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# Evolution of residual stresses in modified epoxy resins for electronic packaging applications

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## Abstract

The bi-material strip bending (BMSB) experiment is successfully employed to monitor in situ, the evolution of residual stresses during curing and thermal cycles of epoxy resins, including neat epoxy, silica-modified and rubber-modified epoxies. In the BMSB experiment, the curvature changes of a bi-material strip specimen consisting of a resin film applied onto a glass slide during a temperature excursion is measured in situ within a temperature chamber. The changes in viscosity and curing kinetics of the resins with temperature are also characterized, which are correlated to the residual stress evolution. Based on the constitutive relation between the residual stress and the elastic modulus change with temperature, the coefficients of thermal expansion of the resins are also determined, which are compared with those obtained from the thermo-mechanical analysis. The resins are also subjected to repeated heating and cooling to study the changes in residual stress due to thermal cycles often encountered in reliability tests of electronic packages.

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## 1. Introduction

One of the most critical reliability issues in the use of polymeric resins for electronic packaging is the high residual stress generated during the assembly processes. Amongst the various sources, the most important are the stresses arising from the volumetric shrinkage of polymer due to the differential coefficients of thermal expansion (CTE) between different components in the packaged assembly. As shrinkage is constrained by adhesion between the components, residual stresses are developed in the package. The stresses generated due to evaporation of solvents and volatile by-products, as well as cross-linking reaction also add to the thermal residual stresses, albeit small [1]. With the continuing demands for miniaturization and higher reliability of consumer electronics, many advanced packages have emerged, amongst which flip chip on board (FCOB) packages are regarded as the choice for many portable and telecommunication products. An FCOB package consists of a silicon chip and a printed circuit board (PCB), which is interconnected

using eutectic solder balls, and an underfill resin is encapsulated along the small gap between the chip and PCB. A schematic diagram of a typical FCOB package is shown in Fig. 1. On one hand, the underfill resin reduces the relative displacement between the chip and PCB and thus the stresses imposed in the solder interconnection that occur during the thermal cycles and mechanical loading. On the other hand, the underfill layer is under significant amounts of tension or compression, depending on the stress-free temperature of the package and the maximum operating temperature.

While the presence of underfill resin improves significantly the life of FCOB packages, the encapsulation and curing process itself creates another problem: high residual stresses are generated in the resin and the surrounding package components after cure. Excessive residual stresses are detrimental to the mechanical and functional performance of FCOB assembly as they often lead to premature failure due to delamination of underfill resin from the other package components and unacceptable bending of the entire assembly. Delamination often initiates from the die-solder ball corners and die-underfill fillet corners [2,3]. To reduce the residual stresses and thus the potential for premature failure, several solutions have been suggested for

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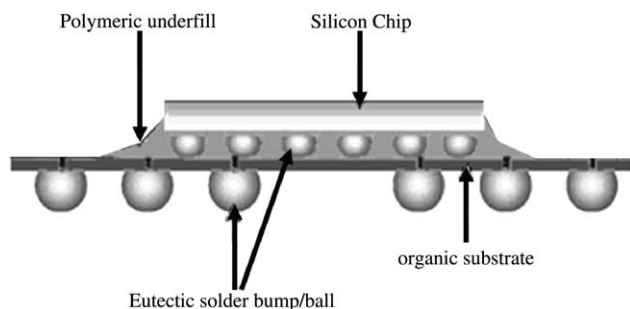


Fig. 1. Flip chip on board (FCOB) package configuration.

the underfill material properties and processing conditions. They include a CTE value of underfill resin similar to that of the solder [4], a low elastic modulus and a low glass transition temperature,  $T_g$ , of resin [5], and a moderate cooling rate [6,7].

Having the material properties and the extents of shrinkage of the epoxy allows the prediction of the residual stress and warpage of the electronic package by modeling the material change during cure. In this paper, the shrinkage stresses induced in epoxy resins containing different types of filler during the manufacturing processes of FCOB packages are characterised. The bi-material strip bending (BMSB) experiment was used within the dynamic mechanical analyzer (DMA) chamber to illustrate in situ, the evolution of residual stresses during curing and the temperature cycles. There is significant analogy between the BMSB and the flip chip package in terms of the geometric configurations and the sources of residual stresses, in which curvature change in the BMSB specimen and warpage in a flip chip package are induced likewise. Similar findings on warpage of composite laminate due to thermal shrinkage are also frequently reported [8–11]. The thermo-mechanical analysis (TMA) and three-point bending tests were conducted to study the effect of filler type on the changes in thermo-mechanical properties of the resins with temperature. Special focus was placed on the study of volumetric changes in these resins during thermal cycles and the underlying mechanisms for the accumulation of shrinkage. The differential scanning calorimetry (DSC) and a rheometer were also employed to characterize the cure kinetics and viscosity of the resins.

## 2. Experiments

The experimental details of the BMSB experiment and flexural tests were described previously [12]. The BMSB specimen consisted of a  $10\ \mu\text{m}$  thick resin layer applied onto a  $18\ \text{mm}$  wide  $\times$   $6\ \text{mm}$  long  $\times$   $110\ \mu\text{m}$  thick glass slide. Glass was chosen as the substrate material for its excellent thermal stability over a wide temperature range with a very low CTE ( $= 5.87\ \text{ppm}/^\circ\text{C}$ ). Different from a typical flip chip device configuration as seen previously in Fig. 1, BMSB configuration allows the assembly to bend

freely without any constraints. The bending of the specimen was merely due to the differences in CTEs between the glass slide and the epoxy. Hence, hereafter the strain of the epoxy layer in this study is referred as the thermal strain of the epoxy experiencing the temperature change from cure temperature to lower temperature, while the stress in the epoxy layer is induced due to the differences in dimensional changes between the glass slide and the epoxy during thermal excursions. In this sense, even though the stress level in the epoxy layer is not directly corresponding to the actual condition in flip chip package, the thermal strain of the epoxy is basically the same in any case, and the residual stress due to the constraints by adhesion between components in the package can then be predicted.

The BMSB specimens were subjected to a temperature excursion that involved heating to  $220\ ^\circ\text{C}$ , isothermal curing at  $220\ ^\circ\text{C}$  for 30 min, followed by cooling to ambient. Repeated heating and cooling cycles were also applied to simulate the thermal cycles often encountered in the manufacturing of FCOB packages and thus evaluate the changes in residual stress profile with temperature cycle. Both the heating and cooling rates used were  $10\ ^\circ\text{C}/\text{min}$ , which were the same as that used in the other thermo-mechanical experiments. A three-point bending configuration with a span length of 15 mm, as shown in Fig. 2, was used to measure the curvature change in the BMSB specimen within a dynamic mechanical analyser (Perkin Elmer Pyris DMA 7e). The DMA instrument consisted of a central core rod connecting to a high sensitivity displacement detector (LVDT), a precise linear high force motor and a low mass, fast-response furnace, as illustrated in Fig. 3. The probe displacement in the mid-span of bi-material strip

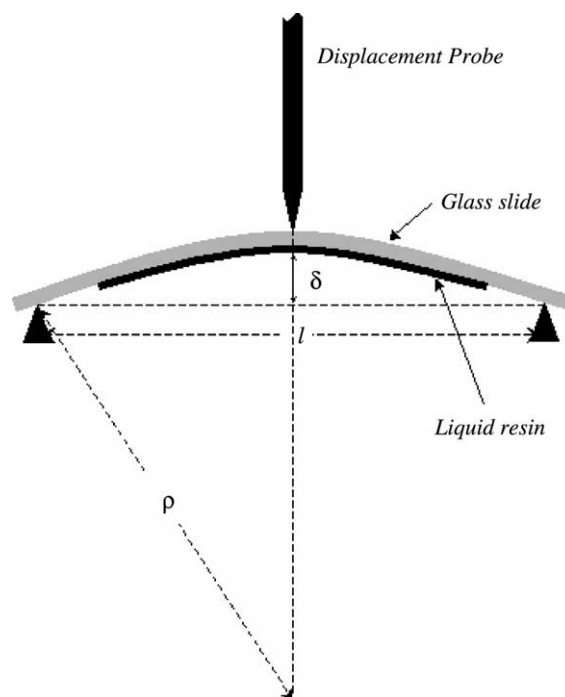


Fig. 2. Schematic drawing of a dynamic mechanical analyzer (DMA).

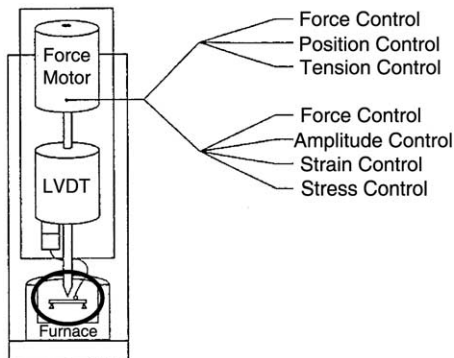


Fig. 3. Bi-material beam bending test configuration.

was continuously monitored against temperature change. The contact force applied by the displacement probe over the glass surface was 3 mN.

Three different epoxy-based resin systems containing different filler types were studied, including unmodified epoxy (Epoxy A), conventional underfill resin (Epoxy B) and no-flow underfill resin (Epoxy C). The unmodified epoxy was D.E.R. 324 (Dow Plastics), which is based on aliphatic glycidyl ether modified bisphenol-A. The underfill resins were formulated from a bisphenol F epoxy and substituted phthalic anhydride as curing agent. Epoxy B contained 50 vol% of fused silica particles that aimed to reduce the CTE while improving the mechanical properties, such as the strength, modulus and fracture toughness. Epoxy C contained liquid rubber particles that were used to improve the fracture toughness and to allow easy spreading during the no-flow flip chip bonding process. Typical scanning electron micrographs of fracture surfaces for the epoxy resins are illustrated in Fig. 4. A flat mirror-like fracture surface is seen for the unmodified epoxy (Fig. 4(a)), whereas the morphologies of uniformly distributed silica (Fig. 4(b)) and liquid rubber particles (Fig. 4(c)) are seen for the modified epoxies. Significant research has been carried out previously to identify the toughening mechanisms of these modified resins [13–15], which will not be further discussed in this paper.

The curing characteristics of resins were also studied by measuring the viscosity using a rheometer (Physica-UDS200) and the curing kinetics using a differential scanning calorimeter (Setaram DSC92) as a function of temperature. The rheometer was operated in the oscillatory parallel-plate geometry with a replaceable aluminium disk at strain amplitude of 5% and an angular frequency of 100/s. The heating rate in both viscosity and DSC measurements was 10 °C/min. Three-point flexural tests were conducted on cured resin samples at a temperature range between ambient and 200 °C to determine the temperature-dependent flexural modulus. 9 mm wide × 18 mm long × 2 mm thick samples were placed on the bending platform in the DMA chamber to allow temperature equilibrium in the sample before loading. The quasi-static operating mode was selected for the DMA to avoid

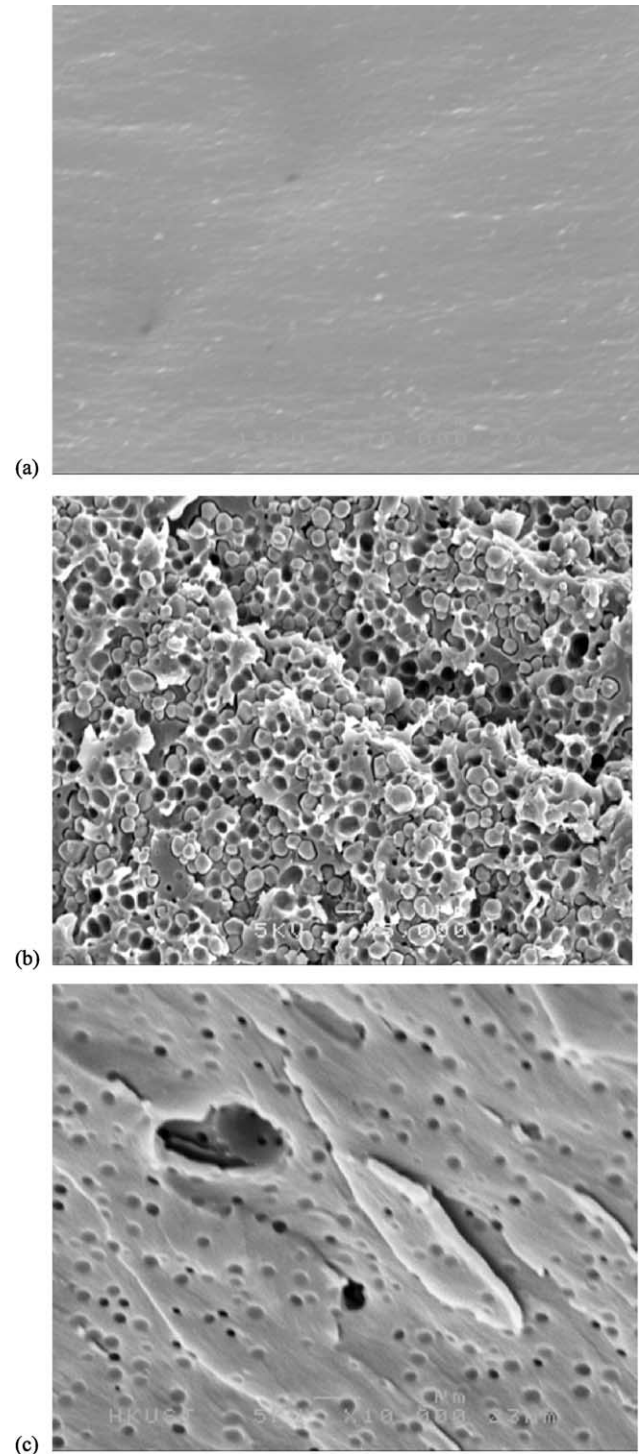


Fig. 4. Fracture surfaces of (a) neat epoxy; (b) silica modified epoxy; and (c) rubber modified epoxy.

potential inaccuracy of flexural modulus obtained from the dynamic loading condition. The applied load was increased to 1.2 N at a rate of 0.1 N/min, and the flexural modulus was determined from the initial linear region of the stress–strain curve within less than 0.02% of the strain. One sample each was tested for each epoxy system. The CTEs of the resins were also measured independently using

a thermo-mechanical analyser (Mettler Toledo TMA/SPTA 840), for direct comparison with the results obtained from the BMSB experiment. The resin sample had a circular shape with approximately 2 mm in thickness. A rigid thin fused silica disc with a very low CTE value ( $\sim 0.5 \times 10^{-6}/^\circ\text{C}$ ) was inserted between the measuring probe of the TMA and the sample to avoid penetration of the probe tip into the sample when the probe was in contact with the sample at a load of 0.01 N. Therefore, the reading obtained from TMA represents essentially the dimensional change of the sample.

### 3. Analysis of residual stresses in a bi-material strip and coefficient of thermal expansion

#### 3.1. Residual stress in a bi-material strip

Based on the simple beam bending theory [16], the residual stresses,  $\sigma_a$ , at a distance  $y$  from the centre of the resin layer for the bi-material strip is approximately given [17]:

$$\sigma_a = \frac{1}{\rho} \frac{E_s h_s}{6(1+m)m} \left[ \left( 1 + \frac{6y}{h_a} \right) nm^3 + \frac{6y}{h_a} nm^2 + 1 \right] \quad (1)$$

where  $E$  and  $h$  are the elastic modulus and thickness; and the subscripts  $s$  and  $a$  refer to the glass substrate and the adhesive resin layer, respectively.  $m = h_a/h_s$  is the thickness ratio, and  $n$  is the moduli ratio  $E_a/E_s$ . For a very thin resin layer compared to the glass slide, i.e.  $h_a \ll h_s$  the residual stress in the resin layer can be further simplified:

$$\sigma_a = \frac{1}{\rho} \frac{E_s h_s^2}{6h_a} \quad (2)$$

The radius of curvature,  $\rho$ , of the bi-material strip can be obtained directly from the bending geometry as a function of mid-span displacement,  $\delta$ , which is temperature-dependent:

$$\rho = \frac{l^2}{8\delta} + \frac{\delta}{2} \approx \frac{l^2}{8\delta} \quad (3)$$

where  $l$  is the span length of the bending platform, see Fig. 2. Substitution of Eq. (3) into Eq. (2) gives:

$$\sigma_a = \frac{4}{3} \frac{E_s h_s^2}{h_a l^2} \delta \quad (4)$$



Fig. 5. Bi-material strip configuration.

#### 3.2. Relation between the residual stress in a bi-material strip and CTE

The bending of a bi-material strip upon cooling from the isothermal cure temperature in Fig. 5 occurs due to the mismatches in CTEs between the glass substrate,  $\alpha_s$ , and resin layer,  $\alpha_a$ .

The generalized thermoelastic stress–strain relations for three-dimensional problems are [18]:

$$\Delta \varepsilon_x - \alpha \Delta T = \frac{1}{E} [\Delta \sigma_x - \nu (\Delta \sigma_y + \Delta \sigma_z)] \quad (5a)$$

$$\Delta \varepsilon_y - \alpha \Delta T = \frac{1}{E} [\Delta \sigma_y - \nu (\Delta \sigma_x + \Delta \sigma_z)] \quad (5b)$$

$$\Delta \varepsilon_z - \alpha \Delta T = \frac{1}{E} [\Delta \sigma_z - \nu (\Delta \sigma_x + \Delta \sigma_y)] \quad (5c)$$

$$\Delta \gamma_{xy} = \frac{\Delta \tau_{xy}}{G} \quad \Delta \gamma_{yz} = \frac{\Delta \tau_{yz}}{G} \quad \Delta \gamma_{xz} = \frac{\Delta \tau_{xz}}{G} \quad (5d)$$

Plane stress will occur in a thin plate when the temperature does not vary through the thickness; therefore, we may assume that  $\Delta \sigma_z = \Delta \tau_{xz} = \Delta \tau_{yz} = 0$ . We may also regard each element as free to expand in the  $z$  direction. As suggested in the method of strain suppression on a thin plate [18], thermal expansions are considered only in the  $x$  and  $y$  directions with the following relationships:

$$\Delta \sigma_x = \Delta \sigma_y \quad \text{and} \quad \Delta \tau_{xy} = 0 \quad (6)$$

Hence, from Eq. (5),

$$\Delta \varepsilon_x = \Delta \varepsilon_y = \frac{\Delta \sigma_x}{E} [1 - \nu] + \alpha \Delta T \quad (7)$$

The stress and strain in Eq. (7) should be interpreted as quantities averaged through the thickness, of which the case is referred to as generalized plane stress [18]. For small curvature, the compatibility condition requires that  $\varepsilon_x$  in the adhesive layer and the substrate are the same:  $[\Delta \varepsilon_x]_a = [\Delta \varepsilon_x]_s$ .

$$\begin{aligned} \Delta \varepsilon_x &= \frac{[\Delta \sigma_x]_s}{E_s} [1 - \nu_s] + \alpha_s \Delta T \\ &= \frac{[\Delta \sigma_x]_a}{E_a} [1 - \nu_a] + \alpha_a \Delta T \end{aligned} \quad (8)$$

where the subscript  $s$  and  $a$  refer to the substrate and adhesive, respectively. For force balance in the absence of the external stresses [19],

$$h_a [\Delta \sigma_x]_a + h_s [\Delta \sigma_x]_s = 0 \quad (9a)$$

Thus,

$$[\Delta \sigma_x]_s = -\frac{h_a}{h_s} [\Delta \sigma_x]_a = -m [\Delta \sigma_x]_a \quad (9b)$$

where  $m = h_a/h_s$ . Therefore, combining Eqs. (8) and (9b) give,

$$[\Delta \sigma_x]_a \{ (1 - \nu_a) + mn(1 - \nu_s) \} = E_a (\alpha_s - \alpha_a) \Delta T \quad (10)$$

where  $n = E_a/E_s$ . By approximation,  $mn \approx 0$ , then

$$\alpha_a = \alpha_s - \frac{[\Delta\sigma_x]_a}{E_a\Delta T}(1 - \nu_a) \quad (11)$$

It follows that once the residual stress  $[\Delta\sigma_x]_a$  (which is the same as  $\sigma_a$  in Eq. (4)) is obtained from the curvature measurement, and the temperature dependent elastic modulus of adhesive,  $E_a$ , is measured, the in situ change of CTE of the adhesive layer  $\alpha_a$  can be determined.

#### 4. Results and discussion

##### 4.1. Temperature dependent flexural moduli

Fig. 6 presents the temperature-dependent flexural moduli of three epoxy resins and glass slide, respectively. The flexural moduli of the resins at room temperature were higher in the order of the rigid filler modified epoxy (Epoxy B), unmodified epoxy (Epoxy A) and rubber modified epoxy (Epoxy C). Epoxy C contains micrometer-scale rubber particles that were mainly responsible for the low modulus [13]. The silica-modified Epoxy B showed the highest modulus over the whole temperature range studied, due to the stiffening/strengthening effects of rigid particles of high content [15]. The neat epoxy resin exhibited the largest drop in flexural modulus when temperature was varied across its  $T_g$  range. The  $T_g$  values obtained from the mid-points of declining portion of modulus curves were approximately 85, 142 and 120 °C, respectively, for Epoxy A, B and C. These values are well compared with those reported by the material suppliers, 82, 148 and 128 °C, respectively. The difference in  $T_g$  was primarily due to the dissimilar epoxy formulation. As expected, the glass slide showed an insignificant variation in flexural modulus when measured at different temperatures.

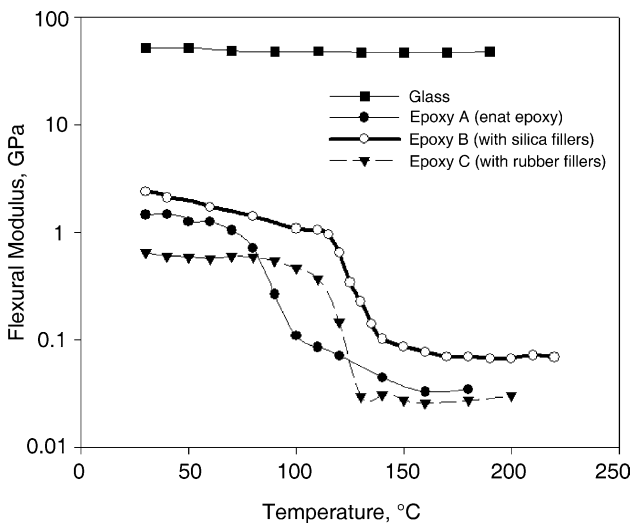


Fig. 6. Flexural moduli of epoxy resins and glass slide as a function of temperature.

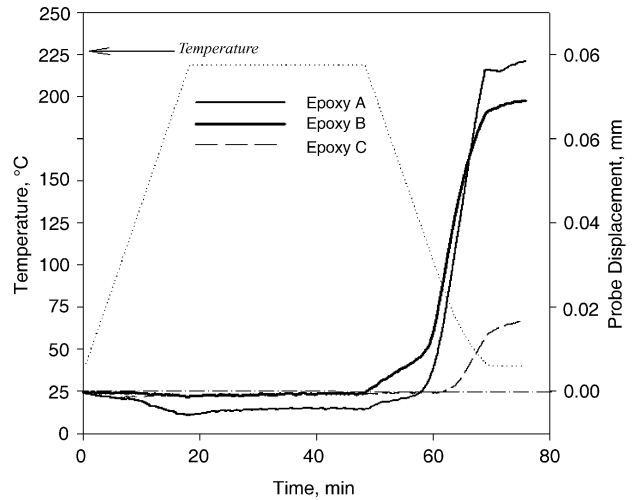


Fig. 7. Probe displacement vs. temperature plots.

##### 4.2. Evolution of residual stresses during initial cure

Fig. 7 plots the probe displacement vs. temperature profiles measured from the BMSB experiment for three resins when subjected to the same curing temperature excursion. The responses among the resins were different, depending on the type of fillers added in the resin and the stage of curing process. For Epoxy B and C, there was little change in displacement during the initial temperature increase and for the majority of isothermal curing at 220 °C. For Epoxy A, there was a drop in displacement (i.e. convex bending) during the initial heating stage. A similar observation was also reported previously [7,8]. The bending of the specimen during the temperature ramp is a reflection of the competitive interactions amongst the contraction of polymeric film due to solvent evaporation, cure shrinkage, and the film expansion. The negative displacement in Epoxy A in this study is thought to be a direct result from resin

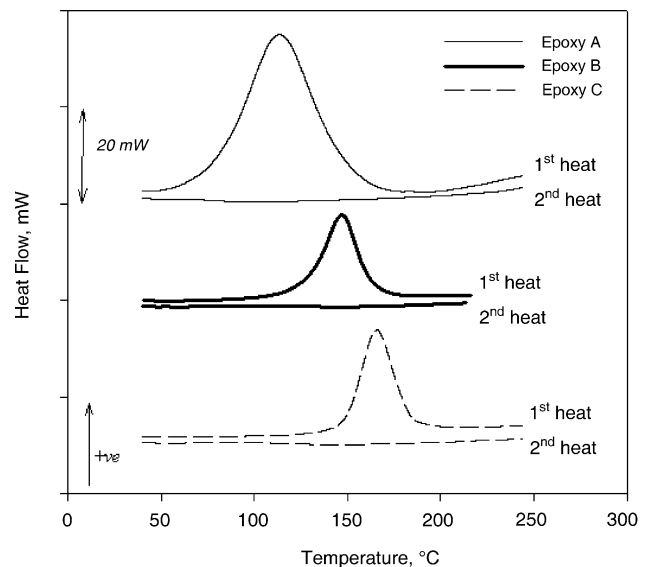


Fig. 8. Curing kinetics of epoxies based on DSC analysis.

expansion at the early stage of cross-linking. This hypothesis is partly supported by the DSC measurements shown in Fig. 8 in that the endothermic reaction of Epoxy A took place much earlier than the other two epoxies. It is also likely that the onset temperature for cure was lower for Epoxy A than the other two epoxies. This observation is further supported by the plots of viscosity vs. temperature as shown in Fig. 9, which were obtained while the temperature was increased monotonically from ambient to 250 °C.

The viscosity of Epoxy A increased drastically when temperature reached 135 °C, the onset temperature of cross-linking reaction in the epoxy [20,21]. Epoxy B and C showed abrupt increase in viscosity at much higher temperatures, 186 and 210 °C, respectively.

Upon cooling from the isothermal curing temperature at 220 °C, the probe displacement started to pick up for all resins. The displacements for all samples exhibited initially a slow increase, followed by a rapid, approximately linear

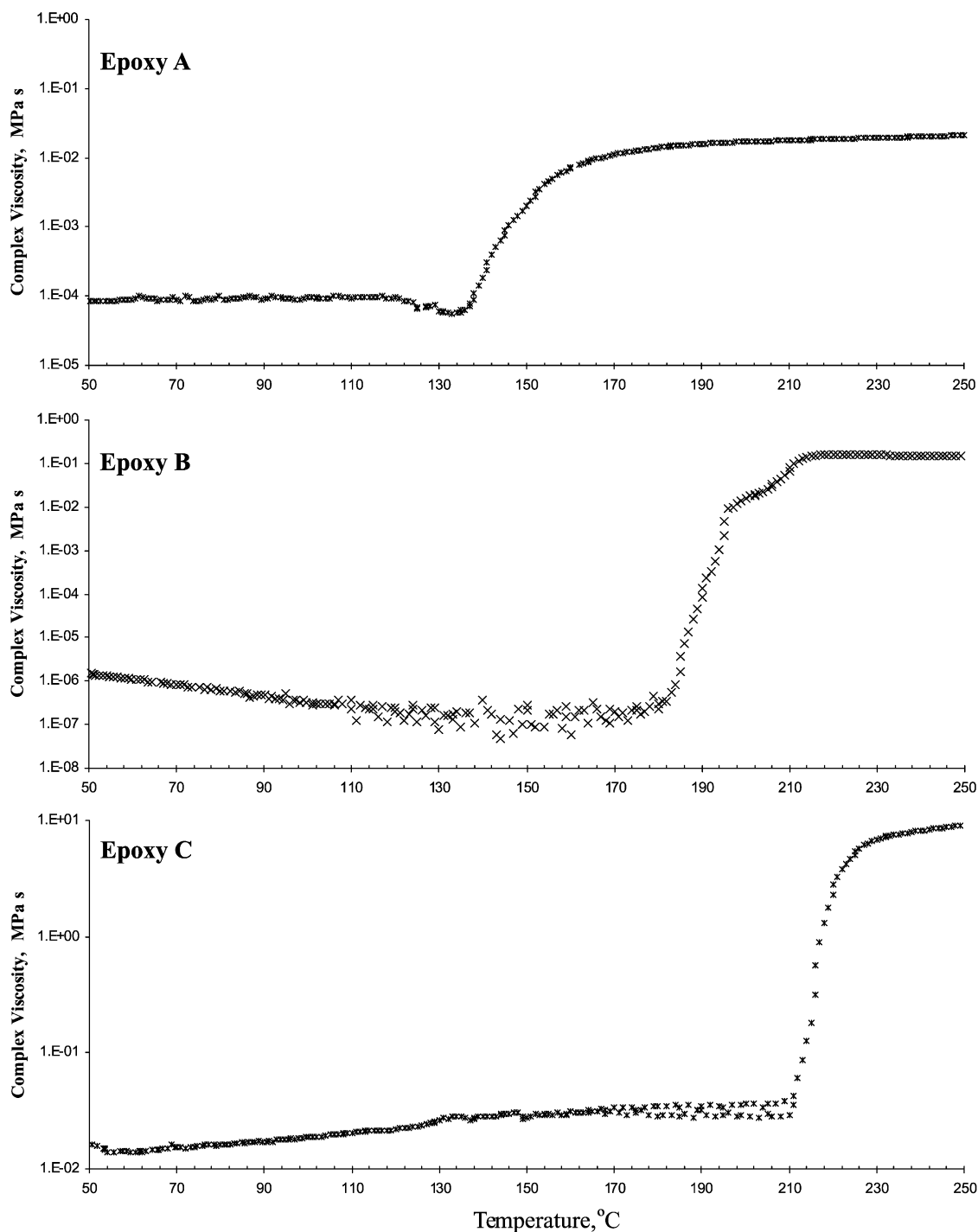


Fig. 9. Change of epoxy viscosity with temperature.

increase at temperatures below about 75–100 °C, before showing plateau values at a dwell temperature of 40 °C. It appears that both the temperature-dependent modulus and CTE of resin played a dominant role in determining the shrinkage behaviour. The plateau shrinkage values were higher in the order of Epoxy A, B and C resins. Epoxies A and B having high flexural moduli at temperatures below  $T_{lg}$  demonstrated much higher thermal shrinkage than Epoxy C containing rubber modifier with a low flexural modulus. The lower shrinkage for the rigid particle modified epoxy than the unmodified epoxy was expected due to the very low CTE of fused silica (typically  $0.5 \times 10^{-6}/^{\circ}\text{C}$ ) compared to neat epoxy (in the range of  $60\text{--}100 \times 10^{-6}/^{\circ}\text{C}$ ). This is in spite the fact that the flexural modulus was higher for Epoxy B than Epoxy A. It is also demonstrated that the incorporation of liquid rubber can, in some circumstances, reduce the shrinkage of epoxy resin, besides enhancing the fracture toughness and reducing the elastic modulus at room temperature. A similar conclusion was also note previously in that there was a systematic reduction in CTE with liquid rubber for a glycidyl ethers of O-cresol novolac (ESCN) epoxy resin [22].

#### 4.3. Response to heating–cooling cycles

Fig. 10 presents the displacement profiles measured during heating–cooling cycles of bi-material strip specimens. Apart from the differences in the general shrinkage behaviour for different resins, isothermal contractions were also noted for all resins during the dwelling period at 40 °C. An established explanation for the isothermal contraction is that when the temperature drops below the  $T_g$ , the structural change in response to a constant temperature is slower than the time required for the actual temperature in the polymer to reach an equilibrium state [23]. The time required for the polymer chains to relax completely is

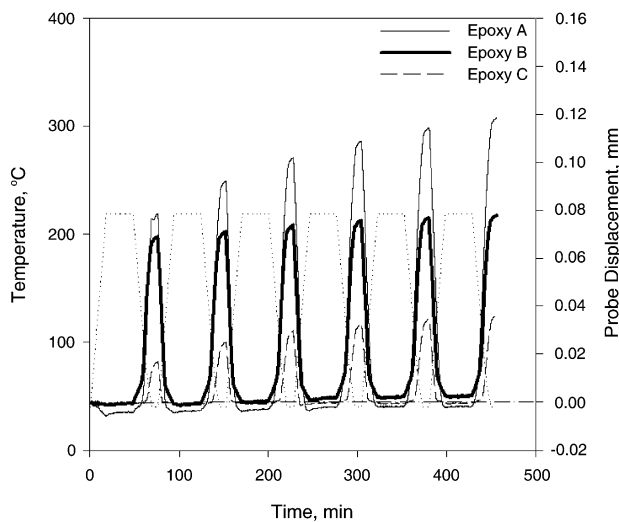


Fig. 10. Probe displacement vs. temperature plots obtained during thermal cycles.

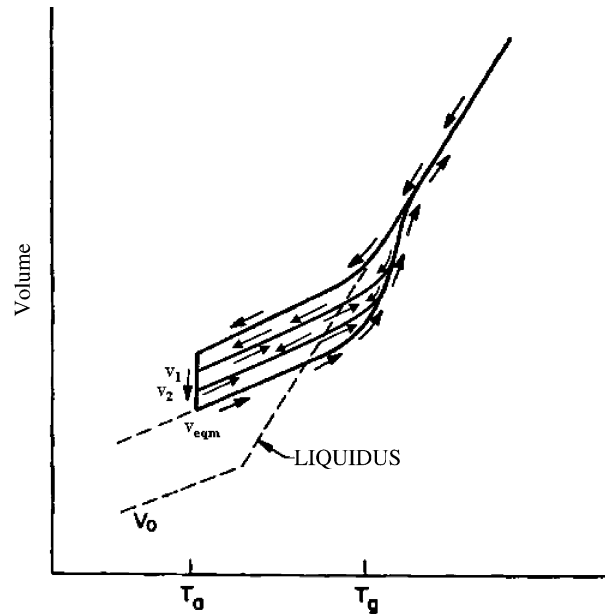


Fig. 11. Schematic diagram of specific volume vs. temperature.

extremely long, and the relaxation is a function of molecular mobility, which in turn depends on the temperature below  $T_g$ . For example, the isothermal contraction in polyvinylacetate (PVA) was found to be most extensive near the  $T_g$  of the polymer. The delay of reaching the equilibrium state is best illustrated by the schematic plot of specific volume vs. temperature as shown in Fig. 11. During the dwell period at a temperature  $T_0$ , the polymer shrinks continuously until its volume reaches the equilibrium state,  $V_{eqm}$ . The possibility of shrinkage contribution due to the uncured portion of epoxy in the previous cure cycle was studied by measuring the residual heat based on DSC, as shown in Fig. 8. There was no evidence of a peak in heat flow obtained on second heating (shown as flat lines) for all epoxy resins studied, confirming negligible residual stresses arising from this source.

In view of our experiment based on the repeated heating–cooling cycles, it is likely that the shrunken volume of the polymer is cumulative for each cycle. Therefore, the changes in the maximum probe displacement of the bi-material strip obtained at dwell temperature 40 °C are plotted as a function of cycle in Fig. 12. All resins showed a similar trend of increasing towards the respective saturation values as the heating–cooling cycle increased. It appears that a longer settling time was required for the neat epoxy containing no reinforcements to reach equilibrium than for the epoxies containing rigid or rubber particles. This observation may suggest that the addition of fillers into epoxy resin depressed the general relaxation behavior of the polymer.

#### 4.4. Measurements of CTE

The dimensional changes were measured independently using a thermo-mechanical analyzer (TMA) and are

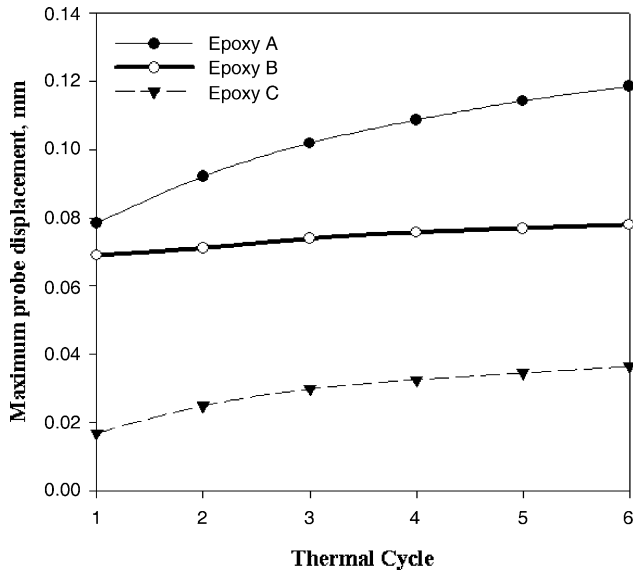
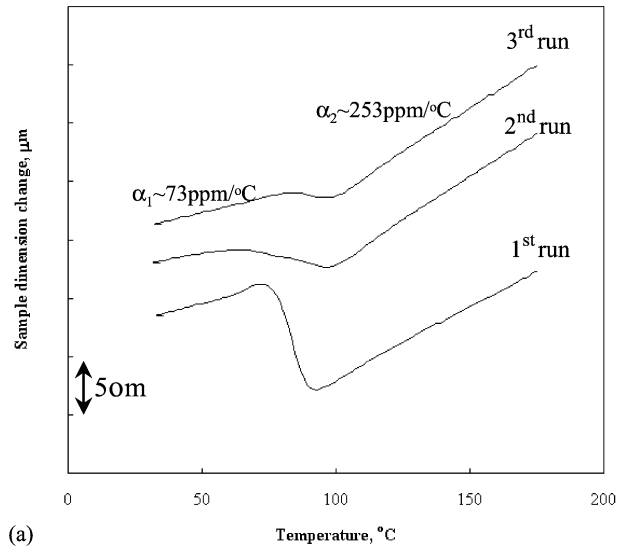


Fig. 12. Maximum probe displacement at 40 °C vs. number of cycles.

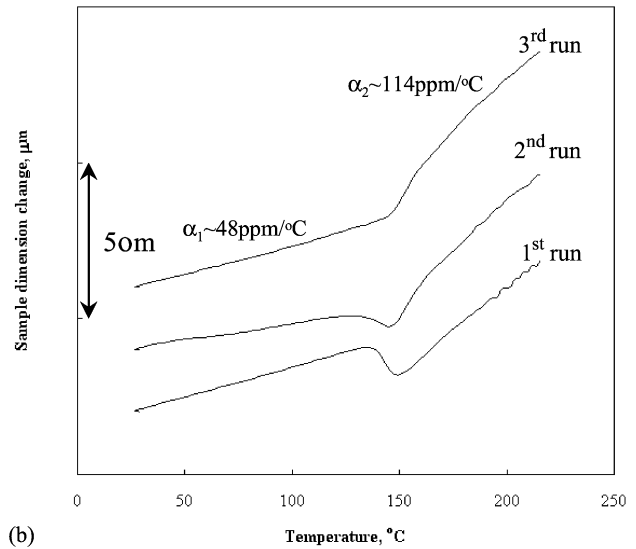
presented along with the CTE values in Fig. 13, where ‘hills’ and ‘valleys’ corresponding to temperatures between 75 and 150 °C were observed. The ‘hill’ and ‘valley’ phenomenon was thought to be attributed to the relaxation of residual stress–strain following the collapse of the frozen-in excess free volume of the polymer [24]. The extra free volume becomes higher with larger dimensional changes upon increasing the cooling rate. The relaxation of free volume became less and the ‘hill’ and ‘valley’ phenomenon gradually diminished as the resin was subjected to repeated heating and cooling. It is noted that the temperature where the hill and valley phenomenon took place was higher in the order of Epoxy B, Epoxy C and Epoxy A. A close examination of the TMA results indicates that the mid-points between the hill and valley were approximately equivalent to the  $T_g$ s of the respective resins, suggesting some correlation between the relaxation process (‘hill’ and ‘valley’ phenomenon) and the thermo-mechanical parameter ( $T_g$ ).

The CTE values measured from the BMSB experiment for temperatures below  $T_g$  were almost identical to those determined from TMA as summarized in Table 1, except for the neat epoxy. The CTE values were higher in the order of Epoxy A, Epoxy C and Epoxy B. The much lower CTE of Epoxy B than the other two resins was expected due to the very low CTE of fused silica contained in Epoxy B. Meanwhile, the CTE values obtained from the BMSB experiments at temperatures above  $T_g$  were approximately 200 °C for both the modified epoxies, which were somehow higher than the corresponding values measured from the TMA. Even so, the general trend with respect

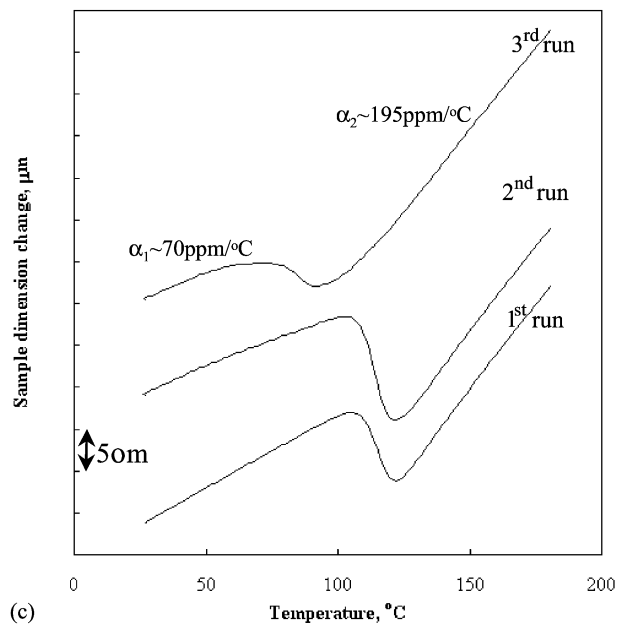
Fig. 13. Dimensional change vs. temperature plots obtained from TMA experiment for (a) neat epoxy; (b) silica modified epoxy; and (c) rubber modified epoxy.



(a)



(b)



(c)



Table 1  
Comparisons of the coefficients of thermal expansion (CTE) obtained from the BMSB experiment and TMA

CTE, $10^{-6}/^{\circ}\text{C}$	BMSB	TMA
Epoxy A	85	73
Epoxy B	50	48
Epoxy C	69	70

to the type of resin remained much the same as the CTE values below  $T_g$ .

### 5. Concluding remarks

The BMSB experiments were successfully used to monitor in situ the evolution of residual stresses in three different epoxy resins, including neat epoxy, silica modified epoxy and liquid rubber modified epoxy. The resin–glass strip assembly was subjected to a curing process and a repeated heating–cooling temperature excursion. The CTEs were determined, which were compared with those obtained from the TMA. Based on the above discussions, the following remarks can be highlighted.

1. At the initial stage of heating, there was a drop in displacement (i.e. convex bending) in the neat epoxy sample, a reflection of slight expansion of resin due to gelation of polymer and crosslinking of polymer molecules.
2. Upon cooling from the curing temperature, the residual displacement increased slowly, followed by a rapid increase due to thermal shrinkage of resin. Both the modulus and CTE of resin played a dominant role in determining the shrinkage behaviour.
3. During the heating–cooling cycles, shrinkage was higher in the order of neat epoxy, silica modified and rubber modified epoxies. There were isothermal contractions for all resins during dwelling at  $40^{\circ}\text{C}$ , which is attributed to a longer time required to reach an equilibrium state in polymer.
4. The ‘hills’ and ‘valleys’ phenomenon were observed in the TMA analyses, which arose from the relaxation of residual stress–strain following the collapse of the frozen-in excess free volume of the polymer.
5. The CTE values measured from the BMSB for temperatures below  $T_g$  were almost identical to those determined from TMA, except for neat epoxy. The CTE values were higher in the order of silica modified, rubber modified and neat epoxies.

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