Cure-Dependent Viscoelastic Behaviour of Electronic Packaging Polymers

Modelling, Characterization, Implementation and Applications

$K_{r}(\alpha,T) + \left[K_{g} - K_{r}(\alpha,T)\right] \cdot \sum_{n=1}^{N} k_{n} \cdot \exp\left[-\frac{t-\xi}{\tau'_{n}(\alpha,T)}\right] \cdot \frac{d\varepsilon_{v}^{ab}}{d\xi} d\xi$

Daoguo Yang

Cure-Dependent Viscoelastic Behaviour of Electronic Packaging Polymers

Modelling, Characterization, Implementation and Applications

Proefschrift

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To my parents

To Lixia, Annie, and Yamin

To my brothers and sisters

Summary

Polymers are widely used in electronic packaging as encapsulants, underfills, adhesives, insulators, and dielectrics, etc. Generally these materials are thermosetting polymers that have to be cured during the fabrication process at elevated temperatures. The curing process will introduce residual stress and warpage in the microelectronic devices, due to the polymerization shrinkage and subsequent cooling down from the curing temperature. During cure these polymers gradually transform from the more or less liquid state into a viscoelastic solid with a relatively high glassy modulus, accompanied with chemical shrinkage. Due to the cross-linking reaction and thermal shrinkage under continuing stiffness increase, stresses will arise in areas where shrinkage is partly prevented by geometrical constraints. Furthermore, if the cross-linked product is cooled down to ambient temperature, the difference in thermal expansion between matrix and adjacent materials will cause additional stresses and deformation.

In order to be able to conduct reliable prediction of the process-induced stress and warpage in electronic packaging, cure-dependent viscoelastic constitutive relations for thermosetting polymers are required. Furthermore, material characterization and numerical implementation of the constitutive models into commercial FEM programs are important for providing a base for large scale thermo-mechanical FEM modelling of electronic packaging. And then a simulation-based optimization on the design for package structure, material parameters, and process conditions can be carried out.

In this thesis, a newly developed cure-dependent viscoelastic model is proposed to describe the mechanical behaviour of thermosetting polymers. In the model, the relaxation moduli are considered as a sum of the equilibrium part (the rubbery moduli) and the transient part. The cure-dependent rubbery moduli are modelled with Adolf's model based on scaling analysis. The transient part is approximated by Prony series, in which the cure dependency is represented through the cure-dependent relaxation amplitude, the normalized Prony coefficients and the cure-dependent relaxation times. Based on our experimental observations that the normalized master curves of the transient part at different cured states virtually fall into one single curve, the model is further simplified by taking the normalized Prony coefficients as cure-

independent. In this way, the model is able to describe a 'quasi' thermo-rheologically simple behaviour but has the advantage of convenient implementation into a general FEM program. The relationship between the mechanical behaviour and the curing profile is established using the well-developed cure kinetics models.

The experimental characterization of the cure-dependent properties including DMA measurements, DSC analysis, and the measurement of the curing shrinkage is presented in Chapter 3. Shear DMA measurements using both isothermal and intermittent curing approaches are performed to characterize the cure-dependent relaxation behaviour. The temperature dependency of the dynamic properties at different curing states is obtained, and the master curve and the shift factor for temperature at each cure state have been established. It is indicated that the temperature effect on the shift factors is independent of degree of cure when the glass transition temperature is chosen as the reference temperature. The temperature effect is described well with the WLF equation if the temperature is above a switching temperature, while below the switching temperature the Arrhenius equation gives a good prediction.

A new concept of "reduced temperature" is proposed in Chapter 3. The equation for the shift factors is modified using the reduced temperature. In this way, the effect of the temperature and the degree of cure on the relation behaviour (shift factors) can then be expressed in an 'integrated' way.

The measurement of relaxation bulk moduli was performed using pressure cell setup and compression disc-shaped DMA. Based on the DMA data and the limited step creep tests, the glassy and rubbery bulk moduli and the relaxation parameters were obtained. Since the obtained data was limited and in particular the data for low degrees of cure could not be established at all, the accuracy of the established cure dependent relaxation bulk modulus appears to be less adequate.

DSC analysis provides sufficient data for obtaining the material parameters for the cure kinetics model and the relationship between the glass transition temperature and the degree of cure. The curing shrinkage is measured using an online density measuring setup. It is found that the density increases almost linearly with the degree of cure for all the resins and the curing shrinkage also shows almost no dependency on the curing temperatures.

Understanding the effect of filler loading on the properties of the filled composites gives great advantages for designers to select materials and to optimize the packaging structure and processing parameter. Therefore, the effect of filler loading on the major material properties is further investigated in Chapter 4. The impact of filler volume fraction on the glassy shear moduli, rubbery shear moduli, the temperature and conversion shift factors, and the curing shrinkage is discussed and summarized. Theoretical predictions based on composite mechanics are carried out and compared with the measurements.

The developed model has been fully implemented into the general FEM code MSC Marc. The incremental form of the cure-dependent constitutive relation is derived, in which the numerical scheme only requires stored data from the previous time step and the evaluation of the stress update expression can be straightforwardly performed adapting an appropriate time integration scheme. This therefore avoids the storage of all the information of the stress history for evaluation of the convolution integral of the model. The cure kinetics, the cure-dependent relaxation functions and the curing shrinkage are implemented by means of user subroutines. With the stress update procedure and the designed user subroutines, an adequate simulation for establishing the curing induced stress and strain fields is obtained.

Model validation is carried out using a disc-shaped test setup, in which the specimen undergoes a 3-D stress state generated by the (partly) constrained curing shrinkage and external loading. FEM simulation indicates that model predictions agree well with the measured data, showing that the model and the FE implementation are reliable for simulation of the cure-induced stresses.

As one of the application cases and to further verify the model, the process-induced warpage during the array-moulding process of QFN packages is investigated both experimentally and numerically. A series of moulding experiments on the package carrier with the model moulding compounds are performed. FE simulations have been performed for the moulding/curing stage and subsequent cooling down phase of a series of QFN packages, for various cure/post-cure histories. The simulated warpage results were compared to the experimentally observed warpage and a reasonable agreement is obtained. Further the inclusion from ageing phenomena in the descriptions should be explored.

As the second application case, the effect of curing process-induced stresses on the thermomechanical reliability of a Flip Chip on Board (FCOB) is investigated. The cure-dependent viscoelastic model is applied to describe the viscoelastic behaviour of the underfill resin during the curing process and subsequent thermal cycling. FEM simulations are carried out to study the cure-induced stress fields and predict the solder joint fatigue life of the test carriers. It is indicated that the cure-induced residual stress/strain state should not be neglected in order to get reliable prediction results.

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Abbreviations

1-D	One-Dimensional
2-D	Two-Dimensional
3-D	Three-Dimensional
CSP	Chip Scale Package
CTE	Coefficient of Thermal Expansion
DGEBA	Diglycidyl Ether of Bisphenol A
DMA	Dynamic Mechanical Analysis
DSC	Differential Scanning Calorimetry
DONE	Design of Numerical Experiments
EMC	Epoxy Moulding Compound
FCOB	Flip Chip on Board
FEM	Finite Element Method
FTIR	Fourier Transform Infrared Spectroscopy
GP	Gel Point
IC	Integrated Circuit
LVDT	Linear Variable Displacement Transducer
PMC	Post-Mould Cure
PQFP	Plastic Quad Flat Package
QFN	Quad Flat Non-lead
TMA	Thermal Mechanical Analysis
TTS	Time-Temperature Superposition
ULFS	Ultra Low Frequency Scanning
VP	Virtual Prototyping

Chapter 1

Introduction

1.1 Electronic packaging and virtual thermo-mechanical prototyping

Electronic packaging is the technology relating to the establishment of electrical interconnections and appropriate housing for Integrated Circuits (ICs). Electronic packages provide a few major functions: interconnection of electrical signals, mechanical protection of the device from mechanical and chemical hazards, providing support for circuits, distribution of electrical power, and dissipation of heat generated by the circuits. The ability of a package to adequately perform these functions depends on the properties of the device as well as the properties of the package.

Thermo-mechanical reliability of electronic packages and assemblies is one of the major concerns in the electronics industry. Currently, thermo-mechanical (thermal, mechanical and thermo-mechanical) related failures account for about 65% of total failures in microelectronics [Zhang, *et al.*, (2006)]. This is expected to become even more critical in future products due to further miniaturization and function integration, which causes increased power dissipation density, higher interconnection density and higher reliability demands.

Based on the root cause analyses from observed failures of microelectronics, it is found that the thermo-mechanical reliability problems originate mostly from the product/process design phase. However, within the electronics industry, the trial-and-error method for thermomechanical design and qualification is still commonly used in product and process development. Several iteration cycles of concept designing, material pre-selection, building and testing of physical prototypes are needed. Clearly, this experience-based design and qualification method cannot lead to competitive products with shorter time-to-market, optimized performance, low costs, and guaranteed quality, robustness and reliability. Therefore, there is an urgent need to develop and exploit virtual prototyping methods.

Virtual thermo-mechanical prototyping methodology fundamentally comprises of two core aspects: one is "accurate and efficient prediction models", and the other is "advanced simulation based optimization methods" [Zhang, (2003)]. In order to establish accurate and efficient prediction models, following major factors, such as product and manufacturing process inputs, material models, failure criteria and damage models, and experimental and numerical methods should be included.

• Product and process input

Input data and design spaces of packages, such as material properties, product geometry, process parameters, and environmental data.

• Materials models

Appropriate material models are needed to describe the material behaviours under various loading conditions. Different materials show different behaviours. Accurate and efficient models are essential for virtual thermo-mechanical prototyping.

- Failure criteria and damage models
- *Experimental methods*

Experiments and tests play an important role in the content of virtual prototyping. First, they are needed in characterizing material and their interface behaviour (material properties, damage initiation, evolution and failure criteria). Secondly, very often, the correctness and accuracy of the developed reliability prediction models need to be verified via experiments for the whole range of the design spaces, and by covering all the critical processes. The results of VP should also be verified, wherein experiments and tests are the direct and obvious options.

• Numerical methods

Because of the complexity of structure and materials involved in the electronic packaging, normally large-scale numerical calculation is needed. Therefore the numerical methods, including model implementation, Design of Numerical Experiments (DONE), and optimization approaches should be established.

1.2 Packaging polymers

Polymers are used extensively in electronics industries. They are often classified into three groups according to their structure and mechanical properties: thermoplastic polymers (crystalline and non-crystalline), elastomers (rubbers), and thermosetting polymers.

Thermoplastic polymers consist of long, linear chains and can be processed by heating. They can be melted above a certain temperature and be pressed into the desired shape and when cooling down, the shape is frozen in. This process does not involve chemical reactions and is thus reversible. Thermoplastic polymer products can be melted and reprocessed to a different shape.

Rubbers are thermosetting polymers with an application temperature above the glass transition temperature and the crystalline melting temperature. Examples are polybutadiene and polyisoprene rubbers (both semi-crystalline). The modulus of crosslinked rubbers depends on the crosslinking density. For typical rubber, the tensile rubbery modulus is of order of 0.1MPa, which is three orders of magnitude lower than the modulus in the glassy state.

In thermosetting polymers, all macromolecular chains are connected by chemical bonds and form a large, three-dimensional network. A thermoset product therefore in fact consists of one, big molecule. The manufacturing of a thermoset product involves the polymerization process or curing process, in which chemical reactions called crosslinking occurs. The crosslinking reaction, which may occur either during or after the growth of the macromolecular chain segments, is also accompanied by a reduction in volume (shrinkage).

Thermosetting polymers are widely used in electronic packaging. They have been used in different forms and as different constituents, such moulding compounds, underfills, and adhesives, insulators, dielectrics, and coatings, etc. In this thesis, we will focus on thermosetting polymers.

Epoxy moulding compound (EMC) is the general name for the epoxy-based composite polymers using transfer moulding as the processing method. It is widely used as an encapsulant for electronic packages to protect the IC chips from mechanical and chemical hazards, due to its low cost and production efficiency. The real composition of EMC is a complex mixture generally comprising of fused silica fillers, epoxy resin and hardeners as well as other proprietary additives such as coupling agent, silicone modifiers, mould release agent, anti-oxidant, colour pigment and flame retardant, etc. [Chung, (1995)]. The cure process associated

with cross-linking of the epoxy resin and hardener is initiated during transfer moulding in which the rheology and mechanical properties of the epoxy mould compound changes drastically. During the transfer-moulding process, the EMC pellet is being melted and pressed under certain pressure into the cavity of a pre-heated mould, typically maintained at between 170°C to 180°C for duration ranging from 45 to 120 seconds. Then the moulded product is released from the mould. To achieve a fully cured state, normally a post-mould cure (PMC) process is required (cured at about 200°C).

Thermosetting polymers are widely used in the form of adhesives in electronic packaging, for example, die-attaches, electrically conductive adhesives, and so on. They can be non-conductive or electrically conductive. They are usually filled with particles.

Underfill is the name of the polymer resins that are used in Flip Chip technology to fill the gap between the silicon chip and the substrate. In Flip chip packages, the IC chip is mounted on a substrate with the chip's active surface (active area) facing to the substrate. A polymer underfill is usually applied to the gap between the chip and substrate. Underfilling the flip chip can help to reduce the effect of the CTE mismatch locally and to couple the die and substrate mechanically, which significantly alleviates the stress on solder joints and thus extends the fatigue life of the flip chip. In addition, the underfill materials can enhance the heat dissipation, thus further increasing the reliability of the flip chip.

In addition to the applications mentioned above, thermosetting polymers are also used as passivation layers, insulators, dielectrics, and coatings, etc.

Generally speaking, no matter what the applications of the thermosetting polymers are, there are a few important issues, among others, need to be well understood:

• The curing process

The curing process is one of the major packaging processes for electronic packages. During the curing process, the polymer transforms from a liquid state into a viscoelastic solid with a relatively high glassy modulus, accompanied with chemical shrinkage. On the one hand, the material properties evolve in the process and the curing profile contributes significantly to the final properties. On the other hand, residual stress and warpage may be induced due to the polymerization shrinkage and subsequent cooling down from the curing temperature. Because of the cross-linking reaction and thermal shrinkage, stresses will arise in areas where shrinkage is (partly) prevented by geometrical constraints. Furthermore, subsequent cooling or thermal cycling will produce additional stress contributions and deformation due to the mismatches in thermal expansion among the materials in the package. The residual stresses may cause reliability issues and package dimensional instability. Interface delamination, cracking of silicon die, package cracking, and cure-induced warpage are often reported.

• The time and temperature dependent behaviour

It is well known that polymers and polymer-based composites show strong temperature and time dependent behaviour. Generally the behaviour is viscoelastic, such that combined phenomena of creep and relaxation occur in packages at various levels. Such behaviour has significant influence on the thermo-mechanical behaviour of plastic IC packages.

• The effect of filler

Polymers are usually filled with fillers to improve mechanical, physical, optical and electrical properties. It is very common in electronic packaging to use silica fillers in conjunction with polymers to increase the elastic modulus and thermal conductivity and decrease the coefficient of thermal expansion (CTE), and cure shrinkage to meet the requirements for electronic packaging. Also addition of silica fillers can reduce the cost. The prediction of mechanical properties based on the knowledge of filler and matrix properties gives great advantages for designers to select the material and to optimize the packaging structure and processing parameters

In the design phase of electronic packaging, the influence of polymer applications on the thermo-mechanical reliability is often judged through thermal and mechanical simulations, under assumed processing and service conditions. For simplicity reasons and/or because of lacking insight into the mechanical processes during fabrication, the impact of the processing induced residual stress fields is usually neglected by assuming a so-called "stress-free" temperature. For example, the curing temperature is often assumed to be the "stress-free" temperature. In that case, all residual stresses are assumed to initiate from the cooling step. Sometimes, this simplification can be partly justified by the fact that part of the cure-induced stress will relax because of the material's viscoelastic behaviour. But in most cases, this assumption may not be appropriate.

The behaviour of these polymer constituents determines the performance, such as functionality and reliability, of the final products. Therefore, the successful development of microelectronics depends to some extent, on the optimal design, selection, and processing of polymer materials. Due to the development trends of microelectronics, the development and application of polymers becomes one of the bottlenecks for the microelectronic industry. With the development and introduction of new packaging materials there are many new requirements to packaged device reliability. Therefore, understanding the thermo-mechanical behaviour of packaging polymers is critical for the development of packages.

In order to be able to conduct reliable curing process optimization and to predict thermomechanical reliability more accurately and further to provide a base for virtual thermomechanical prototyping of electronic packaging, a fundamental understanding of the process of stress build-up during cure is imperative. Therefore, first, a process-dependent material model should be established, and material characterization and numerical implementation should be carried out. And then an optimization based design for package, material parameters and/or process conditions can be carried out.

1.3 The objectives and outline of the thesis

In order to be able to conduct virtual thermo-mechanical prototyping of electronic packages an appropriate description of the mechanical behaviour of polymers during and after the curing process is required. The aim of this work is to establish a cure-dependent constitutive model that should be easily engineering-applicable and be conveniently implemented into a commercial FEM program, eventually to provide a base for thermo-mechanical virtual prototyping of electronic packaging. Therefore, the major objectives of this thesis are:

- Establishment of a cure-dependent viscoelastic model to describe the mechanical behaviour of packaging polymers;
- Characterization of the cure-dependent material properties;
- Implementation of the model into a general finite element code and validation of this model.

This thesis starts with a brief description of linear viscoelasticity theory. In Chapter 2, an extensive literature review on previously developed cure-dependent viscoelastic models is first discussed. Then, a newly developed cure-dependent viscoelastic constitutive model is presented, including establishment of the rubbery moduli, effect of cure and temperature on the relaxation functions, and cure kinetics modelling as well.

Chapter 3 describes the experimental approaches to characterize the cure-dependent viscoelastic parameters of the thermosetting polymers, which are necessary for implementation of the model. The model epoxy system, the test methods, the data analysis, and the results are presented.

Chapter 4 focuses on the effect of filler volume fraction. Based on the experimental results presented in Chapter 3, the impact of filler loading on the glassy shear moduli, rubbery shear moduli, the temperature and conversion shift factors, and curing shrinkage is discussed and summarized. Theoretical predictions based on composite mechanics are carried out and compared with the measurements. A generalized cure-dependent model for the filled epoxy system is formed.

Chapter 5 presents the finite element implementation of the cure-dependent model in the commercial Finite Element Method (FEM) package MSC Marc, and the model validation as well. The incremental form of the constitutive relation is derived. Cure kinetics, cure-dependent relaxation functions and curing shrinkage are implemented by means of user subroutines.

The first application case of the model in electronic packaging is presented in Chapter 6, in which the process-induced warpage during the array-moulding process of QFN packages is investigated. Both experimental measurements and FE modelling are performed for the QFN package moulding process. The effect of filler loading, curing profiles and package structure parameters on the warpage is discussed.

In chapter 7, the modelling methodology for the cure-dependent behaviour of thermosetting polymers is applied to investigate thermo-mechanical reliability of a Flip Chip on Board (FCOB) package. The influence of the residual stresses induced in the curing process on the fatigue life of the solder bumps is investigated. The effect of the cure-induced hydrostatic stress on the fatigue life prediction is discussed.

Finally, in Chapter 8, the thesis is concluded with highlighting the main results from the research work. Recommendations for further work are proposed.

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Chapter 2

Constitutive Modelling of Thermosetting Polymers

2.1 Introduction

As mentioned in Chapter 1, the curing process is one of the major packaging processes in IC manufacturing. In order to be able to conduct reliable curing process optimization and to predict thermo-mechanical reliability more accurately, a fundamental understanding of the process of stress build-up during cure is imperative. Therefore, first, a process-dependent material model should be established and the cure-induced residual stresses and warpage should be predicted and verified with experimental data. And then an optimization based design for package structure, material parameters and/or process conditions can be carried out.

Generally, packaging polymers are epoxy resins filled with fillers and other additives. They show a strong viscoelastic behaviour, which is not only time and temperature, but also cure-dependent. The cure effect may be very significant: the position of the viscoelastic transition region normally shifts for more than 8 decades during cure of the moulding compound. For adequate modelling of the viscoelastic behaviour of thermosetting polymers there are a few important aspects, which should be addressed and better understood:

- The cure kinetics and the relationship between the glass transition temperature T_g and the degree of cure or conversion α, which can relate the mechanical behaviour to the curing temperature and history;
- The effect of conversion and temperature on the evolution of shear and bulk moduli during cure;
- The dependency of chemical shrinkage on the degree of conversion;

• The effect of filler concentration on the material properties.

This chapter starts with a brief recapitulation of the linear viscoelasticity theory, with an emphasis on the spring and dashpot models and the models accounting for the temperature effect. Then, a complete cure-dependent viscoelastic constitutive model, including the rubbery moduli, the cure and temperature dependency of the relaxation behaviour, is proposed. Finally, the relationship between the mechanical behaviour and the curing profile is established by using well-developed cure kinetics models.

The curing shrinkage will be discussed in Chapter 3. The effect of filler concentration on the viscoelastic properties will be presented in Chapter 4.

2.2 Linear viscoelasticity theory

2.2.1 Creep and relaxation

The time dependency of viscoelastic materials can be observed through simple uniaxial tensile tests, among which creep and relaxation are the most commonly used ones.

In a creep test, a constant stress σ_0 is applied to the material at time t_0 . As illustrated in Fig. 2.1, the resulting time-dependent strain response can be described as:

$$\varepsilon(t) = D(t - t_0)\sigma_0 \tag{2.1}$$

where $D(t-t_0)$ is the creep compliance.

In a stress relaxation test, a constant stain ε_0 is applied to the material at time t_0 . A decaying stress response can be seen, as shown in Fig. 2.2, and the stress can be expressed as:

$$\sigma(t) = E(t - t_0)\varepsilon_0 \tag{2.2}$$

where $E(t-t_0)$ is the relaxation modulus.



Figure 2.1: Step creep response, (a) step stress σ_0 applied at time t_0 ; (b) strain response to the step stress



Figure 2.2: Step relaxation response, (a) step strain ε_0 applied at time t_0 ; (b) response to the step strain

2.2.2 The Boltzmann superposition integral

The Boltzmann superposition principle is a widely used starting point for the study of rheological properties of linear viscoelastic materials and is known to be reliable for deformation below plastic yield. The principle states that the material response to the applied loadings is a function of the entire past loading history and each loading step makes an independent contribution to final deformation or stresses. Figure 2.3 illustrates the relaxation response to a multi-step strain loading, in which the incremental strains $\Delta \varepsilon_1$, $\Delta \varepsilon_2$, ..., are added at time t_1, t_2, \ldots , respectively. Then the total stress at time t is given by

$$\sigma(t) = \Delta \varepsilon_1 E(t - t_1) + \Delta \varepsilon_2 E(t - t_2) + \Delta \varepsilon_3 E(t - t_3) + \dots,$$
(2.3)

where $E(t-\xi)$ is the stress relaxation modulus. The contribution of each loading step $\Delta \varepsilon_i$ is the product of the incremental strain $\Delta \varepsilon_i$ and the relaxation function, which depends only on the

interval in time between the loading time t_i and current time t. In considering a continuous loading, Equation (2.3) can be generalized as an integral form:



Figure 2.3: Step relaxation response to a multi-step strain loading, (a) multi-step strains applied at time t_i ; (b) response to the multi-step strains

2.2.3 Typical mechanical models for linear viscoelastic response

Linear viscoelasticity can be represented in principle by models consisting of combinations of Hookean springs and Newtonian dashpot. The spring and dashpot can be used to represent elastic material and Newtonian fluid, respectively. Figure 2.4 shows some simple but important models based on the spring and dashpot. Taken as an illustration example, as shown in Figure 2.4(b), the Maxwell model consists of a spring and dashpot in series. Considering a stress relation test, with boundary condition of $\sigma = \sigma_0$ at time t=0, we have the decaying stress as:

$$\sigma = \sigma_0 \exp\left(-\frac{E}{\eta}t\right) \tag{2.5a}$$

let $\tau = \eta / E$, then

$$\sigma = \sigma_0 \exp\left(-\frac{t}{\tau}\right) \tag{2.5b}$$

in which τ is a characteristic time of the material called the relaxation time. The above equation shows that the stress decays exponentially. Though the Maxwell model can describe the stress relaxation to a first approximation, it is unable to describe the complex relaxation behaviour because it has only one single relaxation term, in addition, for the creep case the model response shows Newtonian flow. This is obviously not true for viscoelastic materials where the creep behaviour is more complex.

Similarly, the Kelvin-Voigt model, which consists of a spring and dashpot in parallel, can represent the time-dependent component of creep to a first approximation, but is unable to describe stress relaxation behaviour.

Model	Constitutive equation	
Hooke's law	$\sigma = E\varepsilon$	(2.6)
Newton's law	$\sigma = \eta \frac{d\varepsilon}{dt}$	(2.7)
Maxwell model	$\sigma + \tau \frac{d\sigma}{dt} = \eta \frac{d\varepsilon}{dt}$	(2.8)
Kelvin-Voigt model	$\sigma = E\varepsilon + \eta \frac{d\varepsilon}{dt}$	(2.9)
The standard linear solid	$\sigma + \tau \frac{d\sigma}{dt} = E_1 \varepsilon + (E_1 + E_2) \tau \frac{d\varepsilon}{dt}$	(2.10)
The Burgers model	$\sigma + a_1 \frac{d\sigma}{dt} + a_2 \frac{d^2 \sigma}{dt^2} = b_0 \varepsilon + b_1 \frac{d\varepsilon}{dt} + b_2 \frac{d^2 \varepsilon}{dt^2}$	(2.11)

Table 2.1 Simple models

For a real viscoelastic material a simple exponential response in relaxation or creep is not adequate to describe the time dependence. More complicated models can be constructed by adding more Maxwell elements or Kelvin-Voigt elements. The most popular models are the generalized Maxwell model and the generalized Kelvin-Voigt model. As shown in Fig. 2.5 and 2.6, respectively, the former consists of a number of Maxwell elements in parallel and the later a number of Kelvin-Voigt elements in series. The relaxation modulus function of the generalized Maxwell model is described as

$$E(t) = \sum_{n=1}^{N} E_n \exp\left(-\frac{t}{\tau_n}\right)$$
(2.12)

in which E_n and τ_n are the modulus of the spring and the relaxation time of the nth Maxwell element. This equation is also referred as the Prony series. The relaxation behaviour of real viscoelastic materials can be described with sufficient accuracy if the number of terms is large

enough. Eq. (2.12) is very convenient for numerical simulation and is also useful for fitting experimental relaxation data.



Figure 2.4: Simple models (a). Maxwell model; (b). Kelvin-Voigt model; (c). the standard linear model; (d). the Burgers model

Regarding to the generalized Kelvin-Voigt model, as shown in Fig. 2.6, the creep compliance function can be derived as

$$D(t) = \sum_{n=1}^{N} D_n \left(1 - \exp\left(-\frac{t}{\tau_n}\right) \right)$$
(2.13)

where D_n and τ_n are the elastic compliance of the spring and the retardation time of the nth Kelvin-Voigt element. The generalized Kelvin-Voigt model is in particular convenient to describe the creep behaviour.



Figure 2.5: Generalized Maxwell model



Figure 2.6: Generalized Kelvin-Voigt model

2.2.4 Time-temperature superposition principle

Polymers and polymer-based composites not only show time dependent behaviour but also strong temperature dependent behaviour. Figure 2.7 illustrates schematically modulustemperature curves for typical linear and crosslinked polymers. At low temperatures polymers are glassy and exhibit a plateau of a relatively high modulus, called the glassy plateau. In this region, the polymers are hard and brittle. Usually, the glassy modulus E_g is decreased slightly with temperature increase [Ferry, (1980)]. As the temperature is increased, the material goes through the transition region and the stiffness drops dramatically. The temperature at which the glass transition occurs is called the glass transition temperature T_g . As the temperature is increased further, the modulus reaches another plateau, to a value called rubbery modulus or equilibrium modulus. For un-crosslinked polymers, such as thermoplastics, the stiffness exhibits only a very short plateau and then decreases to zero and the material behaves like a viscous liquid. For crosslinked polymers, the magnitude of the rubbery plateau depends on the crosslinking density etc. The rubbery moduli dominate the material response at high temperature or at long times.



Figure 2.7: Schematic illustration of modulus-temperature curve

The well-known principle of time-temperature superposition is based on the observation that time-temperature and frequency-temperature effects in polymers are largely equivalent. It implies that the mechanical response at short times (or high frequencies) is analogous to the response at low temperature, and vice versa. For example, increasing temperature will shift the same event to shorter times, or increasing the frequency will shift the same event to lower temperatures. This principle is commonly used to determine viscoelastic properties beyond the range of frequencies covered by experimental measurements. For thermorheologically simple materials, the viscoelastic response at one temperature can be obtained by simply shifting horizontally the viscoelastic curve at another temperature without change of shape. As illustrated in Figure 2.8, the correlation of the curves can be expressed as

$$E(T_1, t) = E(T_2, t/a_T)$$
(2.14)

in which a_T is called the time-temperature shift factor, which is a function of T_1 and T_2 only.

A well known empirical equation for time-temperature superposition is the WLF equation, which was proposed by Willams et al. (1955) to describe the time/frequency shift of viscoelastic parameters with temperature:

$$\log a_T = \frac{-C_1(T - T_{ref})}{C_2 + (T - T_{ref})}$$
(2.15)

where T_{ref} is the reference temperature, C_1 and C_2 are constants whose values depend on the material and choice of the reference temperature T_{ref} . It has been found that if T_g is chosen as the reference temperature, the parameters C_1 and C_2 are constant for many amorphous polymers and are equal to 17.44°C and 51.6°C, respectively.



Figure 2.8: Schematic illustration of time-temperature shift

The WLF equation has a theoretical base in terms of free volume concepts. According to the theory of free volume, the total macroscopic volume V is considered as a summation of the 'occupied volume' V_o and the 'free volume' V_f . Figure 2.9 shows schematically variation of the specific volume of a polymer versus temperature on the basis of dilatometric measurements. A sudden change of the slope of the specific volume can be seen as the temperature approaches the glass transition temperature T_g . Assuming that the occupied volume increases uniformly with

temperature, the discontinuity of the specific volume slope corresponds to a sudden onset of expansion in the free volume.



Figure 2.9: Schematic illustration of relationship of specific volume and temperature

The fractional free volume, $f = V_f / V$, at any temperature T can be written as

$$f = f_g + \alpha_f (T - T_g) , \qquad T \ge T_g$$
(2.16a)

and

$$f = f_g \quad , \qquad \qquad T < T_g \tag{2.16b}$$

where f_g is the fractional free volume at T_g and α_f is the coefficient of thermal expansion of the free volume. The semi empirical Doolittle equation [Ward, (1983)] relates the flow viscosity of amorphous polymers to the free volume in the form of

$$\ln \eta = \ln A + B \frac{V_o}{V_f} \tag{2.17a}$$

where A and B are constants. Rewriting of this equation gives

$$\ln \eta = \ln A + B\left(\frac{1}{f} - 1\right) \tag{2.17b}$$

Thus, the shift factor can be expressed as

$$\log a_T = \log \frac{\eta_T}{\eta_{T_g}} = -\frac{B}{2.303 f_g} \left(\frac{T - T_g}{\frac{f_g}{\alpha_f} + T - T_g} \right)$$
(2.18)

in which η_T and η_{T_g} represent the viscosities of the polymer at temperature T and T_g , respectively. Let $C_1 = B/(2.303 f_g)$ and $C_2 = f_g/\alpha_f$, then equation (2.18) equals the WLF equation.

The WLF equation is typically used to model viscoelastic behaviour at temperatures above the glass transition, but it has been modified to permit application both above and below T_g .

Some time-temperature processes are best described in terms of Arrhenius behaviour [Ferry, 1980], especially when the temperature is below T_g . If the relaxation time obeys an Arrhenius relation of the form $\tau(T) = \tau_0 \exp(E/RT)$, the shift factor is given by

$$\log a_T = \frac{\Delta H}{2.303R} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right)$$
(2.19)

where ΔH is the activation energy and T_{ref} is the reference temperature. Description of relaxation processes in terms of activation energy is usually unsatisfactory at temperature close to and above T_g .

The temperature shift factor can be described in a more general form: the generalized Vogel equation:

$$\log a_T = \frac{C}{T - T_{\infty}} - \frac{C}{T_{ref} - T_{\infty}}$$
(2.20)

where C is a constant, T_{ref} is the reference temperature, T_{∞} is a constant temperature. When T_{∞} is chosen to be $T_{\infty} = T_g - C_2$, the Vogel equation equals the WLF equation. And when T_{∞} is chosen to be $T_{\infty} = 0$ °K, the above equation is the Arrhenius equation. Therefore, the Vogel equation is capable of describing both WLF behaviour and Arrhenius behaviour.

2.2.5 Multi-axial stress states -- 3-D models

The viscoelastic expressions above have been referenced to a simple stress state in which a specimen is subject to uniaxial tension. Under multi-axial stress states, the stress-strain relation can be generalized into following form:

$$\sigma_{ij}(t) = \int_{-\infty}^{t} C_{ijkl}(t-\xi) \cdot \frac{d\varepsilon_{kl}}{d\xi} d\xi$$
(2.21)

For isotropic materials, the relaxation modulus functions have only two independent components: the shear relaxation modulus and bulk relaxation modulus, denoted as $G(t - \xi)$ and $K(t - \xi)$, respectively. The relaxation modulus functions can be written as

$$C_{ii}(t-\xi) = G(t-\xi) \cdot D_{ii} + K(t-\xi) \cdot V_{ii}$$
(2.22)

where $[V_{ij}]$ and $[D_{ij}]$ are the volumetric and deviatoric (constant) coefficient matrices, with

and

$$\begin{bmatrix} D_{ij} \end{bmatrix} = \begin{bmatrix} 4/3 & -2/3 & -2/3 & 0 & 0 & 0 \\ -2/3 & 4/3 & -2/3 & 0 & 0 & 0 \\ -2/3 & -2/3 & 4/3 & 0 & 0 & 0 \\ 0 & 0 & 0 & 2 & 0 & 0 \\ 0 & 0 & 0 & 0 & 2 & 0 \\ 0 & 0 & 0 & 0 & 0 & 2 \end{bmatrix}$$
(2.23b)

The strain can also be split into the volumetric part and the deviatoric part. Then the stress can be expressed as:

$$\sigma_{ij}(t) = \int_{-\infty}^{t} \left[2G(t-\xi) \cdot \frac{d\varepsilon_{ij}^{d}}{d\xi} + K(t-\xi) \cdot \frac{d\varepsilon_{v}^{eff}}{d\xi} \right] d\xi$$
(2.24)

in which ε_{v}^{eff} and ε_{ij}^{d} represent the effective volumetric strain and the deviatoric strains. They can be written as

$$\varepsilon_{v}^{eff} = \sum_{i=1}^{3} \left[\varepsilon_{ii} - \varepsilon_{ii}^{*} \right]$$
(2.25a)

and

$$\varepsilon_{ij}^{d} = \varepsilon_{ij} - \frac{1}{3} \varepsilon_{v}^{eff}$$
(2.25b)

2.3 Cure-dependent constitutive modelling

2.3.1 Literature review

There has been limited work on modelling of the development of thermo-mechanical properties of polymers during cure. Generally, such modelling falls into two categories, i.e. elastic models and viscoelastic models.

Among the elastic models, Plepys *et al.* (1993) used an incremental linear elastic constitutive equation to calculate the residual stresses induced during cure. Several authors have tried to approximate the residual stress-state by assuming the stress relaxation to be much quicker than the evolution of chemical shrinkage [Chambers, *et al.* (1995); Lange, *et al.* (1995); Korotkov, *et al.* (1996)]. Under this assumption an integral form of a rubbery elastic model was adopted using so called 'equilibrium moduli', i.e. the moduli just after transient relaxation. The material characterization was performed by measuring the rubbery modulus and volumetric shrinkage during isothermal curing at the temperatures well above T_g .

Among the efforts on viscoelastic modelling, Lange *et al.* (1997) used a single Maxwell model to account for relaxation behaviour of shrinkage stresses. Cure-dependent relaxation times and (elastic) shear moduli were obtained through torsional DMA measurements. The Poisson's ratio was assumed to be constant. The model results did not give sufficient improvement compared to the earlier published incremental elastic model.

The well-known time-temperature superposition principle has been widely used in modelling the effect of temperature on the viscoelastic behaviour of polymers [Ferry, (1980)]. In analogy to time-temperature superposition, time-crosslinking superposition was used first by Plazek (1966) to reduce creep curves in the terminal zone for natural rubber vulcanates. In that work, the more loosely crosslinked materials were shifted horizontally to longer times associated with the higher molecular weights between cross-link points. Lee and McKenna (1988) used time-crosslinking superposition to describe the effect of crosslinking density on stress relaxation during physical aging in thermosetting networks. Tensile relaxation tests were carried out at temperatures below T_g . The capability of such superposition was observed.

Since then, a few researchers have applied this principle to study the effect of the conversion on the viscoelastic behaviour during cure. Kim and White (1996) studied stress relaxation behaviour of a diglycidyl ether of bisphenol A (DGEBA) resin cured with a multifunctional amine under various conversion levels. Relaxation measurements were carried out on partly cured specimens at different temperatures. The relaxation shear modulus was approximated with Prony series, in which both of the equilibrium modulus and Poisson's ratio were assumed to be constant with degree of conversion. The influence of ongoing cure was handled like long-term chemical aging by applying shift factors on the relaxation times. Complex theoretical considerations were invoked to predict the shift factors at lower degrees of cure.

Plazek and Chay (1991) investigated the viscoelastic properties of fully cured epoxy resin samples with a wide range of crosslinking densities prepared by varying the ratio of monofunctional and terafuctional curing agents in a stoichiometric epoxide-curing agent mixture. Using the method in analogy with the time-temperature superposition (WLF) principle, they have shown that curves of creep compliance of different crosslinking densities could be made to superpose by shifting along the time axis. The curves were found to superpose well at short times (in the glassy region) but deviate at longer times (terminal region). This is not surprising since the glassy modulus is not strongly dependent on chemical conversion whereas the rubbery modulus increases dramatically with conversion.

Simon *et al.* (2000) proposed a model for the viscoelastic properties of an epoxy resin during cure after gelation. They also approximated the shear relaxation modulus with the generalized Maxwell model. The evolution of the rubbery shear modulus was modelled with the theory of rubber elasticity, in which the cure dependency was related through the effective concentration of network chains using the Miller and Macosko approach.

A research group in Sandia National Laboratories has conducted research on modelling the viscoelastic properties of epoxy resins during curing with the aim to establish a structureproperty model for curing resins [Adolf, *et al.*, (1990/1996/1997/1998)]. The shear modulus was considered to be a sum of the equilibrium shear modulus and the decaying portion. In the decaying portion, the relaxation behaviour was represented by the characteristic relaxation time. The characteristic relaxation time was then treated similarly as the WLF temperature dependence, in which the reference temperature was taken to be the glass transition temperature. The glass transition temperature was described by a semi-empirical relationship, which depends on the rubbery shear modulus. A model based on scaling analysis was proposed to describe the evolution of the shear rubbery modulus after gelation.

In our research group, since 1995 much research work on modelling cure-dependent viscoelastic behaviour of thermosetting polymers has been done. A review and discussion will be given in the next separate section.
2.3.2 Background and research progress concerning the modelling of cure-dependent behaviour in our research group

In early effort by our research group to establish a model to describe the behaviour of curing polymers, Kiasat (2000) proposed a fully isotropic constitutive equation for the curing of polyester resin. Both the shear relaxation modulus and bulk relaxation modulus were represented with a Prony's series form. The relaxation times were assumed constant during the entire curing history. The stiffness coefficients were considered to be cure-dependent and represented by a six parameter fitting equation with the curing time as the variable. The parameters of the equations were obtained by fitting to the DMA measurement data from isothermal curing conditions. The relaxation behaviour was described in such a way that the response at any loading time is only dependent on the material behaviour at that time, and the effect of ongoing curing on the subsequent relaxation process is not taken into account.

Ernst et al. (2000/2003) generalized the method and further it was applied for describing cure-dependent viscoelastic behaviour of epoxy resin and for investigating the solder joint fatigue lifetime of a Flip Chip package [Yang et al., (2003)]. A model verification through step relaxation showed that originally the rubbery state was inadequately described, due to the fact that stabilized low frequency DMA measurements (as described in the DMA analyses) are not feasible for continuously increasing stiffness. Later, by using the so-called Ultra Low Frequency Scanning method (see section 3.4.3), this problem could be solved.

Hof (2006) proposed a profound so-called fully cured dependent viscoelastic model, in which the history of state parameters is taken into account in the convolution integral expression. The model does not assume a master curve concept to account for the curing history effects. However, it is hard to be implemented into a FEM program, because the convolution integrals involved should be evaluated for each time step (and each iteration). This would result into a huge storage and data-handling problem. Up to now, only 1-D sample problems were solved and the comparison with approximately fully cure-dependent model results showed only minor differences (for slowly curing compounds).

Almost being parallel to Hof's research work, since 2000 our research work was being carried out with an aim to establish a cure-dependent constitutive model that should be easily engineering-applicable and be conveniently implemented into a commercial FEM program, eventually to provide a base for thermo-mechanical virtual prototyping of electronic packaging. Several publications were made with regard to the development and improvement of our model, the experimental characterization and FEM implementation. In [Yang et al. (2004a/b), Jansen *et*

al. (2004a/b)] we applied time-cure superposition principle to model the mechanical behaviour during isothermal cure. Epoxy resins were cured under isothermal temperature slightly below the ultimate T_g and DMA frequency sweeps were conducted during cure. It was found that the reduced storage modulus ($(G'(\alpha, \omega) - G_r(\alpha))$) at different degree of cure can be shifted along the frequency axis and match well with the master curve of the fully cured materials. Then, in the model, the relaxation modulus was considered of a sum of the rubbery part and transient part. The generalized Maxwell model was applied to model the transient part, while the effect of cure on the relaxation behaviour is taken into account by the cure-dependent relaxation amplitude and the shift factor obtained from the isothermal DMA measurements. This model was applied to predict the cure-induced warpage in the moulding process of QFN packages. As a part of European project Mevipro (Project No.GRD1-2001-40296), our research work was also reported in [Jansen, (2004c/d/e)]. In the subsequent sections of this chapter, our model based on the time (or frequency)-temperature and time (or frequency)-conversion superposition principle will be described. The experimental characterization will be presented in Chapter 4.

It is worth mentioning that recently new doctoral projects have been setup in our research group to study the material behaviour during the snap curing process and further to explore the methods for accurate characterization of the cure-dependent bulk relaxation modulus.

2.3.3 General form of cure-dependent stress-strain relation

In [Ernst et al., 2006], we proposed general state-dependent viscoelastic equations both in relaxation mode and creep mode by using the convolution integral. The relaxation modulus function or creep compliance function can be considered to depend on state variables, such as stress level, temperature, humidity, or degree of cure. With concerns to the application in electronic packaging, the stress level in the packages is relatively low. Therefore, it is reasonable to assume linear viscoelasticity in such applications to reduce the complexity.

Accordingly, the state of stress at time *t* in a curing polymer system is given by:

$$\sigma_{ij}(t) = \int_{-\infty}^{t} C_{ijkl}[\alpha(\xi), T(\xi), (t-\xi)] \cdot \left(\frac{\partial \varepsilon_{kl}}{\partial \xi} - \frac{\partial \varepsilon_{kl}^{*}}{\partial \xi}\right) d\xi$$
(2.26)

where ξ is the curing time or loading time, T the temperature, α the degree of conversion, and ε_{kl} strain. ε_{kl}^* is the initial strain, including thermal and polymerization strains. $(t-\xi)$ represents the time interval between load setup and current time. C_{ijkl} are the relaxation modulus functions or kernel functions, and here they are considered to be the function of curing state (degree of cure), temperature and the history between the curing time (or loading time) and the current time.

Assuming isotropy, the cure-dependent relaxation modulus functions can be decomposed into two independent parts, governed by the shear relaxation moduli and bulk relaxation moduli, respectively. The convolution integral for the stresses at current time t is thus simplified to (see Eq. (2.24)):

$$\sigma_{ij}(t) = \int_{-\infty}^{t} \left[2G[\alpha(\xi), T(\xi), (t-\xi)] \cdot \frac{d\varepsilon_{ij}^{d}}{d\xi} + K[\alpha(\xi), T(\xi), (t-\xi)] \cdot \frac{d\varepsilon_{\nu}^{eff}}{d\xi} \right] d\xi$$
(2.27)

where ε_{ij}^{d} represents the deviatoric strains, with $\varepsilon_{ij}^{d} = \varepsilon_{ij} - \frac{1}{3}\varepsilon_{kk}\delta_{ij}$, and ε_{v}^{eff} is the effective volumetric strain.

Though it is possible that for some cases the relaxation modulus functions in Eq. (2.27) could be measured straightforwardly by experiments, it is not realistic for ongoing curing polymers. Models have to be established to describe the evolution of the relaxation moduli with the curing state. In the following sections, the relaxation modulus functions will be established under some simplifications.

2.3.4 Cure dependent relaxation moduli

During the curing process, the crosslinking polymer transforms from a liquid state into a viscoelastic solid with a relatively high glassy modulus. Figure 2.10 illustrates the typical behaviour of the shear relaxation modulus during cure. G_g is the glassy value (the glassy plateau). The other horizontal plateau is the equilibrium modulus (or rubbery modulus). From the observation, the following characteristics regarding relaxation behaviour of curing polymers can be drawn:

- 1) The glassy plateau is not strongly temperature- or conversion-dependent.
- The equilibrium modulus (or rubbery modulus) shows strong conversion-dependency. It increases from zero before gelation to a certain value at the fully cured state.
- 3) The relaxation time increases as the curing process proceeds.
- 4) The relaxation amplitude, which is the difference of G_g and $G_r(\alpha)$, i.e. $G_g G_r(\alpha)$, changes from G_g before gelation to $G_g - G_r^f$ at the fully cured state.
- 5) It is obvious that the relaxation curves at different degree of cure cannot be formed to be one single master curve by simple horizontal or vertical shifting. It means that the curing polymer shows thermo-rheologically complex behaviour.



Figure 2.10: Typical relaxation behaviour of crosslinking polymer during cure

Thus in the modelling, the strong cure-dependency of the rubbery modulus must be considered. Here, as many researchers did, we split the total relaxation modulus into two parts, i.e., the equilibrium part and the transient part:

$$G[\alpha(\xi), T(\xi), (t-\xi)] = G_r[\alpha(\xi), T(\xi)] + G_d[\alpha(\xi), T(\xi), (t-\xi)]$$
(2.28a)

in which $G_r[\alpha(\xi), T(\xi)]$ is the equilibrium shear modulus, which is cure and temperature dependent. $G_d[\alpha(\xi), T(\xi), (t-\xi)]$ is the transient part or the relaxation part of the total relaxation modulus, which is not only dependent on the cure state and temperature, but also on the history between the curing time or loading time ξ and current time t. For simplification, $\alpha(\xi)$ and $T(\xi)$ are denoted as α and T, respectively. The modelling of the cure-dependent equilibrium modulus will be discussed in section 2.3.3. The transient part will be established in the following and in section 2.3.4.

Because of its numerical efficiency and convenience, Prony series approximations are used. Then the shear relaxation moduli can be described as:

$$G_d[\alpha, T, (t-\xi)] = \sum_{n=1}^N G_n(\alpha, T) \cdot \exp\left[-\frac{t-\xi}{\tau_n(\alpha, T)}\right]$$
(2.28b)

where $G_n(\alpha, T)$ and $\tau_n(\alpha, T)$ are the stiffness coefficient and relaxation time of the n^{th} term. The relaxation amplitude is introduced, then the relaxation modulus can be written as:

$$G[\alpha, T, (t-\xi)] = G_r(\alpha, T) + \left[G_g - G_r(\alpha, T)\right] \cdot \sum_{n=1}^N g_n(\alpha) \cdot \exp\left[-\frac{t-\xi}{\tau_n(\alpha, T)}\right]$$
(2.28c)

in which G_g is the glassy value of the relaxation modulus, which is considered to be not strongly temperature and cure dependent. $g_n(\alpha)$ are the weighting factors, with $\sum_{n=1}^{N} g_n(\alpha) = 1$. The weighting factors could be cure dependent. Equation (2.28c) describes a thermo-rheologically complex behaviour corresponding to the ongoing cure. Due to increasing of the rubbery plateau with ongoing cure, the relaxation behaviour under different degree of cure cannot be obtained by simple horizontal shift along the time axis or frequency axis.

Based on our experimental observations that will be presented in Chapter 3, some simplifications on the equation (2.28c) can be made. Since the normalized relaxation master curves (the transient part) at different cured states can be eventually overlapped into one single by simply horizontal shift (see section 3.4.6), it is implied that the transient relaxation modulus functions follows a thermo-rheologically simple behaviour. Therefore, equation (2.28c) can be simplified by taking the weighting factors as cure independent, as:

$$G[\alpha, T, (t - \xi)] = G_r(\alpha, T) + \left[G_g - G_r(\alpha, T)\right] \cdot \sum_{n=1}^N g_n \cdot \exp\left[-\frac{t - \xi}{\tau_n(\alpha, T)}\right]$$
(2.28d)
which also $\sum_{n=1}^N g_n = 1$.

in v n=1

In analogy to the modelling of the shear modulus, the relaxation bulk modulus is expressed in the same form:

$$K[\alpha, T, (t-\xi)] = K_r(\alpha, T) + \left[K_g - K_r(\alpha, T)\right] \cdot \sum_{n=1}^N k_n \cdot \exp\left[-\frac{t-\xi}{\tau'_n(\alpha, T)}\right]$$
(2.29)

where $K_r(\alpha,T)$ is the equilibrium bulk modulus, K_g is the glassy bulk modulus; k_n are the weighting factors, with $\sum_{n=1}^{N} k_n = 1$; $\tau'_n(\alpha, T)$ is the relaxation time of the n^{th} term, which is not necessarily the same as the relaxation time in the shear modulus description.

Therefore, substituting equations (2.28d) and (2.29) into (2.27), the stress-strain relation can be represented as:

$$\sigma_{ij}(t) = \int_{-\infty}^{t} 2\left\{ G_r(\alpha, T) + \left[G_g - G_r(\alpha, T) \right] \cdot \sum_{n=1}^{N} g_n \cdot \exp\left[-\frac{t - \xi}{\tau_n(\alpha, T)} \right] \right\} \cdot \frac{d\varepsilon_{ij}^d}{d\xi} d\xi + \int_{-\infty}^{t} \left\{ K_r(\alpha, T) + \left[K_g - K_r(\alpha, T) \right] \cdot \sum_{n=1}^{N} k_n \cdot \exp\left[-\frac{t - \xi}{\tau'_n(\alpha, T)} \right] \right\} \cdot \frac{d\varepsilon_{\nu}^{eff}}{d\xi} d\xi$$

$$(2.30)$$

As shown in equation (2.30), because the equilibrium moduli and the relaxation amplitudes in the transient parts are considered to be cure-dependent, the model actually describes a 'quasi' thermo-rheologically simple behaviour.

In Section 2.3.4, the evolution of the cure-dependent equilibrium moduli will described, and in Section 2.3.5, the relaxation times will be expressed as depending on cure and temperature shift factors.

2.3.5 Equilibrium moduli (rubbery moduli)

Basically, there are two approaches to establish models for describing the evolution of the equilibrium shear modulus during the curing process. One is based on the theory of rubber elasticity, in which the rubbery modulus is considered to be proportional to the effective concentration of network chains. Simon et al. (2000) used this model to describe the effect of temperature and conversion on the rubbery shear modulus for an epoxy resin. In their method, the cure dependency was related through the effective concentration of network chains using the Miller and Macosko's approach [Halley and McKay, (1996)].

The other model is based on scaling analysis and was originally proposed by Adolf et al. (1990/1997). Starting from the percolation analysis, they scaled the equilibrium modulus as:

$$G_r \sim \epsilon^{8/3} \tag{2.31}$$

in which \in is the distance-to-threshold, as $\in |p^2 - p_c^2|/p_c^2$, where p and p_c are the bond probability and the critical bond probability at the gel point. Then they came up with a model relating the shear rubbery modulus with the conversion as follows:

$$G_{r}(\alpha,T) = G_{r}^{f}(T) \left[\frac{\alpha^{2} - \alpha_{gel}^{2}}{1 - \alpha_{gel}^{2}} \right]^{8/3}$$
(2.32)

where $\alpha(\xi)$ and α_{gel} are the degree of cure at the curing time ξ and at the gel point, respectively. G_r^f is the rubbery shear modulus at the fully cured state ($\alpha = 1.0$). Note that G_r^f is often temperature dependent for most polymers. Yang *et al.* (2005) applied the model to predict the evolution of the equilibrium shear modulus during the isothermal curing of an epoxy resin and also for the epoxy composites. A good agreement between the experimental measurement and the model prediction was observed.

The degree of conversion at the gel point, α_{gel} , can be determined either by experimental measurements or using theoretical calculation. Winter *et al.* (1987) proposed a general criterion

that can be used to identify the gel point. Flory (1980) proposed an equation to calculate the conversion at the gel point based on the fact that the conversion at gelation is determined by the (average) number of reaction sites of the monomer, and the mixing ratio of the two components. If the reactivity of the functional groups is independent and no side reactions occur, the conversion at gelation is given by the Flory equation as:

$$\alpha_{gel} = \frac{1}{\sqrt{r_E(f_{OH} - 1)(f_{ep} - 1)}} \quad , \tag{2.33}$$

where r_E is defined as the ratio of hydroxyl (or amine) to epoxy groups in the unreacted mixture, and f_{OH} and f_{ep} are the functionalities of hydroxyl (or amine) and epoxy, respectively.

In order to model the cure dependency of the rubbery bulk modulus, we propose an equation similar to Eq. (2.32):

$$K_{r}(\alpha,T) = K_{r}^{l} + \left[K_{r}^{f}(T) - K_{r}^{l}\right] \left[\frac{\alpha^{2} - \alpha_{gel}^{2}}{1 - \alpha_{gel}^{2}}\right]^{8/3}, \qquad (2.34)$$

in which K_r^l is the bulk modulus at liquid state, K_r^f is the bulk modulus at the fully cured state. The extra constant K_r^l in Eq. (2.34) is added to ensure a minimum value for the bulk modulus. A zero value for the bulk modulus would have been unacceptable from a physical point of view since this corresponds to a material with zero resistance to hydrostatic compression. The bulk modulus of liquid moulding compounds is expected to be close to that of other liquids, i.e. in the range from 1 to 3 GPa.

2.3.6 Modelling the effect of temperature and conversion on the relaxation behaviour of curing polymer

The effect of temperature and cure on the relaxation behaviour is usually described through the shift factor, which is either used for 'reduced time' or 'reduced frequency'. For fully cured polymers, as described in section 2.2.4, the time-temperature shift factor is often described by applying the WLF equation and or Arrhenius behaviour or the general Vogel equation. While for curing polymers, the effect of conversion on the temperature dependence of the shift factors must be included. In the early work by Suzuki and Miyano (1977), they found that the activation energy for the shift factors was independent of the degree of cure for an epoxy resin. Similarly, Plazek and Chay (1991) found in their model epoxy system that the viscoelastic shift factors followed the same Vogel temperature dependence independent of the degree of cure when the reference temperature was taken as the glass transition temperature.

As indicated in section 2.3.2, we assume that the transient part or the relaxation part follows a thermo-rheologically simple behaviour. Under this assumption, then the effect of temperature and the degree of cure on the relaxation behaviour can be established by applying the principles of time-temperature and time-cure superposition. The relaxation is expressed as [Simon et al. (2000)]:

$$\tau_n(\alpha, T) = a_{T,\alpha} \cdot \tau_n(\alpha_{ref}, T_{ref})$$
(2.35)

where $\tau_n(\alpha_{ref}, T_{ref})$ is the nth relaxation time corresponding to the reference temperature T_{ref} and reference conversion α_{ref} . $a_{T,\alpha}$ is the shift factor that accounts for the temperature and cure dependence.

When the reference temperature is chosen as the glass transition temperature, according to the general Vogel equation, the temperature shift factor for each conversion level can be expressed as:

$$\log a_T = \frac{A}{T - T_{\infty}} - \frac{A}{T_{ref} - T_{\infty}}, \qquad (2.36)$$

where A is a constant, T_{ref} is the reference temperature, T_{∞} is a constant temperature.

Similar to the approach for the temperature effect, the shift factor for the cure effect is written as:

$$\log a_{\alpha} = \log \frac{\tau_n(T_{g\alpha})}{\tau_n(T_g^{ref})} = -\left(\frac{B}{T_{g\alpha} - T_{\infty}^{'}} - \frac{B}{T_g^{ref} - T_{\infty}^{'}}\right),\tag{2.37}$$

where B is a constant, $T_{g\alpha}$ is glass transition temperature, T_{∞}' is a constant temperature.

Combining the temperature and cure effects, the shift factor is

$$\log a_{T,\alpha} = \left(\frac{A}{T - T_{\infty}} - \frac{A}{T_{ref} - T_{\infty}}\right) - \left(\frac{B}{T_{g\alpha} - T_{\infty}'} - \frac{B}{T_{g}'' - T_{\infty}'}\right).$$
(2.38)

2.4 Cure kinetics modelling

In the above cure-dependent viscoelastic model, the degree of cure is chosen as the governing parameter. The cure kinetics is needed to define the time-temperature dependence of conversion.

2.4.1 Kinetics model

The degree of cure, α , is often defined as:

$$\alpha(t) = \frac{H(t)}{H_u},\tag{2.39}$$

where H(t) is the heat released by the reaction until time t and H_u is the ultimate heat of reaction. All kinetics studies can start with the basic equation that relates the conversion rate to some function of the concentration of reactants:

$$\frac{d\alpha}{dt} = kf(\alpha), \qquad (2.40)$$

in which $d\alpha/dt$ is the rate of conversion; k is the rate constant, and $f(\alpha)$ is a function of α , which depends on the reaction mechanism. Mechanistically, the curing kinetics of thermosetting polymers can be divided into two general categories: nth-order curing reaction kinetics and autocatalytic curing reaction kinetics [Turi, (1997)]. Note that curing is not necessarily limited to one chemical reaction, and the kinetics may be that of an overall process when the chemical reactions occur simultaneously.

For thermosets that follow nth-order curing reaction kinetics, the isothermal reaction conversion rate is proportional to the fraction of material being unreacted $(1-\alpha)$, as expressed in the form shown below:

$$\frac{d\alpha}{dt} = k \left(1 - \alpha\right)^n,\tag{2.41}$$

where n is the reaction rate and k is the rate constant.

Autocatalyzed thermoset cure reactions are characterized by an accelerating isothermal reaction rate, typically reaching a maximum between 20 to 40% conversion. Kamal and Sourour (1976) proposed the following semi-empirical model to take into account both nth-order and autocatalytic curing reactions:

$$\frac{d\alpha}{dt} = k_T \alpha^m (1 - \alpha)^n, \qquad (2.42)$$

where m and n represent the reaction orders, k_T is reaction rate constant following an Arrhenius temperature dependence:

$$k_T = A \, \exp(-\frac{Q}{RT}) \,, \tag{2.43}$$

where A is a constant, Q the activation energy, R the gas constant, and T the absolute temperature.

2.4.2 Diffusion effect

The network formation of a curing thermosetting polymer often depends on both chemical reactivity and mobility of the reacting groups. The mobility is influenced by the viscoelastic state of the changing material. Vitrification occurs when the glass transition temperature reaches the cure temperature. This transformation involves the change of the material from a mobile liquid or rubbery state to a frozen glassy state. Due to the decrease of the mobility of the reacting groups, the rate of conversion may be very slow and become diffusion-controlled. To consider the diffusion effect, a diffusion factor, which is based on free-volume theory, is given as [Chern and Poehlein, (1987)]:

$$f_d(\alpha) = \frac{1}{1 + \exp[C(\alpha - \alpha_c)]} , \qquad (2.44)$$

where C is a material constant and α_c is the critical conversion depending on the curing temperature. For $\alpha \ll \alpha_c$, the reaction is kinetically controlled and the effect of diffusion is negligible. As α approaches $\alpha_{c, f_d}(\alpha)$ begins to decrease and approaches to 0.5 when $\alpha = \alpha_c$. Beyond this point, it continues to decrease and approaches zero, which means that the reaction becomes very slow. The effective reaction rate at any conversion is considered to be equal to the chemical reaction rate (Eq. (2.42)) multiplied by $f_d(\alpha)$.

2.4.3 $T_{\alpha} - \alpha$ relationship

It is well accepted that for many thermosetting polymers there is a unique relationship between the glass transition temperature and the degree of conversion, independent of the cure temperature and thermal history [Turi, (1997)]. The modified empirical DeBenedetto equation is used to describe such a relationship, as:

$$\frac{T_g - T_{g0}}{T_{g\infty} - T_{g0}} = \frac{\lambda \alpha}{1 - (1 - \lambda)\alpha},$$
(2.45)

where T_{g0} is the T_g of the uncured resin ($\alpha = 0$), $T_{g\infty}$ is the T_g of the fully cured resin ($\alpha = 1$), and λ is an adjustable, structure-dependent parameter. When the conversion reaches a high level (for example, above 95% conversion), a quantitative measurement of the residual heat is very difficult due to the small exotherm. In that case, measuring T_g is a more sensitive way to determine the degree of conversion.

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Chapter 3

Experimental

In this chapter, the experimental characterization of the cure-dependent properties of the thermosetting polymers is presented. A model epoxy system with different filler concentrations is used for the study purpose. DSC is used to characterize the cure kinetics and determine the relationship between the conversion level and the glass transition temperature. DMA measurements using isothermal and intermittent curing approaches are performed to characterize the cure-dependent relaxation behaviours and the results are presented. Finally, the measurement of the curing shrinkage is discussed.

3.1 Introduction

In the previous chapter, the cure-dependent constitutive model is proposed (Eq. (2.30)). Before implementation of the model into finite element simulations, experimental characterization has to be performed to investigate the material behaviour and to obtain the cure-dependent parameters. As mentioned in Section 2.1, corresponding to the proposed model, the following cure-dependent behaviour should be investigated experimentally:

- The cure kinetics and the T_g - α relationship;
- The evolution of relaxation moduli that are cure, temperature and filler loading dependent;
- Thermal and chemical shrinkage.

The reaction rate and the degree of conversion as a function of time and curing temperature can be calculated from a kinetics equation. Many techniques can be used to characterize the curing reaction kinetics of epoxy and other thermosets, including Differential Scanning Calorimetry (DSC) [Turi, (1997)] and Fourier transform infrared spectroscopy (FTIR). The later method provides a means for measuring the concentration of reactive groups during polymerization, and the mechanistic models resulting from FTIR data provide the flexibility for predicting the reaction rate at various reactant concentrations. DSC is widely used for characterizing the curing process of thermosetting polymers. Although it gives little or no information on details of the reaction, it is one of the most popular techniques for cure monitoring because of its simplicity and relative rapidity.

Dynamical Mechanical Analysis (DMA) is a thermal-mechanical analysis technique and commonly used in the characterization of polymeric materials. It measures the properties of materials as they are deformed under periodic stress. DMA can measure the complex modulus, compliance and viscosity in several different modes, for example, flexure, tensile, shear, or bending.

It is not an easy task to measure the material properties during the curing process, since the mechanical properties of the material undergo a huge change. During cure, polymers transfer from a liquid at the beginning to a crosslinked solid in the fully cured state, and simultaneously the stiffness is being built up. This imposes restrictions on the choice of possible sample geometries and measurement methods. Basically, people used two different approaches for curing DMA measurements. One is a DMA test on partly cured samples. Samples with different conversion levels are made using quenching to stop curing (for example, [Kim and White, (1996)]) or using different chemical stoichiometric ratios [Plazek and Chay, (1991)]. The disadvantages of this method are that it is time-consuming and the variations in the sample making may have effect on the test results. The other approach is continuously measuring during a part or the whole curing process. In most cases, this approach has been used in the isothermal curing conditions. Eom et al. (2000) used a torsional parallel plate rheometer for measuring the shear modulus during the isothermal curing of an epoxy-amine system. Kiasat (2000) used this method for polyester. Yang et al. (2004a/b) performed DMA measurements on an epoxy system during isothermal curing using a double simple shear test set-up. Due to the dramatic change of the material properties during cure, strict demands for the test machine and the test setup are required to get accurate results.

Hof (2005) proposed a novel continuous DMA approach, 'intermittent cure', in which the curing profile includes a number of cycles of isothermal cure, cooling down and heating up. In between the cure intervals the material is cooled down to room temperature such that the curing is virtually stopped. DMA measurements are then performed during cooling down or heating up.

Such a method enables people to obtain the relaxation behaviour at different degree of cure using one single specimen.

In this chapter, the experimental characterization of the cure-dependent properties of the thermosetting polymers is presented.

3.2 Materials and sample preparation

Epoxy moulding compound for electronic packaging is usually comprised of epoxy resin, hardener and fillers as well as other proprietary additives such as coupling agent, silicone modifiers, release agent, anti-oxidant, colour pigment and flame retardant, etc. It has a complex chemical structure.

In order to focus on the polymer crosslinking behaviour and exclude the influence of other additives, we chose an epoxy resin with the basic chemical structure as in moulding compound as the matrix material. As a model system, the epoxy resin we used in this research is Araldite EPN 1180, a novolac epoxy, which is supplied by Vantico LTD (currently, in Huntsman Advanced materials). It has an epoxy/hydroxy equivalent of $175\sim182$ (g/eq). The hardener is Bisphenol-A supplied by Aldrich-Chemie GmbH & Co (Steinheid, Germany), with an epoxy/hydroxy equivalent of 114.1(g/eq). Triphenylphosphine (TPP) is used as an accelerator for the curing of the epoxy resin. In order to study the effect of filler on the cure-dependent viscoelastic properties of the composites and thermo-mechanical behaviour of the packages, fused silica spheres (FB-940, from Denka) are used as filler to make model EMC's with different filler loading. The filler has a median diameter of 15μ m, with a density of $2.20g/cm^3$. Figures 3.1 to 3.3 show the detailed chemical structures of the materials used in this study.



Figure 3.1: Chemical structure of epoxy resin EPN 1180



Figure 3.2: Chemical structure of Bisphenol-A



Figure 3.3: Chemical structure of Triphenylphosphine (TPP)

A stoichiometric mixing ratio 1:1 between epoxy groups and the hydroxyl groups was used. This gives the resin formulation as follows:

Araldite EPN 1180	100 gram
Bisphenol-A	$\frac{100}{178.5}$ × 114.1 = 63.9 gram
TPP	See table 3.1

Preliminary tests with different concentrations of catalyst TPP were done to get similar reaction kinetics for the matrix resin and the filled materials, and also to get them comparable to those of commercial moulding compounds. Note that the amount of TPP needed increases with increasing filler loading. This suggests that part of TPP is in some way deactivated by the filler. To make a filled composite, a certain amount of silica filler was added to the matrix resin. Three levels of filler loading were used. The final TPP concentrations and the filler loading percentage used in the experiments are shown in table 3.1. The mixing was done in a special mixer (Kenwood, K. beater).

The traditional way of preparing such an epoxy resin is first to heat the epoxy to elevated temperature and dissolve the hardener. Afterwards, cool the mixture to 85°C and add the catalyst. DSC measurements showed that the samples prepared in this way already had remarkable degree of conversion due to the curing progress during the mixing. Therefore, in

order to minimize the initial curing caused by mixing, a two-part mixing procedure was used. As an example, the procedure of preparing the 65% filled EMC is described below:

- 100 gram of EPN1180 was divided into two equal parts and put into two bottles, represented as Part A and Part B. In considering of remaining in the bottle when pouring out, 15% extra of epoxy was added to part A.
- Part A was heated to 165°C using a silicone oil bath. Bisphenol-A was added and well mixed. The mixture was cooled down to 85°C.
- Part B was heated to 90°C using the oil bath and TPP was added and fully stirred. Afterwards it was cooled to 85°C.
- Part A was poured into Part B. The mixture was stirred for about 5 min carefully to avoid possible entrapping air bubbles.
- 5). After mixing, the mixture was transferred into a vacuum oven at 75°C and degassed for about 20 minutes. The degassed mixture was used as matrix resin for filled composites as described in the subsequent step, or cooled down and stored in a freezer at −30°C for later use.
- 6). This step is used for mixing the molding compounds. The container of the mixer was preheated to 80°C. The mixture of matrix resin was poured into the container and then the filler was added and well mixed. The final mixtures were also stored in a refrigerator for later use. For the transfer molding experiments, raw materials in tablet shape have to be made. The procedures for making the tablets will be described in Chapter 6 (Section 6.2.1).

The actual filler loadings for the filled materials were measured using a burning test and the results are listed in table 3.1.

	F00	F40	F50	F65
TPP concentration [g/100 g epoxy]	0.85	1.40	1.60	2.35
Actual filler loading [wt %]	-	42.5%	50.7%	65.6%

Table 3.1: Catalyst concentration and filler loading of the epoxy moulding compounds

3.3 DSC analysis

3.3.1 DSC characterization procedure

DSC has been widely used to obtain the curing process parameters, such as the degree and rate of chemical conversion, glass transition temperature (T_g) . DSC measures heat flow into a material (endothermic) or out of a material (exothermic). The curing process of a thermosetting polymer is an exothermic process. Under the assumption that the heat evolved during cure is proportional to the extent of reaction, the degree of conversion is commonly determined from the residual heat of reaction (ΔH_R) of the partially cured resin, as:

$$\alpha = 1 - \frac{\Delta H_R}{\Delta H_{tot}},\tag{3.1}$$

where ΔH_{tot} is the total heat of reaction associated with the fully cured resin. The rate of conversion can be calculated as:

$$\frac{d\alpha}{dt} = \frac{1}{\Delta H_{tot}} \frac{dH}{dt} , \qquad (3.2)$$

The DSC measurements are performed in a differential scanning calorimeter of TA Instruments (DSC2920). The samples with a size of 8-10mg are prepared and encapsulated in aluminium pans and placed in DSC cell at ambient temperature. Both isothermal and dynamic heating conditions are carried out under a nitrogen flow of 60ml/min. For isothermal cure, the samples were cured under the prescribed temperatures ranging from 90°C to 150°C for different time. After the isothermal run, the samples are cooled down quickly to -40° C, and rescanned at a heating rate of 10°C/min to 300°C to determine the residual heat (ΔH_R). For dynamic cure, six different constant rates as 1, 2, 5, 10, 15 and 20°C/min are used. The samples are first cooled down to -50°C, equilibrated for 2 minutes and then heated to 320°C using the six different rates.

3.3.2 Cure kinetics

Figure 3.4 shows the DSC thermograms from dynamic cure at different heating rates, which represent the released heat reaction as a function of temperature during the heating scanning. Analysis of these data results in the coefficients m and n and the approximate values for the activation energy E and the rate constant k_0 for the cure kinetics model (Eq. (2.42)) [Jansen,

(2004)]. Since these last two parameters are not independent, a fixed value of 77 kJ/mol for the activation energy is chosen. The kinetics parameters are listed in table 3.2.



Figure 3.4: Dynamic DSC thermograms of F65 from scanning with the different heating rates

Figure 3.5 presents the curves of conversion versus the curing time under several isothermal curing temperatures for the four resins. The measured data points are obtained using the isothermal cure mode. The solid lines represent the model predictions using the parameters in table 3.2. Note that the predicted 5 and 10 hours conversion levels for the 90°C experiments were calculated including the diffusion effect. A reasonably good agreement between the measured data the model predictions can be observed. It should be mentioned that the extrapolated data at t=0 does not start at zero conversion. This is because some reaction already took place during the moulding compound mixing process and, possibly, also during the heating up period in the DSC. The initial conversion of the raw moulding materials is taken into account with an extra parameter α_0 . Since the activation energies were chosen to be identical, the rate constants *A* give a good comparison of the relative reaction rates. It can be seen that all reaction rates are of the same order of magnitude and the 50% and 65% rates are highest.

Filler loading	<i>Q</i> [KJ/mol]	A [1/s]	m	n	Initial cure α_0
0%	77	5.11E+6	0.123	1.427	0.134
40%	77	8.53E+6	0.128	1.314	0.214
50%	77	3.32E+7	0.19	1.542	0.136
65%	77	2.61E+7	0.154	1.457	0.287

Table 3.2: Parameters for the cure kinetics



Figure 3.5: Conversion versus curing time, measured and model predicted: (a) unfilled (F00); (b) F40; (c) F50; (d) F65.

3.3.3 Determination of $T_g - \alpha$ relationship

In order to determine the glass transition temperature (T_g) as a function of degree of conversion, a series of isothermal curing and subsequent heat scanning was performed for each material. The samples were cured in the DSC cell at the prescribed temperatures for various periods of time. After each isothermal run the partly cured samples were rapidly cooled down to -40° C, equilibrated and rescanned at a heating rate of 10° C/min to 300° C to determine the T_g and the residual heat (ΔH_R). The corresponding residual heat was used to calculate the degree of conversion. T_g of the uncured sample (α =0) was determined by measuring the T_g of the mixed resin without adding catalyst. To determine T_g of the fully cured materials (α =1), the samples were in dynamic cure with a heating rate of 1° C/min to 300° C, cooled down and rescanned at 10° C/min. The standard heating scan (10° C/min) then reveals both the glass transition and the remaining heat of reaction that is used to calculate the conversion (see the previous section).

Also the T_g of the samples with isothermal curing at 175°C for 2 hours was measured to verify $T_{g\infty}$. The T_g of the fully cured materials were found to be about 118°C. Conversion values higher than 90% were not included due to insufficient resolution of the conversion peak.

Figure 3.6 shows the relationship between T_g and conversion from DSC measurements. It can be seen that the experimental data for the three filled materials generally fall on an approximately single curve, and for the unfilled resin the other single curve could be seen. It can be concluded that there indeed exists a one-to-one relationship between T_g and conversion for all of the resins, which is independent of the cure temperature. The modified DiBenedetto equation (Eq 2.45) is then used as a model to fit the experimental data, as shown in Fig. 3.6 in the solid lines. The fitting parameters are shown in Table 3.3.



Figure 3.6: Relationship between T_g and the degree of conversion for the unfilled and filled materials. The solid curves represent model fitting from the modified DiBenedetto equation (2.45). The symbols represent the DSC measured values.

Filler loading	<i>Т_{g0}</i> [°С]	$T_{g\infty}$ [°C]	λ
F00	12	118	0.54
F40	12	118	0.41
F50	12	118	0.41
F65	12	118	0.41

Table 3.3: The parameters for the DiBenedetto equation

3.4 Characterization of cure-dependent viscoelastic properties

3.4.1 Shear DMA experimental setup

In DMA a variable sinusoidal strain (displacement) or stress is applied, and then the resultant sinusoidal stress or strain is measured. If the material being evaluated is purely elastic, the phase difference between the stress and strain sine waves is 0° (i.e., they are in phase). If the material is purely viscous, the phase difference is 90°. However, most real-world materials including polymers are viscoelastic and exhibit a phase difference between those extremes. This phase difference, together with the amplitudes of the stress and strain waves, is used to determine a variety of fundamental material parameters, including storage and loss modulus, tan δ , complex and dynamic viscosity, storage and loss compliance, transition temperatures, creep, and stress relaxation. DMA can measure the complex modulus, compliance and viscosity in several different modes, for example, flexure, tensile, shear, or bending. Shear DMA measurements (torsion or simple shear) are generally used to establish the shear relaxation modulus curves. Tensile (or elongation) DMA tests are often used to establish the longitudinal relaxation modulus (Young's modulus).

In the following, the experimental setups for measuring the cure-dependent relaxation moduli are described.

The shear DMA measurements are performed in Metravib VA4000 Viscoanalyzer, as shown in Figure 3.7. The equipment can operate either in stress controlled or strain controlled mode with frequencies up to 100Hz and with a force range of 0.1 to 150N. The displacement resolution is $0.1\mu m$. With the attached temperature chamber, test temperature up to 300°C can be applied and controlled.

Due to the special requirement for holding the uncured resins, the commercial test fixtures are not suitable for DMA measurement of curing resins. New shear test setups were developed. The initial shear test fixture consists of the moving part and two L shape Aluminium legs $(26 \times 5.8 \times 1.6 \text{mm})$ connected to the clamping plate with screws, as shown in Figure 3.8(a). This test fixture was seen to work well for relatively low stiffness range of the materials, for instance at low conversion level or at elevated temperature. It gave a large deviation when the sample's stiffness is high due to the limitation of the stiffness of shear fixture itself and the apparatus. To improve the stiffness, a new test fixture consisting of a robust Aluminium frame was fabricated, as shown in Figure 3.8(b). To compensate the effect of the stiffness of the test fixture and the apparatus, stiffness correction in the following form was adopted on the measured data:

$$\frac{1}{K^c} = \frac{1}{K^m} - \left(\frac{1}{K^f} + \frac{1}{K^t}\right),$$
(3.3)

in which, K^m is the measured stiffness value of the sample, K^f and K^t are the stiffness of the apparatus frame and the stiffness of the test fixture, respectively.

In our measurements, the strain control mode is used. Some basic relations of DMA analysis were already derived in [Ernst, (2000)]. Here as an example, the analysis for the relaxation shear modulus *G* is briefly described. Assume sinusoidal deformation started at time ξ_i :

$$\varepsilon_{12}(\xi,\omega) = \varepsilon_{12}^0 \cdot \sin\{\omega \cdot (\xi - \xi_i)\}, \quad \text{for} \quad \xi_i \le \xi \le t$$
(3.4)

where ε_{12}^0 is strain amplitude, ω is the radian frequency. After the starting effects have disappeared, the stress is expressed as

$$\sigma_{12}(t) = 2\varepsilon_{12}^{0} \cdot [G'(\omega) \cdot \sin(\omega t) + G''(\omega) \cdot \cos(\omega t)], \qquad (3.5)$$

in which G' and G'' are the storage and loss shear modulus, respectively. If the stress relaxation behaviour is described by the generalized Maxwell model as shown in Eq.(2.28d), G' and G'' can be approximated as:

$$G'(\omega) = G_r + (G_g - G_r) \cdot \sum_{n=1}^{N} g_n \frac{\omega^2 \tau_n^2}{1 + \omega^2 \tau_n^2},$$
(3.6)

$$G''(\omega) = (G_g - G_r) \cdot \sum_{n=1}^{N} g_n \frac{\omega \tau_n}{1 + \omega^2 \tau_n^2},$$
(3.7)



Figure 3.7: Shear DMA setup, (a). the initial shear test fixture; (b). the new test fixture.



Figure 3.8: Schematic illustration of shear DMA setup

3.4.2 DMA characterization of fully cured materials

The purpose of characterization of fully cured materials is to obtain the viscoelastic behaviour under different conditions (for example at different temperatures). Test methods, such DMA, relaxation and creep tests, are often used for charactering fully cured materials.

In this research work DMA is used to characterize the fully cured resins. Uncured resin (liquid state) is put into the gaps of the shear tool (shown in Fig. 3.8(b)) and cured at 165°C for 5 hours. Then the sample is cooled down with a cooling rate of 1°C/min. DMA measurements are performed during the cooling down. Master curves can be established by using the time-temperature superposition (TTS) or frequency-temperature superposition principle. Because this method has been well documented in literature, the detailed description of the procedure will not be given. Only the major results are shown.

Figure 3.9 shows the shear storage moduli as functions of applied frequencies of the fully cured material (F65) measured from DMA under different temperature levels. According to the frequency-temperature superposition principle, the individual isothermal curves can be shifted along the frequency axis to form a single overlapping master curve.

Figure 3.10 shows the storage modulus versus reduced frequency after being shifted along the frequency axis with reference temperature of 120°C. It can be seen that the frequencytemperature superposition principle is well applicable to our epoxy system.

To obtain the parameters in equation (2.28d) for the fully cured materials, data processing is needed. Here twenty Prony terms for the transient part are used, while the relaxation times τ_n are chosen such that they are nearly logarithmically equally spaced, but also cover the entire relaxation range of the fully cured material. The glassy modulus is determined as the glassy

plateau of the storage modulus. The rubbery modulus is measured using a so-called Ultra Low Frequency Scan (ULFS) DMA, which will be described in Section 3.4.3. These values are listed in table 3.4. The overlapping master curves of the storage and loss moduli are fitted to Eq. (3.8a) and (3.8b) to obtain g_n :

$$G'(\omega_{red}) = G_r^f + (G_g - G_r^f) \cdot \sum_{n=1}^N g_n \frac{\omega_{red}^2 \tau_n^2}{1 + \omega_{red}^2 \tau_n^2}$$
(3.8a)

and

$$G''(\omega_{red}) = (G_g - G_r^f) \cdot \sum_{n=1}^{N} g_n \frac{\omega_{red} \tau_n}{1 + \omega_{red}^2 \tau_n^2}$$
(3.8b)

Table 3.5 presents the relaxation times and the corresponding best-fit normalized Prony coefficients g_n (see Eq. (2.28d)). Figure 3.11 shows the shift factors obtained by shifting the individual curves to construct a master curve. It represents the temperature effect on the relaxation behaviour. It clearly shows different dependency trends at lower and higher temperatures. The turning point is 4 to 10 degrees below the glass transition temperature (measured in DMA, tan δ peak at 1 Hz). Such a change is attributed to a change in relaxation behaviour is mainly driven by free volume mechanism and it follows the WLF behaviour, whereas below this temperature the relaxation behaviour is activation energy driven and the shift factor follows the Arrhenius behaviour. According to the free volume theory [Ward, 1983], above the glass transition temperature T_g the free volume fraction is proportional to $T - T_g$ (see Eq. (2.16a)). And this free volume enables the movement of large molecular segments and the material is in a state of thermodynamic equilibrium. When cooling down, the free volume decreases. When the temperature reaches T_g , the free volume become so small that large molecular motions are impossible, and the material is no longer in thermodynamic equilibrium.

Thus the two parts of the curve are fitted to the WLF equation and Arrhenius equation, respectively. The two equations are rewritten below:

$$\log a_{T} = -\frac{C_{1}(T - T_{ref}^{WLF})}{C_{2} + T - T_{ref}^{WLF}} , \qquad T \ge T_{s}$$
(3.9)

and

$$\log a_T = \frac{\Delta H_T}{2.303R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \qquad T < T_s$$
(3.10)

In above equations, C_1 and C_2 are constants, ΔH_T is the activation energy, T_{ref}^{WLF} and T_0 are the reference temperature for WLF and Arrhenius equation, respectively; T_s is the switching temperature. The fitting values for the parameters are listed in table 3.4.

Apply the same procedure to other resins in our model system. The relaxation behaviours of all the materials are obtained. Figure 3.12 shows the relaxation master curves of the unfilled and filled resins with the same reference temperature of 120°C. The related parameters are also presented in table 3.4 and 3.5. Further discussion about the filler effect on the viscoelastic behaviour will be presented in Chapter 4.



Figure 3.9: Storage shear moduli as functions of frequencies of fully cured F65 under different temperatures



Figure 3.10: Shifted storage shear moduli versus reduced frequencies and the best-fit curves, reference temperature $T_{ref} = 120^{\circ}$ C



Figure 3.11: Shift factor as a function of temperature



Figure 3.12 Relaxation curves of the unfilled and filled resins, reference temperature $T_{ref} = 120^{\circ}$ C.

	F00	F40	F50	F65
$G_{\rm g}$ [MPa]	833	1053	1325	2212
$G_{\it rf}$ [MPa]	4.5	5.7	8.6	32.1
<i>C</i> ₁ [-]	10.7	10.7	10.7	10.7
С2 [К]	40.7	40.7	40.7	40.7
$T_{\it ref}^{\it WLF}$ [K]	391.15	391.15	391.15	391.15
$\Delta H_{\scriptscriptstyle T}$ [KJ/mol]	272.6	239.5	216.4	202.3
T ₀ [К]	397.8	406.2	412.3	423.5

Table 3.4: The parameters

No	Relaxation times	Coefficients g _n				
	τ_n [s]	F00	F40	F50	F65	
1	1.00E-06	0	0	0	1.03E-01	
2	1.00E-05	1.95E-02	0	0	0	
3	3.16E-05	1.02E-01	0	0	4.46E-03	
4	1.00E-04	1.81E-02	0	0	2.09E-02	
5	3.16E-04	1.28E-01	6.13E-02	8.10E-02	2.14E-01	
6	1.00E-03	7.26E-03	1.59E-01	2.01E-01	0	
7	3.16E-03	9.08E-02	1.53E-01	0.00E+00	1.18E-01	
8	1.00E-02	1.01E-01	1.73E-01	3.03E-01	4.68E-02	
9	3.16E-02	1.20E-01	8.30E-02	6.68E-02	1.11E-01	
10	1.00E-01	1.39E-01	1.08E-01	9.07E-02	9.80E-02	
11	3.16E-01	1.14E-01	1.20E-01	1.18E-01	1.18E-01	
12	1.00E+00	1.01E-01	6.57E-02	5.16E-02	9.06E-02	
13	3.16E+00	3.15E-02	5.02E-02	6.02E-02	4.59E-02	
14	1.00E+01	2.29E-02	1.68E-02	1.40E-02	1.99E-02	
15	3.16E+01	0.00E+00	7.60E-03	1.20E-02	5.86E-03	
16	1.00E+02	4.40E-03	9.96E-04	3.06E-05	3.01E-03	
17	3.16E+02	0	1.16E-03	2.59E-03	1.29E-03	
18	1.00E+03	6.39E-04	0	0	0	
19	3.16E+03	3.00E-05	2.00E-04	0	1.48E-04	
20	1.00E+04	8.55E-05	4.38E-06	7.61E-05	0	

Table 3.5: Relaxation times and corresponding normalized Prony coefficients g_n of fully cured resins (see Eq. (2.28d))

3.4.3 Characterization of cure-dependent rubbery shear moduli

1). Experimental approach

For fully cured material, DMA, relaxation and creep tests can be used to measure the rubbery modulus. The tests should be conducted at a temperature well above the ultimate T_g . It is much more difficult to measure the rubbery modulus during the curing process. In that case relaxation and creep tests are not suitable due to the ongoing stiffness build-up as the curing proceeds.

Therefore a novel method called Ultra Low Frequency Scan (ULFS) DMA is used to characterize the rubbery shear modulus during cure. In this method a displacement oscillation with a very low frequency (e.g. 0.001-0.01 Hz) is applied to the sample during isothermal cure at a temperature above the glass transition T_g and the reacting force is measured. Preliminary tests at both 0.005 and 0.01 Hz showed that measured modulus values for these epoxy systems were frequency independent, which shows that we really measure the rubbery plateau values. Figure 3.13 shows schematically the low frequency DMA method for the rubbery measurement. Displacement oscillation with constant amplitude was applied to specimen and reacting force was recorded. As the curing conversion increases, passing through the gel point, the amplitude of the force increases. The rubbery modulus can be calculated either using the force amplitude within one cycle or using the increment of the displacement and force during a certain time increment.



Figure 3.13: Schematic illustration of an Ultra Low Frequency Scan (ULFS) during cure

The DMA tests during cure were performed in a Metravib VA4000 viscoanalyzer using a dual plane shear test setup as shown schematically in Fig. 3.8(b). Displacement was applied by the moving part and the base plate was connected to the force transducer. The measured displacement and force signals were recorded by a data acquisition system and used to calculate the stiffness increase with curing time.

2). Results and discussions

The results of the Ultra Low Frequency Scan method and the applied temperature profile are shown in Figure 3.14. The resin was cured in two steps: first at 130°C for 5 hours and then at 160°C for 2 hours. Afterwards, the sample was cooled stepwise down to 120°C to check the temperature dependency of the fully cured rubbery modulus. The temperature for the first curing

step is chosen such that an appropriate curing rate is obtained and the second curing step with higher temperature enables the resin to be in almost fully cured state. The frequency used is 0.01 Hz. It can be seen that the modulus is zero at liquid state and increases from certain point (the gel point).



Figure 3.14: Rubbery shear modulus versus curing time under two step curing (ULFS method)

Figure 3.15 shows the modulus build-up with conversion level for all materials at 130°C. It can be seen that before 80% conversion, the modulus is very low. After that, it increases quickly during the final conversion period. Nearly two third of the modulus is built up in the conversion range from 90-100%. It also indicates that the filler percentage has significant reinforcement on the rubbery modulus, especially at highly filled state. The 65% filled compound (denoted as F65) shows a sharp increase of rubbery modulus compared to the 50% filled material.

Figure 3.16 shows a comparison of the experimental measurement and the model prediction of the rubbery shear modulus for the materials with different filler loading during 130°C isothermal cure. The evolution of the conversion level with curing time was calculated from Kamal and Sourour's kinetic model (Eq. (2.42) and table 3.2). The solid lines in the figures represent the prediction of Adolf's model (Eq. (2.32)). It is seen that the model predictions match well with the experimental data for F40, F50 and F65. For the unfilled resin, before 95% conversion a relatively large difference between the model prediction and the measured data is seen. In Adolf's model (see Eq. (2.32)), the degree of cure at gel point α_{gel} is required. Here the gel point is obtained using DMA approach (see section 3.4.4) and the kinetics model, which may not match well with the real condition in the DMA measurements (such as sample handling and temperature ramping to the curing temperature). The deviation in prediction of α_{gel} could

result in the difference between the model prediction and the measured data of the rubbery modulus, since Adolf's model is very sensitive to α_{gel} .



Figure 3.15: Rubbery shear modulus evolution with conversion at 130°C for systems with different filler contents.



Figure 3.16: Rubbery shear modulus evolution with conversion at 130°C; (a): F00 and F40; (b): F50 and F60

3.4.4 Gel point

During cure, thermosetting polymers undergo phase transition from liquid to solid at a critical degree of conversion. The gel point for crosslinking reaction is defined unambiguously as the instant when the weight-average molecular weight reaches infinity. At this point, the molecular weight distribution is infinitely broad, with molecules ranging from the smallest unreacted chain to the infinite, sample-spanning cluster. From rheological and mechanical point of view, at the gel point its steady shear viscosity is infinite and its equilibrium modulus is zero. Before the gel point, i.e. $\alpha < \alpha_{gel}$, the polymer is called a sol, because it is soluble in an appropriate solvent.

Beyond the gel point, i.e. $\alpha > \alpha_{gel}$, the polymer is called a gel, and is not soluble even in good solvent.

Understanding and detecting the gel point has both the scientific and practical importance. From a scientific point of view, the material undergoes a dramatic change in material behaviour around the gel point (its steady shear viscosity becomes infinite and the rubbery shear modulus starts increasing from zero). As for our modelling, the degree of conversion at the gel point (α_{gel}) has to be determined in order to predict the rubbery shear modulus (see Eq. (2.32)). From an application standpoint, determining the gel point is helpful for processing because the polymer can be easily shaped or processed before the gel point while it can still flow and the stresses applied can relax to zero. In transfer moulding of plastic IC packaging, knowledge of the gel point would allow estimation of the optimal temperature and time for EMC preheating and for in-mould curing as well.

A few techniques for measuring the gel point have been reported, including DSC, solubility in tetrahydrofuran, rheological measurements, and DMA. The most common rheological methods are to measure the shear equilibrium modulus or the divergence of the steady shear viscosity. However, it is very difficult to measure the equilibrium modulus with enough accuracy at such low equilibrium modulus level, and the method of measuring the diverging steady shear viscosity can only locate the gel point approximately. In the DMA method, the crossover point of the shear storage and loss moduli, G' and G'', is often used to determine the point. However, this method can only be effectively used for some polymers [Boey and Qiang, (2000)].

Winter *et al.* (1986) proposed a general criterion that can be used to identify the gel point. It has been found that the stress relaxation behaviour near the gel point follows a power law:

$$G(t) = St^{-n}; \ \alpha = \alpha_{gel} \tag{3.11}$$

where *S* is a material parameter (Winter *et al.* called it the "strength" of the network at the gel point), which depends on the flexibility of molecular chains and crosslinks, and on the crosslinking density at the gel point. S has the unit of $[Mpa \cdot s^{1/2}]$. *n* is the relaxation exponent and typically has values in the range of 0 < n < 1. Then, the frequency dependence of the storage and loss moduli at the gel point can be deduced to be:

$$G'(\omega) = \Gamma(1-n) \cdot \cos\left(\frac{n\pi}{2}\right) \cdot S\omega^n$$
(3.12a)

$$G''(\omega) = \Gamma(1-n) \cdot \sin\left(\frac{n\pi}{2}\right) \cdot S\omega^n$$
(3.12b)

In a scaling way:

$$G'(\omega) \sim \omega^n$$
 (3.13a)

$$G''(\omega) \sim \omega^n$$
 (3.13b)

While at the gel point the loss factor can be expressed as:

$$\tan \delta = \frac{G'}{G''} = \tan\left(\frac{n\pi}{2}\right) \tag{3.14}$$

From above equations, it can be seen that the storage and loss moduli coincide only when $n = \frac{1}{2}$. For most cases, they are frequency dependent. Whereas the loss factor is frequency independent, therefore this may be used as determining the gel point.

In the present work, Winter's criterion is used to detect the gel point. The DMA measurements are performed under various isothermal temperatures, as described in the previous section. Figure 3.17 shows the curves of G' and G'' plotting versus curing time at 90°C and 105°C. It is seen that the crossover of G' and G'' is frequency dependent and no identical crossover point of G' and G'' exists. The crossover point occurred later with lower frequency. Therefore, for the epoxy system studied, it is not proper to use the crossover of G' and G'' to determine the gel point.

Figure 3.18 presents the curves of the loss factor $\tan \delta$ versus curing time at 90°C and 105°C at different frequencies. It clearly shows that $\tan \delta$ curves of different frequencies crossover at one point, at which $\tan \delta$ becomes independent of frequency. As such, it is possible to define the time at which this occurs to be the gel time for the system.



Figure 3.17: Storage and loss moduli during isothermal cure at 90°C and 105°C, showing frequency dependence of G' and G'' crossover point, (a): $T_{cure}=105$ °C; (b): $T_{cure}=90$ °C.



Figure 3.18: Curves of loss tangent during isothermal cure, showing frequency independent crossover point; (a): $T_{cure}=105^{\circ}C$; (b): $T_{cure}=90^{\circ}C$.

Then the crossover point of $\tan \delta$ is used to estimate the gel time for the resins. The corresponding degree of conversion at the gel point (GP) is calculated according to the cure kinetics model. Table 3.6 lists the conversion values at GP for the filled and unfilled resins. The calculated gel point using the Flory equation (Eq. (2.33)) is 0.62, which shows agreement with the experimental results.

Table 3.6: Degree of cure at gel point

$\alpha_{_{gel}}$	F00	F40	F50	F65
DMA approach	0.62	0.625	0.645	0.63
Flory equation	0.62			

3.4.5 Isothermal cure approach

In the isothermal cure method, the sample is cured under isothermal condition and DMA frequency sweeps are applied continuously during the whole curing process. This measurement can be used for continuous probing of viscoelastic properties during cure. The cure temperature should be carefully chosen in order to be able to follow the changes in the full transition region. If the cure temperature is too high only the changes in the range close to the rubbery plateau are recorded. If the cure temperature is too low the final conversion level is low. After a few preliminary tests, the curing temperature is chosen as slightly below the ultimate T_g of the resins. To obtain higher conversion level, multi isothermal cure steps can be utilized. In addition, if at

the end of isothermal curing a cooling down with frequency sweeps is applied subsequently, then the glassy modulus at the end of cure and the viscoelastic properties of the fully cured resins can be determined.

Shear DMA measurements on the epoxy system are performed using a Metravib Viscoanalyzer VA4000. Continuous frequency sweeps during isothermal cure are used for continuous probing of viscoelastic properties during cure. Seven logarithmically spaced frequencies between 0.1~60Hz are applied. Various cure temperatures are investigated.

To illustrate the procedure, the evolution of the storage and loss shear moduli under 105°C isothermal cure (for various frequencies) with ongoing cure is presented in Fig. 3.19. To describe their dependency on the conversion level, the degree of cure is calculated using the equation (2.42) and the parameters listed in Table 3.2. As discussed in section 2.3, the influence of cure on the relaxation behaviour of thermosetting polymers may show thermo-rheologically complex behaviour, because the rubbery plateau increases with ongoing cure. When we examine the cure dependency, the effect of the evolving rubbery modulus should be taken into account.

In accordance with equation (2.28), the "transient parts" of the storage shear moduli are obtained by subtracting the rubbery modulus. Figure 3.20 illustrates the transient part of the storage shear modulus $(G' - G_r(\alpha, T))$ at different conversion levels as functions of the applied frequencies. Then the individual curves at different conversion can be shifted along the frequency axis to form an overlapping master curve and the cure-dependent shift factor can be obtained. The solid line is the transient part of the storage moduli at the fully cured state $(T_{ref} = 105^{\circ}\text{C})$. The "cure shift factor" a_{α} is obtained after shifting the individual curves to match with the "fully cured" master curve. The dependency of the shift factor on the conversion is shown in Fig. 3.21(a). In Fig. 3.21(b), the shift factor is illustrated as a function of the glass transition temperature. It can be described quite well by the Arrhenius behaviour as:

$$\log a_{\alpha}(\alpha) = -\frac{\Delta H_{\alpha}}{2.303R} \left(\frac{1}{T_{g\alpha}} - \frac{1}{T_0} \right)$$
(3.15)

where ΔH_{α} is the activation energy term corresponding to conversion. The procedure is repeated for various temperatures and for compounds with various filler loadings. The final master curves for the relaxation shear modulus G for various compounds (with different filler %) can be obtained. The fitting parameters for the conversion shift factors are presented in table 3.7.
Though the isothermal approach is relatively simple, the temperature effect on the relaxation behaviour at different curing states cannot be obtained by this method. Alternatively, multi isothermal cure steps (to get fully cured) followed with a cooling down with frequency sweeps can be utilized to measure the temperature dependence of the fully cured material.



Figure 3.19: Evolution of the shear storage and loss modulus of F65 during 105°C isothermal curing



Figure 3.20: Transient parts of storage moduli ($G' - G_r$) versus frequency for various degree of cure + a "fully cured" master curve under 105°C isothermal curing



Figure 3.21: Shift factor versus conversion and glass transition temperature

	F00	F40	F50	F65
ΔH_{α}	492.29	417.06	437.74	399.79
T_{0}	373.33	385.65	368.07	369.68

Table 3.7: Parameters for the shift factors

3.4.6 Intermittent cure approach

The intermittent cure approach was proposed by Hof (2005) and was successfully applied to the unfilled resin and the filled resins [Jansen, (2004)]. Here this approach is used to further investigate the effect of the curing state on the relaxation behaviour. The basic idea of this method is that a temperature profile consisting of isothermal curing sections interrupted by several linear cooling and heating intervals is used and continuous frequency sweeps are applied to the sample during the temperature history. In this way a temperature scan is made at various stages during cure. Note that this method can only be used for slowly curing systems, since it requires scanning to temperatures above the T_g at each cure state without significant reaction. For many commercial resins the reaction already starts in the glassy state such that the viscoelastic range of the master curve cannot be obtained at a single conversion level.

Preliminary trial tests are done before the proper time intervals for each isothermal session are determined to get desired corresponding conversion levels. Figure 3.22 shows the temperature profile used in the intermittent cure. The ramp rate for the heating scanning is 2°C/min and is identical for all the heating stages. DMA measurement data are obtained for each

heat scanning, in which the material is in different degree of cure. Using the data processing procedure similar to that used for the fully cured material (described in section 3.4.2), the master curves of the storage and loss moduli for each of the curing states can be established. Figure 3.23 shows the master curves of the storage modulus at different degree of cure versus the reduced frequency, with an identical reference temperature of 120°C. The master curves of the transient part of the storage modulus can also be established by subtracting the corresponding rubbery modulus. These master curves can be further shifted using a reference conversion to form a 'general' master curve. Figure 3.24 shows the shifted master curves of the transient part of the storage moduli, with an identical reference temperature of 120°C and using a reference conversion of 0.96 (corresponding to T_g of 107°C). The shift factor related to conversion agrees well with the results of the isothermal cure approach. We can see that the master curves of the transient part at different curing states shows a good match by only horizontal shifting.



Figure 3.22: Temperature profile used in the intermittent cure approach



Figure 3.23: Master curves of storage moduli at different conversion levels, established using reduced frequency. The reference temperature is 120°C



Figure 3.24: Master curves of the transient parts of the storage moduli, derived by horizontal shifting using 0.96 as the reference conversion; the reference temperature is 120°C

Figure 3.25 shows all the shift factor curves for establishing the master curves of the corresponding conversions, where 120°C is used as the reference temperature. If the same data is reploted with T_g as a reference temperature, all shift factor curves are seen to merge into a single curve (see Fig. 3.26). Note that the deviations from this overall shift factor curve mainly

occur at the temperature ranges well above $T_{g\alpha}$ or well below $T_{g\alpha}$ (i.e. outside the viscoelastic range) where the shift factor looses its usefulness (shifting is not needed in the glassy and rubbery elastic plateaus). This indicates that for the epoxy system in this study the temperature effect on the shift factors is independent of the degree of cure when the glass transition temperature is chosen as the reference temperature. As mentioned in section 2.3.5, previous research work indicated that for many polymers temperature dependency of the shift factors is independent of the reference temperature was taken as the glass transition temperature.

The shift factors for the temperature and conversion effects can then be expressed in an 'integrated' way by using the new concept of "reduced temperature". The concept of reduced temperature is introduced, as $T_{red} = T - T_{g\alpha}$. The equation for the shift factors (Eq (3.9) and (3.10)) can then be written as:

$$\log a_{T,\alpha} = -\frac{C_1 (T_{red} - T_{ref}^{WLF})}{C_2 + T_{red} - T_{ref}^{WLF}} , \qquad T \ge T_s$$
(3.16)

and

$$\log a_{T,\alpha} = \frac{\Delta H_T}{2.303R} \left(\frac{1}{T_{red}} - \frac{1}{T_0} \right) \qquad T < T_s$$
(3.17)

in which T_{red} is the reduced temperature, with $T_{red} = T - T_{g\alpha}$. The switching temperature T_s is a few degrees lower than the glass transition temperature and the difference ΔT_s (= $T_s - T_{g\alpha}$) is almost the same for different curing states. For the resin of F65, ΔT_s is about -6.55°C.

The measured data shown in Fig. 3.26 can be fitted to equations (3.16) and (3.17). The fitting parameters for each of the materials are given in table 3.11. It is seen that the shift factor is independent of the degree of cure if the glass transition temperature is used as the reference temperature.



Figure 3.25: Shift factors for obtaining the master curves of different curing states, using a reference temperature of 120°C.



Figure 3.26: Shift factors as a function of reduced temperature; reference temperature is the glass transition temperature $T_{g\alpha}$.

	F00	F40	F50	F65
<i>C</i> ₁ [-]	10.7	10.7	10.7	10.7
С2 [К]	40.7	40.7	40.7	40.7
$T_{\it ref}^{\it WLF}$ [K]	0	0	0	0
$\Delta H_{_T}$ [KJ/mol]	121.18	91.02	67.13	55.14
T ₀ [K]	298.05	299.60	313.50	337.51
ΔT_s	-8.72	-5.2	-4.59	-6.55

Table 3.11: The parameters for the shift factors of equation Eq (3.16) and (3.17) using the reduced temperature

3.4.7 Cure dependent bulk modulus

The bulk modulus is one of the fundamental material properties, which relates the stress response to the applied volumetric change. Accurate measurement of the bulk modulus is extremely difficult, especially during cure. Even for fully cured polymers, no standard measurement tools for this property are available.

In principle the relaxation bulk modulus can be derived from the relaxation Young's modulus and the relaxation shear modulus by iteratively solving their Laplace interrelations [Tschoegl, (1989)]. Therefore, as our first attempt to establish the relaxation bulk modulus, longitudinal DMA measurements were performed on partly cured strip specimens. With DMA tests on the strip specimens the relaxation Young's modulus $E(t - \xi)$ is first established. With known relaxation Young's modulus and known relaxation shear modulus $G(t - \xi)$, the relaxation bulk modulus can be obtained by solving the Laplace interrelation. However, difficulties were encountered in handling and clamping of the partly cured specimens. This method appeared to fail for specimens with a relatively low degree of cure or in the rubbery state. Besides, because of measurement inaccuracies combined with loss of accuracy during the iteration process it turned out that the obtained relaxation bulk modulus values showed a large scatter and were inadequate. Therefore this method was discarded and new approaches had to be explored.

In another attempt to obtain the cure dependent behaviour of the bulk modulus, the pressuredeformation approach was used. An experimental setup with a pressure cell was built, as shown in Fig. 3.27(a). This setup consists of a thick-walled steel cylinder filled with oil, a piston, a heating element, a thermocouple and a pressure transducer. The sample specimens with embedded strain gages were placed in the cylinder and the deformations were measured with the strain gages. We first tried the normal strain gages with plastic substrate. It turned out that at higher temperatures the gage substrate becomes of comparable stiffness as that of the specimens, which makes the measurements in that region unreliable. Therefore a special kind of strain gage, called "free grid strain gage", was used to replace the normal strain gages. The free grid strain gage can be completely embedded into the materials. Figure 3.27(b) shows the specimen made of the unfilled resin, in which a free grid strain gage was embedded.

The set-up was installed in a Zwick 1474 test machine and a constant force was applied to the piston for a predetermined period of time. All signals were recorded with the data acquisition system. The bulk relaxation modulus is therefore measured as

$$K(t) \approx \frac{-p}{\varepsilon_{\nu}(t)}.$$
(3.18)

in which *p* is the pressure, ε_v is the volumetric strain. Step pressure loadings up to 90 MPa (900 bar) were applied. The device was calibrated using calibration specimen with known bulk moduli (Quartz, Aluminium and Polystyrene).



Figure 3.27: Pressure cell test setup for measuring the volumetric creep compliance of EMC, (a). schematic illustration of the experimental setup; (b) specimen with embed free grid strain gages.

The bulk creep tests were performed on the fully cured materials using a step loading of 10MPa. The temperatures used in the tests were 20°C (ambient temperature), another four levels

from 80°C to 120°C. Above about 100°C these moduli dropped rapidly, as expected. The strain variations after step loading were recorded for 20 hours and plotted on a logarithmic time scale. Figure 3.28 shows typical creep curves obtained from the measurements, where the pressure history and the measured creep strains for F40 and F65 are presented. After having established the volumetric creep compliance for various temperatures, the corresponding volumetric (or bulk) relaxation modulus curves can be derived by solving their Laplace transform interrelation. The instantaneous values of the moduli at 20°C were taken as the glassy moduli, which are listed in the table 3.12. The relaxation curves obtained at the above-mentioned temperatures can be used to establish a part of the master curves of relaxation bulk moduli (see Figure 3.30), which will be described later.



Figure 3.28: Typical creep curves obtained from the measurements.

From the pressure cell experiment it was found that only the glassy bulk modulus values at higher degree of cure could be obtained. For the rubbery values the disturbance of the samples by the free grid strain gages appeared to be non negligible. Further, a pressure calibration of the free grid strain gages on incompressible materials actually failed so that an appropriate strain gage pressure correction factor could not be established. Therefore the measurement data of the pressure cell test for the rubbery state (120°C) is considered to be less reliable.

Then a disc-shaped specimen test was used to measure the rubbery bulk modulus. Figure 3.29 shows schematically the experimental setup. The stress state in the disc-specimen depends on the aspect ratio of the specimen. Close to the plate surfaces the radial displacements are prevented and if the specimen thickness is small compared to its diameter the specimen will be in a unilateral compression state. In this state both the shear modulus *G* and the bulk modulus *K*

contribute. Lindsey et al. (1963) derived an approximate solution for elastic materials by assuming a uniform stress through the specimen thickness. The axial stress component is given by Eq. (3.19) as:

$$\sigma_{z} = \frac{\varepsilon}{3} \cdot \left\{ (3K - G) + (5G - 3K) \cdot \frac{I_{0} \left(3r \sqrt{\frac{G}{3K + G}} \right)}{I_{0} \left(3a \sqrt{\frac{G}{3K + G}} \right)} \right\},\tag{3.19}$$

where *a* is the outer radius of the specimen, *r* the distance from the centre, ε the axial strain, and I_0 the modified Bessel function, which is given by the equation below [Tuma and Walsh, (1997)]:

$$I_0(x) = 1 + \frac{(x/2)^2}{(1!)^2} + \frac{(x/2)^4}{(2!)^2} + \frac{(x/2)^6}{(3!)^2} + \cdots$$
(3.20)

Then, the axial stiffness K_z is given by:

$$K_{Z} = \frac{\int_{0}^{a} \sigma_{z} \cdot 2\pi r dr}{2\varepsilon}$$
(3.21)

After measuring the axial stiffness of the specimen, with the known shear modulus the bulk modulus can be obtained using Eqs. $(3.19) \sim (3.21)$.



Figure 3.29: Schematic illustration of the experimental setup for rubbery bulk modulus measurement.

Compression DMA tests were performed using the disk-shaped specimen method. These measurements were performed in the Metravib Viscoanalyzer and in Zwick test machine, where different plate diameters were used. In the Metravib Viscoanalyzer, two aluminium plates with a diameter of 4mm were installed. The initial gap between the two plates was about 0.3mm. Uncured resins were injected into the gap between the two plates and fully cured at the elevated

temperatures. Then DMA tests were done at 130°C. Two frequencies of 0.005Hz and 0.01Hz were used and the measured data showed no frequency dependency, indicating that the rubbery properties were measured. In the Zwick test machine, the specimen size was 50mm in diameter and about 2mm in thickness, and the signals of the force and displacement were recorded by the data acquisition system.

Then we tried to establish the master curves of relaxation bulk moduli based on the rubbery bulk modulus and the relaxation curves obtained at the above-mentioned temperatures. The relaxation curves obtained from pressure cell tests can be shifted along the time axis to obtain the bulk modulus master curves. Because these tests only provided the curves at certain temperatures, only a part of the bulk modulus master curve can be acquired. Figure 3.30 (a) shows the master curve and the normalized master curve of F65. Then a Prony series approximation of the normalized bulk modulus curve can be made and the coefficients are presented in table 3.13. Since no full bulk relaxation curves of the other materials were available, we assume that these materials have the same bulk relaxation kernel as F65, in analogy to the relaxation kernel for shear relaxation modulus. This means that the same Prony series data apply in combination with their own glassy bulk moduli and rubbery moduli given in table 3.12.



Figure 3.30: (a) The master curve of relaxation bulk modulus of F65 and (b) the normalized master curve of F65.

	F00	F40	F50	F65
K _g [MPa]	4770	6600	8330	8960
K _r [MPa]	210	258.71	350.72	524.56

Table 3.12: The glassy and rubbery bulk modudli

Relaxation times	Prony coefficients		
$ au_n$ [s]	k_n		
1.0E-05	0.0389		
1.0E-04	0.0287		
1.0E-03	0.0509		
1.0E-02	0.0274		
1.0E-01	0.0872		
1.0E+00	0.0266		
1.0E+01	0.160		
1.0E+02	0.153		
1.0E+03	0.261		
1.0E+04	0.187		
1.0E+05	0.00688		

Table 3.13: Relaxation times and Prony coefficients for the relaxation bulk modulus of F65

It should be noted that the relaxation bulk modulus master curve was constructed on insufficient and/or less reliable data. The experimental methods that we have used for measuring the bulk relaxation modulus have their limitation. It is recommended that new methods to measure the cure dependent bulk relaxation modulus be explored.

Recently, a new project has been setup in our group to further investigate the curedependent viscoelastic behaviour of thermosetting polymers. One of the major aims of this project is the experimental characterization of the cure-dependent relaxation bulk modulus. Recently efforts were done to obtain more reliable data for the bulk relaxation modulus and shrinkage through alternative direct experiments [Ernst, et al, (2006)]. Presently, new methods to measure the cure dependent evaluation of the bulk relaxation modulus are being explored.

3.5 CTE and the curing shrinkage measurement

3.5.1 CTE measurement

The coefficients of thermal expansion (CTE) of the fully cured materials were measured by ATO, Philips Semiconductors, using TMA (TA Instruments TMA 2940). The sample sizes were around 2mm thickness. The applied heating rate and force were 10 °C/min and 1 N, respectively. Table 3.14 lists the CTE values for all the resins. As expected both the glassy and

rubbery CTEs decrease with filler loading. The values of the rubbery CTE are approximately a factor 3 larger than those in the glassy state, which is an observation that holds for most polymers.

Material	CTE (ppm/C)		
ivitatoritar	Below T _g	Above T _g	
F00	65	193	
F40	45	169	
F50	39	158	
F65	26	92	

Table 3.14: CTE of the fully cured materials

3.5.2 Curing shrinkage

We used a specially designed online density measuring setup based on the Archimedes principle to measure the chemical shrinkage of the resins during the curing process. The setup consists of an accurate weighing device, a Teflon cup, an oil bath with controlled heating device, and a data acquisition system. The uncured sample of about 20~30g was carefully weighted and put in the Teflon cup. Then the cup and the sample were put into silicon oil, which has been kept at the desired temperature. The evolution of the sample's density was obtained by measuring the weight change.

The curing shrinkage measurements were carried out under isothermal curing condition at 90°C, 120°C and 150°C for all of the resins. Figure 3.31 shows the density evolution of resin F00 over a time period of 6 hour cured at 90°C and 120°C, and 2 hours at 150°C. At the beginning of the measurements, a large decrease of the measured weight change can be seen because of the thermal expansion of the sample and the Teflon cup during heating from room temperature to the curing temperature. After about 4 minutes, the temperature in the sample becomes uniform. In the case of curing temperature being 150°C, the curing rate is high. During first few minutes, the density shows a decrease due to the thermal expansion. But soon the density increases sharply because of the relatively fast curing rate. When performing data processing, the initial part of the recorded data should be discarded because the temperature disturbance is involved. The other filled resins show similar density evolution behaviour.

The kinetics model described in section 2.4.1 is used to calculate the degree of conversion and a plot of the density change versus conversion can be constructed. Figure 3.32 presents the density change with the conversion. It can be seen that the density increases almost linearly with conversion for the pure and filled resins, which also shows no curing temperature dependency. Such linear relationship was also observed by other researchers [e.g. Zarrelli, et al. (2004)].

Based on the measurement data, we assume a linear shrinkage model for the epoxy resin [Jansen, (2004)], as:

$$\rho^{c+T}(T,\alpha) = \rho_{ref} [1 - 3\beta_L^{g,r}(T - T_{ref}) + 3\gamma_L(\alpha - \alpha_{ref})] \quad , \tag{3.22}$$

where T_{ref} is the reference temperature, α_{ref} is the reference conversion and ρ_{ref} is the density at T_{ref} and α_{ref} . β_L is the linear coefficient of thermal expansion as shown in table and γ_L denotes the linear cure shrinkage parameter. The density parameters can be obtained by fitting equation (3.22) to measurement data. Figure 3.32 presents the density evolution as a function of degree of cure for all the materials at the tested temperatures, together with the model prediction. It shows a good agreement with the experimental values.

F00 F40 F50 F65 1.00 1.00 1.00 1.00 α_{ref} [-] $\rho_{\rm ref}$ [g/cm³] 1.193 1.463 1.560 1.700 T_{ref} [C] 118 118 118 118 0.0167 0.0133 0.010 0.0073 γ_L

Table 3.15: Parameter for the density equation



Figure 3.31: Density evolution of resin F00 during cure at 90°C, 120°C and 150°C.



Figure 3.32: Density evolution versus conversion (a): F00, (b): F40, (c): F50, (d): F65.

3.6 Conclusions

Experimental characterization of the cure-dependent properties of the thermosetting polymers is conducted. A model epoxy system with different filler concentrations is used for the study purpose.

DSC analysis shows that there is a one-to-one relationship between the glass transition temperature and the degree of cure. The T_g - α relationship is well described by the modified DiBenedetto equation. For the cure kinetics, both isothermal and dynamic approaches give similar results. Their cure kinetics generally follow autocatalytic curing reaction kinetics, while Kamal and Sourour's equation gives a satisfactory description of the cure kinetics.

DMA tests are used to detect the gel point. It is seen that the crossover of G' and G'' is frequency dependent and no identical crossover point of G' and G'' exists. Whereas, there exists a point where the loss angle is independent of the frequency. Therefore, the crossover point of $\tan \delta$ is used to estimate the gel time for the resins. The values show a match with the theoretical calculated gel point of 0.62 using the Flory equation (Eq. (2.33)).

The Ultra Low Frequency Scan method is successfully applied to measure the evolution of the rubbery shear modulus. The results show that before 80% conversion, the modulus is very low. After that, it increases quickly during the final conversion period. Nearly two third of the modulus is built up in the conversion range from 90-100%. It also indicates that the filler percentage has significant reinforcement on the rubbery modulus, especially at highly filled state. Theoretical prediction from the rubbery model (Eq. 2.32) agrees with the experimental data.

Both isothermal and intermittent curing approaches are performed to characterize the curedependent relaxation behavior. In the isothermal cure approach, DMA frequency sweeps are applied continuously during the whole isothermal cure. Dynamics properties of the curing polymer as a function of conversion can be obtained. Time-cure superposition principle is applied to the transient part of the storage shear modulus $(G' - G_r(\alpha, T))$. Then the individual curves at different conversion can be shifted along the frequency axis to form an overlapping master curve and the cure-dependent shift factor can be obtained. The cure shift factor a_{α} as a function of the glass transition temperature can be described well by the Arrhenius equation. The major shortcoming of isothermal cure approach is that the temperature effect on the relaxation behavior at different curing states is missing, since useful experiments can only be performed close to T_g . Using the intermittent curing approach enables DMA scanning on the resin of various cured states. The temperature dependency of the dynamic properties at different curing states can be measured, and the master curve and the shift factor for temperature at each cure state can be established. It is indicated that for the epoxy system in this study the temperature effect on the shift factors is independent of degree of cure when the glass transition temperature is chosen as the reference temperature. The temperature effect is described well with the WLF equation if the temperature is above a switching temperature, while below the switching temperature the Arrhenius equation gives a good prediction.

A new concept of "reduced temperature" is introduced. Both the temperature and conversion effects on the relaxation times can then be expressed in an 'integrated' way.

A few experimental techniques have been explored to measure the cure dependent relaxation bulk modulus. The glassy bulk moduli, rubbery bulk moduli, and the normalized Prony coefficients were obtained by using the combined methods. Since the relaxation bulk modulus master curve was constructed on insufficient data, it may be less reliable. It is recommended that new methods to measure the cure-dependent bulk relaxation modulus be explored.

The chemical shrinkage during the curing process is measured by using an online density measuring setup based on the Archimedes principle. The curing shrinkage measurements were carried out at different cure temperatures. The results show that the density increases almost linearly with conversion for the unfilled and filled resins. The curing shrinkage also shows almost no dependency on the curing temperatures.

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Chapter 4

Effect of Filler Volume Fraction

The addition of fillers can significantly change the thermal and mechanical characteristics of a polymer. Understanding the effect of filler loading on the material properties of the filled composites has engineering and scientific importance. This chapter focuses on the effect of filler volume fraction on the overall material properties of the silica spheres filled composites. The effect of the filler volume fraction on the glassy and rubbery moduli, the relaxation behaviour as well as the coefficients of thermal expansion and curing shrinkage is further investigated.

4.1 Introduction

Polymers are usually filled with fillers to improve mechanical, physical, optical, thermal and electrical properties. It is very common in electronic packaging to use silica fillers in conjunction with polymers to increase the elastic modulus and thermal conductivity and decrease the coefficient of thermal expansion (CTE) and cure shrinkage and thus to meet the thermal and mechanical requirements for electronic packaging application. Also addition of silica fillers can reduce the cost.

Understanding the effect of filler loading on the material properties of the filled composites has engineering and scientific importance. It is well known that the residual thermal-mechanical stresses in packaging polymers affect the reliability of electronic plastic packages. These stresses are caused by CTE mismatch between the materials and also by processing. For example, the curing process (crosslinking of the moulding compound) is a critical step for IC packaging. During the curing step the thermosetting polymer gradually transforms from the liquid state into a viscoelastic solid with a relatively high glassy modulus. Before the gel point, the rubbery shear modulus is zero and it increases as the curing proceeds. Cure-induced stresses will arise in the areas where shrinkage is prevented by geometrical constraints. Although part of the residual stress will relax because of the material's viscoelastic behaviour, there is a certain amount of the residual stress, which is dependent on the equilibrium moduli and will not relax to zero within the service time. This part will not relax even at elevated temperature or long time.

Filler loading has significant effect on the material properties of the filled composites and thus has a large influence on the residual stress. First of all, an increase in filler loading increases both the glassy and rubbery moduli and may also have influence on the relaxation behaviour. The second effect is that an increase in filler loading will result in a decrease of both the rubbery and glassy CTEs. The third effect is that the cure shrinkage decreases with the volumetric filler fraction. Therefore, understanding the effect of filler volume fraction on the properties of the filled composites gives great advantages for designers to select material and to optimize the packaging structure and processing parameter.

Making use of the analysis and FE modelling, one can estimate the optimal values for the packaging polymers for a given packaging design. Another task is to develop a material that has the desired properties by using the proper amount of matrix and fillers. Currently, a predictive tool for such purpose is not available and the process has to be carried out on a trial and error basis. This experience-based method can be time consuming and lacks scientific approach. Therefore, prediction of mechanical properties based on the knowledge of filler and matrix properties will be helpful in material development.

One can study the effect of filler on the material properties either through experiments or/and theoretical analysis. Extensive theoretical and experimental work has been done for determining rheological and mechanical properties of filled polymer systems [Ferry (1970); Ward (1983); Nielsen and Landel (1994)]. Within the areas of electronic packaging, in [Qu and Wong (2002)] and [Wang, *et al.* (1999)] a micromechanics approach was used to predict the effective modulus of underfill materials for Flip Chip applications. Such approach was also used for analysis of the thermoelastic behavior of filled molding compound [Uschitsky, *et al.* (2001)]. Most of the previous research has been focused on the elastic properties only.

The measurements on the unfilled and filled resins were described in the previous chapter. In this chapter, a further analysis and discussion of the effect of filler volume fraction (loading) on the viscoelastic properties of the composites will be presented.

4.2 Effect of filler volume fraction on the glassy moduli

The particulate filled moulding compound can be considered as a two-phase composite consisting of an isotropic viscoelastic matrix and randomly distributed isotropic elastic particles. The properties of the composite materials are determined by the properties of the components, the shape of filler, the morphology of the system, and the nature of the interface between the phases.

In Chapter 3, DMA analysis for measuring the viscoelastic properties of the unfilled and filled resins was presented. As shown, for both the filled and unfilled materials, they exhibit two plateaus. At temperatures well below the glass transition temperature T_g or if the test frequency is sufficiently high, the polymers responds with a relatively high modulus, called the glassy modulus. As the temperature is increased through T_g , the material goes through the transition region and the stiffness drops dramatically to a value called rubbery modulus or equilibrium modulus. At these two plateaus, they behave elastically. Both moduli are strongly dependent on the filler volume fraction.

The glassy shear modulus of the moulding compounds is measured by DMA analysis and the values are listed in table 3.4 in the Chapter 3. It is seen that this modulus of the composite increases with the increase of filler loading. The 65% wt filled resin (49.5 vol%, F65) shows a much sharper increase of the modulus compared to F50.

One of the best models describing the modulus dependence on the filler volume fraction for polymer composites is the modified Kerner equation [Nielsen and Landel (1994)]:

$$\frac{M_c}{M_m} = \frac{1 + AB\phi_f}{1 - B\psi\phi_f} , \qquad (4.1)$$

where *M* is any modulus (shear, bulk, and Young's modulus), the subscripts c, f and m refer to the composite, filler and matrix, respectively. A is a constant which takes into account the geometry of the filler phase and the Poisson's ratio of the matrix; B is a constant related to the ratio of the moduli of filler and matrix; ϕ_f is the filler volume fraction; and ψ a reduced concentration.

In the case of spherical filler particles, the constant *A* is defined as a function of the Poisson's ratio of the matrix resin, such as:

$$A = \frac{7 - 5\nu_m}{8 - 10\nu_m} \tag{4.2}$$

And constant *B* is expressed as:

$$B = \frac{M_f / M_m - 1}{M_f / M_m + A}$$
(4.3)

The reduced concentration term ψ depends on the maximum packing fraction ϕ_m of the particles. Nielsen and Landel (1994) defined the reduced concentration term ψ as

$$\psi = 1 + \frac{1 - \phi_m}{\phi_m^2} \phi_f \tag{4.4}$$

The maximum volume fraction ϕ_m of the filler depends, among others, on filler shape, size distribution and state of agglomeration. In most cases, experimental methods such as sedimentation measurements are used to measure ϕ_m . Theoretical prediction of ϕ_m is difficult and is only available for a few cases. For spheres in hexagonal close packing, the theoretical value of ϕ_m is 0.74. Agglomerates and non-spherical particles generally have smaller ϕ_m values than those of spheres. Fillers with a broad size distribution usually have ϕ_m values larger than 0.74.

In the experiments described in Chapter 3, three filler loadings are used, as shown in table 3.1 (in Chapter 3). The corresponding volume fraction can be calculated using the following equation:

$$\phi_f = \frac{\rho_m w_f}{\rho_m w_f + \rho_f (1 - w_f)} , \qquad (4.5)$$

in which ρ_f and ρ_m denote the density of the filler particles and the unfilled matrix (being 2.20 and 1.16 g/cm³, respectively), w_f is the filler loading in percentage of weight. Table 4.1 lists the filler volume fractions of the moulding compounds using Eq. (4.1).

Table 4.1: filler loading of the epoxy moulding compounds in wt% and in volume fraction

	F00	F40	F50	F65
Filler loading [wt %]	0%	42.5%	50.7%	65.6%
Filler volume fraction [-]	0	0.260	0.345	0.495

The modified Kerner equation is applied to predict the glassy shear and bulk moduli of the filled resins. Note that for calculation of the shear modulus, M_f and M_m in Eqs. (4.1) and (4.3) should be substituted with the corresponding glassy shear moduli G_f and G_m , and for the bulk modulus, the glassy bulk moduli K_f and K_m should be used.

With the glassy modulus of the matrix resin and elastic properties of the filler spheres, one can calculate the modulus of a filled composite at any filler loading. According to supplier's data, the Young's modulus and Poisson's ratio of the filler are 778GPa and 0.2, respectively. Figure 4.1 shows the filler volume fraction dependency of the glassy shear modulus obtained from the experimental measurement and calculations using the modified Kerner equation with $\phi_m = 0.74$. It can be seen that the model prediction agrees well with the experimental measurements.

Figure 4.2 presents the measured values of the glassy bulk modulus and as well as the theoretical calculations using the modified Kerner equation. We can see the Kerner equation gives a good prediction for F40 and F50, but shows a difference for F65. The difference could be caused by inaccuracy of the bulk modulus measurement (see section 3.4.7 of Chapter 3).



Figure 4.1: Glassy shear modulus versus filler volume fraction: measured data and model prediction (Eq. (4.1)).



Figure 4.2: Glassy bulk modulus versus filler volume fraction: measured data and model prediction (Eq. (4.1)).

4.3 Effect of filler volume fraction on the rubbery modulus

In Section 3.4.3 of Chapter 3, the ULFS method was applied to measure the evolution of the rubbery shear modulus. The results show that the filler loading has a significant reinforcing effect on the rubbery modulus, especially in the highly filled state. Theoretical prediction from the rubbery model (Eq. (2.32)) gives a good prediction of the evolution of the rubbery modulus during the curing process. However, before using the rubbery model to predict the evolution of the rubbery modulus for a filled resin with arbitrary filler loading, knowledge of the rubbery modulus of the composite at the fully cured state is a prerequisite.

In the rubbery state, the rubbery elastic property of the resin is dominant. Micromechanics approaches can then be used for predicting the properties of the composites. The Mori-Tanaka Method, the differential effective medium theory, and Eilers equation are the widely used theoretical models for prediction of the effective elastic properties of sphere-filled composites [Mura (1987)]. In [Yang, et al., 2005], we used the Mori-Tanaka Method, the differential effective medium theory, and Eilers equation to predict the rubbery moduli of the model moulding compounds. It was found that the variation of fully cured rubbery shear modulus with filler loading turned out to be best described with the Eilers model and for the rubbery bulk modulus the differential scheme method is preferred. Here only the Eilers equation is applied for the modelling.

Eilers equation was based on the relationship between the relative viscosity and the volume fraction of the disperse phase [Eilers (1941)] and is often used to describe the effect of filler on the rubbery modulus. The Eilers expression for the rubbery shear modulus of the composite is:

$$G_{c} = G_{m} \left(1 + \frac{1.25\phi_{f}}{1 - \phi_{f}/\phi_{m}} \right)^{2}, \qquad (4.6)$$

in which ϕ_m is the maximum packing fraction for the filler. As mentioned in section 4.2, here also $\phi_m = 0.74$ is used.

Figure 4.3 shows the experimental results (symbols) and the model predictions of rubbery shear modulus of the fully cured materials with different filler volume fraction. It can be seen that the prediction from the model agrees well with the measured data.

For the rubbery bulk modulus, the Eilers model is not used here since it is only suitable for shear modulus. Here the Kerner's model (Eqs. (4.1) to (4.4)) is used to predict the rubbery bulk moduli of the resins. Note that in this case M_f and M_m in Eqs. (4.1) and (4.3) should be substituted with the corresponding rubbery bulk moduli K_f and K_m should be used. Here again

 $\phi_m = 0.74$ is used. Figure 4.4 shows the measured and predict rubbery bulk moduli. It can be seen that the Kerner's model gives a reasonably good match with the measured value.



Figure 4.3: Rubbery shear modulus versus filler volume fraction: measured data and model predictions.



Figure 4.4: Rubbery bulk modulus versus filler volume fraction: measured data and model predictions.

4.4 Effect of filler volume fraction on the relaxation behaviour

In addition to the reinforcement effect on both the rubbery and glassy plateaus, filler may also have impact on the transition regime. In Section 3.4.2, DMA characterization of the fully cured materials was performed. The master relaxation curves were shown in Fig. 3.12 and the relaxation times and relaxation modulus coefficients (Prony coefficients) were obtained and presented in table 3.5. For convenience, the full master relaxation curves of the unfilled and

filled resins are shown again in Fig. 4.5. We can see that filler increases both the glassy and rubbery moduli of the composites, however filler intends to increase the modulus to a higher extent in the rubbery state than in the glassy state.

Because the transient part determines the transition behaviour, it is worth further examining the transient part. Based on the full master relaxation curves shown in Fig. 4.5, the transient part can be obtained (see Eq. (2.28d)) and is demonstrated in Fig. 4.6. This part actually represents the time dependency and the relaxation magnitude. It shows that higher filler loading tends to increase the relaxation magnitude. Further, the transient part can be normalized by (G_g - G_r). Figure 4.7 shows the normalized transient part of the shear relaxation master curves of the materials with a reference temperature of 120°C. It can be seen that the normalized master curves of all the resins with different filler loading virtually fall into one single curve. This suggests that the filler and the interaction stresses between filler and matrix material do not affect the macroscopic relaxation behaviour and that the actual stress relaxation is governed by the matrix material only. The normalized Prony coefficients are already presented in table 3.5 (see section 3.4.2).



Figure 4.5: Full relaxation master curves of the unfilled and filled resins, reference temperature T_{ref} =120°C (re shown from Fig.3.12).



Figure 4.6: The transient part of the shear relaxation master curves of the materials (reference temperature is 120°C)



Figure 4.7: Normalized transient part of the shear relaxation master curves of the materials (reference temperature is 120°C)

4.5 Effect of filler volume fraction on CTE and curing shrinkage

In Section 3.5.1, the measurement of the CTE for the fully cured resins with different filler volume fractions is described and the measured values are listed in table 3.14. Here, the measured CTE values as a function of filler volume fraction are illustrated in Figure 4.8. As expected, both the glassy CTE and rubbery CTE decrease with filler loading. The values of the

rubbery CTE are approximately a factor 3 larger than those in the glassy state, which is an observation that holds for most polymers.

A number of equations have been proposed for calculating the CTE of a composite from material constants of the matrix and the filler (for example in [Shapery (1968)]). The different equations often give quite different predictions. One of the reasons for the difficulty to accurately predict the CTE of a polymer composite may be that the filler imposes a constraint effect on the matrix and different filler percentages may have a different degree of constraint.

As a first approximation we can assume that the total expansion is just the sum of the expansion of the polymer matrix and that of the filler particles (rule of mixtures):

$$\beta_{c}^{g}(\phi_{f}) = \beta_{v,f} \phi_{f} + (1 - \phi_{f}) \beta_{v,m}$$
(4.7)

where ϕ_f is the filler volume fraction, $\beta_{v,f}$ is the volumetric CTE of filler, $\beta_{v,m}$ is the volumetric CTE's of the matrix resin.

Macroscopically, the filled resins can be assumed to be isotropic. The linear CTE is very closely approximated as one-third of the volumetric expansion coefficient. Thus, the equation of the rule of mixture (Eq. (4.7)) can be expressed approximately in terms of the linear CTE's, giving the linear CTE's of the filled resins as:

$$\beta_c^g(\phi_f) = \beta_f \phi_f + (1 - \phi_f) \beta_m^g \tag{4.8}$$

and

$$\beta_c^r(\phi_f) = \beta_f \phi_f + (1 - \phi_f) \beta_m^r \tag{4.9}$$

where β_f is the linear CTE of filler, β_m^g , and β_m^r are the linear CTE's of the matrix resin at the glassy and the rubbery states, respectively.

The CTE of the fused silica filler is taken as 0.4ppm/C. Fig. 4.8 shows the theoretical prediction of CTE's as a function of filler volume fraction at the glassy and the rubbery states. It can be seen that Eqs. (4.8) and (4.9) give in fact a good approximation for the actually observed CTE's, certainly regarding the fact that the model does not contain fitting parameters. Only the rubbery CTE's for the 40% and 50 wt% filled samples are larger than the rule of mixture predictions. These differences are probably caused by the inaccuracy introduced in the TMA measurements. Small air inclusions may have been trapped in the samples during adding and mixing of the filler. At higher temperature (rubbery state), these air bubbles tend to introduce extra expansion.



Figure 4.8: Coefficient of thermal expansion of the fully cured materials, measured and prediction with Eqs. (4.8) and (4.9).

With regard to the curing shrinkage, as presented in Section 3.4.5, the density of the pure and filled resins during cure shows almost a linear increases with the degree of conversion and shows no curing temperature dependency. The linear coefficients of cure shrinkage were obtained by fitting the experimental data to the shrinkage model (Eq. (3.22) and listed in Table 3.15. A simple model based on the rule of mixture is proposed to describe the dependency of the linear coefficients of cure shrinkage on the filler volume fraction, such as:

$$\gamma_c^c(\phi_f) = (1 - \phi_f) \gamma_m^c \tag{4.10}$$

in which γ_c^c and γ_m^c represent the coefficients of cure shrinkage of the composite and the matrix, respectively. The prediction of the cure shrinkage coefficients using Eq. (4.10) is presented in Figure 4.9. We can see that it agrees reasonably well with the experimental results. In the rule of mixture, due to the fact that the constraint effect from the filler on the shrinkage of the matrix resin is not included, Eq. (4.10) tends to overestimate the curing shrinkage of the composite, especially at higher filler volume fraction.



Figure 4.9: Linear coefficient of curing shrinkage versus filler volume fraction, measured and theoretical prediction with Eq. (4.10).

4.6 Conclusions

The effect of the filler volume fraction on the major thermal and mechanical properties of the silica sphere filled composites is investigated. The following conclusions can be drawn:

Generally speaking, adding filler will increase both the glassy and the rubbery moduli of the composites, however filler intends to increase the modulus in the rubbery state more pronounced than in the glassy state. The modified Kerner equation is applied to predict the glassy shear and bulk moduli of the filled resins. For the glassy shear modulus the model prediction agrees quite well with the experimental measurements. For the glassy bulk modulus the Kerner equation gives a good prediction for F40 and F50, but shows a difference for F65. The difference can be possibly caused by inaccuracy of the bulk modulus measurement.

The variation of the fully cured rubbery shear modulus with filler loading turns out to be well described with the Eilers model, whereas for the effect of filler on the rubbery bulk modulus the modified Kerner equation gives a reasonably good prediction.

The normalized master curves of all the resins with different filler loading virtually fall into one single curve. This suggests that the filler and the interaction stresses between filler and matrix material do not affect the macroscopic relaxation behavior and that the actual stress relaxation is governed by the matrix material only.

The variation of the coefficient of thermal expansion and the coefficient of curing shrinkage with filler volume fraction are conveniently modeled with a simple rule of mixtures.

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Chapter 5

FE Implementation and Model Validation

5.1 Introduction

In practice, electronic products usually consist of different complex structures having a complicated process history. This makes analytical solution for most of the thermal-mechanical problems impossible. Fortunately, with the development of computer and software technology, the finite element method (FEM) has provided a powerful tool for solving such problems with numerical analysis and simulation.

A number of numerical methods and procedures have been developed for the analysis of viscoelastic problems using FEM. As mentioned in Chapter 2, a direct solution of the general viscoelastic constitutive equation with FEM is difficult and causes data storage problems [Ernst *et al.*, 2006]. Therefore, approximate methods have been seeking to circumvent these huge data storage and data handling problems.

Among the approximation methods, using Prony series for approximating the kernel function is the most widely used method. Such a method has been used by many researchers to solve the viscoelastic problems (for example, [Zienkiewicz *et al.*, 1968; Taylor *et al.*, 1970; Puso and Weiss, 1998]). Krishna *et al.* (1995) used this method in modelling the temperature and moisture effect of the packaging polymers on the thermo-mechanical behaviour of a package.

There has been very limited work reported in the literature with regard to the FE modelling of the curing behaviour of viscoelastic materials. Kiasat (2000) first implemented his curedependent viscoelastic model into the FE program Marc for modelling the cure-induced shrinkage stresses in the curing process of fiber-reinforced polyester composites. Based on the material model option (the generalized Maxwell model) provided in the Marc program, the cure-dependent relaxation coefficients and curing shrinkage were implemented through user subroutines. Because the cure kinetics and the cure and temperature effects on the relaxation times were not considered in his model, the implemented approach could only be used for isothermal curing conditions.

In Chapter 2, a cure-dependent constitutive model based on the TTC superposition principle was developed. In order to be able to actually investigate processing induced stress fields in electronic packages the cure-dependent constitutive relations should be implemented into a standard FEM package. Most standard FEM packages facilitate a simple implementation of incremental stress strain relations (or rate equations) for linear viscoelastic materials. In the present work, the commercial standard FEM package MSC Marc is chosen for implementation. MSC Marc has two models that represent viscoelastic materials [Marc version 7.1]. One is a Kelvin-Voigt model, which allows the rate of change of the inelastic strain to be a function of the total stress and previous strain. The other is a general hereditary integral approach, where the stress relaxation form is utilized. These standard procedures only deal with cure-independent material behaviours. In order to be able to perform FE simulations using the developed model, the cure-dependent model and the cure-dependent material properties should be implemented into the FEM package.

5.2 Incremental form of the constitutive equation

In Chapter 2, the cure-dependent constitutive model based on the TTC superposition principle was developed. The stress-strain relation (Eq. (2.30)) is cited here as equation (5.1):

$$\sigma_{ij}(t) = \int_{-\infty}^{t} 2\left\{ G_r(\alpha, T) + \left[G_g - G_r(\alpha, T) \right] \cdot \sum_{n=1}^{N} g_n \cdot \exp\left[-\frac{t - \xi}{\tau_n(\alpha, T)} \right] \right\} \cdot \frac{d\varepsilon_{ij}^d}{d\xi} d\xi + \int_{-\infty}^{t} \left\{ K_r(\alpha, T) + \left[K_g - K_r(\alpha, T) \right] \cdot \sum_{n=1}^{N} k_n \cdot \exp\left[-\frac{t - \xi}{\tau'_n(\alpha, T)} \right] \right\} \cdot \frac{d\varepsilon_v^{eff}}{d\xi} d\xi$$
(5.1)

It should be mentioned that the equilibrium moduli are dependent on the conversion and temperature at the curing time or loading time ξ and the glassy shear modulus and bulk modulus are considered to be temperature and conversion independent. As mentioned in section 2.3.3, the relaxation times for shear relaxation moduli and bulk relaxation moduli are not

necessary the same, but they are considered to have the same dependency of on the conversion and temperature. The dependency of the relaxation times on the conversion and temperature is represented via the shift factors, such as:

$$\tau_n(\alpha, T) = a_{T,\alpha} \cdot \tau_n^{ref} \quad , \tag{5.2}$$

and

$$\tau'_{n}(\alpha,T) = a_{T,\alpha} \cdot \tau'_{n}^{ref}$$
(5.3)

With simplified notation for the equilibrium moduli and relaxation times, Eq. (5.1) is rewritten as:

$$\sigma_{ij}(t) = \int_{-\infty}^{t} 2 \left[G_r + (G_g - G_r) \cdot \sum_{n=1}^{N} g_n \cdot \exp\left(-\frac{t - \xi}{\tau_n}\right) \right] \cdot \frac{d\varepsilon_{ij}^d}{d\xi} d\xi + \int_{-\infty}^{t} \left[K_r + (K_g - K_r) \cdot \sum_{n=1}^{N} k_n \cdot \exp\left(-\frac{t - \xi}{\tau'_n}\right) \right] \cdot \frac{d\varepsilon_v^{eff}}{d\xi} d\xi$$
(5.4)

Usually, in a FE code using an incremental solution strategy, the solution is known at time *t*, and the task is to determine the solution at $t + \Delta t$ using an iterative method. According to the constitutive relation (5.4), a stress-update $\Delta \sigma_{ij}$ for a time step Δt between time *t* and time $t + \Delta t$ is defined by:

$$\Delta \sigma_{ij} = \sigma_{ij} (t + \Delta t) - \sigma_{ij} (t)$$
(5.5)

Substituting t with $t + \Delta t$ in Eq. (5.4), the stresses in time $t + \Delta t$ can be expressed as follows:

$$\sigma_{ij}(t + \Delta t) = \int_{-\infty}^{t+\Delta t} 2 \left[G_r + (G_g - G_r) \cdot \sum_{n=1}^N g_n \cdot \exp\left(-\frac{t + \Delta t - \xi}{\tau_n}\right) \right] \cdot \frac{d\varepsilon_{ij}^d}{d\xi} d\xi + \int_{-\infty}^{t+\Delta t} \left[K_r + (K_g - K_r) \cdot \sum_{n=1}^N k_n \cdot \exp\left(-\frac{t + \Delta t - \xi}{\tau'_n}\right) \right] \cdot \frac{d\varepsilon_{\nu}^{eff}}{d\xi} d\xi$$
(5.6)

The stress increment can be obtained by subtracting expression (5.4) from (5.6), yielding:

$$\begin{split} \Delta \sigma_{ij} &= \sigma_{ij}(t + \Delta t) - \sigma_{ij}(t) \\ &= \sum_{n=1}^{N} \left\{ \left[\exp\left(-\frac{\Delta t}{\tau_{n}}\right) - 1 \right] \cdot \Re_{g}^{n}(t) + \sum_{n=1}^{N} \left[\exp\left(-\frac{\Delta t}{\tau_{n}'}\right) - 1 \right] \cdot \Re_{k}^{n}(t) \right\} \\ &+ \int_{t}^{t + \Delta t} 2G_{r} \frac{d\varepsilon_{ij}^{d}}{d\xi} d\xi + \sum_{n=1}^{N} \left[2g_{n} \exp\left(-\frac{t + \Delta t}{\tau_{n}}\right) \cdot \int_{t}^{t + \Delta t} (G_{g} - G_{r}) \cdot \exp\left(\frac{\xi}{\tau_{n}}\right) \cdot \frac{d\varepsilon_{ij}^{d}}{d\xi} d\xi \right] \\ &+ \int_{t}^{t + \Delta t} K_{r} \frac{d\varepsilon_{v}^{eff}}{d\xi} d\xi + \sum_{n=1}^{N} \left[k_{n} \exp\left(-\frac{t + \Delta t}{\tau_{n}'}\right) \cdot \int_{t}^{t + \Delta t} (K_{g} - K_{r}) \exp\left(\frac{\xi}{\tau_{n}'}\right) \cdot \frac{d\varepsilon_{v}^{eff}}{d\xi} d\xi \right] \end{split}$$
(5.7)
and the history variables $\Re_g^n(t)$ and $\Re_k^n(t)$ are defined as

$$\Re_{g}^{n}(t) = g_{n} \exp\left(-\frac{t}{\tau_{n}}\right) \cdot \int_{\xi=-\infty}^{t} (G_{g} - G_{r}) \cdot \exp\left(\frac{\xi}{\tau_{n}}\right) \cdot \frac{d\varepsilon_{ij}^{d}}{d\xi} d\xi , \qquad (5.8)$$

and

$$\Re_{k}^{n}(t) = k_{n} \exp\left(-\frac{t}{\tau'_{n}}\right) \cdot \int_{\xi=-\infty}^{t} (K_{g} - K_{r}) \cdot \exp\left(\frac{\xi}{\tau'_{n}}\right) \cdot \frac{d\varepsilon_{v}^{eff}}{d\xi} d\xi$$
(5.9)

In the stress update expression, the evaluation can be straightforwardly performed adapting an appropriate time integration scheme. The stress update only requires stored data for the functions of the previous time step $\Re_g^n(t)$ and $\Re_k^n(t)$, and can easily be implemented into a FEM program. With a stress update procedure, based on the above expressions being implemented into a FEM program, an adequate simulation for establishing curing induced stress and strain fields is obtained.

5.3 Implementation of the cure-dependent material behaviour

5.3.1 Calculation of α and $T_{g\alpha}$ as a function of time and temperature

To fully implement the cure-dependent viscoelastic model into MSC Marc program, the degree of conversion α and glass transition temperature $T_{g\alpha}$ have to be calculated first. In case of a complex curing profile, the calculation of α and $T_{g\alpha}$ as a function of time and temperature should be realized for an arbitrary temperature history. Though the model shown in Eqs. (2.42) and (2.43) gives a description of the cure kinetics, it is not convenient to calculate the degree of cure for a complex curing profile directly. Therefore we introduced an equivalent curing time [Jansen (2004)]. Eqs. (2.42) and (2.43) can be rewritten in the form of

$$\frac{d\alpha}{\alpha^m (1-\alpha)^n} = A \exp\left(-\frac{Q}{RT}\right) dt$$
(5.10)

In the above equation, the temperature is a function of time. Then the equivalent cure time is represented as

$$\zeta = \int_{0}^{t} A \exp\left(-\frac{Q}{RT(t)}\right) dt$$
(5.11)

Integration of the left-hand side of Eq. (5.10) yields a conversion dependent function $F(\alpha)$, which should be equal to the equivalent curing time, such that:

$$F(\alpha) \equiv \int_{0}^{\alpha} \frac{d\alpha}{\alpha^{m} (1-\alpha)^{n}} = \zeta$$
(5.12)

The desired conversion is then found by inversion of this equation

$$\alpha(\zeta) = F^{-1}(\zeta) \tag{5.13}$$

For Eq. (5.12), there exists an analytical solution [Jansen, (2004)]]. However, inversion to the required $\alpha(\zeta)$ form is not straightforward. An approximate evaluation method is applied for numerical simulation. The conversion as a function of the equivalent curing time is approximated as Eq. (5.14):

$$\alpha(\zeta) \cong 1 - \frac{1}{2} \exp[-P_1(\zeta + \zeta_0)^{P_2}] - \frac{1}{2} \exp[-P_3(\zeta + \zeta_0)^{P_4}], \qquad (5.14)$$

in which, P_1 to P_4 are parameters, and ζ_0 is the initial equivalent curing time corresponding to the initial conversion α_0 . When the material is at a completely uncured state, then ζ_0 is zero. In other cases, ζ_0 must be calculated according to its initial conversion α_0 before using Eq. (5.14). For instance, in the moulding experiments that will be described in Chapter 6, the uncured filled resins have to be reshaped to tablets with a diameter of 50mm for being used in the transfermoulding machine. The uncured materials were reheated and pressed into a pill shape. During this process additional cure occurred and the initial conversion level has to be taken into account during simulations. Table 5.1 presents the parameters of Eq. (5.14) and the values of the initial conversion and the equivalent curing time corresponding the tablets being used in the moulding experiments.

	F00	F40	F50	F65
P_l	1.1183	0.4571	0.3511	0.3941
P_2	1.1443	0.9819	0.9291	0.938
P_3	0.4247	1.1235	0.974	1.058
P_4	0.9264	1.156	1.2242	1.182
α_0^{pills}	0.3	0.3	0.3	0.3
ζ_0^{pills}	0.500	0.496	0.593	0.539

Table 5.1: Approximate kinetic parameters, for moulding compound pills

A subroutine called 'CUREKINE' is coded. In the subroutine the user can define the desired temperature profile T(t). With this data first the degree of cure at every instant is calculated (using Eqs. (5.11) and (5.14) and the material parameters listed in tables 3.2 and 5.1. With this degree of cure then the corresponding glass transition temperature $T_g(\alpha)$ is calculated (Eq. 2.45 and table 3.3). The updated degree of cure and glass transition temperature are needed for calculating the stiffness functions as well as to calculate the shift factor, thermal strain and curing shrinkage, which will be discussed in the next sub-section.

5.3.2 Cure-dependent stiffness coefficients

In FE program MSC Marc, user defined subroutines can be applied to implement the nonstandard cases. To implement the developed cure-dependent viscoelastic model, user subroutines have to be designed to compute the cure-dependent stiffness coefficients and the shift factors for the temperature and conversion effects.

In our method, the shear and bulk relaxation moduli are represented by normalized Prony series as Eq. (2.30), in which the glassy modulus is assumed to depend only on temperature, whereas the rubbery modulus depends on both the degree of cure and the temperature. A user subroutine is coded to input and calculate the cure-dependent stiffness coefficients for relaxation functions and to enforce a new stiffness matrix assembly.

The evolution of the shear and bulk modulus coefficients during the curing process is defined through the user subroutine 'UBGINC' [Marc manual, Vol. D]. First, the subroutine is coded to input the normalized stiffness coefficients for the fully cured relaxation functions. Then the subroutine 'CUREKINE' is called to obtain the updated conversion and the glass transition temperature. The cure-dependent rubbery moduli are calculated. Note that the cure dependent shear modulus vanishes below the conversion at gelation (α_{gel}) whereas the bulk modulus does not vanish). All terms of the modulus coefficients can then be computed and a new assembly of the stiffness matrix is then carried out.

The effect of temperature and conversion on the relaxation is modelled by a shift factor defined in subroutine 'TRSFAC'. The shift factor equations can be found as Eqs. (3.16) and (3.17) and use the instantaneous glass transition temperature as a reference temperature. Therefore the shift factor not only changes with temperature but also with conversion.

In the subroutine, first the subroutine 'CUREKINE' is called to obtain the updated conversion and the glass transition temperature. Then the "logarithmic shift function", ϕ , is calculated, in which the temperature and conversion (crosslinking) effects are included, such as:

$$\phi(\alpha, T) = -\log_{10} a_{T, \alpha} , \qquad (5.15)$$

where $a_{T,\alpha}$ is the temperature and conversion dependent shift factor, which is defined in Eqs. (3.16) and (3.17). As stated before, the conversion dependency is implemented by taking the cure dependent glass transition temperature as the shifting reference temperature. It should be noted that the terms corresponding to the rubbery moduli (infinite relaxation time) do not change due to the shift procedure.

5.3.3 Thermal and curing shrinkage

In addition to the cure kinetics and the cure-dependent relaxation modulus models, the thermal and curing shrinkage strains have to be included into a thermal-mechanical analysis. For thermal strain, most of the commercial FE software's have a built-in function to calculate the thermal stress. But normally they do not have a function to directly incorporate the curing shrinkage. Therefore, in the modelling of cure-induced stress, the curing shrinkage model definition must be incorporated to calculate the cure shrinkage strains of the resin materials.

Both the thermal strain caused by temperature variation and the cure shrinkage strain caused by chemical crosslinking are introduced by the user subroutine 'ANEXP'. The subroutine is originally used to specify anisotropic thermal strain increments for anisotropic properties. The total strain induced in the curing process is considered as the sum of the thermal strain and the curing shrinkage strain, as:

$$\Delta \varepsilon_{ij}^{eff} = \Delta \varepsilon_{ij}^{th} + \Delta \varepsilon_{ij}^{sh} \quad , \tag{5.16}$$

in which, $\Delta \varepsilon_{ij}^{th}$ is the incremental thermal strain and $\Delta \varepsilon_{ij}^{c}$ the incremental curing shrinkage strain. For the isotropic case, they can be expressed as:

$$\Delta \varepsilon_{ij}^{th} = \beta_L \Delta T \cdot \delta_{ij} \quad (5.17)$$

and

$$\Delta \varepsilon_{ij}^c = -\gamma_L \cdot \Delta \alpha \cdot \delta_{ij}, \qquad (5.18)$$

where β_L is the linear coefficient of thermal expansion (CTE_L), ΔT temperature increment, $\Delta \alpha$ conversion increment, γ_L the linear cure-shrinkage coefficient.

In the subroutine, data for β_L , γ_L and the fitting parameters of the conversion-time relation is input. The subroutine 'CUREKINE' is called to obtain the updated conversion and the glass

transition temperature. Then $\Delta \alpha$ is calculated and the thermal strain increment vector in Eqs. (5.16~18) is defined.

5.4 Model validation

In order to test the correctness of the material models as well as the model implementation, a validation study is required. This should be an experiment on a simple geometry resulting in both shear and (hydrostatic) compression. Below such a setup is established, in which validation experiments will be carried out.

5.4.1 Validation experiment

Figure 5.1 shows the experimental setup for the validation test. Two aluminium plates with a diameter of 50mm are installed in a Zwick 1474 testing machine. The upper plate is fixed and connected to the force transducer. The lower one is connected to the crosshead of the testing machine and the axial displacement is controlled by a Linear Variable Displacement Transducer (LVDT). The data from the LVDT and the force transducer is recorded by a data acquisition system. Uncured resins are injected into the gaps between the two plates and are cured at the desired temperatures. The thickness of the specimen can be adjusted by changing the gap thickness. During cure, stress will be built up in the resin due to the partly constrained state of the geometry. The force recorded by the force transducer represents the axial force acted on the plates by the resins due to curing shrinkage and applied loading.

The stress states in the disc-specimen depends on the aspect ratio of the specimen. Close to the plate surfaces the radial displacements are prevented and if the specimen thickness is small compared to its diameter the specimen will be in a unilateral compression state. In this state both the shear modulus G and the bulk modulus K contribute. Lindsey et al. (1963) derived an approximate solution for elastic materials by assuming a uniform stress through the specimen thickness. Because the strong viscoelastic nature of the thermosetting polymers, a direct theoretical solution for this case is very difficult. Therefore, FE simulations are carried out for verification purposes, which will be described in the next section.



Figure 5.1: Experimental setup for validation tests, (a) photo of the setup; (b) a schematic illustration

A series of experiments were carried out for the unfilled and filled resins. Liquid resin was injected into the gap between the two plates. The displacement-controlled mode was used and the reaction axial force was recorded. Two mechanical loading conditions were used during the curing process:

- Two plates were fixed during the curing process and the axial force acted on the plates was recorded. This force reflects the evolution of the internal force caused by the curing shrinkage.
- 2) The upper plate was fixed. The lower plate was fixed until a certain curing time and after that a step displacement was applied and kept constant during the remained curing process. The displacement profile is shown schematically in Figure 5.2. This will result in a combinational effect of curing shrinkage and stress relaxation of the partly cured material.



Figure 5.2: Displacement profile for step relaxation

5.4.2 FEM simulation

Specimen dimensions are: diameter 50mm, thickness: 2.00mm. An axi-symmetric element is used, as shown in Figure 5.3. With regard to the boundary conditions, in addition to the axi-symmetric boundary condition applied to the axis of symmetry, displacement boundary conditions are applied to the nodes on the top and bottom surfaces. The nodes on the top surface are fixed in all directions, representing that the resin is perfectly adhered to the surface of the upper plate. For the nodes on the bottom surface, in the one hand they are in-plane fixed. On the other hand, the centre node is chosen as tying node; other nodes are tied to the tying node, which makes them have the same axial displacement as the tying node. In this way, the axial displacement is applied through the tying node and the reaction force from the tying node represents the axial force that the lower plate imposes on the specimen, which is used for comparison with the experimental results.

The cure-dependent viscoelastic model for the materials and the model implementation are already described in Chapter 2 and the previous section of the present chapter. For each of the materials, numerical simulations for the loading cases given in section 5.4.1 are performed. The results and discussion will be presented in the next section.



Figure 5.3: Specimen geometry (left) and finite element mesh (right)

5.4.3 Results and discussion

During the isothermal curing, with the increase of the material stiffness, stresses within the specimen is built due to the curing shrinkage that is (partly) constrained by the plates. In the case of applying a step displacement at a certain degree of cure, the stresses caused by the external force and the curing shrinkage, and their relaxation process are all involved.

Figures 5.4 and 5.5 show the force development during cure of the unfilled resin (F00) and the 65% filled resin (F65) at 119°C at fixed condition. From the experimental results, we can see that the cure-induced force starts to increase from zero from the gel point and increases sharply

as the curing proceeds. After a certain curing time (for F00, about 120 minutes and for F65 about 30 minutes), the force shows a drop and starts decreasing. This is because local debonding from the Aluminium plates occurs. For both cases, the model predictions agree well with measured data before the local debonding happens.



Figure 5.4: Evolution of axial force during isothermal curing of the unfilled resin (F00) at 119°C under the condition with both plates fixed



Figure 5.5: Evolution of axial force during isothermal curing of the 65% filled resin (F65) at 119°C under the condition with both plates fixed

In order to avoid the debonding from the plates and to verify the capability to predict the relaxation behaviour under external stress, experiments using a compressive step strain are performed. Figures 5.6 and 5.7 show the experimental results and the FEM predictions of the force development during cure of the four materials at 119°C under step displacements. Before application of the step displacement, stress evolution in the specimen is caused by the combined effect of the curing shrinkage and relaxation. After applying the step displacement, an instantaneous stress increment is seen. Afterwards the stress undergoes relaxation, and

meanwhile the curing shrinkage also induces stress. The force curve after step displacement represents the combined responses of step loading, curing shrinkage, and stress relaxation.

It can be seen from Figs. 5.6 and 5.7 that for the unfilled, 40% and 50% filled resins, the model predictions agree quite well with the measured data except the instantaneous values when the step displacement is loaded. The reasons for causing the difference of the instantaneous values between the experimental and model prediction probably could be: The step loading was applied in displacement-controlled mode. A more or less instantaneous overloading existed in the machine controlling process. And this instantaneous overloading was not considered in the simulation.

Figure 5.7(b) shows the experimental and simulation results for 65% filled material. The results indicate that the model predictions agree quite well with the measured data before and around the step displacement is loaded. At the final stage of cure, the measured data shows a relaxation of the force. The simulation gives to some extent relaxation, but less pronounced. The possible reasons could be: (1). The parameters for curing shrinkage and the rubbery bulk modulus are not accurate enough. As discussed in section 3.4.7, the measurement of the rubbery bulk modulus is rather difficult. Though a few experimental techniques were tried, the relaxation bulk moduli including the rubbery bulk moduli were constructed on insufficient and/or less reliable data. (2). There is no perfect adhesion between the interfaces with the plates. When the tensile stress level in the resins increases due to continuing cure, local debonding may occur, which will cause the measured force to be lower than the simulation values. (3). Entrapped air bubbles in the resin and at the interface. Because F65 has much higher viscosity at uncured state than other resins, air bubbles are easier entrapped when injecting the compound into the gap.



Figure 5.6: Evolution of axial force during isothermal curing at 119°C under step displacement condition. (a). F00: step displacement (δ =-18.2µm) is applied at α = 0.89; (b). 40% filled resin (F40): step displacement (δ =-18.2µm) is applied at α = 0.92.



Figure 5.7: Evolution of axial force during isothermal curing at 119°C under step displacement condition. (a). 50% filled resin (F50): step displacement ($\delta = -20.4 \mu m$) is applied at $\alpha = 0.94$; (b). 65% filled resin (F65): step displacement ($\delta = -9.4 \mu m$) is applied at $\alpha = 0.87$.

5.5 Conclusions

FEM implementation of the cure-dependent viscoelastic model is described in this chapter. In the stress update expression, the evaluation can be straightforwardly performed by adapting an appropriate time integration scheme. The stress update only requires stored data for the functions of the previous time step $\Re_g^n(t)$ and $\Re_k^n(t)$, and can easily be implemented into a FEM program. With a stress update procedure, based on the above expressions being implemented into a FEM program, an adequate simulation for establishing curing induced stress and strain fields is obtained.

Calculation of the cure kinetics and the glass transition temperature T_{ga} is realized in a separate user-subroutine. An equivalent curing time is introduced to make the calculation of the cure kinetics for a complex curing profile more convenient.

The cure-dependent shear and bulk modulus coefficients, the shift factor for the temperature and curing effects, and the curing shrinkage are incorporated through the user subroutines.

Model validation is carried out by using a disc-shaped test setup, in which the specimen undergoes a 3-D stress state generated by the (partly) constrained curing shrinkage and external loading. FEM simulation indicates that model predictions agree quite well with the measured data except for the instant values when the step displacement is loaded. Therefore, it can be concluded that the model and the FE implementation is reliable for simulation of cure-induced stresses, in which thermosetting polymers are involved.

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Chapter 6

Warpage of QFN Packages Induced During the Array Moulding Process

In this chapter, an investigation on the process-induced warpage during the array-moulding process of QFN packages is conducted both experimentally and numerically. A series of moulding experiments for QFN matrix strips with the model moulding compounds are performed. In the moulding experiments, different processing parameters, filler loading and die thickness are used. The warpage is measured by a contact probe coordinate measuring system. The cure-dependent constitutive model is applied to describe the behaviour of the moulding compound during the curing process. The cure-dependent material parameters are incorporated into a finite element code Marc and numerical simulations were carried out for the QFN array-moulding process. The effects of filler concentration, curing temperature profiles and the die thickness on the warpage are studied.

6.1 Introduction

One of the latest developments in packaging technology is the QFN (Quad Flat Non-lead) package. Being both a chip scale package (CSP) and a plastic encapsulated package with lead pad on the bottom of the package, QFN packages provide many advantages over other lead frame package configurations, such as low cost, small size, low profile, high thermal and electrical performance and good production yields. Compared to leaded packages with similar body sizes and lead counts, the QFN offers far superior thermal performance because the lead frame is on the bottom of the package and the die-pad is exposed, resulting into effective

removal of heat. Such structure characteristics also provide excellent electrical performance [Chen *et al.*, 2003]. These features make QFN's suitable for portable communication/consumer products, including cellular phones, digital cameras, PDA's, laptops, wireless transmitters, etc. Therefore, market acceptance of QFN packages has been rapid and their use is expected to grow significantly.

The Philips business carrier HVQFN package is chosen as a demonstrator. Figure 6.1 shows some examples of QFN packages singulated from map moulds and the cross section. The package is composed of an IC die attached to an exposed pad and in a later stage encapsulated with an epoxy moulding compound.



Figure 6.1: QFN packages singulated from map moulds, (a) top and bottom view; (b). Cross-sectional sketch

For reasons of cost reduction many HVQFN's are moulded in so called map moulds; i.e. an array of $m \times n$ devices which are moulded in one mould shot. First, an etched matrix with leadframes and diepads is made on a base strip of metal material (generally a copper alloy). After die–attach and wire-bonding processes similar to conventional leadframe packages, a transfer moulding process is used to encapsulate the matrices with Epoxy Moulding Compound (EMC). After laser marking and plating operations, the QFN units are separated by a sawing process. Figure 6.2 shows an example of a moulded strip for sawing singulation, which contains 5 maps (matrixes) and totally over 200 QFN units. From business point of view (cost-reduction), it is essential to decrease the number of maps, to a 4-map and/or eventually a 1-map assembly. Decreasing the number of maps will increase the space available for products, but as such, will also increase the amount of warpage in the map.



Figure 6.2: Bottom and top view of a moulded strip, which has 5 maps and totally 240 QFN units.

The curing process of EMC and subsequent cooling down will introduce warpage due to polymerization shrinkage and CTE difference of the materials. Warpage is a critical issue for the map-mould technology. Figure 6.3 shows a warped moulded strip after the moulding process. It is expected that with increased density of QFN units, warpage induced in the manufacturing process will be more serious. Such warpage in the map mould will obstruct the delicate sawing process. Furthermore, after sawing, the residual warpage in the QFN package can cause assembly problems and reliability issues. Therefore, it is very important that, first, a process-dependent material model should be established and the warpage should be predicted and verified with experimental data. And then an optimized design for package, material parameters and process conditions can be obtained through virtual prototyping



Figure 6.3: Warpage of a map mould, induced during the moulding process

Warpage due to processing induced residual stresses has long been recognized as an important issue for package reliability. Excessive warpage not only causes device failure issues such as die cracking and interface delamination, but also may cause assembly problems in the subsequent processes, such as dimension instability, non-coplanarity, singulation problems, etc.

Many efforts have been made to predict and/or measure process-induced warpage of packages. Kelly (1994) measured the warpage of a plastic power package and indicated that the package was significantly deformed at the moulding temperature, which is attributed to chemical shrinkage of the moulding compound. In [Yeung and Yuen, (2001)], the impact of processing conditions on warpage prediction of a plastic quad flat package (PQFP) was investigated. It was suggested that low temperature and longer moulding time or high temperature and shorter moulding time would result in less warpage. They also showed that the viscoelastic model predicted the warpage more accurately than the thermoelastic model. In [Dunne and Sitaraman, (2002)], a coupled cure-thermal-stress analysis approach was proposed to predict warpage and stresses during sequential fabrication of electronic packaging structures. They concluded that neglecting the effect of the viscoelastic behaviour of polymers and the influence of the process history on the FE modelling could lead to incorrect predictions. However, due to fast and huge change of the material properties during the curing process, it is still an open and challenging research field to accurately predict the process-induced stress and warpage, especially under complex curing temperature profiles.

In this chapter, an investigation on the process-induced warpage during the map-moulding process is conducted both experimentally and numerically. Parts of this chapter were published before in [Yang, *et al.*, (2004)].

6.2 Moulding experiments

6.2.1 Experimental conditions

The filled resins (F40, F50, and F65) described and characterized in Chapter 3 were used as the moulding compounds. A series of moulding experiments with various combinations of processing conditions and package parameters was conducted and warpage after moulding and post cure was measured.

The transfer moulding was carried out in IMO-BE, Philips Semiconductors. The moulding machine is a Lauffer VSKO 20. In the moulding experiments, an injection pressure of 12 kN was applied, which resulted in a pressure of about 86 Bar. The products were cured in the mould under the pressure for a prescribed time and then de-moulded and cooled down freely to room temperature. Then, the warpage along the chosen longitudinal and lateral cross-sections was measured by using a contact probe coordinate measuring system. Meanwhile, a DSC

measurement was conducted to determine the glass transition temperature, which is a measure for characterizing the de-moulding conversion level. Afterwards, the products were post cured in the oven for 1 hour at 200°C. After cooling down, the product shape was re-measured. Figure 6.4 shows schematically the temperature profile for the moulding and post-curing.

The filler loading, die thickness, moulding temperature and the de-moulding conversion were taken as parameters in the moulding experiments. Each parameter has three levels, as listed in Table 6.1. In order to limit the number of experiments we chose to vary the parameter level only one at a time. As standard conditions were chosen: 65 wt% filled moulding compound, 250 µm die thickness, 5 minutes curing in a mould at 140°C, resulting in a conversion level at mould opening of about 80%. Note that the curing times for the temperature history study were chosen such as to result in the standard de-mould cure levels (80%). In order to obtain the correct curing times several preliminary moulding experiments were performed until the glass transition temperature was about 81°C (corresponding to 80% conversion). Since the curing process is largely affected by the temperature, the exact values of the mould temperatures were verified by introducing small thermocouples inside the mould previous to the moulding experiment. The demoulding conversion level was varied by changing the curing times while keeping the mould temperature at 140°C. Experiments with lower de-mould cure levels than 75% were unsuccessful, since at these levels the moulding compound after mould opening is not stiff enough for the product to be extracted from the mould. After full determination of the moulding conditions from the preliminary moulding experiments, for each experimental condition two or three products were moulded.



Figure 6.4: Illustration of temperature history of moulding process (T_m : moulding temperature t_m : in-mould curing time; T_{pmc} : post-moulding curing temperature; t_{pmc} : post-moulding curing time).

Parameter	Level 1	Level 2	Level 3
Filler loading (%wt)	40	50	65
Die thickness (µm)	180	250	380
Moulding temperature $T_{\rm m}$ (°C)	120	140	160
Conversion after moulding	0.75	0.80	0.90

Table 6.1: Parameter lists in the moulding experiments (Bold text refers to the standard conditions)

6.2.2 Warpage measurement setup

The amount of warpage was determined from measurements of the surface shape using the setup shown in Fig. 6.5 (a). A programmable precision XYZ-table was used, which is equipped with 1 μ m accurate stepper motors. The vertical coordinate was measured with a LVDT sensor.



Figure 6.5: The setup for curvature measurement, (a). The experimental setup; (b). A schematic view of scan lines.

The shape was scanned along the sawing lines (14.5 mm apart, in between the dies, see Fig. 6.5(b)). If the moulding compound was too soft at de-moulding the ejector pins left sink marks on the surface. These sink marks then appear as sharp peaks in the shape pictures. In addition, if the scan lines slightly deviated from the cutting lines the scan entered the region of the die and much broader sink marks could be observed.

Since the sink marks will affect a correct fit to the overall product curvature, they were removed from the data evaluation procedure by using the criterion of 0.5 times the standard deviation from a quadratic fit. Two measures for the average warpage were used. One is the maximum curvature. A quadratic fit in two dimensions was applied to the data without sink marks:

$$h(x, y) = c_0 + c_1 x + c_2 y + c_3 xy + c_4 x^2 + c_5 y^2$$
(6.1)

in which, c_0 to c_5 are fitting parameters. Then, the curvatures in x and y direction as well as a twist are given as:

$$\kappa_x \cong \frac{\partial^2 h}{\partial x^2} = 2c_4 \tag{6.2a}$$

$$\kappa_y \cong \frac{\partial^2 h}{\partial y^2} = 2c_5 \tag{6.2b}$$

$$\kappa_{xy} \cong \frac{\partial^2 h}{\partial x \partial y} = c_3 \tag{6.2c}$$

In all cases these fits gave an accurate description of the product shape. As a warpage measure the maximum of κ_x and κ_y was taken.

The second way of characterizing warpage is by fitting a plane to the data (without sink mark points), subtract this plane from the data and determine the difference between the highest and lowest points. This corresponds to putting the moulded product on a flat table and determining the position of the highest protruding segment. Figure 6.6 presents a typical plot of the measured data and the quadratic fit, in which the full lines are measured coordinates and dashed lines correspond to curved plane fit.



Figure 6.6: Shape of the map mould after post curing, 65 wt% filled moulding compound, 250 mm die thickness, 5 minutes curing in a mould at 140°C,. The full lines are measured coordinates and dashed lines correspond to curved plane fit.

6.2.3 Experimental results and discussion

The warpage results from the moulding experiments are shown in Figures 6.7, 6.8 and 6.9. On the left side are all warpage graphs according to the maximum curvature (k_x , k_y) warpage criterion and on the right are the graphs where the deviations from the average plane are used as a warpage measure. It can be seen that both measures give similar trends in all cases. The curvature directly after de-moulding (dashed lines) is always much lower than after post curing (a factor of 3 to 3.5). The difference in warpage between after de-moulding and after post curing is possibly due to the T_g difference and also the faster stress relaxation in the partly cured product.

Figure 6.7 presents the warpage measurement versus the filler loading after de-moulding and after post curing. It can be seen that the filler loading has a strong effect on the warpage level. The curvature reduces by a factor 2 if the filler content is increased from 40wt% to 65wt%. The decrease is approximately linear. With the increase of the filler loading, both the CTE and the polymerization shrinkage will decrease, which reduces the process-induced warpage.



Figure 6.7: Effect of filler loading on warpage, (a) maximum curvature; (b). maximum plane deviation

Figure 6.8 shows the effect of conversion level at de-moulding on the warpage. It is indicated that high de-moulding conversion tends to reduce warpage. It is perhaps due to the constrained curing in the mould that partly reduces the total warpage. There appears to be no significant effect of the moulding conditions on the warpage after post curing. Unfortunately the interpretation of these measurement series is somewhat obscured by the relatively large uncertainty in the low temperature curing experiment (20 min at 120°C). Note that the demoulding conversion levels were kept equal in these experiments.

High de-moulding conversions (>90%) tend to reduce warpage. The reduction is 30-40% going from 82% de-mould cure to 95%.



Figure 6.8: Effect of de-moulding conversion on warpage; (a) maximum curvature; (b). maximum plane deviation

The effect of die thickness on warpage is shown in Figure 6.9. It can be seen that increasing the die thickness reduces the final warpage. It is due to the fact that the thicker die makes the matrix stiffer. Die thickness only has a slight effect on post-moulded warpage.



Figure 6.9: Effect of die thickness on warpage; (a) maximum curvature; (b). maximum plane deviation

6.3 Finite element modelling

6.3.1 FE model

The package consists of silicon die, EMC, die-attach, leadframe, die-pad. Figure 6.10(a) shows the bottom view of a single map. The HVQFN map mould used in both modelling and measurements has six 10×10 mm dies and the following thickness dimensions:

- total package thickness: 0.85 mm;
- lead thickness: 200 μm;
- glue thickness: $25 \ \mu m$;
- die thickness: 180/250/380 μm.

Parametric 3-D FE models are built for the package with variation of the die thickness. Figure 6.10(b) shows a typical finite mesh. Because of the structure symmetry, only one quarter of the map mould is modelled. The following boundary conditions are used: fixed in x direction $(u_x = 0)$ for YZ symmetric plane; fixed in y direction $(v_y = 0)$ for XZ symmetric plane. The node at the centre bottom is fixed in all directions. The nodes at the bottom of the map mould are fixed in Z direction $(w_z = 0)$ during the curing process, but free during cooling down. The cure-temperature-dependent viscoelastic model proposed in Chapter 2 and 3 is applied here to describe the material behaviour of EMC's during the curing process and cooling down phase.

The silicon die is assumed elastic and isotropic and the leadframe and diepad are considered elastic and ideally plastic. The material properties used in the simulation are shown in Table 6.2. The die-attach is a silver filled conductive adhesive and it has a glass transition temperature of about 38°C. Because it is rather thin compared to the moulding compound, it is expected its viscoelastic behaviour has insignificant influence on the overall stress and strain state in the package. Therefore, in our simulations the die-attach is considered to be temperature-dependent elastic. To measure the temperature-dependent elongation modulus, DMA measurement in single cantilever mode under 1 Hz frequency was performed in IMO-Backend, Philips. Figure 6.11 shows the storage Young's modulus of the die-attach from the DMA measurement, which is used for the temperature-dependent modulus in the simulation. Note that at rubbery state a slight increase of the modulus with temperature can be seen, showing that the rubbery modulus has slightly temperature dependency. A constant Poisson's ratio is assumed for the die-attach.

The thermal history used in the simulation is taken as the same as in the moulding experiments, as already shown in Fig. 6.4. The stress-free state is assumed at the starting of the curing process for all the constituents.

Materials	E (GPa)	ν[-]	$\sigma_y(MPa)$	CTE (ppm/°C)
Silicon die	169	0.26	-	3
Leadframe & die pad	123	0.35	300	16.3
Die-attach	See Fig. 6.11	0.3	-	81, T < 38°C 181, T > 38°C

Table 6.2: Material properties



Figure. 6.10: Geometry and FE mesh; (a). bottom view of a single map mould; (b). 3D mesh used in the FE model of a quarter of the HVQFN map mould



Figure 6.11: Storage Young's modulus of the die-attach from 1Hz DMA measurement.

6.3.2 Simulation results and discussion

Numerical simulation results are presented in the following. Figures 6.12(a) and 6.12(b) show the vertical displacement patterns after moulding and after post-curing, respectively. Figure 6.14 (a) and (b) show the out-of-plane displacement along the x-direction sawing lines (as defined in Figure 6.13) with a comparison to measured data for the packages moulded with 65% filled EMC with 250µm and 380µm die thickness, respectively. The curing profile is the standard moulding conditions, i.e., in mould cure at 140°C for 20 min and the degree of cure at de-moulding 80%. Because only a quarter of the one map mould is used in the FE simulation, a

symmetry of the simulation results along the symmetric axis is used for convenient comparison with the measurements.

A reasonably good agreement between measured and simulated displacements can be observed. For these reference cases the simulated and measured "maximum mean curvature" deviates less than 10%.

However, it turned out that for some of the cases the deviations can be larger. Therefore, a possible explanation was sought. First, from the experiments, it was found that the ejection from the mould had large influence on the warpage, especially when de-mould conversion was low. Not uniform ejection force from the ejector pins would cause irregular initial deformations. Furthermore, when doing the curvature measurements it turned out that the moulded HVQFN maps were either curved in Y-direction or in X-direction. This could even be for samples produced under exactly the same moulding conditions. This is because for curvatures of this magnitude geometric non-linear effects become important (a plane curved in one direction invokes a large increase in bending stiffness in the other direction). For smaller curvatures the warpage was indeed seen to be in both directions of similar magnitude. The other reason may be in the cooling rate. Preliminary cyclic thermal experiments were performed, where fully cured packages were heated above T_g and subsequently cooled down at several cooling rates. Observed warpage appeared to be dependent from the cooling rate. This could not be explained with viscoelasticity only. A strong indication that ageing phenomena are responsible for the deviations remains. This will be subject for additional research.



Figure 6.12: Displacement contour after cooling down to room temperature (a) from moulding (b) from post-cure (65% filled EMC, 380µm die).



Figure 6.13: Illustration of x-direction sawing lines



Figure 6.14: Vertical displacement along the x-direction sawing lines (65% filled). Solid lines are measurements and symbols refer to simulation results. (a). 250µm die and standard moulding conditions. (b). 380µm die and standard moulding conditions.

6.4 Conclusions

In this chapter, an investigation on the process-induced warpage during the array-moulding process of QFN packages was conducted both experimentally and numerically. A series of moulding experiments for QFN matrix strips with the model moulding compounds were performed. In the moulding experiments, different processing parameters, filler loading and die thickness were used. The warpage was measured by a contact probe coordinate measuring system. The cure-dependent constitutive model was applied to describe the behaviour of the moulding compound during the curing process. The cure-dependent material parameters were incorporated into a finite element code MARC and numerical simulations were carried out for the QFN array-moulding process. The effects of filler concentration, curing temperature profiles and the die thickness has a significant effect on the final warpage level. Higher filler

percentage will decrease the warpage. High de-moulding conversion tends to reduce warpage. Increasing the die thickness will also reduce the total warpage.

The aim of this chapter is to find out if the material models presented in Chapter 2 and Chapter 3 and the numerical implementation (Chapter 5) are accurate enough to do predictions about industrial encapsulating process. Such verification is in particular needed for the cure-dependent material parameters that were all determined at temperatures that deviate considerably from those used in "real" moulding processes. The results of this chapter confirm that the present model is capable of giving reliable predictions for real moulding process and show the engineering applicability of the present method for reliability investigation and optimization including the curing effects.

Further it is concluded that warpage is highly sensitive from the cooling rate. Since this sensitivity is not modelled by the present viscoelastic model, future inclusion of ageing phenomena in the descriptions should be explored.

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Chapter 7

Prediction of Solder Fatigue Life in FCOB with Cure-Dependent Underfill Properties

In this chapter, the modelling methodology for the cure-dependent behaviour of thermosetting polymers is applied to investigate thermo-mechanical reliability of a Flip Chip on Board (FCOB) package. Accelerated fatigue tests with thermal cycles from -55°C to 80°C were performed for a specially designed FCOB configuration. Finite element modelling is carried out to study the cure-induced stress fields and predict the solder joint fatigue life of the test carriers. The cure-dependent viscoelastic model is applied to describe the properties of the underfill resin during the curing process and subsequent thermal cycling. The solder bumps are modelled with temperature dependent visco-plastic properties. A combination of a Coffin-Manson based fatigue relation and a creep fatigue model is used to establish the combined fatigue damage. It will be shown that including the effect of curing on the underfill properties has a large effect on the fatigue predictions of the Flip-Chip configuration. In particular, the effect of the cureinduced hydrostatic stress on the fatigue life prediction is discussed. Fatigue prediction results, which are based on a combination of a Coffin-Manson based fatigue relation and a creep fatigue model reveals that the predicted fatigue life matches better with the experimental results than that without consideration of curing for both FCOB packages, but it still underestimates the fatigue life. The main reason for this underestimation is that the used fatigue models are shear strain based and the effect of the hydrostatic stress has not been included, showing that such a compressive hydrostatic stress is significant for the solder fatigue life. Therefore, the cureinduced residual stress/strain state should not be neglected in order to get reliable prediction results

7.1 Introduction

The trend of electronic products is moving toward further miniaturization, better performance, high reliability and low cost. New packaging technologies have being developed and improved to achieve such a goal. Flip chip technology is a packaging technology that the IC chip is mounted on a substrate with the chip's active surface (active area) facing to the substrate. IBM first introduced it in the early 1960s. Before introduction of underfill in the late 1980s, flip chip technology was mainly used in to high-end or special purpose applications, because substrate materials with CTE closely matching that of silicon chip had to be used to avoid over-stress. FCOB technology has extended the use of flip chip devices by using low cost FR-4 type substrate to solve the cost problem. However, this has the disadvantage of extra stresses due to the mismatch in thermal expansion between the silicon die and the polymeric substrate. A polymer underfill is usually applied to improve the reliability of the package, by reducing the stresses of the solder bumps. Underfilling the flip chip can help to constrain the CTE mismatch locally and to couple the die and substrate mechanically, and thus significantly alleviates the stress on solder joints and thus extends the fatigue life of the flip chip. In addition, the underfill materials can enhance the heat dissipation, thus further increasing the reliability of the flip chip.

One of the major reliability concerns with FCOB are the thermal fatigue of the solder bumps caused by mismatch in thermal expansion between the silicon die and the substrate. Many researchers have worked on the prediction of solder fatigue, for example in [Pang, et al. (1998); Okura, et al. (2000); Zhang (1997) and Darbha, et al. (1999)]. As one of the major packaging processes, the curing process of the underfill polymer will induce extra residual stress and strain fields. For simplicity reasons, in thermo-mechanical analyses, the curing induced stress state is usually neglected by assuming a so-called "stress-free" temperature, or a constant hydrostatic stress state in the solder bumps is assumed. To account for the effect of the hydrostatic stress on fatigue life prediction, Darbha et al. (1999) modified an energy partitioning damage model by using a correction factor in the creep damage formulation. The underfill was considered to be elastic and the hydrostatic stress from the curing effect was considered to be the residual stress produced by ramping temperature from the curing temperature to the glass transition temperature. Actually, this does not give the curing stress, but the thermal stress. It was concluded that the effect of the hydrostatic stress is significant. Nevertheless, so far, the effect of the curing process induced stress and strain on the solder fatigue life of FCOB has not been fully understood. The fatigue life of solder joints of FCOB appears to be dramatically influenced by

the mechanical properties of underfill polymers, which are known to be strongly processingdependent.

Therefore, a reliable prediction of solder fatigue will depend on the ability to adequately model the thermo-mechanical properties of the constituents in the package. The process induced stress state and its influence should be well understood.

7.2 Experimental: accelerated temperature cycling tests

Accelerated temperature cycling tests were conducted by Philips to obtain failure data and to investigate failure mechanisms in FCOB assemblies. In order to investigate the effect of underfill, chip size and solder bump stand-off height on the fatigue life of a Flip Chip, a full factorial design-of-experiment (DOE) matrix was developed. Two levels were setup for each factor, i.e., underfill type A and B, 5×5 mm² and 10×10 mm² silicon test chips, 55µm and 82µm of stand-off high. Each test board had 32 test chips, on which the chips were distributed in such a way that all the geometric variables were used.

The 5×5 mm² test chip contains 48 solder bumps and the 10×10 mm² test chip contains 112 solder bumps. The solder bumps are distributed in two rows around the periphery of the die in a staggered configuration, as shown in Fig. 7.1. The pitch of the staggered configuration is 300/600 µm for both sizes of chips. The solder bumped test chips are reflowed to the 1.6mm thick FR-4 substrate. Afterwards, the assemblies are applied with underfill and cured at 130°C for the amount of time specified by the manufacturer.



Figure 7.1: A schematic illustration of the FCOB

After underfilling and curing process, the test assemblies were subjected to thermal cycling from -55°C to 80°C, with a ramp rate of 10°C / minute and 5 minutes dwell time at each extreme. The upper temperature limit of the cycle was chosen below the glass transition temperature of the underfill and also not to cause overstress delamination in the interface of underfill and die-passivation.

During thermal cycling, the resistance of each daisy-chained Flip Chip assembly was measured and monitored real-time for failure. A failure was defined as the occurrence of fifteen transient electrical disturbances recorded by the event detector. The threshold resistance of the event detector was set to 300 Ohms for t≥200 msec, since the maximum resistance of the Flip Chip assembly was below 30 Ohms before the thermal cycling.

After completing the thermal cycling test, a Weibull analysis was conducted to characterize the failure data. In addition, Scanning Electron Microscopy (SEM) analyses on cross sections of related solder bumps were carried out to analyze the failure mechanisms.

7.3 Characterization of cure-dependent properties of underfill resin

The underfill resin (Hysol [®] FP 4526) is a low viscosity, epoxy-based material, designed for capillary underfill on flip chip applications. It is filled with fused silica spheres and the filler loading is 63% in weight filler. The material models presented in Chapter 2 and Chapter 3 are applied to describe the material behaviour of this underfill resin during cure and the subsequent cooling and thermal cycling.

DSC analysis and DMA were applied to measure the cure kinetics parameters and the viscoelastic properties of the resin. The experimental methods were already described in Chapter 3 and here only the experimental results are presented.

Both isothermal and dynamic DSC measurements were carried out. Figure 7.2 shows the relationship between T_g and conversion from DSC measurements, in which the symbol represents the measured data and the solid line represents the model fitting to the modified DiBenedetto equation (Eq. 2.45). The fitting parameters are listed in Table 7.1. It can be seen that there exists a one-to-one relationship between T_g and conversion for this material and the equation gives a good prediction.

The fitting parameters for cure kinetics model are shown in Table 7.2.



Figure 7.2: T_g versus conversion, measured and fit by the DiBenedetto equation

Table 7.1: The parameters for the DiBenedetto equation

$T_{g\theta}, [^{\circ}\mathrm{C}]$	$T_{gf}[^{\circ}\mathrm{C}]$	λ
25.2	144.8	0.3

Table 7.2: Parameters for the cure kinetics of FP4526

E [J/mol]	k ₀ [1/s]	m	n
67.11	4.4E+06	0.785	1.067

DMA is used to characterize shear relaxation of the fully cured resins. Figure 7.3 shows the shear storage moduli as functions of applied frequencies measured from DMA under different temperatures. Figure 7.4 shows the storage modulus versus reduced frequency after being shifted along the frequency axis with reference temperature of 130°C. It can be seen that the frequency-temperature superposition principle is also applicable to this resin.

Based on the DMA measurements, the model parameters can be acquired (see section 3.4.2 for the data processing method). The shear rubbery modulus is determined using ULFS method at 180°C. The glassy modulus is determined as the glassy plateau of the storage modulus. Both are listed in Table 7.3. For the transient part, fourteen Prony terms are used. Table 7.4 presents the relaxation times and the corresponding best-fit normalized Prony coefficients g_n (see Eq. (2.28d)). Figure 7.5 shows the shift factors that account for the temperature effect. It also shows different dependency trends at lower and higher temperatures, in which the two parts of the curve can be well fitted by using the WLF equation and Arrhenius equation, respectively. The fitting parameters are listed in Table 7.3.



Figure 7.3: Storage shear moduli as functions of frequencies of fully cured resin under different temperatures



Figure 7.4: Shifted storage shear moduli versus reduced frequencies and the master curve from the best-fitting, reference temperature T_{ref} =130°C.



Figure 7.5: Shift factor as a function of temperature

Table 7.3: The parameters for viscoelastic model

G_{g} [MPa]	$G_{\it rf}$ [MPa]	<i>C</i> ₁ [-]	С ₂ [К]	$T_{\it ref}^{\it WLF}$ [K]	ΔH_{T} [KJ/mol]	$T_0 {\rm [K]}$
1081.6	83.8	10.6	44.4	406.4	102.9	427.7

Table 7.4: Relaxation times and the normalized Prony coefficients (see Eq. (2.28d))

	Relaxation	Prony		Relaxation	Prony
NO.	times τ_n [s]	coefficients g_n	NO.	times τ_n [s]	coefficients g_n
1	1.00E-08	0.220	8	1	0.157
2	1.00E-06	0.213	9	10	0.0331
3	1.00E-05	0.0575	10	100	0.00310
4	1.00E-04	0.0561	11	1000	0.00087
5	1.00E-03	0.0596	12	10000	0.00309
6	1.00E-02	0.0687	13	1.00E+05	0.00252
7	1.00E-01	0.126	14	1.00E+06	0.00032

Cure shrinkage was measured using a coin shape sample at a curing temperature of 130°C [Hof, et al., (1999); Yang, et al., (2001)]. The evolution of the curing shrinkage strain for the used underfill epoxy is shown in Figure 7.6.



Figure 7.6: Curing shrinkage evolution of the underfill resin

7.4 Solder Fatigue prediction models

Though there are quite a few solder fatigue prediction models available [Lee, et al. (2000)], so far there is no general consensus about the choice of an appropriate model for prediction of fatigue life of a Flip Chip package, since most of the models and their parameters were obtained under specific test conditions and strain/stress states. In the considered FCOB package, the solder joints undergo both plastic and creep strains in the curing process as well as in the subsequent thermal cycles. Therefore, both the plastic and the creep strains should be taken into account for the fatigue prediction.

A Coffin-Manson based relationship, proposed by Solomon (1986), has been successfully applied to underfilled Flip Chip, for instance, by Pang, *et al.* (1998a/1998b). The model relates fatigue life cycles to the plastic shear strain range, as shown in (7.1),

$$N_p = C(\Delta \gamma_p)^{\eta} \tag{7.1}$$

where $\Delta \gamma_p$ represents the plastic shear strain range, N_p represents the number of cycles to failure, and C and η are constants. Based on measurements at -50°C, 35°C and 125°C, Solomon (1986) reported the value of C and η for Sn-Pb eutectic solder. C and η have an averaged value of 1.2928 and –1.96, respectively.

It is commonly accepted that creep may be due to matrix creep and grain boundary sliding. Knecht and Fox (1990) have proposed a fatigue model relating the fatigue life with the solder microstructure and the creep shear strain range due to matrix creep

$$N_{cr} = \frac{C}{\Delta \gamma_{mc}} \tag{7.2}$$

in which N_{cr} is the number of cycles to failure. $\Delta \gamma_{cr}$ is the shear strain range due to matrix creep. C is dependent on failure criteria and the solder microstructure. For the eutectic solders C has a value of 8.9. Shine and Fox (1988) reported that fatigue life due to creep strains shows much correlation to matrix creep but relatively little correlation to grain boundary creep. Thus, the effect on the creep strains due to the grain boundary sliding of the solder bumps is neglected in this paper.

By applying Miner's linear superposition principle, a strain-based fatigue model, which combines the plastic and creep effect, is formulated by Pang, et al. (1998a):

$$\frac{1}{N_f} = \frac{1}{N_p} + \frac{1}{N_{cr}}$$
(7.3)

where N_f represents the number of cycles to failure. N_p and N_{cr} refer to the number of cycles to failure due to plastic fatigue and creep fatigue, respectively.

Because these fatigue models were based on a pure shear state, the equivalent plastic strain and equivalent creep strain should be substituted for the shear strains:

$$\gamma_{eq} = \sqrt{3}\varepsilon_{eq} \tag{7.4}$$

Equations $(7.1 \sim 7.3)$ are applied as indicator for the fatigue failure prediction. It should be noted that because only equivalent strain ranges are used in the above models, the effect of the hydrostatic stress in the solder has been not included.

7.5 FE modelling of the FCOB package

7.5.1 Geometry and FEM mesh

A finite element thermo-mechanical modelling of a FCOB for fatigue predictions was carried out. The same FCOB configuration as used in the accelerated fatigue experiments is applied for the FEM modelling. For simplification, the passivation and metallization layer is neglected. Only the silicon die, the underfill, the solder bumps, the copper pads and the substrate are considered (see Fig. 7.1). In this paper, only one kind of underfill, referred to as underfill A (HYSOL FP4526) is characterized for cure-dependent viscoelastic properties and subsequently used in the FEM-analyses. Underfill A is a polymer composite with epoxy resin as matrix and silica spheres as filler (filler content of 63wt%). It is cured at 130°C for 60 minutes.
2-D plane strain modelling is used. Because of the symmetry, only one half of the structure is simulated. Two FEM meshes are setup for both $5\times5 \text{ mm}^2$ and $10\times10 \text{ mm}^2$ chips. In order to facilitate a comparison between the results of both configurations, equivalent meshes are used around the solder bumps. Only one stand-off high, 82 µm is considered. The FEM meshes are presented in Fig. 7.7. The following boundary conditions are used: the nodes along the symmetry axis are fixed in x direction (u=0), and the node at the left bottom corner is fixed in x and y direction (u=v=0).



Figure 7.7: FEM Mesh (a) mesh for package of 5×5 mm² die (b) close view of the bump, with indication of the specific locations (A, B).

7.5.2 Thermal loading

The Flip Chip is subjected to a thermal loading equivalent to the underfill curing and subsequent fatigue test. At 130°C, the underfill is dispensed and cured for 60 minutes (a-b in Figure 7.8), then the package is cooled down to room temperature at a ramp rate of 10°C /minute and then being hold for 30 minutes (b-c-d) and subsequently temperature cycles (d-e-f-g-h) are applied. Fig. 7.8 shows the temperature profile with six thermal cycles used in the simulation. A stress-free situation is assumed at the curing starting point "a" for the so-called "curing model".

In order to make a comparison between simulation results with and without the curing process being included, another two calculations are made for the $5 \times 5 \text{mm}^2$ and $10 \times 10 \text{mm}^2$ chips, now without consideration of the curing process. These have a loading history "b-c-d-e-f-h". For the "non-curing model", the stress-free state is assumed at the starting point "b" for all the materials in the package. It should be mentioned that more thermal cycles have been used for study on the stability of the strain ranges in the solder joints for both models as well.



Figure 7.8: Temperature profile

7.5.3 Material properties

The experimental characterization of the cure kinetics and the temperature dependent shear relaxation modulus corresponding to our new developed model is described in section 7.3. However the measurement of the cure-dependent relaxation bulk modulus failed due to the adhesion problem in the test fixture. Because our objective of this study is mainly to qualitatively investigate the cure-induced effect on the solder fatigue life, our previous cure-dependent model and the parameters for the underfill resin [Hof, *et al.* (1999); Yang, *et al.* (2001)] are used in the modelling.

The behaviour of eutectic solder joints is modelled as temperature-dependent elastic-plastic and separately rate-dependent creep. The temperature-dependent Young's modulus is given by [Darveaux and Banerji, (1998)]

$$E(T) = 35366 - 151 \cdot T \tag{7.5}$$

where T is the temperature in °C. The yield behaviour is described by the following equation [Pang, et al. (1998)]

$$\sigma_{v}(T) = 49.2 - 0.097T \tag{7.6}$$

where T is the absolute temperature (K).

The creep behaviour is described as [Darveaux and Banerji, (1998)]:

$$\dot{\varepsilon}_{cr} = C_1 \left(\frac{E}{T}\right) \cdot \left[\sinh(\frac{\alpha\sigma}{E})\right]^n \cdot e^{-\frac{Q}{RT}}$$
(7.7)

where $\dot{\varepsilon}_{cr}$ is the equivalent creep strain rate; σ the equivalent stress; *E* Young's modulus; *Q* the activation energy; *R*=8.314Jmol⁻¹*K*⁻¹ is the universal gas constant; *T* absolute temperature; and C_1 , α and *n* are the material constants.

The silicon die and copper pads are assumed to be isotropic, and the FR-4 substrate is considered to be orthotropic. Both are assumed to be temperature-independent and elastic during the loading history. The material properties used in the simulation are shown in Table 7.5.

Materials		E (GPa)	ν	G (GPa)	CTE (ppm/°C)
Silicon die		169	0.26		2.3
Copper Pad		82.7	0.30		16.7
FR-4	In plane	19.7	0.18	3.7	17.6
	Out of plane	9	0.39	2.9	54.2

Table 7.5: Material properties

7.6 Results and discussions

7.6.1 Curing-induced stress and strain

Fig. 7.9(a) shows the evolution of the horizontal stress component σ_{xx} at point A in the underfill and the equivalent von Mises stress at point B in the outmost solder bump during the curing process. The locations of point A and B as well as the coordinate system are illustrated in Fig. 7.7. Fig. 7.9(b) presents the evolution of the horizontal strain component and the cure-induced shrinkage strain in the underfill, and the equivalent plastic strain and equivalent creep strain in the solder bump during the curing process as well.

During the curing process, the constrained shrinkage and the simultaneously increasing stiffness of the underfill resin cause the stresses in the package. The shrinkage of underfill is constrained by the adjacent materials in the package. Adversely, the solder bumps are deformed and stressed by the shrinkage. Meanwhile, the stress relaxation behaviour in the underfill and the plastic deformation and creep in the solder bumps also influence the evolution of stresses during cure and thus influence the final residual stress state.

After starting of the curing for about 4.5 minutes, an intense crosslinking reaction occurs in the underfill. The stresses in the package then increase quickly. At about 15 minutes, most of the crosslinking is finished. Plastic deformation takes place in some local parts with high stresses in the solder bumps. Subsequently, the stress relaxation behaviour in the underfill and creep in the solder bumps prevail over the chemical shrinkage of the underfill. The stresses in the underfill and the solder bumps decline dramatically. Relatively low stress levels are found in the underfill and the solder bumps at the end of curing. However, a high level of creep strain is found in the bumps. It can be seen that the solder creep strain is nearly an order of magnitude larger than the plastic strain for a large part of the bump. The strain component ε_{xx} of the underfill is almost completely determined by cure shrinkage.

Fig. 7.10 represents the contour plot of the shear stress in the whole package at the end of curing. Relatively high stress levels are found in the underfill, the solder bumps and the silicon die.



Figure. 7.9: Stress and strain evolution during cure, (a). stress σ_{xx} evolution in underfill (point A) and equivalent von Mises stress in the solder bump (point B); (b). Strain history in underfill (point A) and in the solder bump (point B).



Figure 7.10: Shear stress (in MPa) distribution in the package at the end of curing (t=60min).

Figure 7.11(a-c) shows the contour plots of the equivalent creep strain in the outermost solder bump at curing time t=12.5min, the end of curing and subsequent cooling down to room temperature. Figure 7.11(d) shows the distribution of equivalent creep strain when directly cooling down from 130°C to room temperature without consideration of curing. It is found that very high creep strain level has been in the solder during the curing process. The distribution and the level of the creep strain caused by the curing process is different from that caused by thermal shrinkage. The thermal shrinkage strain is more concentrated in the corners of the bump, however, in the case of considering the curing process, the distribution of the strain in the solder is much higher (about 8 times higher than that without cure shrinkage) and more uniform.



Figure 7.11: Equivalent creep strain evolution in solder bump (a) at curing time t=12.5min; (b) at the end of curing (t=60 min); (c) subsequent cooling down to room temperature (t=70.5min); (d) Directly cooling down to room temperature from 130°C without consideration of cure shrinkage.

Figure 7.12 shows the contour plots of the equivalent plastic strain at different process phases. Similarly, high plastic strain has been induced in the solder during the curing process. The distribution and the level of the plastic strain caused by the curing process is also different

from that caused by thermal shrinkage. In the case of considering the curing process, the strain in the solder is more than 5 times higher than that without cure shrinkage. Therefore, in FEM modeling, the curing process has a significant effect on both the plastic and the creep strains of the solder bumps, thus influencing the fatigue life prediction results.



Figure 7.12: Equivalent plastic strain evolution in solder bump (a) at curing time t=12.5min; (b) at the end of curing t=60 min; (c) subsequent cooling down to room temperature; (d) directly cooling down to room temperature from 130° C without consideration of curing.

7.6.2 Comparisons between experimental fatigue and model prediction results

Only the test results associated with underfill A are presented in this thesis work. The fatigue test results reveal that the stand-off height of solder bumps has only a slight effect on the durability of the FCOB compared to the chip size. The mean times to failure of the $5\times5mm^2$ chip and the $10\times10mm^2$ chip is 6440 and 5750 hours, respectively. The matching mean numbers of cycles to failure are 10443 and 9324 cycles, respectively. The ratio of mean life of the $5\times5mm^2$ chip versus the $10\times10mm^2$ chip is about 1.12.

The outermost bump in the package is selected for further failure prediction considerations. These values are averaged over the elements in the upper right corner, representing about 8% of the bump volume. Fig. 7.13 shows the time history of the equivalent plastic strains for six thermal cycles with and without consideration of the curing process in the solder bump of the 5×5 mm² chip package, together with the temperature profile for clarification. During the curing process, the magnitude of the equivalent plastic strain generated is about 0.25%. Similarly, Fig. 7.14 presents the time history of the equivalent creep strains with and without the curing process included. It is seen that solder bumps undergo a very high level of creep stain during the curing process, as high as 4%, more than one order higher than the plastic strain. This is due to the fact that the solder bumps are exposed to a high temperature when the curing-induced stresses of the underfill are high. During cooling down from 130°C to room temperature and subsequent dwell time, the creep strain level is decreased. During the following thermal cycles, the creep strain increases as time increases. In the case where the curing process is not included, during the first 3 cycles, the creep strain decreases on average as the time increases. The reason is probably that when the solder is cooled down to room temperature, a very high stress is concentrated at the corner part (Fig. 7.11(d)) and in the first few cycles, the creep strain caused by the thermal cycling counteracts a part of the creep strain caused by the cooling down. As the thermal cycling proceeds, the deformation is more uniform and the deformation of the solder bumps becomes more stable. After three cycles, the creep strain increases as the time increases, with a higher strain range than that with consideration of the curing process.



Figure 7.13: History of the equivalent plastic strains and the temperature profile (averaged over the elements in the upper right corner).



Figure 7.14: History of the equivalent creep strains and the temperature profile (averaged over the elements in the upper right corner).

In a previous paper [Yang, et al. (2001)], the strain ranges of the third cycle were taken for calculation of the fatigue life. This may not be appropriate because it may need longer time for the strain ranges in the solder to become stable if the curing process is included in the simulation. In order to study the stability of the strain ranges, more thermal cycles are applied in the current simulations. Figure 7.15 illustrates the variation of both equivalent plastic and creep strain ranges from the first cycle to 25th thermal cycle. It is seen that with the non-curing model, the strain ranges are nearly stable after six cycles, but with the curing model, more cycles are needed to get stable strain ranges for fatigue prediction.

Table 7.6 lists the equivalent plastic strain range and equivalent creep strain range during the 25th thermal cycle for the 5×5 mm² chip-size package. By using Eqs. (7.1) to (7.3), the number of cycles to failure relating to plastic strain, creep strain and the combination of both can be calculated. Table 7.7 presents the number of cycles to failure with and without consideration of the curing process, respectively.



Figure 7.15: Variation of the strain ranges vs. number of thermal cycles

Table 7.6: Equivalent strain ranges for the 5×5 mm² chip-size FCOB at the 25th cycle

Strain range	Curing	Non-curing
$\Delta \mathcal{E}_{eq_p}$	0.3708%	0.4277%
$\Delta \mathcal{E}_{eq_cr}$	0.0825%	0.1152%

Table 7.7. Lists of number of cycles to failure, experimental and model prediction results for the $5 \times 5 \text{ mm}^2$ chip-size FCOB at the 25^{th} cycle

Fatigue model	Curing	Non-curing
Plastic strain model (Eq. (7.1))	25610	19357
Creep strain model (Eq. (7.2))	6228	4462
Plastic & creep model (Eq. (7.3))	5010	3626
Experimental	10443	

From the previous results it is clear that the fatigue life predictions for plastic strain are much higher than for the creep strain model. That means that creep fatigue plays a predominant role in the whole fatigue life of the solder bumps.

The curing process has a relatively large effect on the fatigue prediction results of all the fatigue models. In Table 7.6 and Table 7.7 it is shown that if the curing process is included in the FEM modelling, the predicted fatigue life is higher than that without consideration of curing.

However, it still underestimates the fatigue life compared with the experimental results. One of the main reasons for the under-estimation is that the used fatigue prediction models (7.1)-(7.3) only account for the deviatoric part of the loaded stress and strain.

The effects of the curing process induced stress/strain on the fatigue lifetime of the solder joints may be explained in two aspects. One is the effect resulting from the deformation and residual stresses in the whole package, i.e. the global effect. The other is the effect of the cure-induced residual stress/strain in the bump itself, the so-called local effect.

Figures 7.16(a) and 7.16(b) show the deformation of the whole package at the end of curing and at the high extreme of the sixth cycle (80°C) (corresponding to "e" in Fig. 7.8), respectively. The deformation caused by the curing shrinkage is obviously different with the deformation caused by thermal stress. Cure shrinkage causes the package, especially the die, to bend upwards, resulting compressive stress at the centre part of the die backside. And also vertically compressive stresses in the solder bumps are induced by the curing shrinkage of the underfill resin. The residual stress/strain will counteract a part of deformation and stress during the subsequent thermal cycling. The magnitude of the bending effect induced during cure will relax partly during cure and subsequent thermal cycling because of viscoelastic effects in the underfill. The bending effect however does not disappear completely and will reach an equilibrium state that are mainly determined by the rubbery properties of the resin. Therefore, by including the curing process in the simulation, the effect of the residual stress and deformation in the whole package on the solder stress/strain and fatigue life prediction, i.e., the global effect can be accessed.





The curing-induced stress field in the solder bumps (the local effect) caused by the cure shrinkage of the underfill can be decomposed into a deviatoric part and a hydrostatic part. The effect of the hydrostatic part will be discussed in the next sub-section. Our simulation shows that the deviatoric part relaxes over time due to creep. In Figure 7.9, it can be seen that the level of von Mises stress in the solder bump decreases steadily as the curing proceeds. At the end of curing, more than 80% of the von Mises stress has been relaxed due to the creep behaviour of the solder bump and relaxation of underfill. During the subsequent cycles, it will relax even further.

7.6.3 Effect of cure-induced hydrostatic stress

Compressive hydrostatic stress is induced in the solder bumps during the curing process because of the curing shrinkage of the underfill. Notice that the solder is in fact completely enclosed by the stiff die at top and substrate at bottom as well as the underfill at the remaining circumference in the surface. If this underfill then starts to shrink, the solder has no way to go and is "squeezed" in a state of hydrostatic pressure. Figure 7.17 shows the evolution of the averaged hydrostatic stress in the solder bump. The stress level increases rapidly after the onset of gelation at about 5 minutes and reaches a maximum of -21MPa at 15 minutes. In the subsequent 45 minutes it decreases slightly due to the relaxation of the underfill. At the end of curing, it has a value of 18.7Mpa.



Figure 7.17. Evolution of the hydrostatic stress in the solder during the curing process

Although most of the deviatoric part of the cure-induced stress in the solder will eventually relax due to creep, the compressive hydrostatic stress does not relax with time. It is commonly accepted that such a compressive hydrostatic stress is favourable for the solder fatigue life because it possibly hinders void nucleation or crack initiation or tends to close microcracks during thermal cycling. Or it will decrease the maximum tensile stress during the low temperature parts of thermal, which may result in a slower propagation of a crack and thus it is beneficial to the fatigue life. Furthermore, it is reported by Dutta *et al.* (2002) that the imposition of compressive hydrostatic stress on the solder joint can effectively reduce coarsening, which significantly influence the strain response. The fatigue prediction models (7.1)-(7.3) used in this study only account for the deviatoric part and are thus unable to take this effect into account. Unfortunately at present, no well-developed models that have considered the effect of the hydrostatic stress are available in literature for solders.

The importance of the hydrostatic stress effect can be estimated with Darbha's model [Darbha *et al.* (1999)]. In that model, the energy partitioning damage model was modified by using a correction factor in the creep damage formulation to take into account the effect of the hydrostatic stress. Assuming that plasticity is not affected by the hydrostatic stress, when a constant hydrostatic stress is applied on the solder, the number of cycles to failure due to creep damage can be computed by

$$\frac{1}{N_{fc}} = \left(\frac{W_c}{W_{co} \left[1 - \frac{\sigma_H}{\sigma_f}\right]^n}\right)^{-1/d'}$$
(7.8)

where N_{fc} is the number of cycles to failure due to creep, W_c creep work density per cycle, W_{co} coefficient, σ_H hydrostatic stress, σ_f fatigue strength, *n* hydrostatic stress exponent, and *d* constant.

In [Darbha, *et al.* (1999)], W_{co} , *n* and *d'* in Eq. (7.8) were obtained from the experimental results of a particular Flip Chip configuration. For a qualitative examination of the influence of the cure-induced hydrostatic stress, we use the values for W_{co} , *n* and *d'* provided in [Darbha, *et al.* (1999)]. The hydrostatic stress at the end of curing is considered as an external pressure and assumed to be constant during thermal cycling. By using Eq. (7.8), a comparison between the situation with and without the hydrostatic stress can be made. This shows that the predicted number of cycles to failure due to creep is more than twice of that without the cure-induced hydrostatic stress included. Therefore, the effect of the cure-induced hydrostatic stress is significant for the fatigue prediction results of the FCOB package. In fact, the magnitude of the hydrostatic stress effect turns out to be just sufficient to explain the discrepancy between our simulation results and the experimental fatigue life. However, it should be mentioned that the

above calculation is a rough estimation and further investigation in modelling and experimental aspects is needed to appropriately incorporate the effect of hydrostatic stress into the fatigue prediction models.

7.7 Conclusions

Accelerated fatigue experiments with thermal cycles from -55°C to 80°C are carried out for a specially designed Flip Chip configuration. Based on a cure-dependent viscoelastic constitutive relation for the underfill epoxy, thermo-mechanical behaviour of the tested FCOB during the curing process and the subsequent temperature cycling is modelled. The fatigue life predictions are based on simulations with and without considering the curing process.

The results show that the creep strain plays a predominant role on the fatigue life of the FCOB. In FEM modelling, the curing process has a significant effect on both the plastic and the creep strains of the solder bumps, thus influencing the fatigue life prediction results. It is indicated that if the curing process is considered in the FEM modelling, more thermal cycles need to be carried out to get stable strain ranges for fatigue life prediction. Fatigue prediction results, which are based on a combination of a Coffin-Manson based fatigue relation and a creep fatigue model reveals that the predicted fatigue life match better with the experimental results than that without consideration of curing for both chip-size packages, but it still underestimates the experimentally found fatigue life. The main reason for this underestimation is that the used fatigue models are shear strain based and the effect of the hydrostatic stress has not been included.

Compressive hydrostatic stress is induced in the solder bump during the curing process. An estimation, based on a modified energy partitioning damage model with a correction factor in the creep damage formulation to take into account the effect of the hydrostatic stress, shows that such a hydrostatic stress is significant for the solder fatigue life. Therefore, the cure-induced residual stress/strain state should not be neglected in order to get reliable prediction results. Further investigation is needed to appropriately incorporate the effect of the hydrostatic stress into the solder fatigue prediction models.

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Chapter 8

Conclusions

8.1 General conclusions

This thesis has presented the research results in four main aspects:

- 1. Development of a cure-dependent viscoelastic model for packaging polymers;
- 2. Characterization of the cure-dependent material properties;
- 3. Implementation of the model into a general finite element code and validation of this model;
- 4. Application of the developed model in FE simulations of packaging carriers.

The general conclusions are summarized as follows:

8.1.1 Conclusions concerning establishment of a cure-dependent viscoelastic model

In this thesis a cure-dependent viscoelastic model has been proposed to describe the mechanical behaviour of thermosetting polymers.

- The newly developed cure-dependent viscoelastic model is presented (Eqs. (2.28) to (2.30)).
- The cure-dependent shear rubbery moduli are modelled with Adolf's model (Eqs. (2.32) and (2.34)). It has been verified by the experimental data.
- The transient part is approximated by Prony series. Based on our experimental observations that the normalized master curves of the transient part at different cured states virtually fall into one single curve, the model is further simplified by taking the Prony coefficients as cure-independent. The influence of temperature and conversion on

the relaxation times is modelled with the time-temperature and time-conversion superposition principle.

- A new concept of "reduced temperature", which is defined as the difference between the temperature and the cure-dependent glass transition temperature, is introduced. By using the "reduced temperature", both the temperature and the conversion effects on the relaxation times can be expressed in an integrated way (Eqs. (3.16) and (3.17)).
- The model has the ability to describe a 'quasi' thermo-rheologically simple behaviour, although the time-temperature and time conversion superposition principle is adopted. This is realized through the cure-dependent rubbery plateau, the cure-dependent relaxation amplitude and the cure-dependent relaxation times.
- The modified DiBenedetto equation (Eq. (2.45)) gives a satisfactory description of the T_g - α relationship for the resins. The cure kinetics is well modelled with the Kamal and Sourour's equation (Eq. (2.42)). Thus the relationship between the mechanical behaviour and the curing profile is established.
- The overall model is convenient to be implemented into a general FEM program.

8.1.2 Conclusions concerning characterization of the cure-dependent material properties

In this thesis the experimental characterization of the cure-dependent material properties includes three parts: DSC analysis for the cure kinetics and $T_g - \alpha$ relationship, DMA measurements for cure-dependent viscoelastic behaviour, and on-line density measurements for the curing shrinkage. In addition to the experimental characterization, the effect of filler volume fraction on the major material properties is investigated by using the composite mechanics approach. From this part of research, following conclusions can be drawn:

- DSC analysis shows that there is a one-to-one relationship between the glass transition temperature and the degree of cure for our model epoxy system. For the cure kinetics, both isothermal and dynamic approaches give similar results. The cure kinetics of the resins generally follow autocatalytic curing reaction kinetics, while Kamal and Sourour's equation gives a satisfactory description of the cure kinetics.
- Shear DMA measurements are successfully used to detect the gel point. Experimental results indicate that the crossover of G' and G'' is frequency dependent. Whereas, there exists a crossover point of tan δ where the loss angle is independent of the frequency.

Therefore, the crossover point of $\tan \delta$ is used to estimate the gel time for the resins. The gel point estimated from this method agrees with the theoretical calculated gel point of 0.62 using the Flory equation (Eq. (2.33)).

- The Ultra Low Frequency Scan method is successfully applied to measure the evolution of the rubbery shear modulus.
- Using the isothermal curing DMA, dynamics properties of the curing polymer as a function of conversion can be obtained. The major shortcoming of isothermal cure approach is that the temperature effect on the relaxation behaviour at different curing states is missing, since useful experiments can only be performed close to T_{g} .
- Using the intermittent curing approach, the temperature dependency of the dynamic properties at different curing states can be measured, and the master curve and the shift factor for temperature at each cure state can be established. The results show that for the epoxy system in this study the temperature effect on the shift factors is independent of degree of cure when $T_{g\alpha}$ is chosen as the reference temperature. The temperature effect is described well with the WLF equation if the temperature is above a switching temperature, while below the switching temperature the Arrhenius equation gives a good prediction.
- The accuracy of the established cure dependent relaxation bulk modulus appeared to be less adequate. In particular data for low degrees of cure could not be established at all.
- The chemical shrinkage during the curing process is measured by using an online density measuring setup based on the Archimedes principle. The results show that the density increases almost linearly with conversion for the unfilled and filled resins. The curing shrinkage also shows almost no dependency on the curing temperatures. The variation of the coefficient of thermal expansion and the coefficient of curing shrinkage with filler volume fraction are conveniently modelled with a simple rule of mixtures.
- Generally speaking, adding filler will increase both the glassy and the rubbery moduli of the composites, however filler intends to increase the modulus in the rubbery state more pronounced than in the glassy state. The modified Kerner equation gives a reasonably good prediction of the glassy shear moduli, the glassy and rubbery bulk moduli of the filled resins. The variation of the fully cured rubbery shear modulus with filler loading turns out to be well described with the Eilers model.

8.1.3 Conclusions concerning numerical implementation of the model into an FEM code and model validation

The developed model has been implemented into the general FEM code MSC Marc.

- In the stress update expression, the evaluation can be straightforwardly performed by adapting an appropriate time integration scheme. The stress update only requires stored data for the functions of the previous time step, and can easily be implemented into a FEM program. With a stress update procedure, an adequate simulation for establishing curing induced stress and strain fields is obtained.
- The calculation of the cure kinetics, the cure-dependent shear and bulk modulus coefficients, the shift factor for the temperature and curing effects, and the curing shrinkage are incorporated through the user subroutines.
- Model validation is carried out by using a disc-shaped test setup, in which the specimen undergoes a 3D stress state generated by the (partly) constrained curing shrinkage and external loading. FEM simulation indicates that model predictions agree reasonably well with the measured data. Therefore, it can be concluded that the model and the FE implementation is reliable for simulation of cure-induced stresses, in which thermosetting polymers are involved.

8.1.4 Conclusions concerning the application cases

- The results show that both of the filler percentage and the die thickness has a significant effect on the final warpage level. Higher filler percentage will decrease the warpage. High de-moulding conversion tends to reduce warpage. Increasing the die thickness will also reduce the total warpage. The simulation results of the package carrier confirm that the present model is capable of giving reliable predictions for real moulding process and show the engineering applicability of the present method for reliability investigation and optimization including the curing effects. Further it is concluded that warpage is highly sensitive from the cooling rate. Since this sensitivity is not modelled by the present viscoelastic model, future inclusion of ageing phenomena in the descriptions should be explored.
- The results show that the creep strain plays a predominant role on the fatigue life of the FCOB. In FEM modelling, the curing process has a significant effect on both the plastic and the creep strains of the solder bumps, thus influencing the fatigue life prediction results. Fatigue prediction results, which are based on a combination of a Coffin-Manson

based fatigue relation and a creep fatigue model reveals that the predicted fatigue life match better with the experimental results than that without consideration of curing for both Flip Chip packages, but it still underestimates the experimentally found fatigue life. The main reason for this underestimation is that the used fatigue models are shear strain based and the effect of the hydrostatic stress has not been included.

 Compressive hydrostatic stress is induced in the solder bump during the curing process. An estimation based on a modified energy partitioning damage model shows that such a hydrostatic stress is significant for the solder fatigue life. Therefore, the cure-induced residual stress/strain state should not be neglected in order to get reliable prediction results. Further investigation is needed to appropriately incorporate the effect of the hydrostatic stress into the solder fatigue prediction models.

8.2 Limitation and recommendations

- 1. The experimental methods that we have used for measuring the bulk relaxation modulus have their limitation. It is recommended that new methods to measure the cure-dependent bulk relaxation modulus be explored.
- The experimental methods to characterize the cure-dependent viscoelastic properties for fast curing polymers (snap curing) should be explored, since in electronic packaging process mostly snap curing is used.
- 3. The temperature dependence of glassy moduli is neglected
- 4. The aging effect (long term effect) and the influence of the cooling rate on the warpage of the QFN package should be investigated.
- 5. The effect of the cure-induced hydrostatic stress on the solder fatigue life should be investigated.
- 6. In the future work, the effect of moisture absorption on the viscoelastic behaviour of packaging polymers should be investigated and could be integrated into the current model.

SAMENVATTING

Polymeren worden alom toegepast in elektronische producten, in de vorm van omhullingmateriaal, underfill, lijmen, isolatoren, dielectrici, enzovoorts. Over het algemeen zijn deze materialen thermoharders, die uitharden op hoge temperaturen gedurende het fabricageproces. Dit uithardingproces introduceert restspanningen en vervormingen in het micro-elektronische product, als gevolg van het krimpen door polymerisatie en de achtereenvolgende afkoeling tot kamertemperatuur. Tijdens het uitharden verandert de polymeer langzaam van een vloeibare substantie naar een visco-elastische vaste stof met een relatief hoge glas modulus en dit gaat samen met een chemische krimp. Deze crosslink reactie met de thermisch krimp te samen met de toenemende stijfheid zorgt ervoor dat spanningen toenemen in gebieden waar de krimp wordt belemmerd door geometrische randvoorwaarden. Eveneens geldt dat wanneer een crosslink product afkoelt naar de omgevingstemperatuur, het verschil in uitzettingscoëfficiënt tussen de thermoharder en de omgevende materialen voor een additionele spanning en vervorming zorgt.

Om in staat te zijn een betrouwbare voorspelling van de procesgeïnduceerde spanningen en vervormingen te plegen, zijn uithardingsafhankelijk visco-elastische constitutieve relaties voor thermoharders nodig. Noodzakelijk ingrediënten zijn experimenten om het materiaal te karakteriseren en een numeriek implementatie van het constitutieve model in commercieel verkrijgbare Eindige Elementen codes. Deze dienen als basis om het thermo-mechanische gedrag van elektronische producten gedurende het fabricageproces te voorspellen. Vervolgens is het mogelijk om het product te verbeteren, denk aan optimalisatie van het ontwerp, materiaal parameters en/of proces condities.

In dit proefschrift wordt een nieuw uithardingsafhankelijk visco-elastisch materiaal model voor thermoharders beschreven. In dit model worden de relaxatie moduli voorgesteld als de optelsom van een evenwicht (de zogenaamde rubberniveau moduli) en een tijdsafhankelijk deel. De uithardingsafhankelijke rubberniveau moduli zijn beschreven met Adolf's model dat gebaseerd is op schaal analyses. Het tijdsafhankelijke deel is benaderd door zogenaamde Prony series, waarbij het uithardingsafhankelijkheid is beschreven door middel van de relaxatie amplitude, de genormaliseerde Prony coëfficiënten en de relaxatie tijden. Door de experimentele observatie dat de genormaliseerde master curven van het tijdsafhankelijke deel bij verschillende uithardingsgraad altijd in één curve vallen, is het model verder gesimplificeerd door de Prony coëfficiënten te beschouwen als uithardingsonafhankelijk. Hierdoor beschrijft het ontwikkelde model een 'quasi' thermo-rheologisch eenvoudig gedrag en heeft daarmee het voordeel van een relatief makkelijke implementatie in een commercieel verkrijgbaar EEM code. De relatie tussen het mechanische gedrag en het uithardingsprofiel is verkregen door gebruik te maken van alom bekende kinetische modellen voor het uitharding van polymeren.

Hoofdstuk 3 van dit proefschrift beschrijft het experimentele gedeelte. De basis voor dit gedeelte wordt gevormd door DMA metingen, DSC analysen en het bepalen van de krimp door uitharding. Afschuif DMA metingen onder iso-thermische en wisselende uitharding condities zijn uitgevoerd om het uithardingsafhankelijke relaxatie gedrag te bepalen. Tevens is het temperatuurafhankelijk dynamische gedrag van het materiaal in kaart gebracht bij verschillende uithardingsgraad. Hiermee zijn de master curven en de temperatuur verschuivingsfactor voor elke uithardingsgraad bepaald. Wanneer men de glas temperatuur als referentie kiest, dan is het effect van de temperatuur op de verschuivingsfactor onafhankelijk van de graad van uitharding. Het effect van de temperatuur is beschreven door twee bekende vergelijking: boven een specifieke temperatuur is de WLF vergelijking gebruikt, daar onder de Arrhenius vergelijking.

Een nieuw concept voor 'gereduceerde temperatuur' wordt voorgesteld in Hoofdstuk 3. De bovengenoemde vergelijking voor de verschuivingsfactor is aangepast gebruik makend van deze 'gereduceerde temperatuur'. Hierdoor kan het effect van de temperatuur en uithardingsgraad op deze factor door middel van een geïntegreerde manier worden beschreven.

De relaxatie bulk modulus is gemeten door middel van een drukcel en compressie DMA opzet, met gebruik van schijfvormige proefstukken. De combinatie van deze experimenten met dataverwerking leidt tot het bepalen van de complete relaxatiecurve, inclusief het glas- en rubberniveau. Echter, een beperkte hoeveelheid data is verkregen, met name bij lage uithardingsgraad. Dit impliceert een beperkte nauwkeurigheid voor de uithardingsafhankelijke relaxatie bulk modulus.

DSC analyses verschaffen de benodigde informatie omtrent de uithardingskinetiek van het materiaal en geven tevens informatie omtrent de relatie tussen de glastemperatuur en de mate van uitharding. De uithardingskrimp is gemeten door middel van een on-line data acquisitie systeem voor de dichtheidsverandering. De resultaten van deze metingen geven een bijna lineair verband tussen de dichtheidsverandering en de uithardingsgraad, onafhankelijk van de uithardingstemperatuur.

Het effect van het vulgehalte in thermoharders is belangrijk voor de ontwerpers bij het kiezen van het materiaal in het elektronisch product en aanverwante fabricageprocessen. Het effect van het vulgehalte op het materiaalgedrag is beschreven in Hoofdstuk 4. Hierbij is dit effect onderzocht op de glas modulus, de rubber modulus (beiden in afschuifrichting), de temperatuur en de verschuivingsfactoren, en de uithardingskrimp. Theoretisch voorspellingen gebaseerd op composiet mechanica zijn opgesteld en vergeleken met de experimentele uitkomsten.

Het ontwikkelde model is volledig geïmplementeerd in de commercieel verkrijgbare Eindige Elementen code MscSoftware Marc/Mentat. Een incrementele vorm voor het uithardingsafhankelijke constitutive gedrag is toegepast waarbij in het numerieke schema alleen de laatste rekenstap wordt opgeslagen om de volgende uit te rekenen. Dit voorkomt een substantiële numerieke opslag van data van de spanningsgeschiedenis. Speciaal geschreven subroutines zijn gebruikt om de uithardingskinetiek, de uithardingsafhankelijke relaxatie functies en de uithardingskrimp numeriek te beschrijven. Het ontwikkelde model is in staat om de spannings- en rekvelden in het materiaal gedurende het uitharden te berekenen.

Het ontwikkelde model is gevalideerd met een serie experimenten waarbij schijfvormige proefstukken in een 3-dimensionale spanningstoestand zijn gebracht door (gedeeltelijk) inklemmen gedurende het uitharden. De Eindige Elementen berekeningen komen goed overeen met deze experimenten waarmee is aangetoond dat deze implementatie voldoen betrouwbaar is.

Als toepassing van het ontwikkelde en gevalideerde model zijn twee relevante onderwerpen vanuit de elektronische industrie onderzocht. Het eerste onderwerp betreft het krom trekken van QFN producten tijdens het fabricageproces. De ontwikkeling in QFN producten is gericht op het efficiënter beleggen van het leadframe, momenteel gebeurt dat in een matrix van 5 keer een serie producten (met onderbrekingen daartussen), dit wilt men veranderen naar een volledige matrix. Het ontwikkelde model is toegepast om de kromming tijdens het molden en uitharden van de volledige matrix QFN producten te voorspellen. Ter verificatie zijn tevens een serie experimenten uitgevoerd. De voorspelde kromming is vergeleken met de experimentele resultaten waarbij een redelijke overeenkomst is gevonden. Het verschijnsel van veroudering is nog een openstaand onderzoeksthema in dit product.

Het tweede onderwerp betreft het effect van uithardingsgeïnduceerde spanningen en de impact daarvan op de uiteindelijke betrouwbaarheid voor zogenaamde Flip Chip on Board (FCOP) producten. Het ontwikkelde model is toegepast om het visco-elastische gedrag van underfill materiaal gedurende het uitharden en de achtereenvolgende betrouwbaarheidstesten (wisseling van temperatuur). De Eindige Elementen berekeningen zijn gebruikt om een voorspelling te doen over het vermoeiingsverschijnsel van soldeer verbindingen. De resultaten verduidelijken een significante bijdrage van uithardingsgeïnduceerde spanningen op dit vermoeiingsverschijnsel en mogen dus niet worden verwaarloosd.

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- Beijer, J.G.J., J.H.J. Janssen, H.J.L. Bressers, W.D. van Driel, K.M.B. Jansen, D.G. Yang, G.Q. Zhang, "Warpage Minimization of the HVQFN Map Mould," accepted to be published in IEEE Transactions on Advanced Packaging.
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Curriculum Vitae

The author, Daoguo Yang, was born in Guangxi, China, on December 4, 1963. In September 1979 he enrolled in Department of Agricultural Machinery, Guangxi Agricultural Institute as a freshman and in July 1983 he received his B.Sc. degree in Engineering. From July 1983 to August 1986, he worked as an assistant engineer in Yangsuo Machinery Factory, Guilin, China. From August 1986 to June 1989, he pursued graduate study in Department of Engineering Mechanics, Zhejiang University, Hangzhou, China and was entitled as Master of Science in Engineering in June 1989.

Since July 1989, he worked first as lecturer and then as associate professor in Department of Mechanical Engineering, Guilin University of Electronic Technology (GUET), China. During the years he worked in GUET, he did a major contribution to the initiation of the research work and education program on microelectronics assembly (SMT) in the university.

In March 1999 he came to the Netherlands as a visiting researcher in the Group Mechanics of Materials, Faculty of Mechanical Engineering & Marine Technology, Delft University of Technology, the Netherlands. Since March 2000, he started his Ph.D. research under the supervision of Prof. L. J. Ernst and Prof. G.Q. Zhang. The research topics included modelling of viscoelastic behaviour of electronic packaging polymers. From January 2003 till December 2005, he worked as a postdoctoral, and during this period of time, he has fully participated in EC project "Mevipro" and a few Philips projects.

Since January 2006, he has joined IMO-BE Innovation, Philips Semiconductors (now NXP Semiconductors) in Nijmegen, the Netherlands. His current work involves virtual thermomechanical prototyping of electronics packaging and assembly.







PROPOSITIONS

Accompanying the thesis

Cure-Dependent Viscoelastic Behaviour of Electronic Packaging Polymers

Modelling, Characterization, Implementation and Applications

Daoguo Yang

- 1. By using a new concept of "reduced temperature", which is defined as the difference between the temperature and the cure-dependent glass transition temperature, both the temperature and the conversion effects on the relaxation times can be expressed in an integrated way.
- 2. Full characterization of cure-dependent viscoelastic properties of polymers requires the determination of at least two distinct functions with sufficient accuracy, such as any combination of two of the following: the (relaxation) Young's modulus, the (relaxation) shear modulus, the (relaxation) bulk modulus and the Poisson's ratio.
- 3. Arbitrarily assuming a time and cure independent Poisson's ratio may lead to large errors in relaxation moduli determinations.
- 4. The curing polymer shows thermo-rheologically complex behaviour, while the transient relaxation behaviour may be thermo-rheologically simple.
- 5. In virtual thermal-mechanical prototyping of a complex electronic package, all the models should be made as simple as possible, but not simpler.
- 6. Reliability prediction of microelectronic products cannot be reliable without proper knowledge of the polymer materials involved.
- 7. In reality, the "stress free state" does not exist.
- 8. Nanoelectronics is not a simple evolution of microelectronics in the sense of down scaling, but is accompanied by an enormous technological revolution.
- 9. The more you know, as you will find, the more you don't know.
- 10. The word "crisis" (危机) in Chinese is comprised of two characters: one is "danger" (危(险)), and the other is "opportunity" (机(会)). Both danger and opportunity exist in a situation of crisis.

These propositions are considered opposable and defendable and as such have been approved by the supervisors Prof. dr. ir. L.J. Ernst and Prof. dr. ir. G.Q. Zhang.

STELLINGEN

Behorende bij het proefschrift

Cure-Dependent Viscoelastic Behaviour of Electronic Packaging Polymers

Modelling, Characterization, Implementation and Applications

Daoguo Yang

- 1. Door gebruik te maken van het nieuwe concept van 'gereduceerde temperatuur', gedefinieerd als het verschil tussen de actuele temperatuur en de uithardingsafhankelijke glastemperatuur, is het mogelijk om het effect van de temperatuur en de uithardingsgraad op de relaxatietijden op een geïntegreerde manier te beschrijven.
- 2. Het volledig karakteriseren van het uithardingsafhankelijke viscoelastische gedrag van polymeren vereist het nauwkeurig bepalen van tenminste twee van de volgende functies: de (relaxatie-) Young's modulus, de (relaxatie-) afschuifmodulus, de (relaxatie-) bulkmodulus en de Poisson's ratio.
- 3. Willekeurig een tijd- en uithardingsonafhankelijke Poisson's ratio aannemen leidt tot grote fouten in de relaxatiemodulibepalingen.
- 4. Een uithardende polymeer vertoont thermo-rheologisch complex gedrag, terwijl het tijdsafhankelijke relaxatiegedrag thermo-rheologisch eenvoudig kan zijn.
- 5. Virtuele thermo-mechanische voorspellingstechnieken voor complexe elektronische producten vereisen modellen die zo eenvoudig mogelijk zijn, maar niet eenvoudiger.
- 6. Betrouwbaarheidsvoorspellingen van micro-elektronische producten kunnen niet betrouwbaar worden gedaan zonder goede kennis van de eigenschappen van de gebruikte polymeren.
- 7. In werkelijkheid bestaat de 'spanningsvrije' toestand niet.
- 8. Nano-elektronica is niet een simpele evolutie van de micro-elektronica in de zin van het steeds maar kleiner maken, maar gaat gepaard met een enorme technologische revolutie.
- 9. Naarmate je meer te weten komt, kom je er achter dat je eigenlijk weinig weet.
- 10. Het woord 'crisis' (危机) in het Chinees bestaat uit twee karakters: het ene staat voor 'gevaar' (危(险)), het andere voor 'kans' ofwel 'mogelijkheid' (机(会)). Beide zijn aanwezig in geval van een crisis.

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