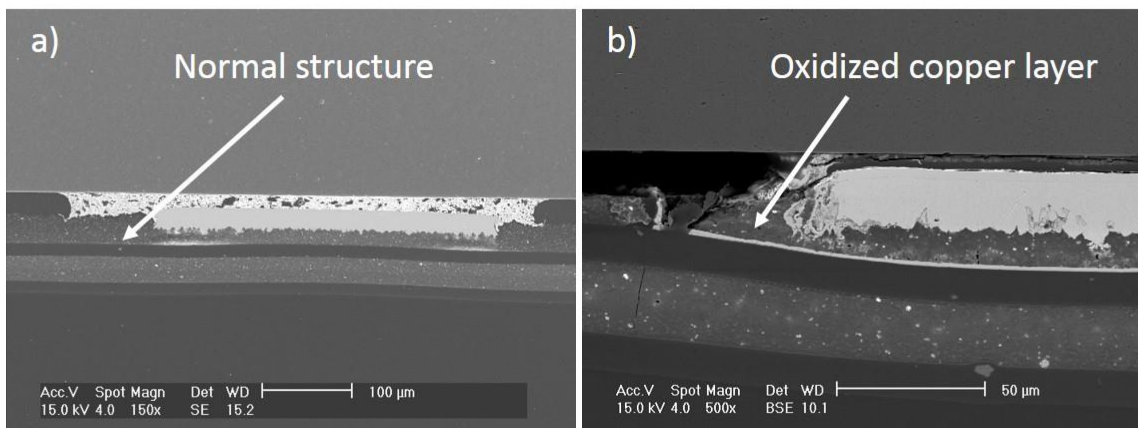


Figure 27. Micrograph of PI PCB with a) normal structure b) Oxidized copper migrating to the interface of PI film.

Thermal Storage at 240°C for PI PCB

Figure 28 shows the CDF for sensor attachments with all ECAs on PI at 240°C (Publication V). As earlier, CDF is used because of the limited number of samples. Most ACAs survived the exposure to 240°C for a relatively long time, as the failures occurred around 100h of testing. The ACPs performed surprisingly well. However, the lot size was quite small, which may have affected the results. For ACAs the failure criteria did not cause much difference, but for ICA the difference was marked. With a 5% criterion all samples failed after only 20h, whereas with a 25% criterion the failure times did not greatly differ from those of ACAs. Thus the resistances of ICAs quickly started to increase, but the total failures occurred much later. Small resistance increases may, however, cause error in the sensing operation of the sensor component. On the other hand, a 5% increase is relatively small.

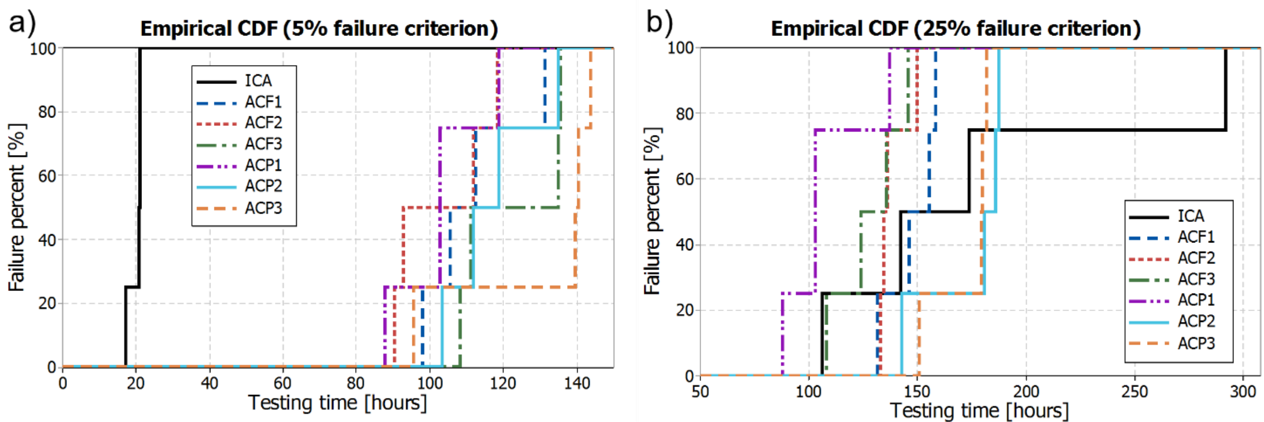
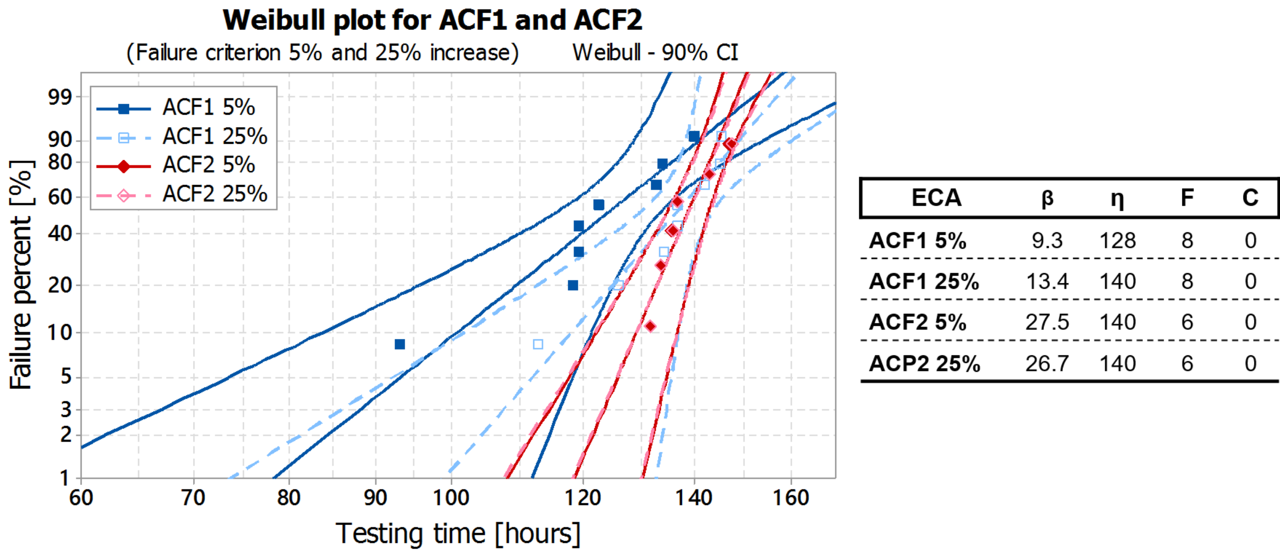


Figure 28. CDF for all ECAs on PI at 240°C with a) 5% failure criterion b) 25% failure criterion.

ACF1 and ACF2 were studied with a somewhat larger test lot size. Figure 29 shows the Weibull distribution. One ACF2 was omitted from the analysis due to an early failure. As with thermal storage at 200°C, the ACF1 samples started to fail earlier than the ACF2 samples, and ACF1 showed a difference between the two failure criteria used. ACF2 with nickel particles was again more reliable. Compared to the testing at 200°C, the characteristic lifetime was much shorter, 140h.



ECA	β	η	F	C
ACF1 5%	9.3	128	8	0
ACF1 25%	13.4	140	8	0
ACF2 5%	27.5	140	6	0
ACP2 25%	26.7	140	6	0

Figure 29. Weibull distribution for ACF1 and ACF2 on PI at 240°C with 90% confidence intervals. Shape and scale factors and number of failed samples (F) and censored, non-failed samples (C).

In the failure analysis of the samples aged at 240°C similar issues emerged as in SST and thermal storage at 200°C. The long exposure at 240°C had caused the samples to be very fragile, and delamination and cracking were seen in every sample. Delamination was also seen with ICA samples and at several interfaces, in contrast to the samples tested at 200°C (Figure 30).

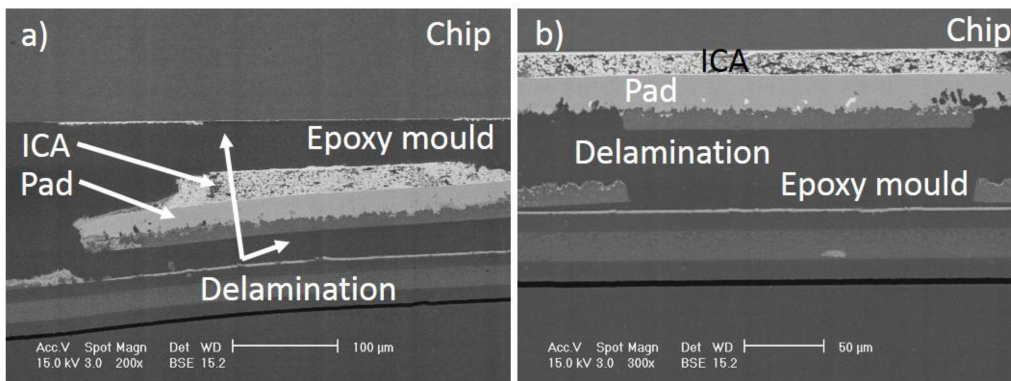


Figure 30. Micrograph of an ICA interconnection after 308h at 240°C a) delamination between the ICA layer and sensor as well as between PI and PCB adhesive layer b) delamination in PI PCB.

Oxidation and migration of the oxide material was again seen. The level of oxidation varied between samples and even pads within the same sample, but after 1,000h of testing most of the copper had oxidized. However, electrically the samples had failed much earlier. In addition to the oxidation, the copper pad structure was seen to already become porous after 300h (Figure 31a) and large voids also formed (Figure 31b). The oxide material was again seen to migrate within the structure, however, in some samples it was seen to migrate though the PI layer and to the PCB adhesive layer, as shown

in Figure 31c. In some of the test samples an oxidation layer was also seen to form on top of nickel and ECA layers (Figure 31d).

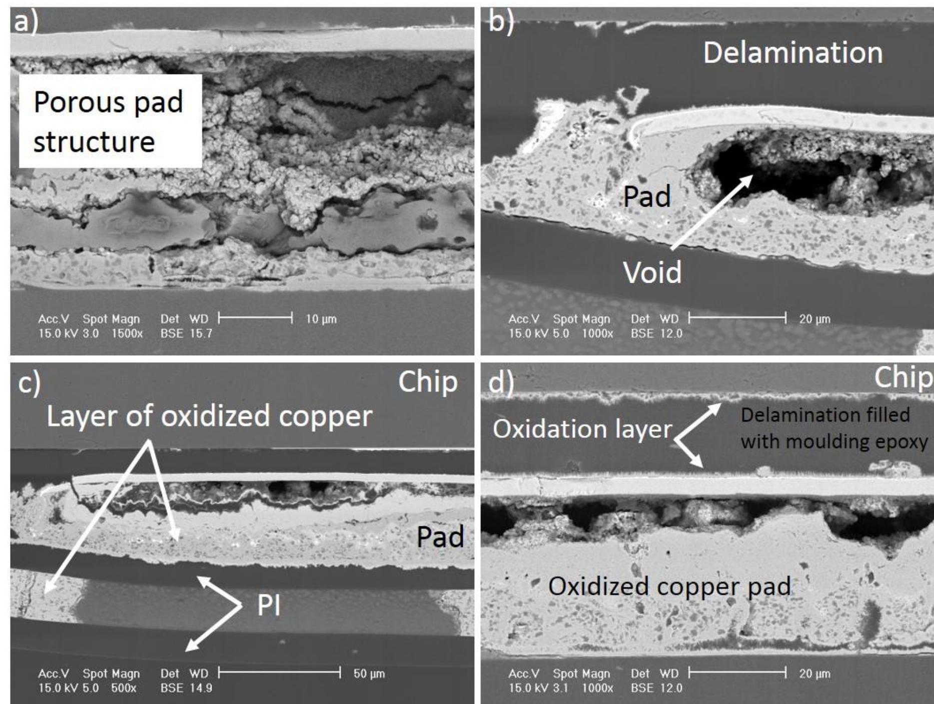


Figure 31. Micrograph of an ACA interconnection after thermal storage at 240°C a) porous pad structure in ACF3 sample after 308h b) Voids in pad in ACF2 sample after 1,000h c) oxide material migrating to the PCB structure in ACF1 sample after 1,000h d) oxidation layer on pad and on ECA in ACF2 sample after 1,000h

The penetration of the oxide material shown in Figure 31c as well as the formation of the copper oxide under the pad on top of PI shown earlier in Figure 27 is an interesting phenomenon. Most likely the void and crack formation within the structure accelerated the penetration of the oxide material, as it was worse at 240°C than in the step stress tests or at 200°C. Copper and copper oxide have been reported to have a tendency to easily diffuse into PI, and the diffusivity is enhanced with increasing temperature [Gre93, Wan99]. This could explain the phenomenon seen.

The progress of oxidation was further studied with samples removed from the test after certain time periods. This was done at both temperatures 200°C and 240°C. Figure 32 presents the propagation at 200°C after 480h, 960h, 1,440h and 1,920h. The propagation at 240°C after 22h, 60h and 124h is shown in Figure 33. At 240°C the propagation was also studied after 144h and 192h.

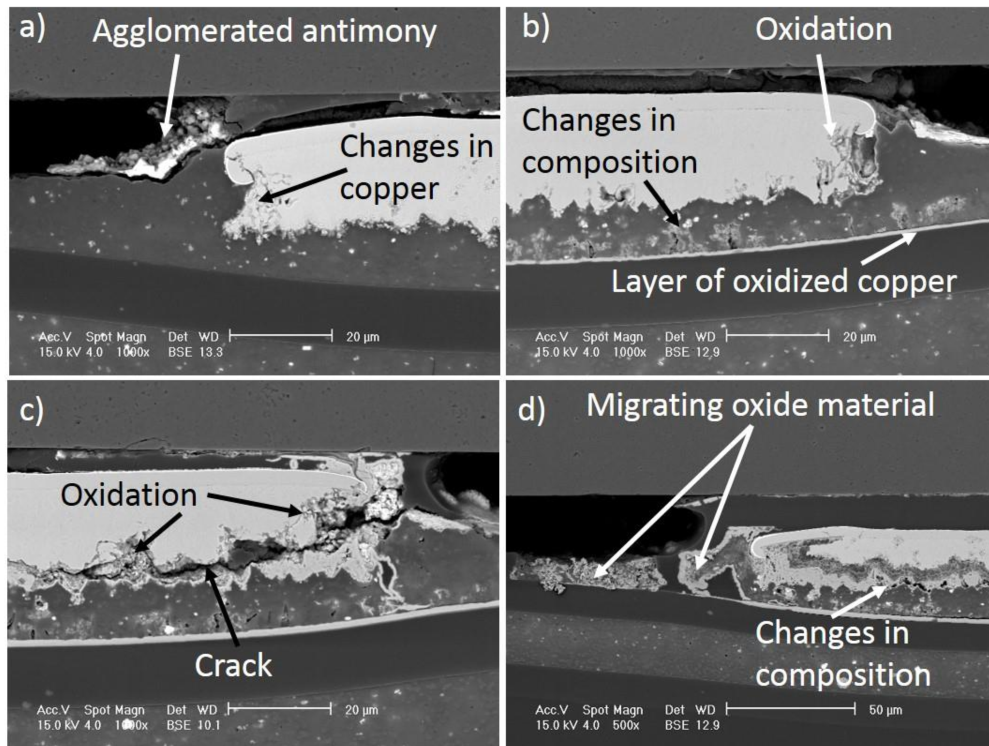


Figure 32. Micrograph of the propagation of oxidation at 200°C in ACF1 after a) 480h, b) 960h, c) 1,440h, d) 1,920h.

At 200°C after 480h and 960h (Figure 32a-b) changes were seen at the sides of the copper pads, most likely due to oxidation. Antimony, presumably added to the PCB as a fire retardant, also started to agglomerate. Cracks in the ACF attachment were seen to form, indicating embrittlement. After 960h the effects had progressed: degradation of the PI PCB adhesive was seen as well as more oxidation in copper and reaction between these materials. A layer of oxidized copper was also seen to have formed on the interface of the PI (Figure 32b). Most of the failures occurred between the two latter removal times; 1,440h and 1,920h (Figure 32c-d). After 1,440h the copper oxidation had progressed, and cracks at the interface of pure copper and oxidized material could be seen in Figure 32c. After 1,920h the structure looked very similar for those already seen in the failure analysis earlier. Consequently, the severe oxidation and material migration could be seen at the same time as the majority of the failures. This would indicate that the degradation of the PI PCB may have caused the failures. However, delamination of the interconnection could soon be seen, and changes in the chemical composition were seen very early in the FTIR analysis. Therefore the structure became fragile quite early, which may also have caused failures. Most likely both of these effects caused the failures together. More stable PCB material therefore would be beneficial to further study the reliability of the package at high temperature.

At 240°C the failures occurred around 100h of testing. In the samples removed from the test no dramatic signs of oxidation were seen even after 124h (Figure 33). The only effects were some initial pad changes and agglomeration of antimony. The only sample having clear signs of oxidation was

the one removed from the chamber after 192h. Therefore the oxidation was seen later than the failures occurred. Consequently, the degradation of the PI PCB did not seem to cause the failures at 240°C. On the other hand, the cracks in the ACF layer were already seen in the samples removed after 22h, and the severity increased with increasing aging time. It seemed that cracking was more severe with ACF1 with the polymer particles than with ACF2, as shown in Figure 33. Nickel particles seemed to be better able to hold the structure together by forming a better interconnection with the contact surface. This possibly explains the difference in failure times between ACF1 and ACF2. The ACF matrix seemed to lose its adhesion and cohesion quite rapidly at 240°C, indicating degradation of the adhesive and leading to fragile structure, cracking and delamination. Therefore the failure mechanisms in the thermal storage tests at 200°C and 240°C seemed to differ from each other, and the results could not be used to determine acceleration factors.

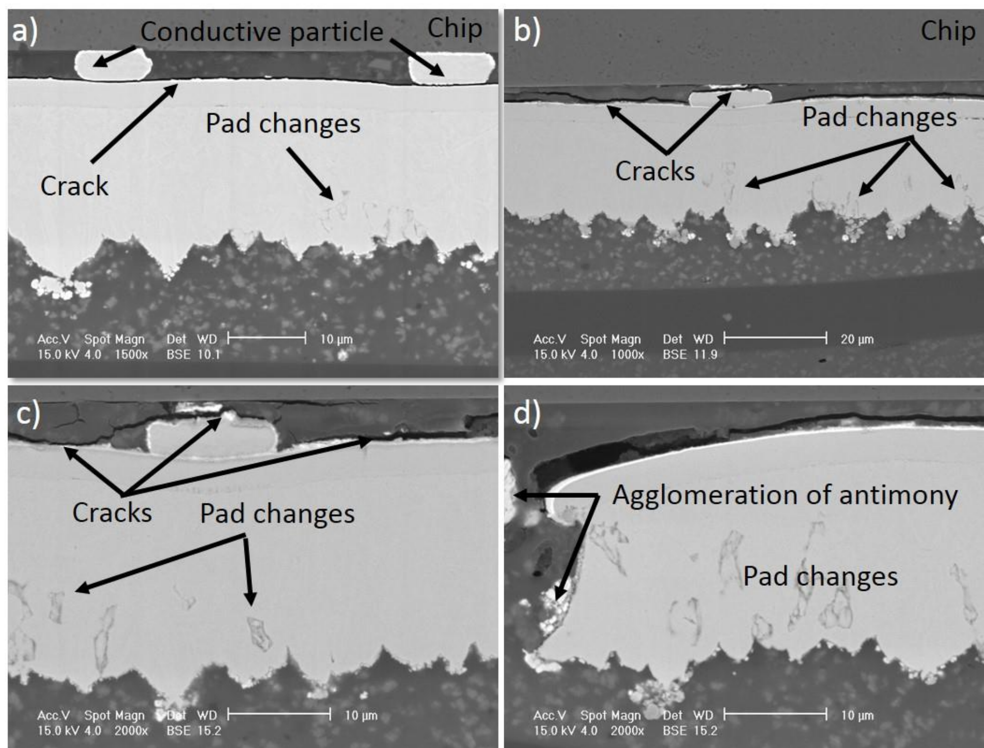


Figure 33. Micrograph of the propagation of oxidation at 240°C in ACF2 sample after a) 22 hours. b) 60 hours. c) 124 hours. d) Pad changes and agglomeration of antimony after 124 hours.

PI PCB used in step stress tests and in the thermal storage tests was shown not to be suitable for high temperatures. As discussed in Chapter 4, no chemical changes in the cover layer were seen according to FTIR, however, the PI PCB adhesive layer was found to degrade rapidly. The copper oxidation and the chemical reactions between the materials affected the reliability, especially at 200°C, and possibly also to some extent at 240°C. However, the PI PCB had the structure of a typical PI PCB widely used at high temperatures, and actually the PCB was purchased as an adhesiveless PCB material, which is clearly was not.

Thermal Storage at 200°C and at 240°C for FR-4 and Rogers PCBs

Due to the stability issues with PI PCB, other PCB materials were also tested in Publication VI. Temperature sensors were attached with ACF1 and ACF2 onto FR-4 and Rogers PCBs. The failure distribution is shown with CDFs. For Rogers tested at 240°C the distribution is also shown with the Weibull plot.

Figure 34 shows the CDF for sensor attachments on FR-4 at 200°C (Figure 34a) and at 240°C (Figure 34b-c). The tests lasted for 3,000h at 200°C and 1000h at 240°C, but as most of the failures were seen very early, a close-ups of the start of the tests are shown. At 200°C most of the samples failed between 25h and 40h of testing. No significant difference was seen between the two failure criteria or between ACFs. ACF2 had one sample with a 5% criterion and two samples with a 30% criterion which did not fail within 3,000h. However, after the test, when temperature was decreased to ambient, these samples also exceeded the failure limits.

At 240°C the ACF1 samples failed very rapidly. Most samples failed after only a few hours of testing, and all before 20h of testing. ACF2 had better reliability, but also more dispersion in the failure times. All the ACF2 samples failed before 100h of testing. Generally the failure times of ACF2 at 240°C with a 5% criterion did not differ greatly from the failures seen at 200°C. Figure 34c shows the failure occurring during the whole thermal storage at 240°C for ACF2. With a 15% failure criterion the failures occurred gradually, and two samples did not exceed the failure limit at all during 1,000h of testing. After testing, when the temperature was decreased to ambient, these samples were also seen to fail. The change in the temperature caused thermomechanical stresses, most likely accounting for the failures seen.

Resistance fluctuation was typical for both ACFs at both thermal storage temperatures with FR-4. For most samples the resistance increased above the failure limits, but then fluctuated around them for long time periods and sometimes until the end of the test. This differed from the behaviour with PI PCB, with which open circuits typically formed quite rapidly after the resistance started to increase.

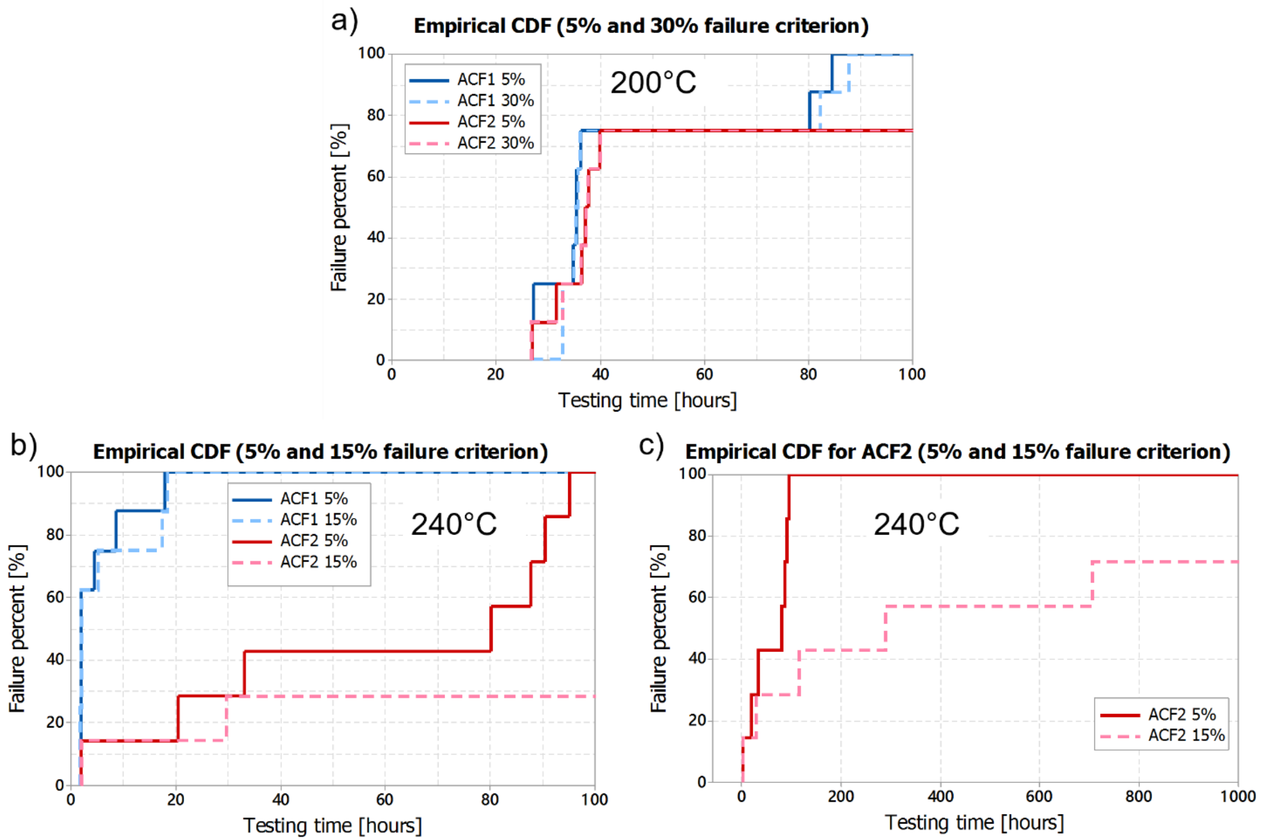


Figure 34. CDF for a) FR-4 at 200°C first 100h b) FR-4 at 240°C first 100h c) CDF for ACF2 on FR-4 at 240°C for 1,000h.

In addition to the poor and unstable electrical behaviour seen with the FR-4 samples, the FR-4 itself was not suitable for high-temperature use. The inner layer started to degrade rapidly at both testing temperatures, as shown in Figure 35a. As the functionality was on the top layer, this degradation did not necessarily cause electrical failures. However, the top layer was also seen to degrade during aging, and the adhesion between copper traces and polymer was seen to deteriorate (Figure 35b). This decreased the reliability of the resistance measurement setup.

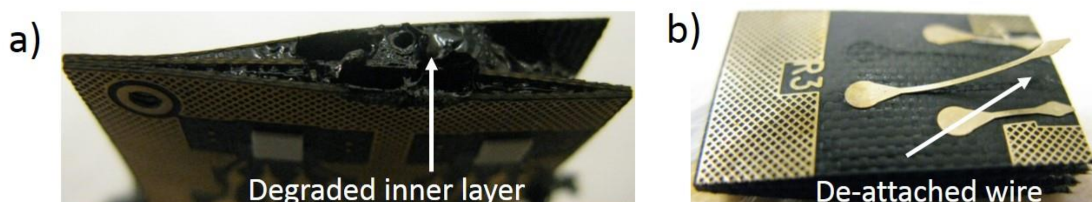


Figure 35. FR-4 degradation on a) inner layer b) top layer.

In failure analysis rapid degradation of the FR-4 PCBs including corrosion of copper, voiding and embrittlement were seen, as shown in Figure 36. Therefore, the FR-4 was not suitable for even short-term exposure to a high-temperature environment above 200°C, although its datasheet stated the T_d to be 370°C. Rapid degradation for FR-4 was also reported in Chapter 4. In the thermal cycling test such dramatic degradation was not seen even at exposure to 180°C, therefore the thermal use limit seems to lie between these two temperatures. Due to the obvious unsuitability of the material for use at high temperatures even for very short periods of time, no detailed failure analysis or analysis of the propagation of degradation and oxidation was conducted.

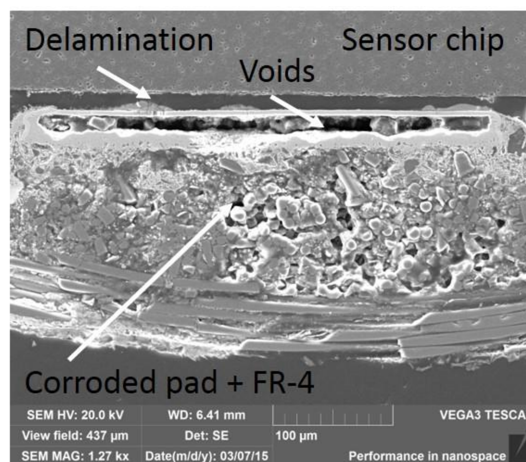


Figure 36. Micrograph of FR-4 degradation after 960h at 200°C.

The reliability achieved with the Rogers PCB was very good. Figure 37a shows the CDFs at 200°C for the 5% failure criterion. Around 60% of ACF1 samples exceeded the failure limit, but only after more than 2,000h of testing. For ACF2 only 25% of the samples failed. Additionally, none of the samples exceeded the 30% failure limit. No early failures were seen with either of the ACFs. When the temperature was decreased to ambient after testing, the resistances of the samples reverted very close to their initial resistance values.

Figure 37b shows the CDFs for Rogers at 240°C. Additionally the Weibull distribution for comparison is shown in Figure 38. All samples failed approximately between 400h and 500h of testing. The characteristic lifetime was approximately 500h with both adhesives and failure criteria. Slightly better reliability was again seen with ACF2. The failures seen were not intermittent; the resistances were seen to fluctuate about 30h around the failure limit after exceeding the limit the first time. After the fluctuation, open circuits were formed, and after testing at ambient the resistance values remained high.

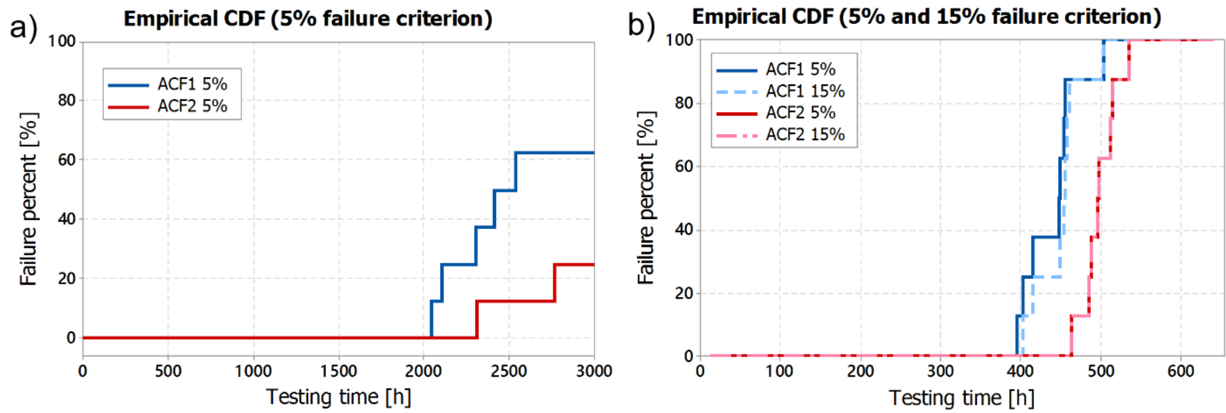
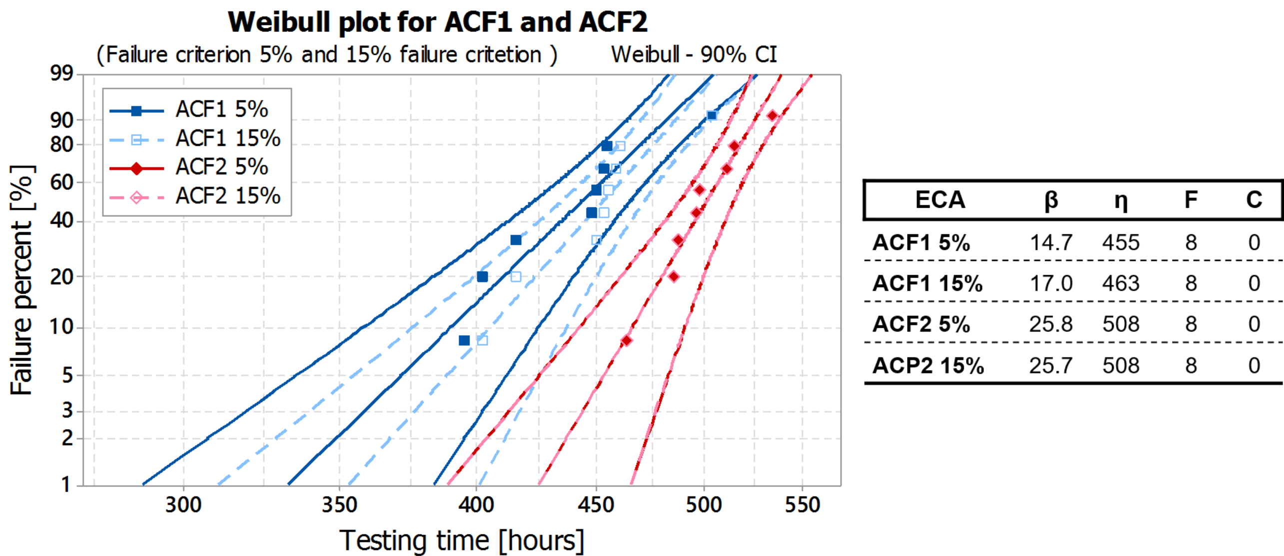


Figure 37. CDF for a) Rogers at 200°C b) Rogers at 240°C.



ECA	β	η	F	C
ACF1 5%	14.7	455	8	0
ACF1 15%	17.0	463	8	0
ACF2 5%	25.8	508	8	0
ACP2 15%	25.7	508	8	0

Figure 38. Weibull distribution for ACF1 and ACF2 on Rogers at 240°C with 90% confidence intervals. Shape and scale factors and number of failed samples (F) and censored, non-failed samples (C).

Similar to PI PCB, the failure analysis revealed delamination between the sensor chip and copper pad in all samples, most likely due to impairment of the mechanical integrity of the ACF. Oxidation of the copper pads was also seen. Similar to the PI, the propagation of degradation and corrosion was studied with samples removed from the test after certain time periods. The propagation at 200°C is shown in Figure 39 and the propagation at 240°C can be seen in Figure 40.

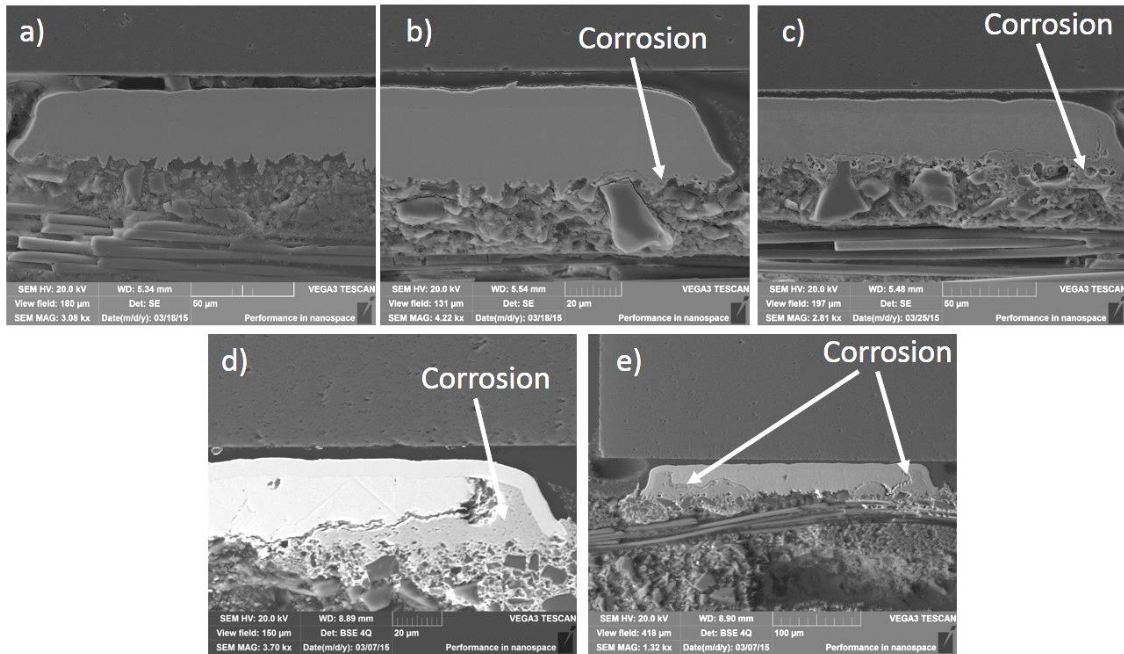


Figure 39. Propagation of corrosion and degradation with Rogers at 200°C after a) 480h b) 960h c) 1,440h d) 1,920h e) 2,400h.

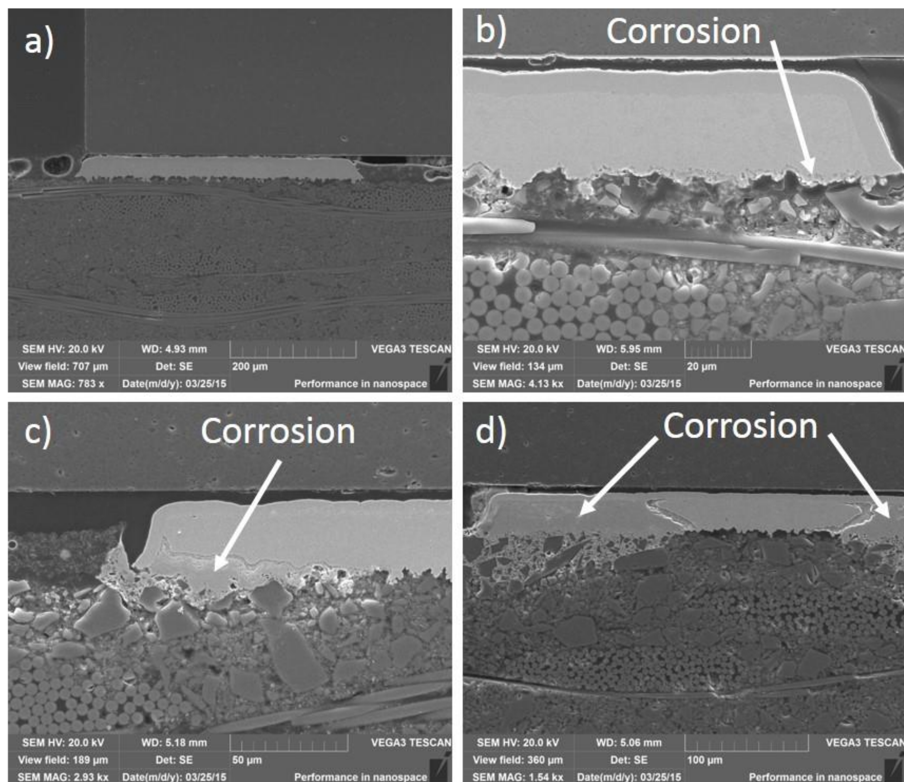


Figure 40. Propagation of corrosion and degradation with Rogers at 240°C after a) 22h b) 60h c) 124h d) 500h.

Delamination was again already seen in the samples with the shortest storage times at both temperatures. Electrically, however, the failures occurred much later at both temperatures. This strongly suggests problems with mechanical integrity at the interconnections. The delamination, however, was less than that with PI PCB, showing the importance of the PCB material for the reliability of the whole package. The first signs of copper corrosion with pad changes appeared at 200°C after 960h and at 240°C after 60h. This seemed to initiate from the bottom of the pad instead of the edges as with PI PCB. Compared to PI PCB, the corrosion seemed to start slightly later with the Rogers, and after the same time periods a greater amount of pure copper was left with the Rogers than with PI PCB. Reaction between the copper and substrate material was also seen with the Rogers, as well as the migrating oxide material. Compared to PI PCB, the reaction seemed to start earlier with the Rogers, but to proceed more slowly.

The reliability of ACAs was much better with the more stable Rogers PCB than with the rapidly degrading PI PCB. With PI PCB most samples had failed before 2,000h at 200°C and before 150h at 240°C. With the Rogers many samples did not fail at all at 200°C and at 240°C the failures occurred at around 500h of testing. The ACF attachment reliability was clearly improved by PCB improvement. Even if the ACF degradation started to occur rapidly, electrical functionality was possible for much longer time. However, the ACF still became fragile at high temperatures, causing the delamination seen in the cross-sections.

Thermal Storage at 180°C, at 200°C and at 200°C for Adhesiveless PI PCB

The high temperature reliability of ECAs was also studied using more stable PI PCB (adhesiveless PI PCB) in Publication VII. A dummy component was used as a test chip to investigate the reliability of a larger chip having more interconnections (90) in the daisy chain than the sensor chips used in the earlier publications. The attachments were done using ACF2 with nickel particles and the reliability was studied at 180°C, 200°C and 240°C.

CDF for the attachments is shown in Figure 41. At 180°C only 9% of samples failed. Testing for 3,000h did not affect the other samples and their resistances reverted to the initial values at ambient temperature after testing. On the other hand, at 200°C more failures were seen as 23% of the samples failed. Most of these failures occurred before 500h of testing, strongly indicating early failures. Therefore the failure mechanism for these failures was most likely different from the failure mechanism the high temperature would have caused in longer testing. The temperature, however, was seen to affect the attachments, as after the testing all the resistances of non-failed samples did not revert to the initial values. Furthermore, at 240°C 85% of the samples failed. Again, there were numerous early failures as half of the samples failed during 360h of testing. There was also a great deal of dispersion, the first sample failing after four hours of testing, whereas three daisy chains did not fail during 3,000h of testing. The long testing had, however, effect on most of these samples.

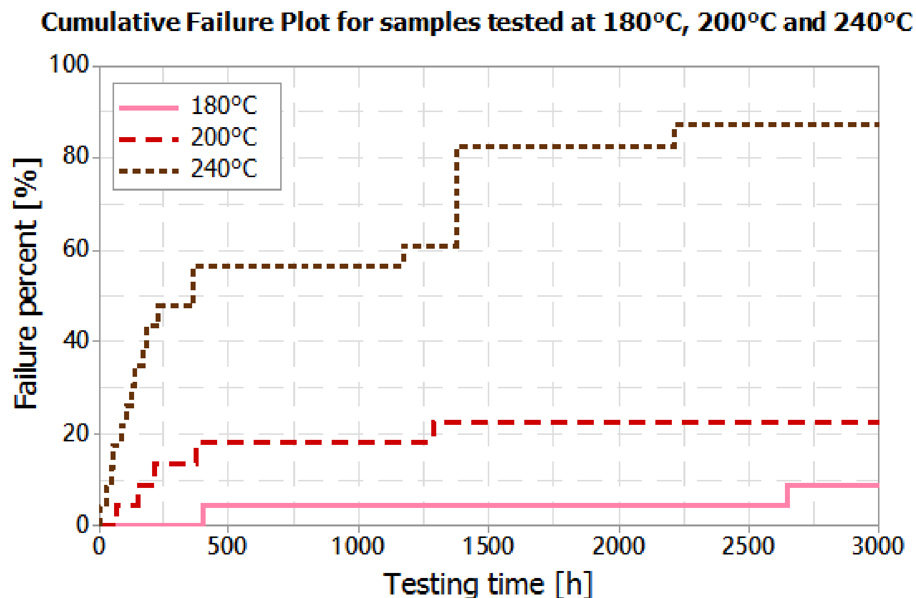


Figure 41. CDF for ACF2 on adhesiveless PI PCB.

When compared to the performance of ACF2 samples on the PI PCB with thick and poor adhesive layer, the reliability was greatly improved. Compared to the Rogers the difference was not as dramatic. Also, at 240°C the difference was less dramatic with each of the PCB materials used due to the degradation of ACF at this temperature. The large number of early failures and a few samples omitted from the analysis due to failure before the test was started indicated some manufacturing defects. Nevertheless, the good quality PI PCB had a critical effect on the reliability, especially when a much larger chip with a much greater number of daisy chains was used. The thermal stresses for the chip were much higher than for the small temperature sensor with a daisy chain of four interconnections. The chip was made of traditional silicon and was bumped, which may have improved the reliability. At 240°C the ACF degraded very fast, which most likely also caused some of the early failures seen. Therefore, prolonged exposure at this high temperature should be avoided. However, 180°C seemed to have no effect.

As with the other thermal storage samples, the progress of degradation and corrosion was studied with additional samples. Figure 42 shows the results. From each thermal storage test the samples were removed after 60h, 120h and 480h of aging. At 180°C (Figure 42b-c) no corrosion or degradation could be seen even after 480h of aging. At 200°C preliminary changes indicating degradation of the thin adhesive layer of the PI PCB were seen after 480h as shown in Figure 42d. At 240°C these changes occurred faster: changes were already seen after 120h (Figure 42e) and the degradation was seen to progress when the testing was continued up to 480h (Figure 42f). Copper corrosion seen in the previous thermal storage test did not seem to occur. However, it was difficult to visually determine whether the copper started to corrode next to the adhesive layer.

According to the thickness measurements the changes were seen only in the adhesive layer. No delamination or cracks were seen in any of the tests after 480h.

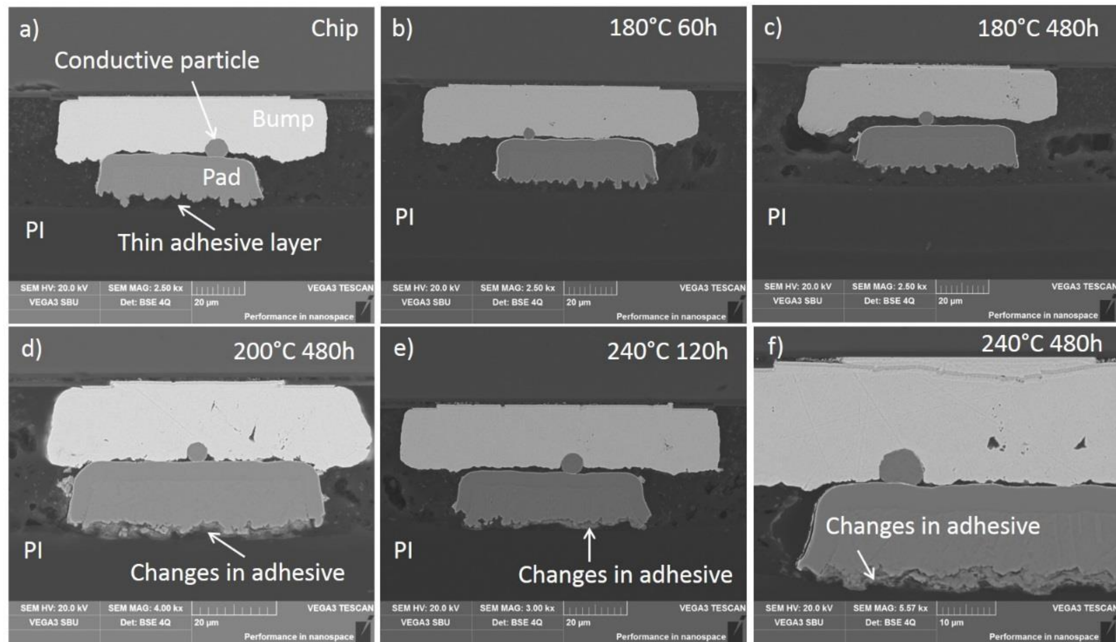


Figure 42. Micrograph of a sample tested at a) non-aged sample b) 180°C for 60h c) 180°C for 480h d) 200°C for 480h e) 240°C for 120h f) 240°C for 480h.

After 3,000h at 180°C a slight degradation of the adhesive layer of the PI PCB was seen in one of the cross-sectioned samples. No delamination was seen. After 3,000h at 200°C and 240°C cracking was seen to be the failure mechanism for the samples having early failures. At 200°C the crack was seen in the interconnection, at 240°C either in the PCB (Figure 43a) or in the interconnection (Figure 43b). No clear failure mechanisms were seen in samples failing later during the test.

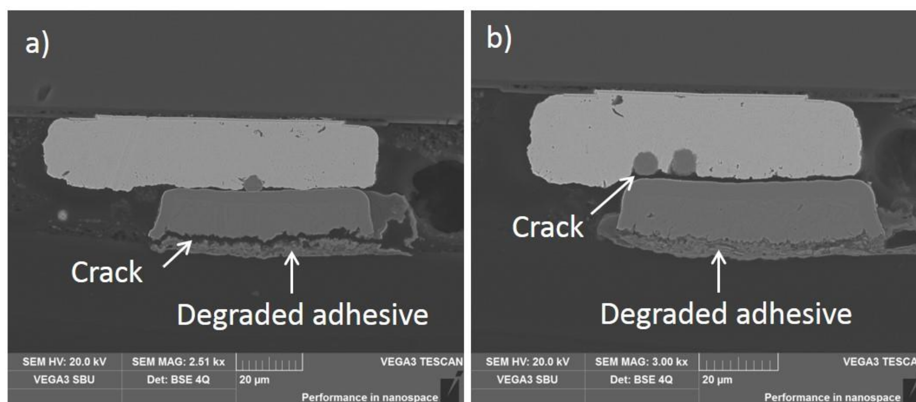


Figure 43. Micrograph of a sample tested at 240°C for 3,000h with a) crack in copper pad b) crack in interconnection.

The mechanical strength of the package was much better with the test structure used in Publication VII than in other thermal storage tests with the temperature sensor. This may be due to the presence of bumps. A larger area of the chip was also covered with ACF due to the structure with peripherally located bumps of the dummy chip. As in other PCBs, the degradation of the adhesiveless PI PCB became more severe at higher aging temperatures. However, cracks due to degradation were only seen after 3,000h at 240°C. This is considerably later than the occurrence of electrical failures. At lower temperatures, or shorter exposures to 240°C no cracking of the PCB was seen.

5.4 Discussion on the Thermal Testing and Reliability of the Polymer-based Sensor Package

More detailed discussion on the results is given in this chapter as regards ECA and PCB materials and also the effect of temperature.

5.4.1 The Effect of the ECA Material

No clear conclusion could be drawn on the differences between the ACAs according to type (ACF vs. ACP). The small test lot sizes made it impossible to determine the differences at a statistically significant level. On the other hand, commercial materials may differ from each other in many other aspects than just the type, and this also affects the results. However, ACF was easier to disperse uniformly in the interconnection, most likely improving the yield and reliability of the attachments. When all ACAs were compared against each other, the ACA matrix seemed to be the most critical factor in ACA performance.

In addition to the matrix, particle type may also affect reliability. As mentioned earlier, ACF1 and ACF2 were manufactured by the same company and differed from each other only in the particle type. According to this work, ACF2 with nickel particles performed better in the high temperature tests. It may be that the high temperature affected the reliability of the polymer particles, thus causing the difference. If the polymer particles degraded due to high temperature exposure, their flexibility most likely decreased, causing them to be more vulnerable to thermomechanical stresses. The TGA measurements in Chapter 4 support the theory of polymer particle degradation due to high temperature: The adhesives had the same matrix, but the onset temperature for ACF1 was lower and weight loss at 240°C higher than that of ACF2. It is also possible that the nickel particles in ACF2 were able to form a stronger connection with bumpless sensor chips than ACF1 with polymer particles.

The ICA samples showed considerable variation in the results of thermal testing conducted in this work, but mainly their reliability was quite poor. The ICAs were used without underfill, and were therefore mechanically unstable, with an open space between the interconnections. This may have

caused the ICA interconnections to be more prone to oxidation and delamination. Additionally, rather small lot sizes were used, rendering the results uncertain. The use of underfill would most likely have improved the reliability. However, as shown in Publication II, underfill does not automatically improve reliability. Additionally, as underfills are polymer materials, they may also degrade at high temperatures, and therefore a suitable underfill material for high temperatures would be needed to optimise the reliability of the ICA interconnections. Due to the sensor structure, the ACA did not cover the whole area of the sensor chips, but only approximately one third of it on the side of the interconnections. Nevertheless, this provided much more mechanical support than the bare ICA interconnections. If underfill were to be used with ICA interconnections, its flow should be limited so that the main part of the sensor structure would still be exposed for sensing purposes.

The sensor attachments with ACA were also very fragile after testing and delamination was seen in every cross-section. Therefore their mechanical strength should also be somehow improved with ACAs. The use of glop top might enhance the adhesion, but as the sensor must be exposed to the environment, the use of a glop top is limited to one side of the component. In Publication VII with silicon chip and better quality PI PCB not even long exposure to 240°C caused similar delamination as that seen with the sensors. It is difficult to determine the reason for the difference between these: The adhesion may have differed due to structural reasons, and with a silicon component the ACA also covered the whole chip area unlike with the alumina component. Additionally, the PI PCB used in Publication VII was of much better quality with no copper corrosion to be seen, unlike all the other PCB materials studied. All these factors may have had a critical effect.

5.4.2 The Effect of PCB Material

PCB material was shown to have an enormous effect on the high temperature reliability of the sensor package. PI PCB with thick adhesive layer was shown to degrade rapidly, and dramatic changes in the structure and materials of the PI PCB were seen to occur. At high temperatures PI PCB was observed to be suitable only for short-term exposures. FR-4 started to degrade even sooner, and this material was not stable and not suitable for even short-term exposures to 200°C or above. The Rogers PCB was seen to offer good reliability at high temperatures. It started to degrade when subjected to high temperature, but after the initial changes no further changes were seen. Consequently, degradation was indeed observed, but it was much less than with PI PCB and FR-4. With good quality PI PCB with a thin adhesive layer, very good reliability was achieved, and the degradation was not significant even after long exposures. However, such types of PI PCBs are more difficult to obtain and often very expensive.

There were differences in the degradation of the PCB materials. In PI PCBs the thermal stability of the adhesive layer used played a significant role, and the thermal stability of the prepreg used in FR-4 was equally important. In addition to these, marked differences were seen in the degradation rate of the copper wirings between different PCB materials. For example, when the PI PCBs were compared, the PI PCB with the thick adhesive layer had clear corrosion after 192h at 240°C, whereas

the adhesiveless PI PCB had no obvious copper corrosion even after 3,000h at 240°C. Copper quality and microstructure were studied to find an explanation for this. In EDS analysis the pad material was analysed to be 100% copper with no major impurities in any of the PCB materials. According to their microstructure, ED copper was used in all PCBs. The only difference observed was the grain size, which was larger for the Rogers and FR-4 and smaller for PI PCBs. It is nevertheless possible that small differences such as impurities due to the manufacturing process were present in some of the PCBs, causing the differences seen. Most likely degradation of other materials also enhanced the corrosion of copper. The difference in copper corrosion between the two PI PCBs was due at least in part to the rapid degradation of the thick adhesive layer in PI PCB. The adhesive may have contained impurities or organic substances vaporising at high temperatures. The degradation of the adhesive may also have produced degradation products. All these may affect the degradation of other materials such as copper.

5.4.3 The Effect of Temperature

Thermal storage at 180°C did not seem to be detrimental to the reliability of the structures studied, and very little or no degradation of the materials was seen at this temperature. Thermal cycling up to this temperature was shown to cause delamination of the samples, but failures occurred mostly after a relatively large number of longlasting thermal cycles.

At 200°C very long exposure times were possible with suitable ECA and PCB materials. With the Rogers and the adhesiveless PI PCB a relatively small number of failures was seen during the long tests. According to the material characterization degradation in the materials gradually occurred. Mechanical strength was a challenge with the sensor chip. However, the shear testing conducted on the Rogers PCB showed that no material present in the sensor package aged and degraded faster than others, and no change due to aging was seen in shear testing fracture surface.

Testing at 240°C seemed to be too high for the structures studied. In shear testing the fracture surface was seen to change from cohesion failure to adhesion failure between 30h and 60h of testing, indicating a drastic and quick degradation of the ACA at this temperature. Severe degradation according to FTIR was indeed seen in ACF1 caused by oxidation and chain scission of the polymer chains. Because temperature enhances chemical reactions, most of the changes and impairments were the same at 200°C and 240°C, but they occurred much faster at higher temperatures. However, the step stress test showed that short exposures to even higher temperatures than 240°C did not cause failures.

Test structures were observed to become fragile during prolonged testing. The chemical changes in ACF1 according to FTIR were seen already after 30h at 200°C and the severity was much more dramatic at 240°C. The tensile strength of ACF1 was seen to clearly decrease after 480h at 200°C and an even bigger drop was seen after 120h at 240°C. The adhesion strength started to slowly decrease after 30h of exposure at both temperatures. The decrease was slow and gradual at 200°C,

but dramatic at 240°C. Electrically the samples withstood much longer exposure times. In this work the mechanical stress during testing was very limited. However, if the structures studied are subjected to mechanical stresses in their actual use environments, the reliability would most likely be poorer than the lifetimes seen in this study.

The degradation began after very short exposures when analysed with FTIR. The electrical failures, however, occurred much later. Nevertheless, it is good to bear in mind that FTIR is a method capable of analysing the surface only. Therefore it is possible that the rapid degradation only affects the surface of the material and not the bulk, therefore causing no major reliability issue for the whole package before the degradation penetrates deeper. The overall results of this work show that the polymer-based package must be considered as a whole. All the materials have an effect on its performance and reliability, and degradation of one part may affect the degradation of another, leading to failures at high temperatures.

6 Conclusions and Final Remarks

The demand for reliable electronics in harsh environments is increasing due to the increased use of electronics, for example in industrial applications. The sensor components used in these applications must function reliably even in harsh environments. Temperature is one of the most detrimental factors for reliability, as increasing temperature is known to accelerate chemical reactions and additionally many material parameters are temperature dependent. Furthermore, all materials have temperature related functional limits. Metals and ceramics typically withstand high temperatures fairly well. Polymers, however, are more complex and their thermal stability is poorer than that of metals and ceramics. Their performance is heavily temperature dependent and due to their chemical composition, most polymers cannot withstand high temperatures without effects on their properties.

Polymer materials are widely used in electronics, for example in PCB materials, interconnection materials (either as underfill providing mechanical support for solder joints or as ECAs), coatings or in component packaging. Epoxy-based materials are most widely used in PCBs, ECAs and underfills. The manufacturing methods for a wide range of polymer materials are widely available and well optimised, such as manufacturing of FR-4 PCBs. Speciality materials, such as ceramics, are much more complicated to manufacture, much less readily available and more expensive. They may also have problems with adhesion and compatibility with other materials. Therefore, from the cost perspective as well as availability, it would be beneficial to use polymer materials at high temperatures. However, as their behaviour is known to be temperature related, they are often assumed to be unsuitable for high temperature applications. This thesis studied the performance and reliability of a polymer-based package with a sensor chip at high temperature. Three main questions were whether polymer materials could be used in high-temperature applications, what kinds of changes in the materials may occur and what kinds of reliability problems may arise.

In this thesis the reliability of polymer package was studied in several high temperature tests. Good reliability in high temperature cycling testing was seen with lifetimes of several hundreds of cycles, even though repeated expansion and contraction caused drastic thermal stresses in the structure.

Of high temperatures 180°C seemed to be low enough, causing only minor reliability problems with polymer materials. Additionally, at 200°C it was possible to achieve good reliability when suitable materials were chosen. The FTIR showed degradation at the surface of polymer materials for all the other materials than neat PI. However, as the mechanical properties were shown to decrease evenly at this temperature, the degradation had most likely not yet propagated throughout the material. The test temperature of 240°C was too high for these materials in longer exposures. The degradation at 240°C was also much more dramatic than at 200°C, as for epoxies the FTIR spectra was fairly similar after 1,920h at 200°C to the spectra after 30h at 240°C. Mechanical testing also showed drastic drops and changes in failure mechanisms at 240°C. Nevertheless, with the right materials most failures occurred after around 500h of exposure. Moreover, step stress testing showed that short

exposures to even higher temperatures did not cause degradation or failures, and no failures were seen after the 24h step stress test.

Several PCB materials were studied. The effect of PCB quality was shown to be highly significant for the reliability of the whole polymer package. With poor PCB quality the failures of the interconnections occurred much earlier than with stable PCB material. Good quality was achieved with both flexible and rigid substrates. If PI PCB is used at high temperatures, it is extremely important to have a very stable adhesive layer in the PCB. Measuring and confirming the material parameters of the data sheets may also be very important. This also applies to ECA materials [Saa16].

Selecting the most suitable ECA material is also important. This often requires testing and comparisons between materials. For example, in this thesis the ACP1 with the highest T_g value was not the best ECA material for high temperature use. Moreover, in all tests and with all substrates ACF2 with nickel particles performed better than ACF1 with polymer particles. This suggests that the high temperature caused degradation of the polymer particles. Thus nickel particles may be more reliable at high temperatures, even though pliable polymer particles have been reported in many studies to be preferable.

Even though with the right PCB and ECA materials the failure free time at high temperatures was fairly long, in long exposures the mechanical integrity was poor. Especially with temperature sensors delamination was seen in all tests. The issue was not as bad with silicon chips. This may have been caused by the superior quality PCB used with the silicon chips or because the silicon chips had bumps, to which it is easier to form a good interconnection. Because the protection of the sensor components with glop tops is often limited and the ACA or ICA and underfill cannot be deposited under the whole sensor component, protecting the structure against mechanical stresses is challenging and should be further studied.

All in all, this thesis showed that a polymer-based electronic package can withstand fairly high temperatures, especially if the exposure time is limited. All materials present in the package, however, must withstand those temperatures. In addition to ECA material, the PCB must also be taken into account as an entity: if poor quality adhesive is combined with thermally stable PI or poor quality prepreg layer is used in FR-4, the PCB will not be suitable for high temperatures even though if it also includes thermally stable parts.

In the future it would be interesting to study the composition of ECA materials suitable for high temperatures. Studying different matrix materials, varying curing agents in thermoset ECAs as well as investigating different conductive particle materials would yield important information and knowledge about the critical issues in the high temperature reliability of ECAs. Degradation of different components of ECAs should also be studied separately. A more detailed characterization of the degradation of the materials present in the sensor package, such as copper on PCBs, would

also be beneficial. Moreover, the possibilities of improving mechanical performance should be studied. Even if not all the sensor components can be covered with glop-top, partial covering may offer the package improved strength against mechanical stresses. Furthermore, determining acceleration factors would yield very important knowledge of the temperature effects. As mentioned in Publication VII, not enough failures in all three tests occurred for the determination of AFs. The determination of AFs requires numerous well-planned tests at different temperatures.

The following paragraphs summarise the main results of the publications.

Publication I, “Thermal Cycling of Anisotropically Conductive Adhesive Interconnections in Demanding Sensor Applications”, studied the effect of widely used cycling test of -40°C/125°C on humidity sensors. Different ACAs, bonding pressures and FR-4 thicknesses were used. The reliability and failures were studied with real-time resistance measurements and cross-sections. With a thin substrate excellent reliability with all bonding pressures was achieved with no failures during 10,000 cycles. With a thicker substrate more failures were seen. The lowest bonding pressure had the best reliability, and the selection of a suitable ACA material was shown to be critical. Clear differences between different ACAs were seen, and the ACA with the best thermal parameters had clearly the poorest reliability. Delamination of the interconnections was seen in the failed samples.

Publication II, “Performance of Electrically Conductive Adhesive Attached Sensors in High Temperature Cycling” studied the high temperature cycling behaviour of temperature sensors in a very slow -55°C/180°C temperature cycling test. Different ECAs were compared, as well as PI and FR-4 substrates. The reliability was studied solely with real-time resistance measurements. Better reliability was obtained with flexible PI substrate, and clear differences between the ECA materials were seen. ACAs in combination with thick FR-4 had poor reliability. ICA performed well with rigid FR-4, but poorly with flexible PI substrate. Underfill did not improve the performance of ICA. With optimal combination of PCB and ECA material, the samples could withstand the cycling test for several hundreds of cycles. When two ACFs with polymer or nicker particles were compared, the ACF with nickel particles was more reliable on both substrates.

Publication III, “Usability of ECA Materials in High Temperature Sensor Applications” studied the temperature limits of ECAs with step stress tests from 180°C to 260°C. Several ECAs were compared using a PI substrate and a temperature sensor. The reliability and failures were studied with real-time resistance measurements and cross-sections. A short test with 15 min steps did not cause electrical or structural changes, nor did 24h steps cause failures. Failures were seen to occur later, when the thermal storage was continued at 260°C after testing. Differences between ECA materials were small. The dwell time of 168h caused failures among ACAs at the 240°C step with small differences between the ACAs, and for the ICA the failures mostly occurred at 260°C. The test showed that ECAs can withstand short exposures to high temperatures very well. In the failure analysis severe degradation of PI PCB was detected. The copper corroded and the adhesive layer of the PCB degraded, which seemed to be the major reliability problem.

Publication IV, “High temperature reliability of electrically conductive adhesive attached sensors on flexible polyimide substrates” studied the effect of thermal storage at 200°C on the reliability of temperature sensors attached with several ECAs on PI PCB. The reliability was studied with real-time resistance measurements and with cross-sections. The ICA failed very quickly, most likely because the flexible substrate and the lack of underfill provided no mechanical support. ACAs started to fail after more than 1,200h of thermal storage. When two ACFs with polymer or nickel particles were compared, the ACF with nickel particles was more reliable in both substrates. In failure analysis similar degradation and corrosion was seen in Publication III, and again the poor stability of the PI PCB was observed to be the main issue. The samples were also observed to be fragile. When the progress of the degradation of PI PCB was studied with samples removed from the test after certain time periods, it was observed that clear degradation was seen to occur approximately at the same time with the observed ACA failures.

Publication V, “Performance of a Polymer-Based Sensor Package at Extreme Temperature” studied the effect of thermal storage at 240°C on the reliability of temperature sensors attached with several ECAs on a PI PCB. The reliability and failures were studied using real-time resistance measurements and with cross-sections. The effect of thermal exposure on the materials was studied with TGA analysis for non-aged ECA materials and with DSC and FTIR for ACF1 and PI PCB aged at 200°C and 240°C. The mechanical properties of ACF1 were studied with tensile testing. ACAs failed after some 100h of exposure to 240°C. When two ACFs with polymer or nickel particles were compared, the ACF with nickel particles were more reliable. Similar corrosion as with other high temperature tests was seen in the failure analysis, and the samples were very fragile. With samples removed from test after certain time periods it was observed that failure occurred before the severe degradation of PI PCB was seen. TGA showed no marked mass loss at the testing temperatures. No changes for PI were seen with DSC or FTIR, but the adhesive layer of PI PCB were observed to degrade fast and changes at both temperatures were seen after 30h. Changes in FTIR spectra for ACF1 were also already seen after 30h. The tensile strength of ACF1 was observed to clearly decrease at 200°C after 480h and at 240°C after 120h. Consequently, the reason for failures at 240°C was most likely the degradation of ECA matrix leading to embrittlement.

Publication VI, “High-Temperature Storage Testing of ACF Attached Sensor Structures” studied the effect of thermal storage at 200°C and 240°C on the reliability of temperature sensors attached with ACF1 and ACF2 on Rogers and FR-4 PCBs. The reliability was studied with real-time resistance measurements, samples removed from the test after certain time periods and with cross-sections. The adhesion strength of the ACFs was studied with shear testing. The effect of thermal exposure on the materials was studied with TGA analysis for non-aged PCB materials and with DSC and FTIR for aged PCB materials. FR-4 was found to be unsuitable even for short exposures at high temperatures. Sample variation was seen in the failure times at both temperatures with this PCB. With the Rogers PCB the failures started to occur after 2,000h at 200°C and around 400h at 240°C. ACF2 was somewhat more reliable. The high temperature caused the samples to be fragile. Copper

pads were also seen to corrode with the Rogers, but this was less than with PI PCB. Adhesion was seen to gradually decrease at 200°C, and the failure mechanism regardless of aging was partially cohesion and partially adhesion. At 240°C the adhesion decreased more rapidly, and between 30h and 60h the failure mechanisms changed from cohesion to adhesion failure, indicating the degradation of ACF. TGA showed no marked mass loss at testing temperatures. DSC indicated stability problems for FR-4, and the FTIR spectra for FR-4 lost its shape very quickly, both supporting the poor thermal stability seen with the test samples. The Rogers was quite stable, also according to material characterization. Changes in the FTIR spectra were seen for the Rogers after 120h at both temperatures, but after this the material seemed to be stable.

Publication VII, “Performance of Anisotropically Conductive Adhesive Attachments on Adhesiveless Polyimide Substrate during High-Temperature Storage Tests” studied the effect of thermal storage at 180°C, 200°C and 240°C with a high quality PI PCB with a very thin adhesive layer (PI PCB adhesiveless). Additionally, a larger chip and longer daisy chain were used with ACF2. The reliability was studied with real-time resistance measurements, samples removed from the test after certain time periods and with cross-sections. At 180°C the reliability was very good with only a few failures. At 200°C and 240°C the failure rate increased, and there were several early failures, especially at 240°C. The reliability was much better than with temperature sensors, even though thermal stresses most likely were a lot greater due to the larger component size. No corrosion of the copper pads was seen even after long exposure at 240°C, and the degradation of the PI adhesive on the PCB was slight. Cracking of the PI PCB only occurred at 240°C after much longer exposure than the majority of the electrical failures were seen. Delamination was only seen in the samples failing early, but which were further tested after the failure occurrence for a prolonged period.

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