Investigation of Cure Stresses in Non-conductive Adhesive Interconnects

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Abstract

Non-conductive adhesives (NCAs) offer cost reduction, simplicity, and flexibility over other electrically conductive adhesives (ECAs) due to an absence of conductive fillers and reduced processing requirements. However, although NCAs are a very promising potential alternative to metallic solder interconnections, there continue to be significant challenges that need to be addressed for their widespread implementation. This investigation focuses on a fundamental study of the mechanical, thermal and rheological properties of NCAs during cure process, the formation of the electrical connectivity, and the mechanisms governing long-term reliability of NCA flip chip interconnects.

The reaction kinetics of fast cure non-conductive adhesives has been systematically investigated using differential scanning calorimetry (DSC). Good agreement between the autocatalytic kinetic model and experimental results has been demonstrated. The degree of cure at gelation was determined around 55%. Vitrification was directly measured by rheological experiments. A time-temperature transformation (TTT) cure diagram was constructed based on the gelation and vitrification time.

A new method by means of thermal mechanical analysis (TMA) was developed for the in-situ measurement of cure shrinkage of NCAs. By comparing the heat flow as measured by DSC, the cure shrinkage induced by the crosslinking reaction was validated. A linear relationship between the cure shrinkage and degree of cure was clearly indicated. Coefficient of cure shrinkage (CCS) was proposed to be a material constant to describe cure shrinkage, and applied to various regions of the TTT diagram.

A multi-step force technique was used to determine the shear mechanical properties during cure. It is observed that cure at lower temperature leads to higher storage modulus, whereas, cure at high temperature could result in the modulus buildup within a small range of degree of cure. Cure-induced stresses were incrementally calculated based on the measured shrinkage and storage moduli and expressed as a function of degree of cure. A new method for direct measurement of cure-induced stresses by using the iso-strain mode of a dynamic mechanical analyzer (DMA) has been developed. Procedures for numerical simulation of the evolution of cure stresses are presented through a novel implementation of a thermal-cure analogy finite element analysis. CCS and degree of cure are proposed to be analogous to coefficient of thermal expansion (CTE) and temperature in thermal-
mechanical analysis, respectively. The proposed analogy method prediction can be easily made using the commercial finite element software. A good agreement of simulation and the direct experimental measurement is exhibited. Cure-induced stress at lower cure temperature could be larger than thermal stress. Final stress increases with increasing cure temperature and reaches a plateau at higher temperature, where the increase of thermal stress is diminished by the drop of cure-induced stress.

In-situ measurement of the development of contact resistance during the bonding process was developed by using a mechanical tester combined with a four wire resistance measurement system. With decrease of bonding temperature, the drop of contact resistance induced by cure shrinkage becomes larger, while cooling-induced drop of resistance becomes smaller. There appears to be good agreement of the evolution of contact resistance and the directly observed cure stress build-up.

It was found that the evolution of adhesion strength was largely dependent on the build-up of mechanical properties. At low and medium degrees of cure, cohesive and adhesive failures were respectively observed, while at high degrees of cure, adhesion strength surpassing the shear strength of the solder mask was observed. The sharp increase in adhesion strength was observed to coincide with the gelation point, thus suggesting that the contributors to adhesion strength include mechanical interlocking as well as chemical bonding.

Methodologies developed and analysis performed in this project have provided a means to understand the ‘birth’ of the NCA flip chip interconnect. They can be further applied to cure shrinkage analysis in optoelectronics and other applications where either cure strain related displacement or stresses may have significant impact on the optimal performance of these materials or devices.
Chapter 1 Introduction

1.1 Background

Solder-bumped flip chip interconnection was first introduced in 1964 by IBM. This technology, referred as controlled-collapsed-chip-connection (C4) technology, was essentially unique to IBM in the 1970s, but gained wider utilization in the 1990s as the advantage of higher I/O density from its area array capabilities became apparent. In adopting the C4 process, many researchers have introduced material and process modifications to try to improve the process, cost, the electrical, thermal, mechanical properties and reliability. There are two significant improvements that have contributed to making flip chip a particularly rich and vital field for development, namely the introduction of organic substrates and underfill encapsulation. In plastic packages, the former can greatly reduce packaging cost, while the latter has effected a tenfold improvement in fatigue life compared to a package without underfill [1-4].

An ongoing and consistent driving force in the modern microelectronics packaging industry is the drive towards smaller, faster, and more reliable integrated systems, at equivalent or lower prices. After four decades of development, flip chip technology is well positioned to meet these needs. Flip chip technology is an interconnection technique that directly mounts a silicon die with its active area face down to a substrate or a printed circuit board. Higher I/O and increased interconnect density are achieved by the area array architecture in flip chip packages. Package height can also be reduced since no clearance above the die is required for wires or mold compound. These give rise to great
reduction in package size (as can be seen from Fig. 1.1). At the same time, due to the pronounced reduction in electrical path length, flip chip interconnection provides faster speed and excellent electrical performance, such as lower parasitic capacitance, inductance and resistance (Fig. 1.2). Flip chip interconnects are superior in thermal performance since it enables more thermal enhancement methods by having thermal vias throughout the substrate. Furthermore, all the connections are made simultaneously rather than serially as in wire bonding. Therefore great savings in manufacturing time and cost can be made.

![Type Area](attachment://types.png)

**Fig. 1.1** The package size comparison of various package types [4].

![Conduction Path](attachment://conduction.png)

**Fig. 1.2** Comparison of conduction path of wire bonding and flip chip.
Chapter 1 Introduction

Tin-lead solder materials have been used for surface mounting technology and flip chip interconnection for many decades. However, there are increasing environmental and health concerns on the toxicity of lead. Depending on the level of lead ingestion, lead can damage the human kidney, liver, blood and central nervous system. Legislation has been passed in Europe to ban the use of lead in solder in 2006. As a response to this legislation, great effort has been made by the industry and academia to develop lead-free and environmentally-friendly soldering materials to replace lead-based solders. However, several limitations of lead-free solders including reliability, relatively high cost, poor wettability, and higher reflow temperature have impeded efforts to replace lead-bearing solders with lead-free solders. In addition, joint embrittlement and fatigue are serious concerns in lead-free solder applications as embrittlement of solder joints after reflow and fatigue cracks induced by temperature cycling are among the major causes of lead-free solder joint failure [5-7].

The other alternative to lead-bearing solder is electrically conductive adhesives (ECAs), which provide environmentally friendly lead-free flip chip interconnections and can also be used for surface mounting of IC packages. In flip chip interconnects, ECA assemblies can offer great potential benefits including greater flexibility, easier processing, lower processing temperature, finer pitch, and lower cost. ECAs are composite materials that consist of a polymer matrix and conductive fillers. According to the amount of conductive fillers, there are three types of ECAs: (a) isotropic conductive adhesives (ICAs), (b) anisotropic conductive adhesives (ACAs, or Z-axis adhesives), and (c) non-conductive adhesives (NCAs) [8-9].
ICAs are usually manufactured with filler concentration sufficiently greater than percolation threshold, typically >75%, to guarantee low resistance with allowance for manufacturing tolerances and thereby can conduct current equally in all directions. Typically, ICAs with Ag filler particles are used and the adhesive is application of the adhesive is performed by stencil printing, dipping, or dispensing. However, limitations to the use of ICAs include pad pitch and the need for an underfill encapsulant from reliability considerations.

As opposed to the ICAs, the amount of conductive fillers in ACAs is below the percolation threshold. The conductive particles added into the polymer matrix are metallic or metal-coated polymer spheres. The metals used are most often Au or Ni. By compressing the bumps in the pre-applied ACA, the metal particles enable electrical connectivity in the z-direction between the IC and the substrate pads via the ACA particles.

Contrary to other ECAs, there are no conductive particles in NCAs. The NCA interconnections are formed through mechanical contact between the bump on the silicon chip and the pad on the substrate. The compressive stress induced during the curing process of NCAs results in a very low contact resistance thus enabling electrical connectivity between the chip and the substrate. In solder based flip chip interconnects, metallic solders provide both electrical and mechanical functions for the whole system. In ACAs and ICAs the mechanical and electrical functions are provided by conductive fillers and the adhesive matrix respectively, whereas for NCAs, the conductive path is provided by mechanical contact between the IC bump and the substrate pad. Although the mechanical and electrical functions are provided separately by different constituents of
Chapter 1 Introduction

the ECAs, there is an intrinsic relationship between the mechanical and electrical properties. Long term stable and reliable mechanical properties provided by the adhesive matrix are the basis of good conductivity. Therefore, investigation of the characteristic of adhesive matrix is of paramount importance for the ECA interconnected systems.

ICAs have been used for decades as die attach adhesives and ACAs have also found applications since the 90’s in LCD driver assemblies [10]. NCAs on the other hand are a more recent addition to the ECA family, and there are very few reports on NCA interconnects. Furthermore, a lack of fundamental understanding of the reliability mechanisms of NCA interconnects has impeded the widespread implementation of this technology. Although NCAs promise simpler processing than ICA and ACAs, the lack of conductive particles in NCAs have resulted in more stringent mechanical, thermal, and rheological property requirements of NCAs as compared with other ECAs. The major challenges in NCA interconnects may be summarized as [8-10]:

1. The curing and cooling process of the adhesive matrix and its effect on the mechanical properties are not well understood. The history of cure and its impact on electrical connectivity is an issue of utmost importance and has not been sufficiently investigated.

2. Standards and methodologies to measure cure shrinkage and cure force build up have not been developed and are not available either in the literature or from any standards organization (e.g. ASTM, IPC, JEDEC etc). As presented earlier in the chapter, the compressive cure force caused by the adhesive cure is the sole force that creates electrical conductance in NCA flip chip.
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3. A methodology to model the cure process and estimate the build up of compressive stress (and thus the electrical conductivity) is not available and has not been addressed in the literature.

4. The adhesion strength build-up and degradation mechanisms under service have not been documented.

5. The failure modes and mechanisms are not well elucidated due to the limited failure analysis data. The impact of static and cyclic loading and the viscoelastic relaxation behavior on the reliability is not understood.

Therefore, extensive studies on the characterization of adhesive and its effect on the reliability are necessary to develop a better understanding of the mechanisms underlying these issues and to improve the performance and expand the application of NCAs.

1.2 Objectives

This work aims to conduct fundamental study on the mechanical, thermal and rheological properties of NCAs for flip chip interconnections, and to study their effects on the long term reliability of polymeric flip chip assembly. The objectives of the current investigation may be summarized as:

1. To conduct fundamental study on the cure kinetics, time-temperature transformation, and rheological properties

During the curing process, the NCAs will transform from the liquid state into the solid state and involve polymerization and crosslinking. Gelation and vitrification are the two most important changes during this process [7-10]. Gelation corresponds to the incipient formation of an infinite network and is accompanied by a dramatic increase in viscosity and the development of modulus. Vitrification is understood as a change from rubber
state to glass state due to the consequence of increasing molecular weight and further crosslinking. At early stages of polymerization, shrinkage does not cause any stresses because of the flow nature and lack of any mechanical modulus of the liquid. After the critical gel point, the material begins to develop a significant modulus. If there is a constraint on the system boundary, cure-induced stresses will develop. As the reaction proceeds, vitrification characterized by liquid or rubber-to-glass transition sets in and cure stresses develop monotonically with conversion after the vitrification point [4-5]. The development of cure stress is highly related to the two events. Therefore, a detailed study on cure kinetics and time-temperature transformation to correlate the extent of cure, reaction rate and cured state is of great importance for providing a deep understanding of cure shrinkage and cure-induced stresses.

2. To develop characterization tools and methodologies for characterizing the evolution of chemical shrinkage and cure stress during curing process

In a NCA flip-chip joint, the conductivity after bonding is completely dependent on the direct mechanical contact between the IC bump and the substrate pad. The compressive cure force caused by the adhesive cure is the sole force that creates electrical conductance in NCA flip chip. As discussed previously in this section, a standard methodology for this characterization does not exist. Therefore, in this study, the characterization tools will be developed to measure cure shrinkage. Moreover, a direct measurement of cure stress is very necessary and will be developed to validate the calculation from the theory and finite element modeling.

3. To establish a simulation technique to model the formation of NCA flip-chip interconnects
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To date, most of the work reported only on the theoretical approach for calculating cure stresses, there has been little work to simulate the evolution of cure stress. The implementation of finite element analysis for the development of cure stress is still lacking due to the lack of characterization technique and poor understanding of the characteristics of shrinkage-induced stress. In some cases, we are much more interested in the evolution of stresses as well as the stress distributions. Besides, simulation technique is strongly needed to solve the practical problems with complex geometries and boundary conditions. Therefore, in this study, a new simulation methodology will be developed to model the evolution of cure-induced stresses.

4. To correlate the compressive stress obtained during the cure process and the electrical contact resistance

The in-situ measurement of resistance during the curing and cooling process gives a clear indication between the evolution of resistance and the build up of contact force. Eventually, the mechanical compressive stress formed during the cure process has to be translated to the electrical contact resistance for practical interpretation and to investigate the reliability of flip chip interconnects with NCAs. In this study, an experimental set-up will be developed using a microforce tester combined with a resistance testing system to correlate the compressive stress with contact resistance.

1.3 Report Organization

This study is divided into six chapters and each chapter is briefly discussed as follows:

Chapter 1 gives a brief introduction of background information related to this research and presents the motivations and objectives.
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Chapter 2 deals with a literature review covering various topics related to this research work.

Chapter 3 provides a short description to the various experimental techniques and modeling and simulation methods employed in this study.

Chapter 4 is the core part of this study. It will focus on the results and analysis. Extensive discussions are also made on this chapter.

Chapter 5 summarizes the important conclusions and main findings of this research work.

Finally, the recommendations for future work are outlined in chapter 6.
Chapter 2 Literature Review

2.1 Overview of Electrically Conductive Adhesives

Since the metal-filled thermoset polymers as the first patented electrically conductive adhesives in the 1950s [17], conductive adhesive joining has been used for many years in chip-on-glass (COG) applications [18]. Only in recent years have efforts been made to develop this technology for low-cost flip chip applications. Electrically conductive adhesives (ECAs) offer several potential advantages over solder. They are environmentally friendly since there is no Pb and flux associated, and offer lower cost due to the lower processing temperature and simple assembly process. However, thorough understanding of the design, reliability, material and manufacturing characteristics of various conductive adhesive technologies is still lacking. Therefore, basic and applied studies of the process, structural and material characterizations are critical for the successful applications of the ECA technology [19].

There are three main classes of ECAs – isotropic conductive adhesives (ICAs) which conduct electricity equally in all directions like solder; anisotropic conductive adhesives (ACAs) which conduct only in the Z-axis, and non-conductive adhesives (NCAs) which maintain pressure contacts between the bumps and pads by the compressive force of the adhesive after cure [19].

2.1.1 Anisotropic Conductive Adhesives
Anisotropic conductive adhesives (ACAs), also known as z-axis conductive adhesive, consist of conductive particles dispersed in an adhesive matrix. These conductive particles are used to provide the adhesive with electrical conductivity and can be pure metals such as gold, silver or nickel, or metal-coated particles with plastic or glass cores. The conductive particle loading is way below the percolation threshold [10, 20], only 5-10 volume percent [21-22]. Diameters of the conductive particles typically range from 3-15 μm.

The low loading in ACA ensures no direct contact between individual particles. It is only after pressurization during assembly that electrical conduction becomes possible in the pressurization (z-axis) direction. The particle density is controlled to provide enough particles on the conduction pads to ensure reliable z-axis electrical conduction after assembly, yet low enough to ensure electrical insulation along the x-y axis [23]. The adhesive matrix is used to form mechanical bond at the interconnection and can be both thermosetting and thermoplastic polymer. The principal advantage of thermoplastic adhesive is reworkable and the relative ease of processing and. However, there are many disadvantages for thermoplastic adhesive such as low adhesion strength and poor resistance to thermal shock or thermal cycling. Thermosetting adhesives, such as epoxy and silicone, form a three dimensional crosslinked structure when cured under certain conditions. The ability to maintain strength at high temperature and robust adhesive bonds are the principal advantage of these materials. However, because the cure reaction is not reversible, rework or repair of joint might be a problem.

ACAs have been primarily used in liquid crystal display panels for a long time [10, 24-26]. Recently, intensive research and development work have been carried out in the field of flip chip technology using ACAs as a soldering alternative [27-29]. The ACA bonding
process used for flip chip interconnects is illustrated in Fig. 2.1. In addition, ACAs were also studied for possible use for surface mount technology to replace solders [30].

Fig. 2.1 Assembly process of flip-chip interconnects using ACAs.

2.1.2 Isotropic Conductive Adhesives
Isotropic conductive adhesives (ICAs) are composites of polymer resin and conductive fillers. In order to achieve desirable conductivity, volume fraction of the conductive filler in an ICA should be equal to or slightly higher than the critical volume fraction, the percolation threshold. Too high filler could compromise the mechanical properties of the adhesives. The loading content in a typical ICA formulation is about 25-30 percent. Silver is by far the most popular conductive filler due to excellent thermal stability with its conductive oxide comparing with other conductive fillers. Nickel with its lower cost than silver and better thermal stability than copper, can offer an appropriate alternative to silver for incorporation into ICAs. In addition, silver-plated copper and short carbon fibers have also been used as conductive fillers in ICAs [31-32]. The adhesive matrix of ICAs is similar to that of ACAs. Both thermoplastic and thermoset resins can be used for ICA formulations. The main thermoplastic resin used for ICAs is polyimide resin.
However, most ICAs are based on thermosetting resins. Epoxy resin is most commonly used in thermosetting ICA formulations due to its superior properties. Silicone, cyanate esters and cyanoacrylates are also used in ICAs.

The principal applications of ICAs are die attach, flip chip interconnection and surface mount technology. The main function of die attach is to mechanically attach the backside of IC to the substrates. Sufficient adhesion is required to bond the IC and thermal stability is also important for the long term reliability. ICAs are currently being used for flip chip bumping or bonding. In order to use ICAs in flip chip applications, the material must be precisely applied onto the points to be electrically connected and not allowed to flow and short circuit between circuit lines [33-34]. To precisely deposit the ICA paste, screen or stencil printing is most commonly used. However, printing for flip chip applications would require very accurate pattern alignment. To overcome this problem, the transfer method may be used. For this technique, raised studs or pillars are required on either the die or the substrate. The ICA is then selectively transferred to the raised areas only, by contacting the face of it to a flat thin film of the material which adheres to the prominent surfaces. The thin film is produced by screen printing, and the transfer thickness may be controlled by changing the printed film thickness [35]. The complicated process for ICAs is the main drawback for this technology. Furthermore, a nonconductive adhesive often has to be applied to function as an underfill, like in the soldering process. Fig. 2.2 shows the bonding process for ICA.
2.1.3 Non-conductive Adhesives

Non-conductive adhesives (NCAs) are attracting great attentions as potential solder replacements in microelectronic packaging. Typically, NCAs are thermosets or B-stage epoxies (or blends), which are not filled with any conductive particles. Since conductive fillers are not required, NCAs are by far the cheapest materials as compared to isotropic conductive adhesives (ICAs) and anisotropic conductive adhesives (ACAs). NCAs also act as the function of underfill to compensate the mismatch of CTE between the chip and substrate. There are no conductive particles in NCAs, the nonconductive adhesive bonding relies upon direct mechanical contact between the two conductor surfaces [36]. The natural surface roughness of the two mating materials provides a number of metal-to-metal contact spots giving electrical continuity. After the connections are made, shrinkage in the cured adhesive and the mechanical properties of the involved materials will be responsible for the compressive force needed to maintain the electrical contacts [37]. However, the coplanarity requirements for this type of interconnection are very strict as there are no conductive particles to fill the gaps left between contact surfaces after placement [38]. The focus of this study is flip chip interconnections using NCAs,
therefore the conduction mechanisms and failure mechanisms will be elaborated in the following paragraph. The assembly process of flip chip interconnect using NCA is shown in Fig. 2.3.

![Assembly process of flip-chip interconnects using NCAs.](image)

**Fig. 2.3 Assembly process of flip-chip interconnects using NCAs.**

### 2.1.3.1 Conduction Mechanisms

In a NCA flip-chip joint, the conductivity after bonding is completely dependent on the direct mechanical contact between the bump under the chip and the corresponding pad on the substrate. This mechanical contact is solely responsible for providing electrical continuity. The contact force, responsible for this electrical continuity is caused by the elastic deformation created by the initial applied bonding pressure and the residual shrinkage stress due to the crosslinking shrinkage during the curing process [39]. However, it can be easily observed that the interfaces between the NCAs and silicon passivation layer or the substrate experience a tensile stress (Fig. 2.4). So, both the cohesive strength within the adhesive and the adhesion between the adhesive and the parts to be bonded must be sufficient to maintain this compressive force.
2.1.3.2 Failure Mechanisms

All failures are electrical failures eventually. However, the cause for these failures may be thermal, mechanical, electrical, chemical or a combination of these. No matter what the failure mechanism is, it is important to understand the underlying causes for the failure mechanism and to design against such a failure mechanism. The reliability of NCA joint is a critical issue that must be considered carefully before the adhesives can be widely used in a production setting. As mentioned previous, in a NCA joint, the electrical conductivity between the two electrodes relies on mechanical contact and its compressive stress. The use of NCA interconnection technique therefore implies different failure mechanisms compared to that of the traditional solder connections.

Liu et al [26] reported that there are basically two failure mechanisms that can destroy the adhesive contacts. The first is the formation of non-conductive film on the contact areas. The second is the loss of mechanical contact between the conductive elements. This can
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be due to either loss of adherence, or relaxation of the compressive force. Chung et al [40] suggested that unlike intermetallic joints involved in solder joints with alloy forming along the interface for electrical transport, the NCA bonding is Van Der Waal in nature between two polar surfaces. Poor wetting and delamination will dramatically increase the electrical resistance. The same deleterious effects could be resulted if insulating oxide layer of more than a few angstroms is formed between the bonding pads and adhesives. Chung et al [40] also reported that the long-term reliability depend on the internal stresses built up during the curing process. The extent of the stress build up is determined by the curing temperature, the operating temperature ranges, the modulus of elasticity of adhesive, CTE mismatches of adhesive and adherents, the thickness and area of bonding [40]. R. Aschenbrenner et al [33, 37] investigated the reliability and failure mechanisms of non-conductive film (NCF) joints with gold ball bumps on flexible substrates upon exposures to thermal cycling and storage at high temperature and humidity. They observed that humidity tests caused the strongest increase of contact resistance for NCF. They attributed these phenomena to the diffusion of water molecules into adhesive layer as well as into the interface between substrate and adhesive. This causes an irreversible decrease of mechanical and adhesive strength, a reversible increase of plasticity, decrease of Tg and swelling. The thermal expansion of the adhesive and its swelling in the z-axis direction due to humidity as well as mechanical stress from the environment will tend to diminish the compressive forces between the conductive components. Studies by Liu et al [26] revealed another effect of humidity, which is the oxidation of the metal on interconnection materials. R. Nagle et al [35] evaluated three different groups of adhesive flip-chip interconnect techniques. They claimed that the coplanarity requirements for NCA interconnection are stricter than for ICA and ACA as there is no conductive filler material to fill gaps left between contact surfaces after placement, causing poor electrical
connection. Therefore, in order to achieve high reliability, it is important to have compliance in the interconnection to compensate for non-planarities of the substrate and thermal mismatch of the interconnection materials.

The typical failure mechanisms for NCAs flip chip interconnects are summarized below:

**Failure induced by stress relaxation:** stress relaxation in non-conductive adhesive is most commonly happened phenomenon [41]. The relaxation characteristic of the adhesive is of paramount importance in the reliability of the interconnection and will result in the degradation of mechanical contact between the bump and the substrate metallization, and then lead to the corresponding increase in the electrical contact resistance.

**Failure induced by adhesion strength:** Poor adhesion strength due to the inappropriate curing profile or degradation of adhesion strength owing to the ingress of moisture has a catastrophic effect on the flip chip interconnects. Strong adhesion strength between the adhesive and silicon or substrate is the basis of long term reliability.

**Failure induced by delamination:** delamination always occurs along the interface of dissimilar materials. In several cases, delamination may be present in packages due to various processing issues, such as in adequate surface preparation, inadequate cleaning and presence of contaminants, inadequate baking, moisture and volatiles, inadequate material dispensing, non-planarity and topological variations in the surface, etc [42].

**Failure induced by moisture ingestion:** the reliability of NCAs flip chip interconnection is limited by the adhesive’s sensitivity to moisture penetration. Moisture induces the hygroscopic swelling of adhesive and damages the mechanical properties of
adhesive. The diffusion of water molecules into the interfaces between adhesive and substrate or silicon will reduce the bonding strength and thereby result in the delamination along the interfaces [42]. Another deleterious effect of humidity is the formation of the oxidation layer on the bump and pad and then increases the contact resistance dramatically.

**Failure induced by thermal expansion:** fatigue induced by the thermal mismatch is the most common mechanism of failure for solder joints. However, the deformation upon heating could reduce the contact force between the bump and pad. The fatigue model for predicting the lifetime of adhesive interconnects is thus completely different compared with that for solder joints. Such models to understand and predict lifetimes of adhesive interconnects are not available and have contributed to the thwarting implementation of these interconnect schemes.

These failure mechanisms have not been investigated in detail. Therefore, to be able to reduce the chance of these failures and to fully implement flip chip interconnections using NCAs, a comprehensive understanding of the curing behavior, stress build up, adhesion strength and their relation with reliability is essential. The following paragraphs will give a detailed review on these considerations.

### 2.2 Time-Temperature Transformation Cure Diagram

The isothermal time-temperature transformation cure diagram shown in Fig. 2.5, first introduced by Gillham et al [11-12], is a useful intellectual framework for analyzing and determining cure processes. This diagram displays the time to reach various events during isothermal cure. During the curing process, the NCAs will transform from the liquid state...
into the solid state and involve polymerization and crosslinking. Gelation and vitrification are the most important changes during this process. Gelation corresponds to the incipient formation of an infinite network and is accompanied by a dramatic increase in viscosity and the development of modulus. Vitrification is always understood as a change from rubber state to glass state due to the consequence of increasing molecular weight and further crosslinking. The reaction rate will be significantly retarded due to the change from a chemical controlled reaction to a diffusion controlled reaction. If the cure temperature is lower than the ultimate glass transition temperature $T_{gr}$, the material will first gel and then vitrify. On the other hand, if the cure temperature is above $T_{gr}$, the material cures rapidly without vitrification. In this case, the chemical kinetics governs the progress of the reaction. At the particular cure temperature of $gelT_g$, the material will gel and vitrify simultaneously. $gelT_g$ also indicates the upper temperature at which the thermosetting polymer can be stored. In addition, as a thermosetting material cures, its glass transition temperature, $T_g$, increases from an initial value $T_{g0}$ due to increasing molecular weight, after gelation, $T_g$ increase due to increasing crosslink density, as well as to increasing number- average molecular weight and to the decrease in chain ends. Curing parameters such as cure temperature and time determine the curing behavior and cured state.
2.2.1 Bondability Diagram

Based on TTT cure diagram, a bondability diagram that can establish optimum cure schedules for die attach materials was proposed [43]. The extent of reaction was used to determine the minimum and maximum time of curing. The time required to reach extent of reaction 90% is the minimum time for developing sufficient mechanical strength, and that to reach 95% extent of reaction, is considered as the maximum time to avoid the material degradation and also to satisfy the manufacturing economics. The minimum cure temperature is the onset cure temperature. The maximum cure temperature is the leadframe oxidation temperature. The outgassing, gelation and cure stress data also contributed to the construction. The bondability diagram for die attach materials will provide a good insight for the construction of the processing diagram of non-conductive adhesive that should consider the optimization of time, temperature and pressure.
2.2.2 Gelation and Vitrification

The gelation point is worthy to study because it is the onset of mechanical strength and cure stress. Moreover it is a termination point of voiding and resin bleed [43]. Gelation does not involve any chemical change in the curing process, and therefore cannot be detected by techniques sensitive to chemical reaction, such as DSC. However, the mechanical and rheological properties of the reaction medium do change during gelation, which can therefore be detected by methods based on changes in these properties [44-46].

There are several methods available for determining the gelation point. Viscometry defines $t_{gel}$ as the time at which the viscosity tends toward infinity [44, 47], whereas torsional braid analysis (TBA) defines it as the time needed to reach the maximum $\tan \delta$. Thermal mechanical analysis (TMA) has been utilized to determine the gel time by applying a periodic force and the gel time was defined as the time required for the material to change from liquid to solid state [45]. By means of dynamic mechanical tests, gelation can be detected: (a) as the crossover of storage modulus and loss modulus where $\tan \delta=1$ in ASTM standards [48]; (b) as the point at which $\tan \delta$ becomes independent on the frequency by means of multi-frequency technique [49-53]. As can be seen from the above, there are many ways of defining gelation or gelation time. Curing times and $t_{gel}$ obtained through different techniques may not be directly compared [45].

Vitrification is a gradual, thermo-reversible process and its detection will vary with the technique employed. There are two main methodologies for the determination of vitrification, calorimetric and dynamic mechanical analysis. For calorimetric method, the material is cured at different times and temperatures. The $T_g$ is determined by using DSC, TMA or DMA and the degree of conversion, by DSC, from residual heat. A single master curve $T_g(\alpha)$ is then established. The time required to reach a given degree of conversion
can be established through any of the classical kinetic procedures, since the reaction is controlled chemically before vitrification. Recently, the modulated density scanning calorimetry (MDSC) was used to directly determine the vitrification \cite{14,54}. The second methodology consists of curing the sample by a technique which is sensitive to vitrification, such as TBA, DMTA, etc. In this case, the vitrification time is determined directly as the time needed for the material to reach a maximum \tan \delta value at a given curing temperature \cite{46}. A recent study compared vitrification times measured by calorimetric and rheological measurements \cite{14}. Criteria for direct measurement of vitrification are as follows: (1) onset of frequency dependence in storage modulus, (2) peak in \tan \delta at 1 Hz, (3) peak in loss modulus at 1 Hz and (4) end of frequency dependence in storage modulus. By comparing the different vitrification measurements, it was observed that the calorimetric vitrification times were expected to be somewhat longer than the vitrification times obtained from rheological measurements \cite{14}.

2.3 Cure Shrinkage

Volumetric shrinkage of a typical thermosetting resin occurs during the curing process because molecules move from a van der Waals distance of separation to a covalent distance of separation. For the flip chip interconnects using electrically conductive adhesive, the cure shrinkage plays a very important role during the conductivity establishment \cite{55-57}. Particularly for the flip chip interconnects using non-conductive adhesive, the cure shrinkage of non-conductive adhesive is critical for the formation of final compressive stress in the contacts between the bump and the pad. Therefore, it is very important to investigate the evolution of cure shrinkage during the curing process.
However, measuring the cure shrinkage during reaction is fairly difficult. A variety of testing techniques have been applied to measure the volumetric change or dimensional change of crosslinking process of light-cured resin or thermal-cured resin. Initially, mercury based dilatometers (Fig. 2.6) were used [58-59]. The potential hazard associated with mercury vapor in the glass tube led to the development of water based dilatometers [60]. Water-based dilatometers are also very dependent on temperature stability and may be influenced by water absorption by the resin. Thereby a non-contact gas pycnometry method [61] was employed to determine the volume changes during the polymerization of materials in a dry state and showed the similar accuracy and less labour intensive than liquid-based dilatometric methods. However, this method measures only the final amount of shrinkage and is not able to monitor in-situ chemical shrinkage. The buoyancy technique (Fig. 2.7) [62] monitors the sample buoyancy as its density increases with respect to the constant density fluid during the curing process. The resin was sealed in a silicone rubber bag and kept from contacting with the fluid, but the maximum temperature is limited to 200°C due to the use of silicone bag and silicone fluid. Other methods include online monitoring of the dimensional change of polymers or composites during cure by embedded optical sensors or laser beam scanning [63-64]. Thermomechanical Analyzer (TMA) was also used to measure the dimension changes of electrically conductive adhesive [55-56]. This techniques based on measuring linear shrinkage using contact displacement transducers can be much less labour intensive, but may have potential errors associated with the effect of gravity or the load of the measuring system on the result or non-uniform shrinkage [61]. Comparing with ACAs and ICAs, NCAs without addition of metallic fillers have lower viscosity, so it could be expected that it is not possible to measure the polymerization shrinkage of NCAs by means of TMA. This study will propose a simple method of using TMA to measure the
cure shrinkage of NCAs. This method will overcome the shortcomings of a number of techniques discussed above.

![Diagram of computer-controlled mercury dilatometer](image1)

**Fig. 2.6 Schematic diagram of computer-controlled mercury dilatometer [58]**

![Diagram of in-situ measurement setup](image2)

**Fig. 2.7 Schematic of setup for in-situ measurement of cure shrinkage [62]**
2.4 Residual Stress

The conductivity of flip chip interconnects using NCAs is strongly dependent on the compressive stress developed during the curing and cooling process. The cure stress is generated due to the development of crosslinking shrinkage and mechanical stiffness during the curing process. The cooling stress is due to the thermal shrinkage formed when cooling from the cure temperature to room temperature. Cure shrinkage is an inherent property of thermosetting materials since the secondary intermolecular bonds between monomer molecules convert to primary covalent bonds with smaller interatomic distances. Thermal shrinkage is formed due to the coefficient of thermal expansion. By increasing the temperature during cure, the expansive thermal strain, arising from the large CTE could, in theory, exactly balance the contractive cure shrinkage strain [65].

Moreover, the build-up of mechanical properties is strongly influenced by the degree of reaction during the curing process. From the TTT cure diagram, during the curing process, the system passes through several discernible stages. It can be seen that at the early stage of cure, the material is essentially in liquid state incapable of sustaining an external load. With increase of cure, the system acquires an equilibrium modulus which is essentially elastic upon gelation. After gelation, if cure temperature is above the glass transition temperature, the system will continue the reaction until completion. On the other hand, if cure temperature is below the glass transition temperature, the system will vitrify. At the early stages of reaction, the shrinkage does not produce any stress because of the flow of the liquid. However, after the critical gel point, the material begins to develop a significant modulus. If there is a constraint on the system boundary, curing stress will be generated due to the crosslinking shrinkage during reaction. It was reported that the residual stresses due to the cure shrinkage may contribute up to 30% of the total residual
stresses. Hence, cure stress can not be neglected when modeling isotropic stresses [66].

There are several constitute relationships proposed in attempts to model the stress evolution during curing process.

Plepys and Farris [67-68] utilized incremental linear elastic (ILE) constitutive equation to calculate the residual stresses directly during cure for thermosetting materials polymerizing under conditions of dimensional constraint. ILE is based on the linear thermoelasticity that is modified to include the volumetric changes associate with polymerization and written in incremental (or differential) form, as shown by equation (2.1):

\[
E(T, p)\frac{d\sigma_y}{d\varepsilon_y} - \delta_y \left[ \alpha(T, p) dT - \tau(T, p) dt \right] = \left[ 1 + \nu(T, p) \right] d\sigma_y - \delta_y \nu(T, p) d\sigma_{xx} \tag{2.1}
\]

where \(d\sigma_y\) is incremental stress, \(d\varepsilon_y\) is incremental strain, \(E(T, p)\) is modulus as a function of temperature and extent of reaction, \(\alpha(T, p)\) is thermal expansion coefficient as a function of temperature and extent of reaction, \(dT\) is temperature increment, \(dt\) is time increment, \(p\) is extent of reaction, \(\tau(T, p)\) is linear rate of shrinkage due to reaction as a function of temperature and extent of reaction, \(\nu(T, p)\) is Poisson’s ratio as a function of temperature and extent of reaction, and \(\delta_y\) is the Kronecker delta.

If the sample is subjected to one-dimensional constraints, equation (2.1) reduces to:

\[
d\sigma_{11} = -E(T, p)\left[ \alpha(T, p) dT - \tau(T, p) dt \right]
\]

\[
(\sigma_{22} = \sigma_{33} = 0, \sigma_{11} = 0)
\]
For a two-dimensionally constrained sample, the stress in the constrained directions is given by:

\[ d\sigma_{11} = d\sigma_{22} = \frac{-E(T, p) [\alpha(T, p) dT - \tau(T, p) dt]}{1 - v(T, p)} \]  

\[(d\sigma_{33}=0, d\varepsilon_{11}= d\varepsilon_{22}=0)\]

For a three-dimensionally constrained sample, the stress is the following equation:

\[ d\sigma_{11} = d\sigma_{22} = d\sigma_{33} = \frac{-E(T, p) [\alpha(T, p) dT - \tau(T, p) dt]}{1 - 2v(T, p)} \]

\[= -K(T, p) [3\alpha(T, p) dT - 3\tau(T, p) dt] \]  

\[(d\varepsilon_{11}= d\varepsilon_{22}=d\varepsilon_{33}=0)\]

They have found that dynamic cure can resulted in lower residual stress than isothermal cure due to thermal expansion during the heating ramp compensates for some of the shrinkage that occurred during cure. They also showed that one-dimensional cure stresses were generally small in comparison to thermal stresses.

Jakob Lange et al [69-71] investigated the residual stress build-up over time during curing and on cooling in thermoset films. According to the cure temperature, the different constitutive equations were used to calculate the residual stress. If the cure temperature is higher than \(T_g\), the system is in the gelled state and the modulus is essentially elastic, and exhibits little time-dependence. Therefore, the incremental linear elasticity can be used to
describe the evolution of cure stress. The prediction is performed incrementally, where each increment of cure shrinkage causes a contribution to the residual stress and the total residual stress is obtained by a summation over the curing process. Below $T_{ge}$, the modeling of stress is complicated by the vitrification process in that stress build-up and stress relaxation both proceed simultaneously. A simple elastic analysis is unable to take the time-dependence into account. So, a viscoelastic stress model was used by taking simultaneous build-up and relaxation of stress into account (shown in equation (2.5)).

\[
\frac{d\sigma}{dt} = 2G_0(t)\frac{dc}{dt} - \sigma - 2\int G_\infty(t)\frac{dc}{dt} \frac{dt}{\tau(t)}
\]

(2.5)

where the first term is the stress production and the second is the viscoelastic decay. $G_0(t)$ is the instantaneous (unrelaxed) shear modulus, $G_\infty(t)$ is the relaxed shear modulus, $\tau$ is the relaxation time, $dc$ is the shrinkage.

Adolf and Martin, et al [65, 72-74] stated that most calculations ignore stresses generated during cure. A general temperature and state-of-cure dependent viscoelastic constitutive model (equation (2.6)) was developed to calculate the evolution of stresses in crosslinking polymers.

\[
\sigma = 2\int_x ds \left[ G_x \left( \int_0^{\frac{du}{T(u)}} \right) + \psi \left( T, s \right) \right] \frac{d}{dt} \left( \frac{1}{3} tr\gamma \right) I + \int_x ds K \left( \int_0^{\frac{du}{T(u)}} \right) \psi \left( T - T_0, I - \phi \left( p - p_{st} \right) \right) I
\]

(2.6)
where $G(t) = G_d(t) + G_s$ is the shear modulus, $K(t)$ is the bulk modulus, $\gamma$ is the strain tensor, $p$ and $T$ are the extent of reaction and temperature, $T_0$ is the temperature at the gel point $p_{gel}$ and $I$ is the identity tensor. $\psi$ is a constant equal to the product of the glassy bulk modulus, $K_g$, and the glassy volumetric coefficient of thermal expansion, $\alpha_g$ (both independent of extent of reaction). $\phi$ is also a constant equal to the product of the rubbery bulk modulus, $K_r$, and the total volumetric strain due to cure alone, $\Delta V_{rxn}$ (which is negative in sign). The four terms in equation (2.6) represent stresses arising respectively from imposed shear strains, imposed bulk strains, thermal expansion (or contraction) strains, and cure shrinkage strains. They suggested that if the goal is to minimize the stress at the final cure temperature then the final cure temperature should exceed the glass transition temperature of the fully-cured polymer. In this case, the rubbery modulus will determine the final stress level, rather than the much higher glassy modulus. However, this exacerbates the thermal stresses upon cool-down.

A thermo-viscoelastic model [66, 75] was reported for calculating the residual stress involved in both viscoelasticity and the effects of shrinkage due to cure and subsequent cooling. The equation (2.7) describes the time, temperature and conversion dependence of the shear modulus using the Maxwell elements.

$$K(t,T,x) = K_r + \left[ K_g - K_r \right] \sum_{i=1}^{\infty} g_i e^{-t/(\tau_i)}$$  (2.7)

where $K_r$ and $K_g$ are the rubbery and glassy values of the bulk modulus, both of which are assumed to not be a strong function of temperature or conversion, and $t$ is time. $\tau_i$ is the $i$th relaxation time and $g_i$ is the weighting factor for the $i$th relaxation time, such that $\sum g_i = 1$. 

\[ \text{EQUATION} \]
1.0. $\sigma_{T;x}$ is shift factor. Given the assumed dependence of the bulk modulus on time, temperature and conversion, the residual stresses can be calculated according equation (2.8) during and after cure:

$$\sigma_{res} = - \int_{t'}^{t} K(t', T, x) \left( \frac{1}{V} \frac{dV}{dx} \frac{dx}{dt} + \frac{1}{V} \frac{dV}{dT} \frac{dT}{dt} \right) dt$$

(2.8)

where $V$ is in specific volume, $dV/dx$ is taken to be a constant associated with the change in volume due to a unit change in conversion, $t-t'$ is the time from which a strain is applied, $dx/dt$ is the rate of reaction given by the cure kinetics, $dV/dT$ is the thermal expansion coefficient, $dT/dt$ is the heating rate. Integration is performed only after gelation. The model has been applied to predict the evolution of residual isotropic stresses in three-dimensionally constrained thermosetting materials.

2.5 Adhesion

As can be seen from the assembly of flip chip interconnects using NCAs, there are several interfaces, including adhesive/passivation, adhesive/substrate, adhesive/bump and adhesive/pad and these interfaces might be the weak locations for potential delamination. Therefore, it is very necessary to understand the adhesion strength and the bonding mechanism between the adhesive and the adherent. There are several adhesion theories available to explain the adhesion phenomenon. The adhesion mechanism include: adsorption theory, mechanical interlocking, electrostatic attraction, diffusion theory, chemical bonding. However, it should be emphasized that, depending on a specific case of the surfaces involved, different mechanisms may be involved in adhesive bonding, and no unified theory can apply to all cases.
2.5.1 Adsorption Theory

The adsorption theory states that adhesion is due to the intimate interatomic and intermolecular attractive forces between adhesive and adherent. These attractive forces may be ascribed to van der waals forces, hydrogen bonds. This adhesion mechanism has been experimentally demonstrated in many adhesive joints [76-77]. In order to obtain good adsorption, good wetting is essential and can reach the intimate contact.

2.5.2 Mechanical Interlocking

This theory points out that surfaces on a microscale are very rough. Therefore, when a liquid adhesive is dispensed between two surfaces, it penetrates into the crevices and pores and then solidifies. Thus, the surface layers on both sides interlocks with each other and provides a mechanical bond. Therefore, the bonding strength is unlikely to be very high in transverse tension, but the strength in shear may be significant dependent on the degree of roughness [76-77]. Roughness or an increase in the surface results in increased mechanical interlocking of the adhesive to the adherend. Although experiments do demonstrate improved adhesion associated with the roughening process, it is thought that this mechanism is only partially responsible for the adhesion in the cases involving the adherend surface having characteristics that are conducive to mechanical interlocking. The mechanical interlocking mechanism must have a certain effect on the strength of an adhesive bond, based on the facts that adhesive bonding formed on roughened surfaces are typically stronger (with all other factors being equal), as compared to well polished surfaces. However, the strength with a mechanical interlocking bonding is lower than that of a chemical bonding. Pure mechanical interlocking is not enough in most cases.
2.5.3 Electrostatic Attraction

The electrostatic theory states that electrostatic forces are formed in the form of an electrical double layer at the interface and are considered to be a contributing factor in the resistance of debonding of the adhesive and the adherent. Thus, the adhesive bond in this case can be related to a charged capacitor, with the adhesive strength described in terms of the force that is required to separate the plates of the capacitor. The strength of the interfaces will depend on the charge density. However, this attraction is unlikely to make a major contribution to the final bond strength of the interface. Adhesives and adherends containing polar molecules or permanent dipoles are probable to form such electrostatic bonding.

2.5.4 Diffusion Theory

Diffusion is operational in the case of bonding between polymers having mutual solubility. So this theory requires that both the adhesive and adherend are polymers, which are capable of movement and are mutually compatible and miscible. The bonding is formed between the two surfaces by the diffusion of the polymer molecules on one surface into the molecular network of the other surface. The bonding strength will depend on the amount of molecular entanglement and the number of molecules involved. However, the diffusion theory may not be applicable where the polymer and adherend are not soluble or the chain movement of the polymer is constrained by the highly crosslinked, crystalline structure or when under glass transition temperature.

2.5.5 Chemical Bonding

The chemical bonding mechanism suggests that primary, chemical bonds may form across the interface. Chemical bonding is strong and may make a significant contribution
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to the intrinsic adhesion in some cases. The chemical reaction at the interface is of particular interest for polymer matrix composites because it offers the major explanation for the use of coupling agents on the substrate [78]. The bond energy in physical bonding is approximately 8-16 kJ/mol, chemical bonding, on the other hand, involves primary forces and the bond energy in the range of approximately 40-400 kJ/mol [76].

2.6 Effect of Moisture on Adhesive and Adhesion

The flip chip system using NCAs may be exposed to various environmental conditions during their service life. The performance of the adhesive systems may deteriorate to a certain extent upon exposure to harsh environments for a certain period of time. Moisture/water is the most commonly encountered service environment, and must be considered a critical factor in determining the long-term durability of adhesively bonded joints. The moisture/water will not only weaken the cohesive strength of adhesive, but also damage the bonding strength of various interfaces.

2.6.1 Effect of Moisture on Adhesive

Moisture absorbed in a polymer matrix can lead to a wide range of effects. Some effects on the polymeric materials are reversible and can be erased on removal of water. Others are irreversible and result in permanent changes in the performance of polymers. Water absorption into polymer materials can cause plasticization and swelling, which are both reversible processes. Water acting as a plasticizer can depress the $T_g$ of the polymer matrix and reduce the strength and modulus of the adhesive. Many studies [79-85] have also shown that water causes permanent chemical and physical changes.

2.6.2 Effect of Moisture on Adhesion
Chapter 2 Literature Review

Water can also weaken the strength of adhesive joints by attacking the adhesive/substrate interface. It has been proposed that there must be a critical water concentration within the adhesive layer below which environmental attack on the adhesive joint does not occur. For an epoxy system, it is estimated that the critical water concentration is about 1.35%-1.45%, and the critical humidity is around 50-65% [86-87].

Lefebvre et al [88] discovered in their study of an epoxy/glass model system that the critical humidity was around 70% RH, at which point an abrupt loss of adhesion, a sudden increase in water solubility and swelling in the epoxy, and a decrease in the mobility of dissolved water occur. They attributed these phenomena to chemical reactions between adsorbed water molecules and the OH groups of the polymer, which cause the breaking of inter-chain hydrogen bonds and displacing adsorbed OH groups from the surface of the substrate, as well as result in other observed changes.

Several mechanisms have been proposed to explain the degradation of the adhesive joint interface due to water absorption, though no single mechanism is applied to explain all the failure phenomena. Gledhill and Kinloch [89] suggested that for adhesive joints, the intrinsic stability of the adhesive/substrate interface in the presence of an absorbed liquid may be evaluated from a consideration of the thermodynamic work of adhesion. Usually, the work of adhesion for a dry adhesive/substrate has a positive value, indicating thermodynamic stability of the interface. However, the introduction of water may induce a negative value of the work of adhesion, which indicates that the interface is unstable and the adhesive may be easily displaced from the substrate by water. Water can also chemically degrade the interface by interacting with the adhesive and the substrate or probably chemical bonds across the interface. It has been observed by many researchers...
that the presence of water/moisture can hydrolyze aluminum oxide and result in the formation of a hydrated oxide layer between the underlying substrate and the adhesive, which is mechanically weak and is the failure location in many adhesive joints. Studies have suggested that a boundary layer of adhesive exists adjacent to the substrate surface and this boundary possesses a different physical and chemical structure such as lower crosslink density [93] or a lower concentration of filler particles [94]. Brockmann et al [95] proposed that the mechanism of environmental attack through hydrolysis of this boundary layer of the adhesive might be important for aluminum alloy joints, though most researchers currently suggest that water attack on the metal oxide layer is a more likely failure mechanism of adhesive joints. In some circumstances, substrate corrosion may occur in adhesive joints and act as a factor that weakens the performance of the adhesive joint. Examples for gross corrosion have been reported for rubber/steel joints exposed to seawater or salt-spray [96] when an electrochemical potential is present and also in electrically conductive adhesive joints where the conductive adhesive is bonded to the non-noble metal surface [97-98].

2.7 Viscoelastic Relaxation of NCAs

NCAs are viscoelastic materials, which exhibit both elastic and viscous behaviors. As a result of their viscoelastic nature, NCAs exhibit behavior during deformation, which is both temperature and time (frequency) dependent. The deformation is reversible but time dependent and associated with the distortion of polymer chains from their equilibrium conformations through activated segment motion involving rotation about chemical bonds. For example, if cured NCA is subjected to a constant load, the elastic modulus exhibited by the material will decrease over a period of time. This occurs because the polymer under a load undergoes relaxation or molecular rearrangement in an attempt to minimize
localized stresses. In an NCA joint, the stress relaxation over time will result in the degradation of contact pressure and thus increase the contact resistance or even cause complete loss of electrical contact.

2.7.1 Measurement of Viscoelastic Relaxation Behavior

Dynamic mechanical analysis (DMA) is one of the best thermal analysis techniques for using this time/temperature predictive approach. This technique involves subjecting the material to some type of forced periodic stress or strain oscillation, and measuring the corresponding response as a function of the frequency of the oscillation. These tests measure a complex modulus – for example $E^*(\omega)$, which is composed of two components, one $E'(\omega)$, in phase with the forced oscillation, and the other, $E''(\omega)$, out of phase with the forced oscillation. The relationship between these components is:

$$E'(\omega) = \sqrt{E'^2(\omega) + E''^2(\omega)}$$  \hspace{1cm} (2.8)

The in-phase component, $E'(\omega)$, is called the storage modulus (stiffness) and is a measure of the ability of a viscoelastic material to store energy. The out-of-phase component, $E''(\omega)$, is called the loss modulus and is a measure of the ability of the material to dissipate energy. The ratio of the two components defines a frequently used quantity, called the loss tangent:

$$\tan \delta = \frac{E''(\omega)}{E'(\omega)}$$ \hspace{1cm} (2.9)

During the process of characterizing the mechanical response of a viscoelastic material as a function of time, one finds that complete characterization requires information obtained from experiments conducted over a very broad time scale. For most polymeric materials (particularly amorphous or semicrystalline polymers) this range is of the order of 10 to 14 decades of time. To experimentally obtain such data is not inconceivable, but it is highly
impractical. Therefore, a satisfactory method of extrapolation is obviously a matter of great importance. Time-temperature superposition principle or the method of reduced variables is one of the most widely used methods to project long-term properties under a variety of conditions and shall be further discussed.

2.7.2 Time-Temperature Superposition

As discussed earlier, the viscoelastic functions of materials depend on temperature, as well as time. As such, the relaxation function may be written as:

\[ E = E(t, T) \]  \hspace{1cm} (2.10)

The underlying basis for time/temperature superpositioning is the demonstrated equivalency between time (or frequency) and temperature. It has been demonstrated that viscoelastic data collected at one temperature can be superimposed upon data obtained at a different temperature simply by shifting one of the curves along the time (or frequency) axis.

The superposition principle is based upon the premise that an increase in temperature will accelerate molecular relaxation and segmental motion, bringing the system more rapidly to equilibrium and accelerates all types of viscoelastic relaxation processes (see Figure 2.8). The time over which these processes occur can be reduced by conducting the measurement at elevated temperatures and transposing the data to lower temperatures.
If all the processes contributing to the viscoelasticity of the material are accelerated to the same extent by a temperature rise, then a relaxation function of the following form may be obtained:

$$E(t, T) = E(\zeta, T_0)$$

(2.11)

where \( \zeta = \frac{t}{a_T} \) = reduced time

\( a_T \) = shift factor

Thus, viscoelastic changes which occur relatively quickly at higher temperatures can be made to appear as if they occurred at longer times or lower frequencies simply by shifting the data with respect to time (or frequency). Materials that obey the above time-temperature superposition (TTS) are termed thermorheologically simple. In addition, TTS is only valid in the linear visco-elastic region (LVR). Within the LVR, the material structure is maintained in tact (unbroken).

2.7.3 Master Curve and Shift Factor
Viscoelastic data can be collected by performing frequency multiplexing experiments where a material is analyzed at a series of frequencies. By selecting a reference curve and then shifting the other data with respect to time (or frequency), a "master curve" can be generated, as shown in Figure 2.9. A master curve is of great value since it covers times or frequencies outside the range easily accessible by experiment.

\[
T_1 < T_2 < T_r < T_3 < T_4 < T_5
\]

Fig. 2.9 The generation of a master curve.

The degree of horizontal shifting (i.e. time) required to shift a given set of data upon a reference can be mathematically described with respect to temperature. These can generally be described with the following two empirical relations:

### WLF Equation

Polymers tend to follow the well-known empirical Williams-Landel-Ferry (WLF) equation:

\[
\log(a_T) = -\frac{C_1(T - T_r)}{C_2 + (T - T_r)} 
\]  

(2.12)

where

- \( T_r \) = reference temperature (K)
- \( T \) = measurement temperature (K)
- \( a_T \) = shift factor
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C_{1}, C_{2} = constants

For many amorphous polymers, it has been found that C_{1} = 17.4, C_{2} = 51.6 where T_{r} has been taken as the glass transition temperature (T_{g}). The WLF time-temperature superposition has some limitations. Most important is the fact that its applicability is generally limited to a temperature range of T_{g} to T_{g} + 100°C. In addition, it does not directly fit many copolymers, highly crystalline polymers, or polymer composites.

Arrhenius Relation

If the temperature dependent processes obey Arrhenius relation, then the shift factor is given as

$$\ln(a_T) = \frac{E}{R} \left( \frac{1}{T} - \frac{1}{T_{r}} \right)$$

(2.13)

where $E$ = activation energy associated with the relaxation transition

$R$ = gas constant ($R = 8.314$ J/mole °C)

The Arrhenius equation is typically used to describe the viscoelastic events outside the WLF range or the glass transitions associated with semicrystalline polymers. Frequently, it is used to obtain the activation energy associated with the glass transition event.

Fitting the experimentally determined shift factors to a mathematical model permits the master curve to be shifted to any desired temperature. Thus, data that was collected and referenced to a high temperature can be shifted to low temperature and vice versa.
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3.1 Materials

The NCA used in this study was an epoxy based adhesive, XS8436 supplied by NAMICS Japan. It composed of a bisphenol A type epoxy resin and amine system. In the previous research [41-42, 99], the flip-chip assembly process and the reliability under thermal and moisture condition with this material have been studied by NTU and Philips group. It has been show that all the NCA interconnects can pass the minimum requirement of 1000 cycles for temperature cycling as well as the temperature-humidity cycling under JEDEC standard. However, due to the lack of the understanding of the formation process, we are still not able to predict the behavior of the NCA flip chip interconnects. In this condition, a comprehensive research on the formation of NCA flip chip interconnects, which is involved in a very complex polymerization process consisting of cure shrinkage evolution and development of mechanical properties, is strongly needed. Therefore, in order to further understand the material properties and behaviors of the curing process, we choose this material as our main research source. In some situations, other materials were also used for the purpose of comparison and to support the general conclusion for a wide range of applications.

3.2 Experimental Procedures

3.2.1 Cure Kinetics
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The experiments were carried out in a TA Instruments 2010 Differential Scanning Calorimetry (DSC) with an inert nitrogen atmosphere purging the sample cell. The sample size was around 5 mg and sealed in aluminum pans. For isothermal measurements, samples were loaded into DSC cell at room temperature, and then heated to 40°C, which is well below the onset cure temperature at 50°C/min, and kept at this temperature for three minutes for stabilization. After the equilibration, the system was ramped up to the desired cure temperature at 100°C/min and dwelled at this temperature until the chemical reaction was completed. The total area under the exothermic curve was the heat of reaction ($H_I$). After the completion of reaction, the system was cooled to room temperature and then the residual heat ($H_R$) was obtained by heating to 280°C at 10°C/min.

The isothermal cure tests were performed from 120 to 160°C. The degree of cure at time $t$ was defined as

$$\alpha(t) = \frac{H(t)}{H_I + H_R}$$

(3.1)

The curing rate at time $t$ was determined by

$$\frac{d\alpha}{dt}(t) = \frac{dH(t)/dt}{H_I + H_R}$$

(3.2)

For dynamic cure measurements, samples were kept at -50°C for equilibration and then heated to 280°C at ramp rates between 5 and 20°C/min.

3.2.2 Rheological Measurement
To measure the gelation point of NCAs, ARES rheometer equipped with a dual range force rebalance transducer was utilized in the parallel plates geometry (disposable plates of diameter 25 mm, and 1 mm sample thickness), with air convection temperature control (accuracy ±0.1°C). The temperature of the sample was measured by inserting a thermocouple probe inside the rheometer shaft. The plates were zeroed at the test temperature to ensure that the gap between the plates is consistent and the uncured adhesive was placed in between the plates with a gap of 1 mm. Multiple waveform dynamic tests for determining the gel point with a single measurement were performed from 80°C to 100°C. This consists of performing simultaneous time sweeps at different frequencies for a given temperature. The applied strain amplitude is 1% that is within the linear viscoelasticity (1% to 20% [49]) for each frequency.

In fact, with this technique, the multiwave strain generation is based upon the Boltzmann superposition principle which, in simplified terms, states that two or more mechanical waves can simultaneously pass through a curing material independent of each other. Since each wave acts independently, the total linear strain, $\gamma$, applied on the sample is the sum of several independent strains, each described by its corresponding Fourier series:

$$\gamma = \sum_{i=1}^{n} \gamma_i \sin(\omega_i t)$$

$$\omega_i = \omega_f$$

$$\omega_i = \omega_f$$

$$\omega_i = \omega_f$$

$$\sum_{i=1}^{n} \gamma_i \leq \gamma_e$$

The frequencies $\omega_i$ chosen are the harmonics of a fundamental frequency $\omega_f$. The strain relation (Equation 3.3) expresses the requirement that the sum of the individual strain...
amplitudes stays below a critical amplitude $\gamma_c$ corresponding to the linear viscoelastic limit. From the stress response to this compound strain, the individual stresses at each discrete frequency can be obtained by means of a discrete Fourier transform. This combined information on the latter leads to the determination of the gel point. In this study, a total of three wave forms (1.0, 5.0, 10.0 Hz) were used to create the composite strain input. After the gelation had been determined, the experiments were repeated and terminated at time to gelation ($t_{gel}$). These partially cured adhesives were then subjected to DSC scans to determine the degree of cure ($\alpha_{gel}$) from the residual heat according to the cure kinetics study described above.

3.2.3 Cure Shrinkage Measurement

Volumetric shrinkage of a typical thermosetting resin occurs during the curing process because molecules move from a van der Waals distance of separation to a covalent distance of separation. Whether cure shrinkage has detrimental or beneficial effect on the system, is strongly dependent on the system. For the molding compound or underfill used in solder-bumped flip chip interconnects [100], cure shrinkage should be minimized because the residual stress might cause the delamination and warpage of the package. For the flip chip interconnects using electrically conductive adhesive, on the other hand, the cure shrinkage plays a very important role during the conductivity establishment [55-57]. Particularly for the flip chip interconnects using NCAs, the cure shrinkage of the adhesive is critical for the formation of the final compressive stress of contacts between the bump and the pad. Moreover, the conductivity of flip chip interconnects using NCAs is strongly dependent on the compressive stress. Therefore, it is essential to investigate the evolution of cure shrinkage during the curing process.
In this study, a simple method of using Thermomechanical Analyzer (TMA) to measure the cure shrinkage of NCAs was developed. This method will overcome the shortcomings of using dilatometer and show the less labour intensive advantage than the buoyancy technique. Furthermore, this novel testing method is able to provide reliable and accurate results and eliminate the concern of using contact method.

Fig. 3.1 shows the schematic diagram of the measurement setup by means of TMA. The sample preparation is simple, yet crucial for the measurement accuracy. First TMA was used to measure the thickness of the two silicon covers, with 7 mm x 7 mm square dimensions, at room temperature. A very small amount of NCA was dispensed at the center of the bottom silicon covers and sandwiched between the two silicon covers. A uniform adhesive layer with very thin thickness (around 10-20 µm, depending on the applied force and the amount of adhesive), can be obtained by rubbing the two silicon covers carefully. In order to prevent the adhesive from squeezing out, the amount of adhesive should be no more than 5 mg. Sample with uniform adhesive layer was then placed on the sample platform of TMA. The thickness of the adhesive layer can be determined by measuring the total thickness of the sandwiched sample. The measurement of thickness change was conducted under isothermal cure. A two-step cure profile with heating rate 10°C/min from room temperature to 60°C and 5°C/min from 60°C to the desired curing temperatures (90°C, 100°C and 110°C) was utilized to reduce the temperature overshoot problem. DSC scans with the same two-step cure profile were performed to make a comparison between TMA cure process and DSC. In order to study the effect of applied load and weight of silicon cover on the testing results, the load of 0.005N and 0.05 N were applied to the probe. Five samples were used for each testing condition.
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3.2.4 Shear Storage Modulus Measurement

It has already been established that the cure stress build-up is governed by the shear modulus and cure shrinkage. Dynamical mechanical analyzer was always used to measure the mechanical properties during the curing process. However, there are two problems associated with the method [101]. Firstly, due to the mechanical sensitivity of the transducer, the loads required to measure the mechanical properties, e.g., storage and loss moduli, are dominated by the sample support rather than the resin itself during the early stage of curing. Secondly, when curing enters into the vitrification stage, it is very difficult to accurately detect the high load or small deformation involved in determining the mechanical properties in glassy state. Therefore, a multi-step force technique was used to measure the mechanical properties which could be accurately detected from the liquid state to the glassy state.

RheoStress 300 from HAAKE with two parallel plates with diameter 10 mm was employed to measure the evolution of mechanical properties. The plates were zeroed to ensure that the gap between the plates is consistent and the uncured material was placed...
in between the plates with a gap of 1 mm. The testing was conducted in oscillation mode with a frequency of 1 Hz. Three stress amplitudes (20, 50 and 100 Pa) were applied to the different cure stages or cured states. With the increase of mechanical properties, the stress amplitude was increased to result in a detectable deformation. The duration of different stress amplitudes varied with different cure temperatures. The isothermal cure tests were performed from 90 to 160°C.

3.2.5 Cure Stress Measurement

Understanding and quantitative description of cure stresses are crucial for the conductivity establishment of NCA flip chip interconnects. Several methods have been developed to measure the build-up of cure stress for thermosetting polymers. These include beam-bending technique [69-70], steel ring method [102], thin-walled tube [66, 72], thick-walled tube [103], instrumented sphere method [104], etc. However, the above methods cannot measure the cure stresses directly and cure stresses have to be computed based on the measured strain or deflection value. Furthermore, there are other problems such as the effect of the adhesive used for the bonding of strain gauge, the lower resolution which may not be high enough to detect the small cure stresses. Therefore, a novel method which can directly measure the build-up of cure stresses was developed by means of DMA.

Fig. 3.2 shows the experimental set-up for the direct cure stress measurement. DMA experiments were performed using a TA Instruments Q800 dynamic mechanical analyzer (DMA) (Fig. 3.2 (b)). NCA was dispensed between two quartz rods with a diameter 3 mm and length of 15 mm as seen in Fig. 3.2 (a). The thermal tape is used to help to maintain
the iso-strain. The build up of cure stress was monitored using the DMA operated in the tension iso-strain mode. The detailed experimental procedures are as follows:

(a) Schematic view of quartz rod method by using DMA
(b) Q800 DMA
(c) Experimental set-up for cure stress measurement
(d) Cured quartz rod samples

Fig. 3.2 Experimental set-up for cure stress measurement by means of DMA and sample preparation.

Testing procedures:

1. Place the thermal tape between the fixed clamp and moveable clamp (force probe).
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2. Mount the quartz rods at the fixed clamp and moveable clamp, respectively. And control the gap of the two rods around 1 mm.

3. Use a needle to dispense the adhesive in between the two quartz rods.

4. Run the testing by using the iso-strain method with a magnitude of 0.1% strain.

The measurement was conducted under isothermal cure. DMA temperature chamber may need a long time to equilibrate because of its larger size compared with TMA. Therefore, we utilized a three-step cure profile that is different from TMA. The samples were tested at a heating rate 5°C/min from room temperature to 80°C and then held isothermally for ten minutes. Finally, the samples were heated again with a heating rate 2°C/min from 80°C to the desired curing temperatures (90°C, 100°C and 110°C).

3.2.6 Contact Resistance Measurement

In order to establish the relationship between the cure force obtained during the cure process and the electrical contact resistance, eventually, the mechanical compressive stress formed during the cure process has to be translated to the electrical contact resistance for practical interpretation and to investigate the reliability of flip chip interconnects with NCAs. Therefore, the evolution of the electrical conductivity which could reflect the impact of cure stress and thermal stress should be monitored during the curing process. In these studies, an experimental set-up which can conduct in-situ measurement of the development of contact resistance during the bonding process of test chips was developed by using a microforce tester combined with a 4-wire resistance measurement system.

3.2.6.1 Fabrication of Test Chip and Substrate
Chapter 3 Experimental Materials, Procedures, Modeling & Simulation

The chips and substrates used are the same structure and fabricated on 8 inch Si wafers at IME cleaning room. In order to be able to align the chip with substrate easily and accurately, the test chips & substrates with single bump have been fabricated with a 2 mm diameter and 20 μm height. The test chips with single bump as shown in Fig. 3.3 were fabricated according to the following procedures:

1. USG 2000 A deposition of silicon wafer
2. Sputtering of a Ti/Cu blanket layer with a thickness of 1000 A
3. Silicon nitride deposition with a thickness of 1000 A
4. Photoresist deposition with a thickness of 15 μm and development of photoresist
5. Silicon nitride etch
6. Electrical plating of Cu
7. Strip of photoresist
8. Dicing of test chip with a dimension of 30×7 mm

Fig. 3.3 Schematic view of the cross-section of test chip.

3.2.6.2 In-situ Contact Resistance Measurement Set-up

Fig. 3.4 shows the experimental set-up for the in-situ resistance measurement of NCA flip chip interconnects with a test chip and substrate. Instron 5848 microforce tester with the load control mode was used to apply a 10 N load by using a 50 N load cell. It has a position control resolution better than ± 0.05 micron and load measurement accuracy of at least 0.2% of the load cell capacity. A four wire resistance measurement system which
has high resolution was used to measure the evolution of contact resistance during the bonding process. The detailed experimental procedures are as follows:

Testing procedures:

1. Sample preparation (Fig. 3.4 (c))
2. Align the probe with the bump of the substrate (Fig. 3.4 (d))
3. Mount the substrate on the platform inside the temperature chamber
4. Dispense the NCA around the bump
5. Align the chip with the substrate
6. Start the resistance measurement system and simultaneously apply a 10 N load at a speed of 1 N/min on the top of chip and enable the electrical conduction between the chip and substrate
7. Equilibrate at 10 N for 10 minutes and then start the temperature chamber at a heating rate 5°C/min to the desired temperature
8. Hold the temperature for a certain duration and then cool down to the room temperature
9. Remove the applied load

For the purpose of baselining the measurements, a test run was performed with the same procedures except without dispensing the adhesive in between the chip and substrate. The in-situ measurement of resistance during the curing and cooling process gives a clear indication between the evolution of resistance and the build up of contact force.
(a) Schematic view of experimental set-up for the in-situ contact resistance measurement.

(b) Experimental set-up combining microforce tester with resistance measurement system
3.2.7 Adhesion Strength Measurement

Since the electrical conductivity relies entirely upon the mechanical contact between the bump and pad, the requirements of mechanical and rheological properties for the non-conductive adhesive used in the adhesive interconnects are more stringent than the underfill materials used in the traditional solder flip chip. According to the previous research, many researches have used die shear test to investigate the adhesion strength of underfill with die and substrate. It has been reported that the adhesion strength decreased with the increase of test temperature and degraded after aging in a high temperature and high humidity environment [105]. It was revealed that the adhesion strength could be enhanced by the addition of silane coupling agents [106] or other adhesion promoters [107]. It was also found that the adhesion strength between the die passivation layer and the underfill was stronger than that between the underfill and substrates. However, there are limited reports [108-109] on the study of the evolution of the adhesion strength during the curing process. Due to the difficulty in controlling the shear height [110] that could affect the shear force and the premature fracture caused by the possible bending of the
substrate under shear strength in a die shear test, the single lap tensile joint, which was regarded as the most convenient method for testing the quality of adhesive bond [111], was used in this work for testing the adhesion strength between the non-conductive adhesive and the substrate with solder mask.

Substrates used for the adhesion test were made up of bismaleimide triazine (BT) epoxy, 0.03 μm electroless Au, and standard Ball Grid Array (BGA) solder mask materials. Surface pretreatment is a very important step governing the quality of an adhesive joint. In order to minimize the influence of the moisture and contaminants on the surface, the substrates were baked at 125°C for 24 hours followed by plasma cleaning prior to sample preparation. The schematic diagram of the test specimen is shown in Fig. 3.5. The lap joint specimens were prepared according to the ASTM standards D1002. The dimensions of the substrates were 25 mm in length and 5 mm in width. The overlap length between the two substrates was 5 mm. A silicon spacer was used to control the adhesive thickness at 0.4 mm. The samples were clamped together and put into the oven for curing. For ease of control of the curing process, curing was performed at 90°C for different durations. As soon as the curing was completed at the desired time, the sample was taken out for shear testing. The shear test was conducted on Instron 5567 in tension mode at a tensile speed of 1 mm/min. After the shear test, DSC was used to measure the residual heat of the adhesive and then the degree of cure can be calculated as mentioned above. Five samples were used for each testing condition.
3.3 Modeling & Simulation

3.3.1 Autocatalytic Model

In order to predict the degree of cure at any time for a given temperature, several phenomenological models have been proposed. The simplest one is the $n^{th}$ order kinetics equation:

$$\frac{d\alpha}{dt} = k(T)(1 - \alpha)^n$$  \hspace{1cm} (3.5)

where $n$ is the reaction order and $k(T)$ is the temperature dependent rate constant which obeys the Arrhenius relationship:

$$k(T) = k_0 \exp\left(-\frac{E}{RT}\right)$$  \hspace{1cm} (3.6)

where $k_0$ is the Arrhenius frequency factor, $E$ is the activation energy, $R$ is the universal gas constant. The cure kinetics can also be expressed using the autocatalytic model as:

$$\frac{d\alpha}{dt} = (k_1(T) + k_2(T)\alpha^m)(1 - \alpha)^n$$  \hspace{1cm} (3.7)

where $k_1(T)$ and $k_2(T)$ are rate constants; $m$ and $n$ are reaction order. If the initial reaction rate is zero, the equation can be simplified as:

---

Fig. 3.5 Schematic diagram of lap joint sample preparation.
Chapter 3 Experimental Materials, Procedures, Modeling & Simulation

\[ \frac{d\alpha}{dt} = k(T)(1-\alpha)^n \alpha^m \]  \hspace{1cm} (3.8)

From the equations above, the overall reaction rate can be expressed as a function of temperature and degree of cure:

\[ \frac{d\alpha}{dt} = k(T) f(\alpha) = k_0 \exp(-\frac{E}{RT}) f(\alpha) \]  \hspace{1cm} (3.9)

By integrating equation (3.9), the function of degree of cure can be obtained:

\[ F(\alpha) = \int_{0}^{\alpha} \frac{d\alpha}{f(\alpha)} = k_0 \exp(-\frac{E}{RT}) \]  \hspace{1cm} (3.10)

By taking the natural logarithm, the equation can be expressed as:

\[ \ln t = \ln(\frac{F(\alpha)}{k_0}) + \frac{E}{RT} \]  \hspace{1cm} (3.11)

It can be seen from equation (3.11) that the time necessary to reach the degree of cure can be determined at the desired dwell temperature for a given degree of cure.

In these studies, the autocatalytic model (equation (3.8)) was used as the kinetic equation to describe the curing process.

3.3.2 Isothermal Cure Simulation by Dynamic Cure

In order to correlate the isothermal method with the dynamic, it is assumed that the reaction rate equation (3.9) is still valid for dynamic cure measurements. Therefore, the equation can be rearranged as:

\[ \frac{d\alpha}{dt} = \frac{d\alpha}{dT} \frac{dT}{dt} = \beta \frac{d\alpha}{dT} = k_0 \exp(-\frac{E}{RT}) f(\alpha) \]  \hspace{1cm} (3.12)

where \( \beta \) is heating rate. By integrating equation (3.12), the equation can be expressed as:

\[ F(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{k_0}{\beta} \int \exp(-\frac{E}{RT}) dT \]  \hspace{1cm} (3.13)
Chapter 3 Experimental Materials, Procedures, Modeling & Simulation

According to the reference [112], the integral equation (3.13) can be expressed by means of polynomial form and rearranged as:

\[
\log \beta = \log \left( \frac{k_c E}{F(\alpha) R} \right) - 2.315 - 0.4567 \frac{E}{RT} \tag{3.14}
\]

As can be seen from equation (3.14), there is a linear relationship between the logarithm of the heating rate and the reciprocal of temperature. As such, from the plot of \(\log \beta\) versus \(1/T\) for a given degree of cure, the activation energy and \(\log (k_c E/F(\alpha) R)\) can be obtained from the slope and intercept, respectively. Therefore, the value of the intercept \(\ln(F(\alpha)/k_0)\) and the slope \(E/R\) of equation (3.11) can be determined by these two results. Consequently, the dynamic measurement can be used to describe the isothermal cure behavior.

3.3.3 Cure Stress Modeling

To date, most of the work reported only on the theoretical approach for calculating cure stresses on the basis of elasticity or viscoelasticity, there has been little work to simulate the evolution of cure stress. In some cases, we are much more interested in the evolution of stress as well as the distribution of stresses. As stated by Martin and Adolf [74], cure stress calculations must be done with finite element codes because many real applications involve complex geometries (e.g., electrical circuits). In addition, in the case of complex boundary conditions, finite element analysis is an effective way, while theoretical and direct experimental approach may not be readily carried out. Curing is a very complex phenomenon and one tends to think that it ought to be described with a very complicated model. On the other hand, many material parameters are needed and also require complex characterization techniques which are difficult to obtain. Also the propagation of errors may lead to little practical values [65]. A balance need to be struck. Indeed, the best solution is one that is the simplest yet adequate for the job. Therefore, in order to make
the complex cure-induced stress issue simple, we developed a thermal-cure analogy method by introducing a new physical property - coefficient of cure shrinkage (CCS) - whose definition will be presented in the following chapter.

**Thermal-cure Analogy**

Fig. 3.6 shows the experimental procedures for the characterization of material properties during the curing process. The evolution of mechanical properties was measured with rotational parallel plate rheometer. Therefore, modulus as a function of degree of cure can be determined based on the cure study with DSC. In addition, the cure shrinkage was measured by means of TMA and thus the relationship between cure shrinkage and degree of cure was established. The detailed procedures for both the modulus and cure shrinkage measurement can be found in the previous sections.

(a) Characterization of the build-up of storage modulus. Combining rheometer measurement and cure kinetics study with DSC can yield an evolving storage modulus as a function of degree of cure.
(b) Characterization of cure shrinkage. Combining the measurement of dimension change by means of TMA and cure kinetics study with DSC can yield a linear relationship of cure shrinkage and degree of cure.

Fig. 3.6 Schematic drawing of the experimental procedures for the characterization of material properties to establish a finite element simulation methodology based on thermal-cure analogy.

A linear relation between the degree of cure and cure shrinkage after gelation point was found as can be seen from Figure 3.6. It is this linearity that endorses the use of a single physical parameter, the coefficient of cure shrinkage (CCS ($\gamma$)), to characterise the rate of cure shrinkage of a material. Mathematically, cure shrinkage strain can be defined as:

$$\delta(p) = \gamma \cdot p \quad (3.15)$$

Therefore, a simple thermal-cure analogy has been developed (Table 3.1) so that cure-mechanical modeling can be performed using the thermo-mechanical function of any FEA software. Degree of cure ($p$) and CCS ($\gamma$) in the cure process are analogous to temperature and CTE in the thermal-mechanical finite element modeling respectively.
Chapter 3 Experimental Materials, Procedures, Modeling & Simulation

Thereby, the storage modulus as a function of degree of cure could be analogous to the function of temperature.

Table 3.1 Thermal-cure analogy for cure-mechanical modelling

<table>
<thead>
<tr>
<th>Properties</th>
<th>Thermal</th>
<th>Cure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Field variable</td>
<td>Temperature, $T$</td>
<td>Degree of cure, $p$</td>
</tr>
<tr>
<td>Coef. of thermal expansion</td>
<td>$CTE, \alpha$</td>
<td>$CCS, \gamma$</td>
</tr>
<tr>
<td>Storage modulus</td>
<td>$E(T)$</td>
<td>$E(p)$</td>
</tr>
</tbody>
</table>

Through the analogy, we convert the complex curing process to simple thermal-mechanical process. Therefore, we can easily utilize the thermal-mechanical function of commercial finite element software to model the curing process and study the impact of curing on the practical geometries for 2D or 3D.
Chapter 4 Results and Discussion

4.1 Cure Kinetics

4.1.1 Isothermal Cure

Table 4.1 shows the information of cure reaction times according to the DSC heat flow curve at different temperatures including the onset time ($t_{onset}$) when the reaction initiated, peak time ($t_{peak}$) at which the reaction reached the maximum rate and the end time ($t_{end}$) at which the chemical reaction was completed. Heat generated from the reaction is also shown in the table. Fig. 4.1 shows the residual heat measured after the first isothermal cure. It can be seen that complete cure could be achieved for the first isothermal run for cure temperatures beyond 140°C. It is worthwhile to find that with the increase of cure temperature, complete cure can be obtained within a shorter time, but the heat generation decreased. This is because the heat generated at initial stage of reaction could not be recorded at high temperature. The evolution of degree of cure can be determined according to equation (3.1) and the results at different temperature are shown in Fig. 4.2. Fig. 4.3 shows that reaction rate increases with increase of degree of cure and then a maximum of reaction rate occurs. With further increase of degree of cure, the reaction rate will decrease due to the decrease of epoxide group as well as the diminishing of free volume. With increase of temperature, the reaction rate increase. However, as can be seen from the graph due to the limitation of equipment, it is quite difficult to obtain the accurate reaction rate for the fast cure at higher temperature. The figure also shows that the cure reaction of the non-conductive adhesives was very fast if cure at high temperature.
Table 4.1 Variations of reaction time and heat generated at different isothermal cure temperatures

<table>
<thead>
<tr>
<th>$T_{\text{cure}}$ (°C)</th>
<th>$t_{\text{onset}}$ (min)</th>
<th>$t_{\text{peak}}$ (min)</th>
<th>$t_{\text{end}}$ (min)</th>
<th>$H_T$ (J/g)</th>
<th>$H_R$ (J/g)</th>
<th>$H_{\text{total}}$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>4.81</td>
<td>5.41</td>
<td>8.64</td>
<td>278.5</td>
<td>24.85</td>
<td>301.08</td>
</tr>
<tr>
<td>130</td>
<td>4.68</td>
<td>5.05</td>
<td>6.71</td>
<td>306.3</td>
<td>10.5</td>
<td>316.97</td>
</tr>
<tr>
<td>140</td>
<td>4.64</td>
<td>4.91</td>
<td>6.41</td>
<td>283.4</td>
<td>1.97</td>
<td>284.512</td>
</tr>
<tr>
<td>150</td>
<td>4.67</td>
<td>4.84</td>
<td>6.23</td>
<td>277.4</td>
<td>0</td>
<td>277.4</td>
</tr>
<tr>
<td>160</td>
<td>4.61</td>
<td>4.79</td>
<td>6.04</td>
<td>271.9</td>
<td>0</td>
<td>271.9</td>
</tr>
</tbody>
</table>

Fig. 4.1 Residual heat measured with dynamic cure after the first isothermal run.
Fig. 4.2 The degree of cure versus time at different cure temperatures.

Fig. 4.3 Reaction rate versus degree of cure at different cure temperatures.
Chapter 4 Results and Discussion

According to the autocatalytic model (equation (3.8)), the kinetic parameters, \( k(T) \), \( m \) and \( n \), can be estimated by fitting the isothermal data. Values of these parameters are shown in Table 4.2. With knowledge of the cure process at several isothermal temperatures and having developed the temperature dependence of the kinetic parameters, the reaction rate and degree of cure at any given temperature and time can be predicted using this autocatalytic model. Fig. 4.4 and Fig. 4.5 show the reaction rate versus time and degree of cure at different isothermal cure temperatures, respectively. It is obvious from the comparison of experimental and the autocatalytic kinetic model prediction that if the cure temperature is below 140°C, a good agreement between the kinetic model prediction and experimental result was demonstrated for certain duration, after which the divergence was shown. The reason for this deviation could be ascribed to the occurrence of vitrification transformation and as such the reaction rate was significantly retarded due to the change of cure behavior from chemical reaction dependence to diffusion controlled reaction.

As mentioned earlier, if the cure temperature is above \( T_g \), the material does not vitrify. However, it is more appropriate to think of \( T_g \) as a region with an onset, a midpoint and an associated breadth. The dynamic mechanical analysis (DMA) was used to determine the glass transition temperature which is defined as the maximum value of \( tan(\delta) \). It can be seen from Fig. 4.6 that \( T_g \) is 115°C. Therefore, it is not surprising that vitrification occurred at 120 and 130°C.

Table 4.2 Kinetic parameters of the autocatalytic model obtained from isothermal cure

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>( k(T) )</th>
<th>( m )</th>
<th>( n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>3.14</td>
<td>0.61</td>
<td>1.31</td>
</tr>
<tr>
<td>130</td>
<td>5.21</td>
<td>0.62</td>
<td>1.12</td>
</tr>
<tr>
<td>140</td>
<td>6.23</td>
<td>0.56</td>
<td>1.13</td>
</tr>
<tr>
<td>150</td>
<td>10.08</td>
<td>0.60</td>
<td>1.37</td>
</tr>
<tr>
<td>160</td>
<td>9.46</td>
<td>0.59</td>
<td>1.36</td>
</tr>
</tbody>
</table>
Fig. 4.4 The reaction rate versus time at isothermal cure temperature (a) 120°C, (b) 130°C, (c) 140°C, (d) 150°C, (e) 160°C: Comparison of experimental and the autocatalytic kinetic model prediction.
Fig. 4.5 The reaction rate versus degree of cure at different cure temperatures: Comparison of experimental and the autocatalytic kinetic model prediction.

Fig. 4.6 The measurement of glass transition temperature using DMA.

In addition, the autocatalytic model is only valid for chemically controlled reaction and can not be used to describe the diffusion behavior. Therefore, the point of time when the
deviation took place could be utilized to determine the time to vitrification. On the other hand, it is noted that for cure temperature above 140°C there is a perfect agreement of experimental and kinetic model prediction for the entire reaction process. This could be due to the fact that the vitrification phenomenon did not take place at temperature above the glass transition region and the whole reaction process was chemically controlled.

### 4.1.2 Dynamic Cure

Fig. 4.7 shows the degree of cure against temperature at different heating rates. As can be seen, the higher the heating rate, the higher the onset temperature and the complete cure temperature. Based on the relationship between the degree of cure and temperature, the temperatures at various degree of cure can be estimated for a given heating rate. According to equation (3.14), the linear relationship between the logarithms of heating rate and the inverse of temperature for degree of cure from 5% to 100% was shown in Fig. 4.8. Table 4.3 shows the kinetic parameters at various degree of cure (where $K_I = \log k_0 E/(F(\alpha)R)^{2.315}$, $K = \ln(F(\alpha)/k_0)$). It can be noted that the activation energy varies with the degree of cure. Similar findings have also been reported [44-45]. Fig. 4.9 (a) to (e) shows the comparison between the experimental results of degree of cure versus time with the prediction from the dynamic cure. It was found that there is a good agreement throughout the curing reaction between the isothermal experimental results and the predictions when cured at 140°C. However, divergence occurs at high degree of cure when curing at both higher temperature and lower temperature. The reason for the disagreement below 140°C may be attributed to the occurrence of vitrification that could make the cure reaction become extremely slow. On the other hand, vitrification does not occur at temperature above Tg. However, owing to the inherent system limitations of the DSC equipment, the actual temperature of the specimen is unable to reach the pre-set
temperature within a short time. The higher the curing temperature, the larger is the lag between the actual and pre-set temperatures. Therefore, the difference between the isothermal experiment and the prediction was observed with the increase of curing temperature.

Table 4.3 The kinetic parameters calculated at various degree of cure

<table>
<thead>
<tr>
<th>Degree of Cure</th>
<th>5%</th>
<th>10%</th>
<th>30%</th>
<th>50%</th>
<th>70%</th>
<th>80%</th>
<th>90%</th>
<th>95%</th>
<th>100%</th>
</tr>
</thead>
<tbody>
<tr>
<td>K1</td>
<td>12.85</td>
<td>12.50</td>
<td>11.86</td>
<td>11.42</td>
<td>11.11</td>
<td>11.08</td>
<td>11.4</td>
<td>12.02</td>
<td>18.57</td>
</tr>
<tr>
<td>E/R</td>
<td>9748.7</td>
<td>9579.8</td>
<td>9207.5</td>
<td>8917.7</td>
<td>8711.8</td>
<td>8728.3</td>
<td>9063.2</td>
<td>9683.4</td>
<td>16475</td>
</tr>
<tr>
<td>E</td>
<td>81.05</td>
<td>79.65</td>
<td>76.55</td>
<td>74.14</td>
<td>72.43</td>
<td>72.57</td>
<td>75.35</td>
<td>80.51</td>
<td>136.98</td>
</tr>
</tbody>
</table>

Fig. 4.7 The degree of cure versus temperature at different heating rates.
Fig. 4.8 Relationship of logarithms of heating rate versus the inverse of temperature and its linear fit at degree of cure from 5% to 100%.
Fig. 4.9 The degree of cure versus the reaction time at isothermal cure temperature (a) 120°C, (b) 130°C, (c) 140°C, (d) 150°C, (e) 160°C: Comparison of the experimental results with the prediction from the dynamic cure.
4.2 TTT Cure Diagram

4.2.1 Gelation

Fig. 4.10 shows $\tan \delta$ measured by multiwave dynamic rheological method at 1, 5 and 10 Hz for isothermal cure temperature 100°C. The point at which $\tan \delta$ is independent of frequency is clearly indicated as the gelation point and its corresponding time is regarded as gelation time. The gelation time at different cure temperatures are tabulated in Table 4.4. As can be seen from the table, gelation time will decrease with the increase of cure temperature. From the DSC measurement of the partially cured adhesives, it was found that the degree of cure at the gel point ($\alpha_{gel}$) is 55%.

![Diagram showing $\tan \delta$ vs. time at different frequencies](image)

Fig. 4.10 $\tan \delta$ measured by multiwave dynamic rheological method at 1 Hz, 5 Hz and 10 Hz during isothermal cure at 100°C. The point at which $\tan \delta$ is independent of frequency is indicated as gelation point.

4.2.2 Vitrification
Chapter 4

Results and Discussion

To establish the relationship existing between the degree of cure and glass transition temperature, samples were partially cured at various times at cure temperature 90°C, and the $T_g$ of the partially cured material and degree of cure were then evaluated by means of a dynamic post curing. Fig. 4.11 shows the DSC plots of dynamic cure in order to measure $T_g$. It was commonly accepted that as a thermosetting cure, the glass transition temperature will increase from a minimum, $T_{go}$, to a maximum value, $T_{gI}$, which corresponds to the fully cured material. From Fig. 4.11 (a) and (c), $T_{go}$ and $T_{gI}$ can be determined as -21.47 and 111.15, respectively. Using this approach, the relationship of $T_g$ vs the degree of cure (Fig. 4.12) can be determined. There are various theoretical approaches to study the effect of crosslinking on $T_g$. One of the most widely accepted has been proposed by Nilsen and Dib Benedetto [113] with the following relationship:

$$\frac{T_g - T_{go}}{T_{gI} - T_{go}} = \frac{\lambda \alpha}{1 - (1 - \lambda) \alpha}$$  \hspace{1cm} (4.1)

$\lambda$ is taken as an adjustable structure-dependent parameter between 0 to 1. Pascault and Williams [114] show that $\lambda$ is theoretically equivalent to $\Delta C_{pr}/\Delta C_{p0}$, where $\Delta C_{pr}$ and $\Delta C_{p0}$ are heat capacity of the glassy and rubbery states, respectively. Curve fitting of $T_g$ versus degree of cure using the DiBenedetto equation yields a $\lambda$ of 0.616 (Fig. 4.12). The $T_g$-degree of cure relationship can further be used to establish the vitrification curve in TTT cure diagram. The vitrification times were calculated using the isoconversional lines obtained by dynamic curing in the previous cure kinetics study (Table 4.4).

In addition to the approach described above, in this paper, vitrification of NCAs was also determined using rheological techniques. Both the peak in $tan \delta$ at 1 Hz (criterion 1) and
peak in storage modulus ($G''$) at 1 Hz (criterion 2) can be defined as the vitrification point. A low strain (0.2%) was used due to the significant increase of stiffness during the vitrification process that could surpass the capacity of the transducer. Fig. 4.13 shows the direct observation of vitrification point based on the two criteria for cure temperature 100°C. It can be clearly seen that the vitrification point defined by criterion 1 was detected in advance of that defined by criterion 2. The times to vitrification from cure temperature 80°C to 100°C are listed in Table 4.4.
Fig. 4.11 $T_g$ measured by DSC. (a) uncured adhesive, (b) partially cured adhesive, and (c) completely cured adhesive.
Fig. 4.12 Relationship between $T_g$ and degree of cure. Curve fitting using DiBenedetto equation.

Fig. 4.13 Direct observation of vitrification point using rheological techniques for isothermal cure temperature 100°C. Peak in $\tan \delta$ is vitrification one and peak in loss modulus is vitrification two.
Table 4.4 Gelation and Vitrification times at cure temperature 80-100°C

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>80</th>
<th>85</th>
<th>90</th>
<th>95</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gel Times (s)</td>
<td>873.4±30</td>
<td>629±30</td>
<td>495.6±30</td>
<td>378.1±20</td>
<td>312.4±20</td>
</tr>
<tr>
<td>Vitrification Times (s) (Tg-degree of cure relation)</td>
<td>1148.4±20</td>
<td>852±20</td>
<td>648±20</td>
<td>524.4±20</td>
<td>420±20</td>
</tr>
<tr>
<td>Vitrification Times (s) (peak in tan δ)</td>
<td>987±20</td>
<td>726±20</td>
<td>567±20</td>
<td>447±10</td>
<td>379±10</td>
</tr>
<tr>
<td>Vitrification Times (s) (peak in G″)</td>
<td>1270±40</td>
<td>897±40</td>
<td>697±40</td>
<td>520±20</td>
<td>439±20</td>
</tr>
</tbody>
</table>

4.2.3 TTT Cure Diagram

The TTT isothermal cure diagram can be obtained from the contours of the time to gelation and to vitrification as a function of cure temperature. The TTT cure diagram of NCA is shown in Fig. 4.14, plotted according to the gelation and vitrification times. It is quite difficult to construct the TTT cure diagram for NCA due to its fast cure rate. Therefore, experimental results at lower cure temperatures were extrapolated to higher temperatures to construct a complete TTT cure diagram. It is generally accepted that gelation occurs at a fixed degree of cure which is independent of cure temperature [45]. According to the multiple frequency experiments and the subsequent DSC testing, the gelation happened at 55% degree of cure approximately. On the other hand, the isoconversional lines of the 55% degree of cure and full cure can be plotted according to the cure kinetics parameters. \( \frac{g}{T_g} \) can be determined to be 40°C by equation 4.1. Therefore, the entire TTT cure diagram with the various cure states could be determined. Autocatalytic modeling method was used to determine the vitrification at cure temperature beyond 100°C. From the TTT cure diagram, the NCAs can be completely cured within one minute at cure temperature beyond 160°C.
Fig. 4.14 Entire TTT cure diagram indicated with cured states.
4.3  Cure Shrinkage

4.3.1  Isothermal Cure

4.3.1.1  Dimension Change

Fig. 4.15 shows the dimension changes measured by TMA at temperature from 90°C to 110°C. There is a clear indication from the graph that the change in thickness of the NCA can be divided into four distinct regions. The thickness drops in the initial stage (region I) and then becomes stable (region II). In region III, there is a gentle decline of thickness followed by another flat region (region IV). The first drop is due to the fall of NCA’s viscosity and the applied load. To validate the effect of viscosity on the initial drop of thickness, the rheometer was used to measure the evolution of viscosity during the isothermal cure at 90°C. As can be observed from Fig. 4.16, viscosity will drop first with the increase of temperature and then become stable. With further increase of temperature, the viscosity will increase dramatically with the occurrence of crosslinking reaction. The trend of viscosity change with temperature is a common phenomenon for epoxy and amine system [50]. With the stabilization of the viscosity, there is a corresponding flat stage for the dimension that is not affected by the applied load of TMA and the weight of silicon cover. The viscosity will go up as soon as the crosslinking reaction initiates. At the same time, the crosslinking shrinkage that is resulted from the transformation of van der Waals to covalent bonds begins to evolve with the proceeding of reaction. DSC with the same cure profile of TMA was used to verify whether the shrinkage happened during the crosslinking reaction. It is clearly evident from Fig 4.15 (a) to (c) that the dimension changes occurred in region III corresponds to the exothermic curve of DSC perfectly, thus strongly demonstrated that the second slight drop was because of the cure behavior of materials. With the increase of temperature, the cure time will diminish due to the high
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reaction rate, and the dimension change shows the similar trend with the heat flow obtained with DSC. In region IV, there is almost no heat generated from the crosslinking reaction that was quenched by the occurrence of vitrification. From the cure kinetics study, it is found that when cure under 140°C, the reaction will be changed from chemical control to diffusion control and thereby become very slow. Consequently, there is no more dimension variation and hence the dimension change curve shows a flat region again.

(a)
Fig. 4.15 Dimension change measurement with TMA at temperature 90°C (a), 100°C (b), 110°C (c); DSC with the same cure profile of TMA was used to validate the shrinkage happened during the crosslinking reaction.
4.3.1.2 Shrinkage vs. Degree of Cure

In order to investigate the relationship of shrinkage with degree of cure, the variation of degree of cure with time was obtained according to the method described in the cure kinetics study part. From the dimension change curve, it can be seen that the thickness of NCA will be reduced before curing due to the drop in region I. Therefore, after taking into the effect of the initial drop into consideration and performing a vertical translation of "zeroing" the dimension change in region II, the cure shrinkage that happened at region III could be obtained. Fig. 4.17 shows the evolution of crosslinking shrinkages at cure temperature 100°C for samples with different thickness at the range of 10 to 20 μm. The measurements are quite reproducible although some random errors might be resulted from the measurement of the very thin thicknesses. The relationships between the cure shrinkage with time and degree of cure with error bars at cure temperature 90°C, 100°C and 110°C are shown in Fig. 4.18 and Fig. 4.19, respectively. Table 4.5 shows the results.
of statistical analysis of shrinkage measurements at the maximum degree of cure under different temperatures. Generally, with the increase of temperature, the maximum of degree of cure showed increase, however the maximum cure shrinkage was found to reduce instead. The reason for the reduction of cure shrinkage may be attributed to the effect of expansion of materials at higher cure temperature. The expansion of materials will compensate the increase of cure shrinkage due to the increased degree of cure. Fig. 4.20 combines the cure shrinkages under different temperatures so as to present the evolution of shrinkage more clearly.

Fig. 4.17 Evolution of cure shrinkages obtained from the dimension changes measured by TMA at temperature 100°C for samples with very thin thickness at the range of 10 to 20 μm.
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(a)

(b)

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Fig. 4.18 Cure shrinkage vs time with error bars at cure temperature 90°C (a), 100°C (b) and 110°C (c).
Fig. 4.19 Cure shrinkage vs degree of cure with error bars at cure temperature 90°C (a), 110°C (b) and 110°C (c).
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![Graph showing cure shrinkage at 90°C, 100°C, and 110°C](image)

Fig. 4.20 The relationship of cure shrinkage of NCA with time at cure temperature 90°C, 100°C and 110°C.

Table 4.5 Results of statistic analysis of cure shrinkage measurements

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Maximum Degree of Cure (%)</th>
<th>Cure Shrinkage (%)</th>
<th>Standard Deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>82</td>
<td>3.76</td>
<td>0.22</td>
</tr>
<tr>
<td>100</td>
<td>86</td>
<td>3.71</td>
<td>0.24</td>
</tr>
<tr>
<td>110</td>
<td>89.7</td>
<td>3.59</td>
<td>0.32</td>
</tr>
</tbody>
</table>

The cure shrinkage is a reflection of cure behavior of material and thereby it is much more practical and useful to find the relationship of cure shrinkage with the degree of cure.

Fig. 4.21 shows the relationship of cure shrinkage and degree of cure at cure temperature 100°C. It is clearly indicated that there are three distinct stages for the build-up of cure shrinkage. At lower degree of cure, cure shrinkage shows a slow linear increase with...
degree of cure. With further increase of degree of cure, the increase of cure shrinkage become faster but still shows a linear relation with degree of cure. The turning point (degree of cure =55%) where the change of the slope happens corresponds to the gelation point. The degree of cure at the gelation point of the NCA has been determined to be around 50% and the measurement was described earlier (section 4.2.1). Similar findings have been reported in other publications [62, 66]. The relationship of evolution of volume with degree of cure from the pressure dilatometry measurements was obtained in reference [66]. The observed slower increase of shrinkage at lower cure degree of cure was attributed to the errors in conversion axis. The bilinear relationship between the cure shrinkage and the degree of cure was observed by a gravimetric method [62]. A match between the change in the rate of cure shrinkage and the gelation point was also demonstrated. In our study, the observed lower shrinkage rate prior to the gelation point is thought to be the result of the compensation by the easy molecular rearrangement of the polymer chains before the acquisition of substantial modulus [115]. Upon gelation, the adhesive will transform from liquid to solid and stop flowing. At the same time, the cure behavior will become more intense and involve more polymer chains rearrangement. The observed linear relationship between cure shrinkage and degree of cure may extend until the occurrence of vitrification. The cure reaction will change from chemical control to diffusion control upon vitrification, and therefore the cure shrinkage leveled off. Assuming that there is no vitrification and complete cure can be obtained, the curve can then be extrapolated to 100% degree of cure and the total cure shrinkage of 5.6% could be determined. Fig. 4.22 combines the measured cure shrinkage with degree of cure at different cure temperatures. Although the cure shrinkage at the three cure temperatures follows the same predictable trend, the effect of cure temperature on the cure shrinkage was clearly indicated in our study. It can be expected that the volume of adhesive shrinks
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due to the crosslinking reaction during the curing process, however the cured materials are in an expansion condition. Therefore, with the increase of cure temperature, the measured shrinkage will reduce due to the compensation of expansion of materials. This is the reason why the measured cure shrinkage at low temperature is larger at the same degree of cure. It is worthy to note that the effect of cure temperature on the cure shrinkage would become larger upon gelation. This is also attributed to the liquid state before gelation and its flowability and possible molecular rearrangement of polymer chains. In addition, although there exists the effect of temperature on cure shrinkage after gelation, the slopes of the linear relationship between the cure shrinkage and the degree of cure at different cure temperatures are almost the same and the rate of cure shrinkage is independent on the cure temperature. This finding is very important for the subsequent calculation of curing stress because the curing stress only forms after gelation due to the development of modulus. The independence of cure shrinkage on the cure temperature after gelation can also be used to predict the cure shrinkage when curing at higher temperature. It is assumed that there is no vitrification and the degree of cure at gelation point is independent of the cure temperature (55% is regarded as the degree of cure at gelation point from Fig. 4.22). Then the cure shrinkage after gelation point can be determined as $(1-55\%) \times 0.095=4.275\%$.

From a practical point of view, to reduce the cost and increase the output, NCA is usually ramped up to 200°C and cure for one minute during the assembly process. However fast cure reaction poses a great challenge for the accurate measurement of cure shrinkage. Therefore, in order to determine cure shrinkage at higher cure temperature, a methodology is proposed by measuring cure shrinkage at lower temperatures with slow
reaction rate and then extrapolated to high temperatures with the linear relationship of cure shrinkage and degree of cure.

![Image of Figure 4.21](image)

Fig. 4.21 Cure shrinkage vs degree of cure at cure temperature 100°C.

![Image of Figure 4.22](image)

Fig. 4.22 The relationship of in-situ measured cure shrinkage of non-conductive adhesive with degree of cure at cure temperature 90°C, 100°C and 110°C.
4.3.2 Dynamic Cure

Fig. 4.23 shows the dimension changes measured with TMA from room temperature to 250°C at heating rate 5°C/min and then cooling down to room temperature at cooling rate 2°C/min. It can be seen from the graph that the dimension drops in the initial stage. It has been elaborated in the previous section that the initial drop is due to the applied load of the TMA probe and the fall of viscosity upon heating. Thermal expansion of the liquid in this stage is negligible. With the increase of temperature, the viscosity will become stable and then increase due to the occurrence of polymerization reaction. The thermal expansion due to the increase of temperature will contradict with shrinkage induced by the polymerization. Therefore, a flat region without dimension change is clearly observed following the first drop. Then the polymerization reaction will become dramatic and reaction rate will increase. Consequently, cure shrinkage becomes dominant over thermal expansion. Thereby, the second drop is manifest as the cure shrinkage. The dimension changes occurring in this region corresponds well with the exothermic curve of DSC. However, it can be seen from the figure that the temperature range of polymerization presented by TMA cure shrinkage is smaller than that manifested by DSC heat flow. The reason is that thermal expansion will take effect during the entire dynamic cure process. While, from the previous isothermal study, cure shrinkage region shown by TMA curve is almost equal to the heat flow shown by DSC curve. Therefore, we can conclude that cure shrinkage measured by means of dynamic cure process is smaller than that measured by isothermal cure due to the influence of thermal expansion. Therefore, when extracting the net shrinkage through dynamic cure method, the thermal expansion should be taken into consideration. As the polymerization reaction becomes complete, the crosslinked material is in gelation state. As can be seen from the graph, the dimension increases gradually with
the increase of temperature. As temperature increases and reaches around 170°C, a sudden expansion is clearly observed. The temperature range for the sudden expansion is around 170-200°C. After the sudden expansion region, the material expands gradually with temperature as before. After reaching 250°C, the system is cooled at 2°C/min to room temperature. The dimension decreases gradually with the drop of temperature. From the cooling curve of dimension change, it can be clearly seen that the observed sudden expansion, after the polymerization reaction, is nonreversible. It can finally contradict the cure shrinkage which occurs due to the polymerization reaction. The inset in Fig. 4.23 shows the thermal stability of the cured material detected by thermogravimetric analyzer (TGA) and indicates that the occurred expansion is not because of the degradation of the material.

![Graph showing dimension change and heat flow](image)

Fig. 4.23 Comparison of dimension change measured with TMA and heat flow detected by DSC. Inset shows the degradation point measured by TGA.
Fig. 4.24 shows the dimension change for the Henkel and Toshiba adhesive. Cure shrinkage region is clearly observed according to the dimension change. However, the sudden expansion shown with Namics adhesive (Fig. 4.23) does not present for both Henkel and Toshiba adhesive. Therefore, one can conclude that the non-reversible expansion occurred at the end of cure reaction with Namics adhesive is a material-related phenomenon. The analysis of microstructure from the molecular level may be beyond the scope of the research. However, the directly observed polymerization shrinkage and expansion which occur at two different temperature ranges is a significant property which could be further utilized for the future development of shrinkage-controllable high performance materials. Therefore, it merits a further study from the molecular level and a deep understanding of the expansion mechanism.
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Fig. 4.24 Dimension change for Henkel and Toshiba adhesives during dynamic cure: (a) Henkel adhesive, (b) Toshiba adhesive.

Fig. 4.25 shows the comparison of dimension change at various heating rates. The dimension changes at different temperature ranges are still consistent under different heating rates. In other words, heating rate does not affect the dimension change. It further confirms the observation of both shrinkage and expansion occurred in the heating process. The inset (a) shows the dimension change during cooling of the samples cured with different heating rates. Tg can be determined from the variation of coefficient of thermal expansion (CTE). The measured Tg (115°C) agrees well with the previous DMA results. Therefore, the sudden expansion occurred from 170 to 200°C is not due to the glass transition.
Fig. 4.25 Dimension change under different heating rates. Inset (a) shows the determination of glass transition temperature during the cooling process, while Inset (b) shows glass transition measured with dynamic mechanical analyzer.

The dimension changes were further measured under complex temperature profile. During the first run, the sample is heated from room temperature to 150°C at 5°C/min and then cooling down to room temperature. During the second run, the sample is heated again from room temperature to 250°C. It can be seen from Fig. 4.26 that only shrinkage is exhibited in the first run. Due to the completion of polymerization reaction at the first run, the material is actually in solid state at the beginning of second run. Therefore, the dimension evolves in the second run along the same path as the cooling in the first run. When temperature approaches the expansion region (170-200°C), the sudden expansion occurs, which is obviously larger than the thermal expansion. Thereby, it can be concluded that the polymerization reaction will not affect the expansion that occurs at the end of the cure reaction. The most important thing is that the shrinkage induced by the
polymerization reaction can be reduced by the introduction of such kind of expansion. The shrinkage-controllable material can be thereby achieved by varying the cure temperatures.

![Graph showing dimension change with temperature](image)

Fig. 4.26 The first run shows the dimension change from room temperature to 150°C and cooling down to room temperature. The second run shows dimension change from room temperature to 250°C.

### 4.3.3 Effect of Applied Load

Concerns about the potential errors associated with the effect of gravity on the Si slide and the load of the measuring system on the results need also to be considered. In order to investigate the effect of applied load, dimensional changes of the adhesive at various applied loads were measured at 25°C which ensures an absence of any cure reaction. Fig. 4.27 shows the dimension changes with different thicknesses under applied load 0.05 N. The dimension initially drops due to the applied load and the weight of silicon slide, but then shows a steady state that does not change with the applied load. It is recommended that the adhesive thickness be maintained to less than 30 µm to ensure that the time to stabilization does not become excessively long (> 10 minutes) so as to overlap with the...
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onset of cure. Fig. 4.28 shows dimension changes with 20±1 μm thickness under different applied loads. As expected, the initial drop increases with the increase of applied load. However, the time to stabilization is not affected due to the increase of applied load. It is evident that the applied load only influences the initial dimensional change and the stabilization is achieved at about the same time for all loads.

It can further be observed (Fig. 4.29) that the applied load 0.005 N and 0.01 N shows relatively larger dimensional changes when compared with larger applied loads. This may be attributed to the inability of the TMA probe to maintain contact with the upper silicon slide due to the structural changes induced by the cross-linking reaction. A load of 0.05 N is able to detect the gelation point whereas higher loads in general are likely to overestimate the shrinkage due to the superimposed compressive force caused by the applied load. Thus the load of 0.05 N is arguably the optimal load because it suitably tracks the changes in shrinkage, is able to allow detection of the gel point, and does not confound the measurement of shrinkage with an excessive external load.

![Graph showing dimension changes with different thicknesses under applied load 0.05 N at temperature 25°C without cure reaction.](image)

Fig. 4.27 Dimension change with different thicknesses under applied load 0.05 N at temperature 25°C without cure reaction.
Fig. 4.28 Dimension change with 20±1 μm thickness under different applied loads from 0.005 N to 0.1 N.

Fig. 4.29 Cure shrinkage as a function of degree of cure under different applied loads at cure temperature 100°C.
4.4  Modulus

It has already been established that the stress build-up during curing process is governed by the evolution of elastic modulus as well as cure shrinkage. There are two problems which are associated with the current mechanical measurement methods [101]. The mechanical sensitivity in the pregel polymerization and inability to accurately measure the high load or small deformation in the glassy state. Thus, a technique capable of measuring the mechanical properties from the liquid state to the glassy state is strongly needed. In order to overcome the two problems, a multi-step force technique was utilized to measure the shear mechanical properties during cure. Using this method, it was possible to track the entire polymerization from the liquid to the vitrification state in a single experiment.

4.4.1  Modulus vs. Time

Fig. 4.30 shows the evolution of storage modulus from cure temperature 90 to 160°C. As can be seen from Fig. 4.30 (a), when cure temperature is below 120°C, modulus increases slowly due to the occurrence of vitrification. At lower cure temperature, the modulus buildup dominates over relaxation. With increase of cure temperature, the modulus evolves rapidly and then reaches a plateau where modulus relaxation is equal to the modulus buildup due to cure reaction. A very interesting phenomenon occurs when cure temperature is above 120°C (Fig. 4.30 (b)), where modulus relaxation is obviously observed at the end of the cure reaction. According to the previous cure kinetics study, at cure temperatures higher than 140°C, vitrification does not take place and the fully cured state is readily achieved. Therefore, with further increase of cure temperature, modulus accumulation from the cure reaction gradually fades away and finally vanishes. Storage...
modulus becomes mainly a function of temperature and time. It is indicated in Fig. 4.30 (b) that with increase of cure temperature, the magnitude of modulus relaxation becomes larger. The comparison of modulus build-up from cure temperature 90 to 160°C is shown in Fig. 4.30 (c).

The variation of the maximum storage modulus as a function of cure temperature (as determined from Fig. 4.30(c) and plotted in Fig. 4.31) indicates that the maximum modulus increases with increase of cure temperature and then reaches a peak at cure temperature of 120°C. The maximum modulus then drops with further increase of cure temperature due to the complete cure reaction and the dominance of relaxation. It is also observed that cure temperature, where the peak modulus occurs, coincides with the $T_g$ of this material (Fig. 4.7). In other words, when cure temperature is equal to $T_g$, the material can obtain a maximum storage modulus during the cure process. If the cure temperature is below $T_g$, modulus increases due to vitrification that enables a slower cure reaction as well as a reduced modulus relaxation. If the cure temperature is above $T_g$, modulus decreases due to the large relaxation.
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3.5x10^8n

-20 0 20 40 60 80 100 120 140 160 180 200
Time (min)

(a)

(b)
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Fig. 4.30 Modulus as a function of time measured with a multi-force step technique: (a) cure temperature 90-120°C, (b) cure temperature 120-160°C, and (c) cure temperature 90-160°C.

Fig. 4.31 The maximum modulus measured by means of multi-force step technique from cure temperature 90°C to 160°C.
4.4.2 Modulus vs. Degree of Cure

A novel simulation methodology based on the thermal-cure analogy has been proposed to simulate the cure process. The most important parameter introduced in the equations is the degree of cure. Both cure shrinkage and modulus are therefore expressed as a function of degree of cure.

Fig. 4.32 shows experimental data used for characterizing storage modulus as a function of degree of cure. Storage modulus as a function of time was obtained by using the rheometer (Fig. 4.32 (a)). Gelation point is defined as the crossover of storage modulus and loss modulus. The time to the end of cure reaction was determined as when the maximum modulus occurs. According to previous study, when cured beyond 140°C, the material can obtain complete cure. Therefore, we can deduce that degree of cure should be 100% when maximum modulus occurs. Thus, the time from gelation point to the end of cure reaction was determined to be 78 seconds at cure temperature 160°C. Fig. 4.32 (b) shows the degree of cure as a function of time, which was generated from the heat flow obtained from the DSC curve. As previously reported, the degree of cure at the gelation point has been determined as 55%. The time from gelation point to the end of cure was determined as 72 seconds by DSC. The cure time from the gelation to complete cure exhibited by both rheometer and DSC are in fair agreement. Thereby, the relationship of storage modulus and the degree of cure can be determined by combining the two graphs and shown in Fig. 4.32 (c) and (d). The modulus shown in Figure 4.32 is the Young’s modulus that was determined from the shear modulus.
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(a) Modulus (Pa) over time (min).

(b) Degree of Cure over time (min).

Gel-Fully Cure:
- (a) 78 s
- (b) 72 s
Fig. 4.32 The experimental procedures for the characterization of the build-up of storage modulus as a function of degree of cure: (a) the evolution of storage modulus at cure temperature 160°C measured by means of a parallel plate rheometer; (b) DSC measurements at cure temperature 160°C for characterizing cure kinetics; (c) storage
modulus as a function of degree of cure in a linear scale, and (d) storage modulus as a function of degree of cure in a logarithm scale.

Based on the same technique, modulus as a function of degree of cure at other cure temperatures can be obtained and shown in Fig. 4.33. As can be seen from the graph, cure at lower cure temperatures leads to higher storage modulus at the same degree of cure comparing at higher cure temperature. As cure progresses, vitrification occurs when the glass transition temperature, $T_g$, of the system increases and becomes equal to the cure temperature. At this condition, the mobility of the reacting groups is hindered and restricted with the reduction of free volume, thereby leading to a slow reaction, with the reaction rate now controlled by diffusion rather than being controlled by chemical factors. Also the material will be further strengthened due to the vitrification transformation.

According to the previous TTT cure diagram study, the degree of cure at gelation and vitrification point was obtained and shown in Fig. 4.34. The isoconversional phenomenon at gelation point was clearly observed. Whereas, with increasing cure temperatures, vitrification occurred at higher degrees of cure and at shorter vitrification times. Therefore, due to the vitrification and increase of degree of cure, modulus will increase with increasing cure temperature. However, when cure temperature rises above the glass transition temperature, vitrification transformation becomes weaker and weaker, and the amount of reacting groups becomes fewer and fewer. On the other hand, modulus relaxation becomes larger and larger due to the higher temperature. Consequently, modulus reaches a maximum value at glass transition temperature and then drops at higher cure temperatures.
Fig. 4.33 Modulus as a function of degree of cure from cure temperature 90 to 160°C.

Fig. 4.34 Degree of cure at gelation and vitrification as determined from time-temperature transformation.
4.5 Cure Stresses

4.5.1 Analytical Study

According to the time-temperature-transformation (TTT) cure diagram, the material passes through several discernible stages during the curing process. At the early stage of cure, the material is essentially in a liquid state, incapable of sustaining an external load. With increase of cure, the system acquires an equilibrium modulus which is essentially elastic upon gelation. After gelation, if cure temperature is above the glass transition temperature, the system will continue the reaction until completion. On the other hand, if cure temperature is below the glass transition temperature, the system will vitrify. At the early stages of reaction, shrinkage does not cause any stress because of the flow nature of the liquid. However, after the critical gel point, the material begins to develop a significant modulus. If there is a constraint on the system boundary, curing stress will be generated due to constrained cure shrinkage.

The buildup of cure stress can be calculated incrementally from the change of cure shrinkage and modulus [67-69]. If the sample is subjected to one-dimensional constraints, the cure stress may be expressed as equation (4.2):

\[ d\sigma = -E(T, p) \left[ \frac{\partial \alpha(T, p)}{\partial T} dT - \frac{\partial \delta(T, p)}{\partial p} \frac{\partial p}{\partial t} dt \right] \]  

(4.2)

where \( d\sigma \) is incremental stress, \( E(T, p) \) is the modulus, \( \alpha(T, p) \) is the coefficient of thermal expansion, \( dT \) is temperature increment, \( dt \) is time increment, \( p \) is degree of cure, and \( \delta(T, p) \) is cure shrinkage. It should be noted that the modulus, CTE, and cure shrinkage are all expressed as functions of temperature and degree of cure. For the case of isothermal cure, equation (4.2) can be reduced to:

---

\[ d\sigma = -E(T) \left[ \frac{\partial \alpha(T, p)}{\partial T} dT - \frac{\partial \delta(T, p)}{\partial p} \frac{\partial p}{\partial t} dt \right] \]  

(4.2-i)

---

\[ d\sigma = -E(T) \left[ \frac{\partial \alpha(T, p)}{\partial T} dT - \frac{\partial \delta(T, p)}{\partial p} \frac{\partial p}{\partial t} dt \right] \]  

(4.2-ii)

---

\[ d\sigma = -E(T) \left[ \frac{\partial \alpha(T, p)}{\partial T} dT - \frac{\partial \delta(T, p)}{\partial p} \frac{\partial p}{\partial t} dt \right] \]  

(4.2-iii)

---

\[ d\sigma = -E(T) \left[ \frac{\partial \alpha(T, p)}{\partial T} dT - \frac{\partial \delta(T, p)}{\partial p} \frac{\partial p}{\partial t} dt \right] \]  

(4.2-iv)

---

\[ d\sigma = -E(T) \left[ \frac{\partial \alpha(T, p)}{\partial T} dT - \frac{\partial \delta(T, p)}{\partial p} \frac{\partial p}{\partial t} dt \right] \]  

(4.2-v)

---

\[ d\sigma = -E(T) \left[ \frac{\partial \alpha(T, p)}{\partial T} dT - \frac{\partial \delta(T, p)}{\partial p} \frac{\partial p}{\partial t} dt \right] \]  

(4.2-vi)

---

\[ d\sigma = -E(T) \left[ \frac{\partial \alpha(T, p)}{\partial T} dT - \frac{\partial \delta(T, p)}{\partial p} \frac{\partial p}{\partial t} dt \right] \]  

(4.2-vii)

---

\[ d\sigma = -E(T) \left[ \frac{\partial \alpha(T, p)}{\partial T} dT - \frac{\partial \delta(T, p)}{\partial p} \frac{\partial p}{\partial t} dt \right] \]  

(4.2-viii)

---

\[ d\sigma = -E(T) \left[ \frac{\partial \alpha(T, p)}{\partial T} dT - \frac{\partial \delta(T, p)}{\partial p} \frac{\partial p}{\partial t} dt \right] \]  

(4.2-ix)

---

\[ d\sigma = -E(T) \left[ \frac{\partial \alpha(T, p)}{\partial T} dT - \frac{\partial \delta(T, p)}{\partial p} \frac{\partial p}{\partial t} dt \right] \]  

(4.2-x)

---

\[ d\sigma = -E(T) \left[ \frac{\partial \alpha(T, p)}{\partial T} dT - \frac{\partial \delta(T, p)}{\partial p} \frac{\partial p}{\partial t} dt \right] \]  

(4.2-xi)

---

\[ d\sigma = -E(T) \left[ \frac{\partial \alpha(T, p)}{\partial T} dT - \frac{\partial \delta(T, p)}{\partial p} \frac{\partial p}{\partial t} dt \right] \]  

(4.2-xii)

---

\[ d\sigma = -E(T) \left[ \frac{\partial \alpha(T, p)}{\partial T} dT - \frac{\partial \delta(T, p)}{\partial p} \frac{\partial p}{\partial t} dt \right] \]  

(4.2-xiii)

---

\[ d\sigma = -E(T) \left[ \frac{\partial \alpha(T, p)}{\partial T} dT - \frac{\partial \delta(T, p)}{\partial p} \frac{\partial p}{\partial t} dt \right] \]  

(4.2-xiv)

---

\[ d\sigma = -E(T) \left[ \frac{\partial \alpha(T, p)}{\partial T} dT - \frac{\partial \delta(T, p)}{\partial p} \frac{\partial p}{\partial t} dt \right] \]  

(4.2-xv)

---

\[ d\sigma = -E(T) \left[ \frac{\partial \alpha(T, p)}{\partial T} dT - \frac{\partial \delta(T, p)}{\partial p} \frac{\partial p}{\partial t} dt \right] \]  

(4.2-xvi)

---

\[ d\sigma = -E(T) \left[ \frac{\partial \alpha(T, p)}{\partial T} dT - \frac{\partial \delta(T, p)}{\partial p} \frac{\partial p}{\partial t} dt \right] \]  

(4.2-xvii)

---

\[ d\sigma = -E(T) \left[ \frac{\partial \alpha(T, p)}{\partial T} dT - \frac{\partial \delta(T, p)}{\partial p} \frac{\partial p}{\partial t} dt \right] \]  

(4.2-xviii)

---

\[ d\sigma = -E(T) \left[ \frac{\partial \alpha(T, p)}{\partial T} dT - \frac{\partial \delta(T, p)}{\partial p} \frac{\partial p}{\partial t} dt \right] \]  

(4.2-xix)

---

\[ d\sigma = -E(T) \left[ \frac{\partial \alpha(T, p)}{\partial T} dT - \frac{\partial \delta(T, p)}{\partial p} \frac{\partial p}{\partial t} dt \right] \]  

(4.2-x).
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\[ d\sigma = E(p) \frac{\partial \delta(p)}{\partial p} \frac{\partial p}{\partial t} \]  

(4.3)

Considering that cure stress begins to build up after gelation, the total cure stress is obtained by integration of equation (4.3):

\[ \sigma = \int_{t_{ge}}^{t_{end}} E(p) \frac{\partial \delta(p)}{\partial p} \frac{\partial p}{\partial t} dt \]  

(4.4)

where \( t_{ge} \) is the time when after gelation, \( t_{end} \) is the time when cure is completed. Equation (4.4) can be further reduced to:

\[ \sigma = \int_{\delta_{ge}}^{\delta_{total}} E(\delta) d\delta \]  

(4.5)

where \( \delta_{ge} \) is the cure shrinkage at the gelation point, \( \delta_{total} \) is the total cure shrinkage.

Figure 3.6 shows the experimental procedures for the characterization of material properties during the curing process. In order to further investigate the relationship of shrinkage with degree of cure, the cure shrinkage rate (cure shrinkage per degree of cure) is defined as the coefficient of cure shrinkage (CCS). As shown in Fig. 4.35, CCS1, CCS2, and CCS3 correspond to CCS at the three regions which consist of material states from the pre-gelation, gelation to vitrification, to the post-vitrification. As can be seen from the Table 4.6, the linear relationship between the cure shrinkage and the degree of cure at different cure temperatures from gelation to vitrification point is found to be the same. Then we can conclude that CCS2 is essentially a material constant and independent of cure temperature. Therefore, the independence of CCS on cure temperature can be used to predict the cure shrinkage when curing at higher temperature.
Fig. 4.35 The relationship of cure shrinkage with degree of cure at cure temperature 100°C.
Insets: Dimension change and heat flow measured using TMA and DSC, respectively.

Table 4.6 Determination of CCS at cure temperature 90, 100 and 110°C

<table>
<thead>
<tr>
<th>Cure Temperature (°C)</th>
<th>CCS1 (Prior to Gelation)</th>
<th>CCS2 (Gelation)</th>
<th>CCS3 (Vitrification)</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>0.024</td>
<td>0.095</td>
<td>0.062</td>
</tr>
<tr>
<td>100</td>
<td>0.0171</td>
<td>0.095</td>
<td>0.064</td>
</tr>
<tr>
<td>110</td>
<td>0.0157</td>
<td>0.095</td>
<td>0.066</td>
</tr>
</tbody>
</table>

By combining the cure shrinkage as a function of degree of cure (Fig. 4.22 and Fig. 4.35) and modulus as a function of degree of cure (Fig. 4.33), modulus buildup as a function of cure shrinkage can thereby be determined (Fig. 4.36 (a)). It should be noted that it is quite difficult to directly measure cure shrinkage above 110°C due to the fast reaction. Cure shrinkage at higher cure temperatures was therefore deduced from the linear relationship of cure shrinkage and degree of cure that is independent of cure temperature. Thereby, one can determine the cure stress according to equation (4.5), from the area under the
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curve of the modulus vs cure shrinkage. Fig. 4.36 (b) shows the evolution of cure stress as a function of degree of cure from cure temperature 90 to 160°C. With the increase of cure shrinkage and build-up of stiffness, cure stress will develop gradually above gelation point and then increase dramatically with the further increase of degree of cure. Similar results have been reported for the case of UV-cured dental material and thin film coatings [15-16]. It is also observed from Fig. 4.36 (b) that cure at low temperature could result in high cure stress. When cured at lower temperature, vitrification occurs at lower degree of conversion as shown in Fig. 4.34. As the vitrification approaches, the material undergoes a change from rubbery to glassy state. Modulus then rises with the slower reaction. While, at higher cure temperature, vitrification occurs at higher degree of conversion and modulus builds up dramatically within a small conversion. Hence, only a small fraction of cure shrinkage is involved in the formation of cure shrinkage when cured at high temperature based on the linear relationship of cure shrinkage and degree of cure. Moreover, significant stress relaxation arises at higher cure temperatures. Consequently, cure stress is larger at lower cure temperatures due to the earlier occurrence of vitrification. With increase of cure temperature, the majority of the overall cure stress is formed in the final stage of crosslinking [16]. Another observation is that at the same degree of cure, cure stress at low cure temperature is higher than that at high cure temperature. It is obvious that stress relaxation increases at high cure temperature.

Gelation and vitrification play a significant role in the cure stress development. A good understanding of the two events in the formation of cure stress can provide improved insights of using new methods to control the shrinkage and stresses. Gelation marks the beginning of cure stress. Therefore, to reduce the cure-induced stresses, gel point should occur at a higher degree of cure according to the correlation of stress and degree of...
conversion. A smaller CCS is beneficial to diminish cure stresses. While, in comparison with gelation, the involvement of vitrification in cure stresses is more complex. On the one hand, vitrification is the main momentum for the buildup of shear mechanical property. On the other hand, inhibited cure shrinkage is also observed when the material progresses in vitrification region. Different conversions at vitrification point occur when cured at different cure temperatures. Therefore, the effect of gelation and vitrification need to be taken into consideration.

![Graph showing modulus vs. cure strain for different cure temperatures]

(a)
4.5.2 Experimental Measurement

For UV-cured materials, it is relatively easier to conduct direct cure force measurement due to a negligible contribution of the heating process [15]. However, it is quite difficult to perform direct cure stress measurement for the thermal-cured materials due to the much more complex cure process during sample heating. To date, the reported methods cannot measure the cure stresses directly and cure stresses have to be computed based on the measured strain or deflection value. The accuracy of the measured cure stress is largely dependent on the resolution of strain gauges as well as the thickness and stiffness of the sample holder. Low resolution strain gauges and related methods may not be capable of detecting the generation of cure stresses as the material transitions through the gelation, vitrification, and rubber or fully cured states. Moreover, the use of adhesive for the
bonding of the strain gauges adds to the complexity of the measurement process and may confound cure stress measurement making it thereby difficult to interpret the experimental data. On the other hand, experimental understanding and accurate quantitative description of cure stresses are crucial for the validation of the theoretical prediction as well as the establishment of simulation procedures.

In this section, we report a newly developed method that can directly measure the cure stress buildup based on the iso-strain mode of DMA. In combination with DSC measurements, cure stress buildup as a function of degree of cure was established. The influence of gelation and vitrification on the evolution of cure stress is also discussed.

4.5.2.1 Cure Force vs. Time

Fig. 4.37 shows the typical evolution of cure force at cure temperatures of 90, 100 and 110°C. It can be clearly seen that the cure force develops after a certain time interval. Initially, a small force around 0.2 N is observed which is induced by the applied 0.1% strain on the thermal tape. This force is crucial to activate the iso-strain mode testing and helps to maintain the moveable probe at a constant position until the two quartz rods are bonded by the epoxy and obtain sufficient mechanical strength capable of withstanding an external load. Without the aid of the thermal tape, the moveable probe itself could not be held at a constant position. It is also clearly seen that the initial force keeps almost constant even during the heating process. For cure at 90°C, the cure force builds up after approximately 41 minutes, whereas, curing at 100°C and 110°C, results in the build up of cure force after about 32 and 29 minutes respectively. In other words, with increase of cure temperature, cure force develops earlier. In principle, the onset of cure force marks the formation of gelation which is capable of sustaining an external load. Therefore, this
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trend confirms that the observed increase of force is induced by the polymerization process of the material. The cure force then evolves with the progression of cure reaction and finally reaches a plateau. It can be observed that it takes longer time (127 min) from gelation to the saturation of the cure force when cured at 90°C. On the other hand, curing at 100 or 110°C results in the saturation of the cure force at much shorter times (42 min and 20 mins for curing at 100°C and 110°C respectively). In order to make a comparison with the evolution of cure force, DSC measurements with the same temperature profile as DMA were conducted from cure temperature 90 to 110°C. It is clearly seen from Fig. 4.37 (a), (b) and (c) that cure stress develops noticeably at the final portion of the polymerization reaction where the heat flow is quite low. From our previous report, the gelation point occurs at around -55% degree of conversion. It is reasonable that the observed gelation point from cure force buildup lags a little behind DSC due to the larger temperature chamber of the DMA. Therefore, this technique also provides another new way to be able to conduct direct determination of gelation point based on the observed cure stress buildup.

Fig. 4.38 shows the comparison of cure stresses buildup from temperature 90 to 110°C with error bars. It can be clearly seen that the measurement with this method is quite reproducible and with good accuracy. It is observed that curing at lower temperatures leads to higher cure stresses.
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(a)

(b)
Fig. 4.37 Evolution of cure force and heat flow measured by means of DMA and DSC respectively at cure temperature (a) 90°C, (b) 100°C, and (c) 110°C.

Fig. 4.38 Evolution of cure stresses with error bars at cure temperature 90°C, 100°C, and 110°C.
4.5.2.2 Cure Stress vs. Degree of Cure

It is apparent that cure stress buildup during curing process is governed by the evolution of elastic modulus as well as cure shrinkage. According to the previous research, a linear relationship between cure shrinkage and degree of conversion was experimentally observed. The evolution of modulus as well as the cure stresses are also a function of conversion. Therefore, it is more appropriate and useful to describe cure stress as a function of degree of cure. Fig. 4.39 shows the evolution of cure stress as a function of degree of cure. With the increase of cure shrinkage and build-up of stiffness, cure stress will develop gradually above gelation point and then increase dramatically with the further increase of degree of cure. As cure progresses, vitrification occurs when the glass transition temperature, $T_g$, of the system increases and becomes equal to the cure temperature. At this condition, the mobility of the reacting groups is hindered and restricted with the reduction of free volume, thereby leading to a slow reaction, with the reaction rate now controlled by diffusion rather than being controlled by chemical factors. Besides, the mechanical properties will undergo a dramatic increase in the vitrification regime. The two important features are clearly exhibited by heat flow and cure force in Fig. 4.37, respectively. Heat flow shows that the polymerization reaction is inhibited, while the cure force intensively develops. According to the previous study, the degree of cure at vitrification point was determined to be $\sim 67\%$, $\sim 75\%$ and $\sim 82\%$ at cure temperature 90, 100, and 110°C, respectively. As shown in the inset of Fig. 4.39, cure stresses prior to vitrification are quite small. It can be seen that cure stresses induced by vitrification are ten more times than that resulted from gelation. Therefore, cure stresses buildup prior to vitrification are actually negligible. As vitrification approaches, the material undergoes a change from gel-like to glassy state while the modulus rises with the
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slower reaction. On the other hand, at higher cure temperature, vitrification occurs at higher degree of conversion and modulus builds up dramatically within a small cure range. Hence, only a small fraction of cure shrinkage contributes in the formation of cure stress when cured at high temperature based on the linear relationship of cure shrinkage and degree of cure. Moreover, significant stress relaxation may arise at higher cure temperature. Consequently, cure stress is larger in samples cured at lower cure temperatures due to the earlier occurrence of vitrification. It may also be noted that at the same degree of cure, lower cure temperatures lead to higher levels of cure stresses.

![Graph showing cure stresses](image)

Fig. 4.39 Evolution of cure stresses as a function of degree of cure. Inset: the initial portion of cure stresses.
4.5.3 Simulation

4.5.3.1 1D Simulation

The detailed description of the simulation methodology has been presented in the previous chapter. The commercial software ANSYS 8.0 was employed to carry out the thermal-cure analogy. One dimensional simulation results based on the thermal-cure analogy methodology are shown in Figure 4.40. It is clearly seen that the simulation agrees well with the analytical results. Therefore, the novel simulation methodology has been validated and can be used further for the 2D or 3D simulation. Cure shrinkage may be considered to be similar to thermal shrinkage such that the magnitude of shrinkage can be fully described by a single physical property, coefficient of cure shrinkage and coefficient of thermal expansion respectively. This similarity between cure shrinkage and thermal shrinkage forms the basis for the cure-mechanical modeling technique described above. However, the following assumptions and simplifications are implicit in the methodologies for the cure stress modeling presented in this paper: (i) cure shrinkage is isotropic; (ii) degree of cure is uniform, (iii) the heat generated from the cure reaction does not significantly affect shrinkage.
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Fig. 4.40 Comparison of analytical and simulation results for cure stress as a function of degree of cure from cure temperature 90 to 160°C.

4.5.3.2 2D Simulation

The experimental structure presented above is an axisymmetric 3-D structure. Therefore, we can build up the model in equivalent 2-D form. As shown in Fig. 4.41, 2D finite element models with a fixed boundary condition on both the top and bottom were built to simulate the curing process and used to validate the direct experimental measurements. PLANE82 element was used and the axisymmetric analysis was performed. Two different meshing sizes were used. For the coarse meshing, the model has totally 88 elements and 303 nodes. While, for the fine meshing, the model has totally 2200 elements and 6791 nodes. The material properties were expressed as temperature-dependent which was analogous to conversion-dependent. Degree of cure at gelation point was assumed to be the stress-free conversion.
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Fig. 4.42 shows stress distribution along the normal direction for 2D and an expanded 3D geometry at the end of polymerization reaction when curing at 90°C. It can be clearly seen that the maximum tensile stresses occur at the corner. Then we defined a path at the location with a height 0.1 mm (A-A’) for the coarse meshing (in Fig. 4.41(a)) and 0.02 mm (B-B’) for the fine meshing (in Fig. 4.41(b)), respectively. The stresses in normal direction were mapped on the path. Hence, cure force can be determined by the integration of cure stress. Fig. 4.43 shows the comparison of cure force buildup as a function of degree of cure from cure temperature 90 to 110°C for the two types of mesh sizes and the two locations. It can be clearly seen that cure force buildup at the two locations presents a good agreement with each other. Therefore, the buildup of cure force at one of the two paths can be used to simulate the experimentally measured cure force which was detected by the force probe of DMA. Fig. 4.44 shows the comparison of experimental and simulation results for cure force buildup. When using the 2D axisymmetric geometry to simulate the experimental structure, a good agreement between the simulation and experimental measurement is shown in Fig. 4.44. Therefore, it further proves that the incremental constitution equations are accurate to predict the evolution of cure process.

(a)
Fig. 4.41 2D finite element model with a fixed boundary condition on both the top and bottom: (a) coarse meshing; (b) fine meshing.

Fig. 4.42 Stress distribution along the normal direction for 2D (a) and expanded 3D geometry (b) at the end of polymerization reaction at cure temperature 90°C.
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Fig. 4.43 Comparison of cure force buildup as a function of degree of cure for different meshing sizes from cure temperature 90 to 110°C.

Fig. 4.44 Comparison of experimental and simulation for cure force buildup.

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4.5.3.3 NCA Flip Chip Assembling

A finite element analysis of the NCA flip-chip package was performed to determine the cure-induced stresses by using thermal-cure analogy method. A 2-dimensional model was built. Due to the symmetric nature of a flip chip package, it is sufficient to consider a half package for 2-dimensional model. Figure 4.45 shows the diagonal cross-section of a NCA package, and Figure 4.46 shows the meshed model. The dimensions of flip chip package used in analysis are shown in Table 4.7. The material properties of the analysis at cure temperature 90°C are shown in Table 4.8. During the curing process, only the adhesive can shrink. CTEs of the other components are thereby assumed to be zero. It is obvious that cure-induced stresses are actually caused by the CCS mismatch which is analogous to the thermal stresses induced by CTE mismatch.

![Fig. 4.45 Schematic view of NCA flip chip diagonal cross-section.](image1)

![Fig. 4.46 Meshed 2D finite element model.](image2)
Table 4.7 Package construction used in FEA modeling

<table>
<thead>
<tr>
<th>Flip Chip Components</th>
<th>Length (mm)</th>
<th>Width (mm)</th>
<th>Thickness (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon</td>
<td>2</td>
<td>2</td>
<td>0.6</td>
</tr>
<tr>
<td>Substrate</td>
<td>2.5</td>
<td>2.5</td>
<td>0.3</td>
</tr>
<tr>
<td>Bump (D)</td>
<td>0.08</td>
<td>0.08</td>
<td>0.025</td>
</tr>
<tr>
<td>Pad (D)</td>
<td>0.155</td>
<td>0.155</td>
<td>0.025</td>
</tr>
<tr>
<td>NCA</td>
<td>2</td>
<td>2</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Table 4.8 Material properties for NCA flip chip assembly at bonding temperature 90°C

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Silicon</th>
<th>Substrate</th>
<th>Bump</th>
<th>Pad</th>
<th>NCA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modulus (Pa)</td>
<td>131e9</td>
<td>18e9</td>
<td>207e9</td>
<td>150e9</td>
<td>E(T)=E(p)</td>
</tr>
<tr>
<td>Poisson's Ratio</td>
<td>0.25</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.49</td>
</tr>
<tr>
<td>CTE(°C⁻¹)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>p&lt;0.67, CTE(T)=CCS(p)=-0.095; p&gt;0.67, CTE(T)=CCS(p)=-0.062</td>
</tr>
<tr>
<td>Density (Kg/m³)</td>
<td>2330</td>
<td>1200</td>
<td>2000</td>
<td>2000</td>
<td>1200</td>
</tr>
</tbody>
</table>

Figure 4.47 shows the stress contour of bump and pad along the normal direction. It can be seen that the contact surface of bump and pad is in compression state. The maximum compressive stress occurs at the corner as shown in the figure. Figure 4.48 further shows the evolution of compressive stress during the curing process at locations A, B, C, D, E, F, and G as indicated in Fig. 4.46. The cure-induced compressive stress at the contact can be more than 15 MPa. From another angle, stress distribution at the contact interface of bump and pad has been shown in Fig. 4.49. Stress at the center is smaller than that at the edge. Degree of cure of the adhesive plays a very important role in the formation of the compressive stress. With increase of degree of cure, compressive stress evolves rapidly.
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![Stress Distribution Diagram](image)

A = -397E+07  
B = -340E+07  
C = -282E+07  
D = -225E+07  
E = -168E+07  
F = -110E+07  
G = -530275  
H = 63400  
I = 617075

Fig. 4.47 Stress distribution along the normal direction for bump and pad at the end of polymerization reaction at cure temperature 90°C.

![Stress Evolution Graph](image)

Fig. 4.48 Evolution of compressive stress at different locations during the assembly process at temperature 90°C.
Fig. 4.49 Stress distribution at various degree of cure during the assembly process at temperature 90°C.
4.6 Cooling Stresses

In order to understand the stress generated during the entire assembly process, the thermal stress during cooling need also be studied. The calculation of cooling stress is much more straightforward. The experimental study to determine the tensile modulus and CTE at the end of cooling has been performed. The rheometer with two parallel plates as presented in previous section was used to measure the storage modulus at the end of cooling. Then, the material was detached from the plates and the thermal expansion measurement was carried out immediately with thermal mechanical analyzer (TMA).

Figure 4.50 shows the modulus prior to cooling and at the end of cooling for the specimens isothermally cured from 90 to 160°C. The storage modulus before cooling was extracted from Fig. 4.30 and the detailed explanation can be found in section 4.4. The storage modulus at the end of cooling increases with increasing cure temperature and reaches a plateau at higher cure temperature. As indicated in Table 4.9, the final degree of cure increases with increase of cure temperature. At lower temperature, degree of cure plays a main reason for the buildup of modulus. When the material approaches complete cure (~100% degree of cure) at high cure temperature, the modulus will not change and may decrease due to the degradation of material when holding at high temperature for a long time. Another important observation in Fig. 4.50 is that the difference of the modulus prior to cooling and at the end of cooling becomes larger and larger with increasing of cure temperature. At lower cure temperature, cure reaction happens in the vitrification regime and most of the crosslinked materials are in glassy state. When cooling from the cure temperature to the room temperature, there is little transition from the rubber state to glassy state. Therefore, the modulus does not change much when
cooling down to the room temperature. While, when curing at high temperature, most of the crosslinked materials are in rubbery state. During cooling process, all the material in rubbery state will transform to glassy state and a large change of modulus occurs during the glass transition.

CTE measurements have been conducted with the same samples as the modulus measurement. Fig. 4.51 shows the normalized dimension change for the isothermal cured samples from temperature 90 to 160°C. The normalized dimension change is actually the thermal strain during cooling process. According to the dimension change, CTE can be calculated. It is very difficult to determine the glass transition temperature based on the measurement of modulus during cooling. However, glass transition temperature can be determined based on the CTE measurement. CTE1 and CTE2 represent CTE below and beyond glass transition, respectively. CTE1, CTE2, and Tg for materials cured at various temperatures are listed in Table 4.9. As can be clearly seen in Fig. 4.52 that CTE1 of the materials cured at different temperatures are almost same. While, an interesting phenomenon is observed for the case of CTE2. When curing at lower temperature (90°C), CTE2 becomes large due to a large part of unreacted materials. With increase of cure temperature, CTE2 becomes small due to the increase of degree of cure. When curing at higher temperature (160°C), majority of glassy state transformed to rubbery state and CTE2 thereby becomes larger.

Based on the measured modulus at the end of cooling and CTE, one can easily calculate the thermal stress due to the temperature change. In order to make a comparison with cure-induced stress which has been calculated in the previous section, Fig. 4.53 shows cure stress, thermal stress, and final stress as a function of cure temperature. It can be
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clearly seen that cure-induced stress at low cure temperature could be larger than thermal stress. With increase of cure temperature, cure-induced stress becomes smaller and has been discussed in the previous section. While, a rapid increase of thermal stress is initially observed with increase of cure temperature. With further increase of cure temperature, thermal stress evolves slowly due to the small storage modulus at high temperature. For the case of final stress, it can be seen that it increases with increase of cure temperature and reaches a plateau at higher temperature, where the increase of thermal stress is diminished by the drop of cure-induced stress.

Fig. 4.50 Comparison of modulus prior to cooling and at the end of cooling for the adhesive isothermally cured from temperature 90 to 160°C for a certain time.
Fig. 4.51 Normalized dimension change during cooling at a rate 2°C/min for the adhesive isothermally cured from temperature 90 to 160°C.

Fig. 4.52 CTE of the isothermally cured adhesive from temperature 90 to 160°C.
Fig. 4.53 Stress caused by curing and cooling process from temperature 90 to 160°C.

Table 4.9 Cure conditions, material properties, and stresses induced by curing and cooling

<table>
<thead>
<tr>
<th>Cure Temperature (°C)</th>
<th>Cure Time (hour)</th>
<th>Degree of Cure</th>
<th>Modulus At the beginning of cooling (Pa)</th>
<th>Modulus At the end of cooling (Pa)</th>
<th>CTE1 (ppm/°C)</th>
<th>CTE2 (ppm/°C)</th>
<th>Cure Stress (MPa)</th>
<th>Thermal Stress (MPa)</th>
<th>Total Stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>3</td>
<td>0.87</td>
<td>1.05E8</td>
<td>1.3E8</td>
<td>68.13 (T&lt;70)</td>
<td>197.5 (T&gt;70)</td>
<td>1.18</td>
<td>0.83</td>
<td>2.01±0.02</td>
</tr>
<tr>
<td>100</td>
<td>2</td>
<td>0.89</td>
<td>1.99E8</td>
<td>2.24E8</td>
<td>66.6 (T&lt;80)</td>
<td>80.38 (T&gt;80)</td>
<td>1.05</td>
<td>1.14</td>
<td>2.19±0.03</td>
</tr>
<tr>
<td>110</td>
<td>1</td>
<td>0.92</td>
<td>2.60E8</td>
<td>3.12E8</td>
<td>67.58 (T&lt;85)</td>
<td>73.96 (T&gt;85)</td>
<td>1.32</td>
<td>1.74</td>
<td>3.06±0.05</td>
</tr>
<tr>
<td>120</td>
<td>1</td>
<td>0.95</td>
<td>2.91E8</td>
<td>3.62E8</td>
<td>68.05 (T&lt;92)</td>
<td>82.35 (T&gt;92)</td>
<td>1.06</td>
<td>2.32</td>
<td>3.38±0.08</td>
</tr>
<tr>
<td>140</td>
<td>1</td>
<td>0.98</td>
<td>1.88E8</td>
<td>3.46E8</td>
<td>68.83 (T&lt;95)</td>
<td>97.13 (T&gt;95)</td>
<td>0.63</td>
<td>2.49</td>
<td>3.12±0.05</td>
</tr>
<tr>
<td>160</td>
<td>1</td>
<td>0.99</td>
<td>0.45E8</td>
<td>3.53E8</td>
<td>69.48 (T&lt;106)</td>
<td>360.7 (T&gt;106)</td>
<td>0.38</td>
<td>2.86</td>
<td>3.24±0.03</td>
</tr>
</tbody>
</table>
4.7 Contact Resistance

In order to establish the relationship between the cure force obtained during the cure process and the electrical contact resistance, eventually, the mechanical compressive stress formed during the cure process has to be translated to the electrical contact resistance for practical interpretation and to investigate the reliability of flip chip interconnects with NCAs. Therefore, an experimental set-up which can conduct in-situ measurement of the development of contact resistance during the bonding process of test chips was developed by using a mechanical tester combined with a four wire resistance measurement system.

Fig. 4.54 shows the evolution of contact resistance at a cure temperature of 100°C with an applied load of 10 N. The temperature and external load profile are also displayed in Fig. 4.54. It is evident from the graph that resistance change can be divided into seven distinct regions. The drop of contact resistance in the first region is induced by the applied load. The electrical connection of a NCA joint can be explained according to the well-know theory of electrical contacts [116]. According to the theory of contact resistance, the contact resistance consists of a constriction resistance and a film resistance. The constriction resistance is caused by the confinement of the current flow on to small metal-metal contact areas caused by surface roughness of mating surfaces. Whereas, the film resistance is due to the poor conductivity of passivating films that may form on the contacting surfaces. In the case of the copper bumps and pads used in this study, the oxidized copper layer forms the film resistance. When the bump and pad are pressed together, the electrical connection is achieved by the small contact spots which are dependent on the roughness of the contact surface and the applied pressure. The area and
the number of contact spots will increase with the increase of applied pressure. Therefore, the contact resistance drops with the increase of applied load, followed by a flat region where the resistance becomes almost constant under a fixed applied load. In region III, with the elevation of temperature at a ramping rate 5°C/min, the contact resistance increases with a linear relationship with the temperature due to the temperature coefficient of resistance. When the temperature holds constant at 100°C, there is no change observed in region IV. According to the time-temperature-transformation cure diagram, curing stress will be generated at the gelation point due to the constrained cure shrinkage and detectable stiffness. Therefore, the observed slight decline in region V is caused by a contraction force which is induced by the polymerization reaction of the adhesive. In order to further confirm the effect of cure stress on the contact resistance, prior to the actual measurement of the bonding process with adhesive, a calibration measurement has been performed without dispensing the adhesive in between the bump and pad. The same temperature and force profile were used. It can be seen in the inset of Fig. 4.54 that the contact resistance for the calibration measurement shows the same temperature coefficient of resistance during the heating process and remains constant when the temperature is held constant. By comparing the evolution of contact resistance for the two measurements, it is clearly seen that the drop in region V is induced by the cure reaction. It is also found that the drop of contact resistance lasts for about 30 to 40 minutes and then become constant in the final portion. In region VI, a large drop of contact resistance occurs during cooling process because of the temperature coefficient of resistance as well as thermal stress induced by thermal shrinkage of the adhesive. In region VII, the applied load was removed at the end of cooling. It can be readily observed that the contact resistance does not change after removing the applied load. Cured adhesive provides a strong mechanical bond between the bump and the substrate. Following the evolution of contact resistance
through the cure process in the presence of an externally applied force, one can discern that the compressive stress that realizes the electrical connection between the bump and pad comprises of the applied pressure, cure shrinkage stress, and the thermal contraction stress.

Fig. 4.55 shows the comparison of contact resistance at bonding temperatures of 90, 100, and 110°C. Due to the difficulty in the definition of bonding area of the adhesive, which strongly depends on the amount of adhesive, the gap filling, and the alignment of bump and pad, it may not be reasonable and possible to compare quantitatively the reduction magnitude of the contact resistance for the different samples bonded at different temperatures. Nevertheless, qualitatively speaking, it can be seen that when bonding at lower temperatures, cure stress induced drop of contact resistance makes up an important portion of the total resistance change. With increasing bonding temperature, cure stress induced drop of contact resistance becomes smaller and lasts for a shorter time due to the rapid cure reaction. On one hand, with increase of bonding temperature, the drop of contact resistance caused by the temperature coefficient of resistance and thermal contraction force increases. On the other hand, as previously reported in Fig. 4.38, curing at lower temperature could lead to higher cure stresses which were directly measured by the DMA probe. The reason for the occurrence of large cure stresses at low temperatures is due to the earlier onset of vitrification transformation during the curing process. Also, according to the previous study, the cure-induced stress can be larger than cooling stress when bonding at 90°C. In comparing Fig. 4.55 and Fig. 4.38, there appears to be a good agreement of the cure reaction duration at the three temperatures reflected by the measured cure stress and the contact resistance, respectively.
Fig. 4.54 Evolution of contact resistance during the bonding process at temperature 100°C under 10 N. Inset: comparison of contact resistance with and without adhesive bonding.

Fig. 4.55 Comparison of evolution of contact resistance at bonding temperature 90, 100 and 110°C.
4.8 Adhesion Strength

The compressive stresses between the bump and pad enable the electrical connection of the chip and substrate. However, the tensile stress induced during the curing and cooling process along the interface between the adhesive and chip or substrate may cause a severe reliability issue. Therefore, the adhesion strength is critical and values a further study.

Figure 4.56 shows the evolution of shear strength with the curing time at cure temperature 90°C measured with the use of single lap joint samples. The degree of cure obtained for sample cured with oven was compared with that for sample using DSC for curing in Fig. 4.57. It was found that the degree of cure with time measured separately agrees well with that measured consecutively with one sample. Figure 4.58 shows the evolution of shear strength as a function of degree of cure. It should be mentioned here that samples with degree of cure up to 84% were cured at 90°C, while samples with degree of cure beyond 84% were cured at 160°C. This is because the maximum degree of cure that can be obtained at 90°C was only 86.2% even after curing for one hour. Higher curing temperature is required to obtain high degree of cure at relatively short curing time. It can be easily observed that there were two obvious development stages of the shear strength. The shear strength increased slowly with the increase of degree of cure at the early stage. However, when the crosslinking reaction proceeded to a certain degree of cure (around 55%), the strength was observed to rise dramatically until it reached the maximum degree of cure. According to the gelation measurement, the gelation point, which associated with a 55% degree of cure, agrees well with the sharp inflection in the shear strength versus degree of cure graph (Fig. 4.58). This clearly indicates the important effect of development of mechanical properties of adhesive on the evolution of adhesion strength.
Consequently, it appears that two kinds of bonding mechanisms could be dominant in the two stages. The primary bonding mechanism before gelation point is weak physical bonding that involves van der waals forces, dipolar interactions and hydrogen bonding. Beyond the gelation point, the chemical bonding and development of the storage modulus will make a dominant contribution to the adhesion strength. It should be pointed out that the failure modes of the lap joint shear test change with increasing degree of cure. When the degree of cure is less than that at the gelation point, the failure mode is a mixture of cohesive failure and adhesive failure as seen by interfacial separation. The cohesive bonding became much stronger with the increase of crosslinking density and thus cohesive failure mode diminished with increasing degree of cure. As a result, the failure was mainly adhesive in nature with the epoxy separated completely from the substrate. With further increase of reaction conversion, the adhesion strength could surpass the shear strength of the solder mask and cause the solder mask to peel off from the substrate, as evident from the optical micrograph (Fig. 4.59) of the failure surface for completely cured specimen.

![Graph of shear strength vs. time](image.png)

Fig. 4.56 The evolution of shear strength with time during the curing process.
Chapter 4  
Results and Discussion

Fig. 4.57 Comparison of curing process with DSC and oven.

Fig. 4.58 The evolution of shear strength with the degree of cure during the curing process.
Fig. 4.59 The fractured surface of BT substrate with solder mask for different degree of cure: (a) 0.45, (b) 0.66, (c) 0.84.
Chapter 5 Summary and Conclusions

The following conclusions may be drawn based on the experimental and numerical analyses performed in this project:

1. **Cure kinetics & TTT cure diagram**
   - A good agreement between the autocatalytic kinetic model prediction and experimental results was demonstrated for isothermal curing.
   - Due to high reaction rates at high temperatures, cure kinetics cannot be accurately determined. The prediction based on the dynamic method compared favorably with the experimental isothermal scans for curing up to 140°C.
   - A multiple frequency rheological technique was used to study the gelation behavior of NCAs. The degree of cure at the gelation point was determined to be close to 55%.
   - Vitrification times were directly measured by rheological experiments.
   - A TTT cure diagram was constructed based on the measured gelation and vitrification times.

2. **Cure shrinkage**
   - A modified simple experimental procedure by means of TMA was developed for the in-situ measurement of cure shrinkage. By comparing the heat flow of DSC, the cure shrinkage induced by the crosslinking reaction was validated.
   - Applied load and viscosity did not affect the measurement of cure shrinkage.
   - The sharp changes of slope of cure shrinkage versus degree of cure were observed to coincide with the gelation and vitrification, respectively and thus the transformations from sol to gel and to a vitrified state were detected.
   - A linear relationship between the cure shrinkage and degree of cure was clearly indicated.
Chapter 5

Summary and Conclusions

- Coefficient of cure shrinkage (CCS) was proposed to be a material constant to describe the cure shrinkage. CCS1, CCS2, and CCS3 correspond to CCS at the three regions which consist of material states from the pre-gelation, gelation to vitrification, and the post-vitrification.
- CCS2 is independent of cure temperature and can be used to predict the cure shrinkage when curing at higher temperatures.

3. Modulus

- At lower cure temperatures, storage modulus increases slowly due to the occurrence of vitrification. With increase of cure temperature, modulus evolves rapidly and then reaches a plateau where modulus relaxation is equal to the modulus build-up. When cured above 120°C, modulus relaxation is obviously observed at the end of cure reaction.
- Modulus as a function of degree of cure has been established. Cure at lower temperature leads to higher storage modulus at the same degree of cure due to the earlier occurrence of vitrification.
- Cure at high temperatures could result in the modulus buildup within a small degree of cure range

4. Cure Stresses

- Cure-induced stresses were incrementally calculated based on the measured shrinkage and storage moduli and expressed as a function of degree of cure.
- Cure at lower temperature could lead to a larger cure stress. At the same degree of cure, cure stress at low cure temperature is larger than that at high cure temperature due to the vitrification.
- A new method for direct measurement of cure-induced stresses by using the iso-strain mode of DMA has been developed.
- The cure stress buildup was observed to occur after certain duration and correspond to the gel point. It is directly observed that a majority of cure stresses develop in the vitrification regime
Chapter 5  Summary and Conclusions

- Experimental results clearly show that cure at lower temperatures could lead to higher cure stresses due to the earlier onset of vitrification.
- A novel modeling methodology based on thermal-cure analogy has been proposed for numerical simulation of the evolution of cure stresses.
- CCS and degree of cure are proposed to be analogous to CTE and temperature in thermal-mechanical analysis, respectively. Mechanical properties as a function of degree of cure are analogous to the temperature-dependent properties.
- Simulated cure stresses as a function of degree of cure agree well with the direct experimental measurements.

5. Cooling Stresses
- The storage modulus at the end of cooling increases with increasing cure temperature and reaches a plateau at higher cure temperatures.
- Cure-induced stresses at low cure temperatures could be larger than thermal stress.
- Final stress increases with increasing cure temperatures and reaches a plateau at higher temperature, where the increase of thermal stress is diminished by the drop of cure-induced stress.

6. Contact Resistance
- A drop of resistance induced by cure stress during the bonding process is clearly observed. The evolution of contact resistance agrees well with experimentally directly observed cure stress build-up.
- With decrease of bonding temperature, the drop of contact resistance induced by cure shrinkage becomes larger, while cooling-induced drop of resistance becomes smaller.

7. Adhesion Strength
- Before gel point, adhesion strength increased slowly to around 0.8 Mpa. Beyond the gel point, adhesion strength increased dramatically. The adhesion strength
surpassed the shear strength of the solder mask when the degree of cure reached 80%.

- Two different bonding mechanisms could govern the evolution of adhesion strength. The bonding mechanism before gelation point was weak physical bonding. Beyond the gelation point, the chemical bonding and development of the storage modulus will make a dominant contribution to the adhesion strength.

- There were three failure modes according to the evolution of shear strength. The failure before gelation point was the mixture of cohesive and adhesive failure. With increasing degree of cure, the failure was mainly adhesive in nature with the epoxy separated completely from the substrate.

According to this research, cure stress decreases with increasing cure temperature and becomes negligible as compared with cooling stress. For a fast cure material cured with a slow ramping rate, the material is actually dynamically cured. Dynamic cure may result in lower residual stress than isothermal cure owing to the thermal expansion during the heating ramp compensating for some of the chemical shrinkage. However, cure shrinkage and stress are fundamental phenomena and are very common and ubiquitous in applications ranging from microelectronics and optoelectronics packaging to biomaterials amongst others. A 1 μm displacement caused by the cure-induced stresses in optoelectronics packaging may result in up to 20% loss in coupling efficiency [117]. Therefore, the methodologies and analyses contributed by this project can further be applied to cure shrinkage and stress analysis in optoelectronics and other applications where either cure strain related displacement or stresses may have significant impact on the optimal performance of these materials or devices.
Chapter 6 Recommendations for Future Work

1. Study on the non-uniformity of degree of cure
Degree of cure plays a very important role in the simulation of cure-induced stresses. The established methodologies in this study assume a uniform degree of cure. Actually, degree of cure is not uniform due to the temperature gradient. Therefore, in order to accurately simulate the structures with complex geometries and boundary conditions, degree of cure with time at any location need to be determined. Then the distribution of degree of cure can be analogous to the temperature distribution. Finally, the cure stress can be calculated according to the thermal-cure analogy methodology.

2. Study on the relationship between cure profile and NCA interconnect reliability
It has been found in this study that adhesion strength, cure shrinkage, mechanical properties, and cure stress are highly related with cure temperature and time. It is desirable to cure under high temperature in order to save processing time and energy, but it may lead to too high residual stress as well as degradation. On the other hand, low temperature curing may result in incomplete cure and be detrimental to the adhesion strength. In order to obtain an optimal cure profile, the reliability study should be conducted for the samples with different cure profiles.

3. Develop constitutive relationships to model NCA failure when subjected to accelerated reliability testing
Chapter 6 Recommendations for Future Work

In an adhesive joint, the failure mechanisms are different from the conventional metallic solder interconnections. Coffin-Mason relationship may not be applicable to predict the lifetime of the adhesive interconnection. Due to the relaxation of polymeric material, the stress relaxation over time will result in the degradation of contact force and thus increase the contact resistance or even cause complete loss of electrical contact. Moreover, the subcritical debonding of passivation layer/NCA under monotonic and cyclic loading is another issue. The moisture absorption diffusion and hygroscopic swelling properties of adhesive matrix could be detrimental to the adhesion and result in the adhesive joint degradation. Therefore, based on the above work proposed, constitutive models including the stress relaxation behavior, adhesion strength, moisture absorption, and hygroscopic swelling then need to be constructed to predict the NCA joint failure and lifetime.

4. Apply the newly developed methodologies to wide ranging practical applications

Thermosetting adhesives become more and more important in the semiconductor industry from wafer level to packaging level. Functional and structural applications of such polymeric materials range from glass fiber composites to advanced functional polymers used in optoelectronics and microfluidic applications. Cure-induced stresses are very common and ubiquitous in such applications. Polymerization shrinkage in dental materials is a critical issue and the contraction stress that occurs during the curing process could cause the debonding and lead to clinical failures [118,119]. One of the significant problems in composite laminates is the development of process-induced stresses which lead to warpage of composite structures and could initiate the failure of the laminates [120-122]. Alignment shift in the optical packaging [117] is a severe issue in the optical
fiber attached with adhesive. It is envisioned that the newly developed approach could be successfully applied to such practical applications where cure-induced stresses is encountered.
References


References


References


References


References


References


References


References


References


References


References


Appendix 1  Ansys Programs

----------Cure stress simulation using thermal-cure analogy ------
----------One dimension, Cure temperature is 90°C ----------------
/filename,Cure
/Title,Cure Stress Simulation

/prep7
ET,1,Link10
R,1,1
!---------------------------------------------Create Mode---------------------
N,1,0,0
N,2,0,0.1e-3
E,1,2

!Define NCA material property as a function of temperature (degree of cure)
MPTEMP,1,0.5,0.51,0.52,0.53,0.54,0.55
MPDATA,EX,1,1,346258.8,467394.9,620196.6,808193.5,1.0212E6,1.249E6
MPDATA,PRXY,1,1,0.49,0.49,0.49,0.49,0.49,0.49
MPDATA,ALPX,1,1,-0.095,-0.095,-0.095,-0.095,-0.095,-0.095

MPTEMP,7,0.56,0.57,0.58,0.59,0.6,0.61
MPDATA,EX,1,7,1.543601E6,1.889199E6,2.279599E6,2.760401E6,3.312006E6,3.953199E6
MPDATA,PRXY,1,7,0.49,0.49,0.49,0.49,0.49,0.49
MPDATA,ALPX,1,7,-0.095,-0.095,-0.095,-0.095,-0.095,-0.095

MPTEMP,13,0.62,0.63,0.64,0.65,0.66,0.67
MPDATA,EX,1,13,4.834402E6,5.855598E6,7.056801E6,8.411991E6,1.019599E7,1.21E7
MPDATA,PRXY,1,13,0.49,0.49,0.49,0.49,0.49,0.49
MPDATA,ALPX,1,13,-0.095,-0.095,-0.095,-0.095,-0.095,-0.095

MPTEMP,19,0.68,0.69,0.7,0.71,0.72,0.73
MPDATA,EX,1,19,1.41E7,1.64E7,1.89E7,2.15E7,2.47E7,2.788802E7
MPDATA,PRXY,1,19,0.49,0.49,0.49,0.49,0.49,0.49
MPDATA,ALPX,1,19,-0.062,-0.062,-0.062,-0.062,-0.062,-0.062

MPTEMP,25,0.74,0.75,0.76,0.77,0.78,0.79
MPDATA,EX,1,25,3.13E7,3.41E7,3.845599E7,4.26E7,4.576797E7,5.08E7
MPDATA,PRXY,1,25,0.49,0.49,0.49,0.49,0.49,0.49
MPDATA,ALPX,1,25,-0.062,-0.062,-0.062,-0.062,-0.062,-0.062

MPTEMP,31,0.8,0.81,0.82,0.83,0.84,0.85
MPDATA,EX,1,31,5.64E7,5.946398E7,6.499197E7,7.134797E7,7.659603E7,8.145998E7
MPDATA,PRXY,1,31,0.49,0.49,0.49,0.49,0.49,0.49
Appendix 1

Ansys Programs

MPDATA, ALPX, 1, 31, -0.062, -0.062, -0.062, -0.062, -0.062, -0.062
MPDATA, MPTEMP, 37, 0.86, 0.8605, 0.8612, 0.8618, 0.8622, 0.87
MPDATA, MPDATA, EX, 1, 37, 9.0432E7, 9.07E7, 9.17E7, 9.11E7, 9.1E7, 9.4E7
MPDATA, PRXY, 1, 37, 0.49, 0.49, 0.49, 0.49, 0.49, 0.49
MPDATA, ALPX, 1, 37, -0.062, -0.062, -0.062, -0.062, -0.062, -0.062

MP, DENS, 1, 1200

!------------------ Apply boundary condition---------------------
! Fix the two nodes
D, 1, all
D, 2, all

! Define the degree of cure at the gelation point as the stress free point
tref, 0.5

!---------------------------Solution-------------------------------
/solu
outres, all, all
antype, static, new
nlgeom, on
solcon, on, off
autots, off
ncnv, 0
neqit, 30

!-------------------Set Initial Conditions-----------------------
! Apply the temperature (degree of cure) as a function of time
KBC, 0
TM_Initial=0 ! Initial time value
TM_End=74 ! The end time

*Do, TM, TM_Initial, TM_End, 1
/Solu
BF, all, temp, TM*0.005 + 0.5
Time, TM
Solve

!-------------------Set this step as the stress free temperature (degree of cure) and then calculate
!------------------------the incremental value for the next step.
Tref, TM*0.005 + 0.5
j = j + 1
save
*enddo
Finish
Appendix I

Ansys Programs

!--------- Cure stress simulation using thermal-cure analogy--------
!--------- Two dimension, Cure temperature is 90°C--------
!--------- Simulate the experimental model--------

/filename,Cure
/Title,Cure Stress Simulation

/prep7
RECTNG,0,1.1E-3,0,8E-4

! Define NCA material property as a function of temperature (degree of cure)

MPTEMP,1,0.5,0.51,0.52,0.53,0.54,0.55
MPDATA,EX,1,1,346258.8,467394.9,620196.6,808193.5,1.0212E6,1.249E6
MPDATA,PRXY,1,1,0.49,0.49,0.49,0.49,0.49,0.49
MPDATA,ALPX,1,1,-0.095,-0.095,-0.095,-0.095,-0.095,-0.095

! (CTE (analogy with CCS) is constant)

MPTEMP,7,0.56,0.57,0.58,0.59,0.6,0.61
MPDATA,EX,1,7,1.543601E6,1.889199E6,2.279599E6,2.760401E6,3.312006E6,3.953199E6
MPDATA,PRXY,1,7,0.49,0.49,0.49,0.49,0.49,0.49
MPDATA,ALPX,1,7,-0.095,-0.095,-0.095,-0.095,-0.095,-0.095

MPTEMP,13,0.62,0.63,0.64,0.65,0.66,0.67
MPDATA,EX,1,13,4.834402E6,5.855958E6,7.056801E6,8.411991E6,1.019599E7,1.21E7
MPDATA,PRXY,1,13,0.49,0.49,0.49,0.49,0.49,0.49
MPDATA,ALPX,1,13,-0.095,-0.095,-0.095,-0.095,-0.095,-0.095

MPTEMP,19,0.68,0.69,0.7,0.71,0.72,0.73
MPDATA,EX,1,19,1.41E7,1.64E7,1.89E7,2.15E7,2.47E7,2.778802E7
MPDATA,PRXY,1,19,0.49,0.49,0.49,0.49,0.49,0.49
MPDATA,ALPX,1,19,-0.062,-0.062,-0.062,-0.062,-0.062

MPTEMP,25,0.74,0.75,0.76,0.77,0.78,0.79
MPDATA,EX,1,25,3.13E7,3.41E7,3.845599E7,4.26E7,4.767979E7,5.08E7
MPDATA,PRXY,1,25,0.49,0.49,0.49,0.49,0.49,0.49
MPDATA,ALPX,1,25,-0.062,-0.062,-0.062,-0.062

MPTEMP,31,0.8,0.81,0.82,0.83,0.84,0.85
MPDATA,EX,1,31,5.64E7,5.946398E7,6.499197E7,7.134797E7,7.659603E7,8.145998E7
MPDATA,PRXY,1,31,0.49,0.49,0.49,0.49,0.49,0.49
MPDATA,ALPX,1,31,-0.062,-0.062,-0.062,-0.062,-0.062
Appendix 1

Ansys Programs

MPTEMP,37,0.86,0.8605,0.8612,0.8618,0.8622,0.87
MPDATA,EX,1,37,9.0432E7,9.07E7,9.17E7,9.11E7,9.1E7,9.4E7
MPDATA,PRXY,1,37,0.49,0.49,0.49,0.49,0.49,0.49
MPDATA,ALPX,1,37,-0.062,-0.062,-0.062,-0.062,-0.062,-0.062

MP,DENS,1,1200

!------------------------Meshing-------------------------------------
ALLSEL,ALL
Esize,0.02e-3
AMESH,ALL ! MESH ALL AREA

!-----------------Apply boundary condition--------------------------

!Apply the symmetry boundary condition
Nsel,s,loc,x,0
Dsym,symm,x,0

!Fix the upper line
Nsel,s,loc,y,0
d,all,all,0

!Fix the bottom line
Nsel,s,loc,y,8E-4
d,all,all,0

nsel,all

!Define the degree of cure at the gelation point as the stress free point
tref,0.5

!------------------------Solution------------------------------------

/solu
outres,all,all
antype,static,new
nlgeom,off
solcon,on,off
autots,off
ncnv,0
neqit,30

!------------------------Set Initial Conditions---------------------

!Apply the temperature (degree of cure) as a function of time

KBC,0
Appendix 1

Ansys Programs

TM_Initial=0 ! Initial time value
TM_End=37 ! The end time

*Do,TM,TM_Initial,TM_End,1
/Solu
BF,all,temp,TM*0.00984+0.5
Time,TM
Solve

!----- Set this step as the stress free temperature (degree of cure) and then calculate
!----- the incremental value for the next step.

Tref,TM*0.00984+0.5
i=i+1
save
*enddo
Finish

/POST1
PATH,STRESS1,2,,80 ! DEFINE PATH WITH NAME = "STRESS1"
PPATH,1,379 ! DEFINE PATH POINTS BY NODE
PPATH,2,114

Set,37 ! Read result at step 2
PDEF,i,S,Y ! Mapping stress in y direction on the path
Pcalc,mult,m,i,XG ! Calculate R*SY
Pcalc,INTG,f,m,XG,6.28 ! Integrate and obtain the cure force

Finish
Appendix I Ansys Programs

!------------------Cure stress simulation using thermal-cure analogy------------------
!------------------NCA Flip Chip Assembly, Cure temperature is 90°C------------------

/filename, Cure
/Title, Cure Stress Simulation

/prep7
!----------------------------------Create Mode----------------------------------
!Substrate
RECTNG, 0, 2.5E-3, 0, 0.3E-3
!Pad
RECTNG, 0.9225*1E-3, 1.0775*1E-3, 0.3E-3, 3.25E-4
!Bump
RECTNG, 0.96E-3, 1.04E-3, 3.25E-4, 3.5E-4
!Silicon
RECTNG, 0.2E-3, 3.5E-4, 4.9E-4
!NCA
K, 100, 0, 0.3e-3
K, 101, 0.9225E-3, 0.3e-3
K, 102, 0.9225E-3, 3.25E-4
K, 103, 0.96E-3, 3.25E-4
K, 104, 0.96E-3, 3.5E-4
K, 105, 0, 3.5E-4

a, 100, 101, 102, 103, 104, 105, 100
K, 200, 2.5E-3, 0.3e-3
K, 201, 1.0775E-3, 0.3e-3
k, 202, 1.0775E-3, 3.25E-4
K, 203, 1.04E-3, 3.25E-4
K, 204, 1.04E-3, 3.5E-4
K, 205, 2E-3, 3.5E-4

a, 200, 201, 202, 203, 204, 205, 200
AGLUE, all
!----------------------------------Material Properties----------------------------------
!Si material properties----------------Material\#1
MP, EX, 1, 131E9
MP, PRXY, 1, 0.3
MP, ALPX, 1, 0
MP, DENS, 1, 2330

!NCA material properties----------------Material\#2
!Define NCA material property as a function of temperature (degree of cure)
Appendix 1

Ansys Programs

MPTEMP, 1, 0.5, 0.51, 0.52, 0.53, 0.54, 0.55
MPDATA, EX, 2, 1, 3.462588, 4.673949, 6.201966, 8.081935, 1.0212E6, 1.249E6
MPDATA, PRXY, 2, 1, 0.49, 0.49, 0.49, 0.49, 0.49, 0.49
MPDATA, ALPX, 2, 1, -0.095, -0.095, -0.095, -0.095, -0.095, -0.095

!--------- (CTE (analogy with CCS) is constant)

MPTEMP, 7, 0.56, 0.57, 0.58, 0.59, 0.6, 0.61
MPDATA, EX, 2, 7, 1.543601E6, 1.889199E6, 2.279599E6, 2.760401E6, 3.312006E6, 3.953199E6
MPDATA, PRXY, 2, 7, 0.49, 0.49, 0.49, 0.49, 0.49, 0.49
MPDATA, ALPX, 2, 7, -0.095, -0.095, -0.095, -0.095, -0.095, -0.095

MPTEMP, 13, 0.62, 0.63, 0.64, 0.65, 0.66, 0.67
MPDATA, EX, 2, 13, 4.834402E6, 5.855598E6, 7.056801E6, 8.411991E6, 1.019599E7, 1.21E7
MPDATA, PRXY, 2, 13, 0.49, 0.49, 0.49, 0.49, 0.49, 0.49
MPDATA, ALPX, 2, 13, -0.095, -0.095, -0.095, -0.095, -0.095, -0.095

MPTEMP, 19, 0.68, 0.69, 0.7, 0.71, 0.72, 0.73
MPDATA, EX, 2, 19, 1.41E7, 1.64E7, 1.89E7, 2.15E7, 2.47E7, 2.778802E7
MPDATA, PRXY, 2, 19, 0.49, 0.49, 0.49, 0.49, 0.49, 0.49
MPDATA, ALPX, 2, 19, -0.062, -0.062, -0.062, -0.062, -0.062, -0.062

MPTEMP, 25, 0.74, 0.75, 0.76, 0.77, 0.78, 0.79
MPDATA, EX, 2, 25, 3.13E7, 3.41E7, 3.845599E7, 4.26E7, 4.576797E7, 5.08E7
MPDATA, PRXY, 2, 25, 0.49, 0.49, 0.49, 0.49, 0.49, 0.49
MPDATA, ALPX, 2, 25, -0.062, -0.062, -0.062, -0.062, -0.062, -0.062

MPTEMP, 31, 0.8, 0.81, 0.82, 0.83, 0.84, 0.85
MPDATA, EX, 2, 31, 5.64E7, 5.946398E7, 6.499197E7, 7.134797E7, 7.659603E7, 8.145998E7
MPDATA, PRXY, 2, 31, 0.49, 0.49, 0.49, 0.49, 0.49, 0.49
MPDATA, ALPX, 2, 31, -0.062, -0.062, -0.062, -0.062, -0.062, -0.062

MPTEMP, 37, 0.86, 0.8605, 0.8612, 0.8618, 0.8622, 0.87
MPDATA, EX, 2, 37, 9.0432E7, 9.07E7, 9.17E7, 9.11E7, 9.1E7, 9.4E7
MPDATA, PRXY, 2, 37, 0.49, 0.49, 0.49, 0.49, 0.49, 0.49
MPDATA, ALPX, 2, 37, -0.062, -0.062, -0.062, -0.062, -0.062, -0.062

MP, DENS, 2, 1200

!BT substrate material property

MP, EX, 3, 18E9
MP, PRXY, 3, 0.4
MP, ALPX, 3, 0
Appendix 1

Ansys Programs

MP,DENS,3,1200

! Bump material property --------------------- Material#4

MP,EX,4,207E9
MP,ALPX,4,0
MP,PRXY,4,0.3
MP,DENS,4,2000

! Pad material property --------------------- Material#5

MP,EX,5,150E9
MP,PRXY,5,0.3
MP,ALPX,5,0
MP,DENS,5,2000

! Element Types
ET,1,Plane82

! Meshing Operations

! Bump
Asel,S,Area,,3
AATT,4,,1
Esize,0.01e-3
AMESH,ALL

! Pad
Asel,S,Area,,8
AATT,5,,1
Esize,0.01e-3
AMESH,ALL

! NCA
Asel,S,Area,,9
AATT,2,,1
Esize,0.02e-3
AMESH,ALL
Asel,S,Area,,10
AATT,2,,1
Esize,0.02e-3
AMESH,ALL

! Silicon Area
ASEL,s,area,,11
AATT,1,,1
Esize,0.1e-3
AMESH,ALL
Appendix 1

---Substrate---
Asel,S,Area,,7
AATT,3,,1
Esize,0.1e-3
AMESH,ALL

---Apply boundary condition---
Nsel,s,loc,x,0
Dsym,symm,x,0
Nsel,s,loc,y,0
d,all,uy,0
nseI,all

---Solution---
!Define the degree of cure at the gelation point as the stress free point
tref,0.5
/solu
outres,all,all
antype_static,new ! Set analysis
ngeom,on
solcon,on,off
autots,off
nenv,0
neqit,30

---Set Initial Conditions---
!Apply the temperature (degree of cure) as a function of time
KBC,0
TM_Initial=0 ! Initial time value
TM_End=74 ! The end time
i=1
*Do,TM,TM_Initial,TM_End,1
/solu
BF,all,temp,TM*0.005+0.5
Time,TM
Solve
!----- Set this step as the stress free temperature (degree of cure) and then calculate
!----- the incremental value for the next step.
Tref,TM*0.005+0.5
i=i+1
save
*enddo
Finish
Appendix 2  

Publications


Appendix 2

Publications

Effect of Degree of Cure and Surface Condition on the Interfacial Adhesion Strength of Non-Conductive Adhesives Used in Flip Chip Interconnects, ICMAT 2005 (Poster).


