Linear thermal expansion, thermal ageing, relaxations and post-cure of thermoset polymer composites using modulated temperature thermomechanometry

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Abstract The glass transition temperature (Tg) regions of polymers and composites were studied using static force thermomechanometry and modulated temperature thermomechanometry (mT-TM). Modulated temperature allowed measurement of linear thermal expansion coefficient and glass transition as reversing phenomena, independent of any residual cure and relaxations that are non-reversing in nature. The reversing dimension change curves were well defined with continuous expansion that increased after Tg, though sensitivity decreased with crosslinking and fibre content. The non-reversing dimension change curves showed the maximum variation and revealed complex changes, and the non-reversing characteristics were confirmed by repeated scans, both upon cooling or re-heating. Non-reversing curves showed contractions with increasing temperature. Lissajous figures demonstrated that temperature modulation deviated significantly from linear response in the temperature range below Tg, and during the Tg range, steady state was not maintained. Measurements made in mT-TM mode were compared with modulated force TM where Tg was revealed as a peak in loss modulus or $\tan(\delta)$, whilst reversing events were consistent with changes in storage modulus.

Keywords Thermomechanical analysis · Crosslink · Reversing · Thermal equilibrium · Glass transition

Introduction

Thermoset polymer composites are preferred for many applications because of their strength, dimensional stability, resistance to heat, solvents and corrosive environments. They usually have a high glass transition temperature (Tg) that approaches a maximum at full cure. Full cure is difficult to achieve as illustrated by a time–temperature–transformation phase diagram. Initial Tg and cure can be measured using differential scanning calorimetry (DSC) [1]. Post-cure can be measured and quantified using DSC. However, glass transition, relaxations and thermal ageing [2] give a low response with DSC, particularly when the polymer is highly crosslinked and mobility restricted by the fibrous filler phase.

Heat capacity is a characteristic thermodynamic property of a substance related to the temperature, and hence thermal vibrations, degrees of freedom of the molecules and the thermal equilibration or fictive temperature. Heat capacity at constant pressure (p) and moles (n) (Cp) is defined as shown in Eq. 1 where enthalpy $= H$ and temperature $= T$.

$$C_p = \left[\frac{\mathrm{d}H}{\mathrm{d}T}\right]_{n,p} \qquad (1)$$

The coefficient of thermal expansion (α) is a volumetric (V) change defined by Eq. 2 and is analogous to the heat capacity in revealing changes in the state of materials and their approach to equilibrium with temperature. The linear coefficient of thermal expansion (α_l) shown in Eq. 2 is more convenient to measure and reveals the same properties as the volumetric coefficient for an isometric material.

$$\alpha_V = \frac{1}{V_0}\left[\frac{dV}{dT}\right]_{n,p} \qquad \alpha_L = \frac{1}{L_0}\left[\frac{dL}{dT}\right]_{n,f} \qquad (2)$$

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Thermomechanical (TM) measurements are sensitive to changes in the structure of polymers [3]. TM measurements are often performed using a modulated force (mf-TM) to obtain storage and loss modulus, and the damping factor [4, 5]. The glass transition and other lower temperature transitions are revealed by mf-TM as a peak in the loss modulus or damping factor. The Tg is obtained as an inflection in the coefficient of thermal expansion (CTE) measured by static force (zero force or contact force only) thermo-mechanometry (sf-TM) [6, 7]. CTE is usually measured by linear expansion rather than volumetric expansion. The technique of sf-TM can provide additional information when a modulated temperature (mT) is superimposed upon the linear temperature programme [8, 9]. Application of mT-TM gives an average dimension change, a modulated dimension change, a reversing dimension change (in-phase with the temperature modulation) and a non-reversing dimension change (out-of-phase). Experimental conditions for mT-TM will be discussed including scans performed on heating and cooling.

A second scan gives a better defined sf-TM curve with a distinct Tg inflection as expected for this type of experiment, though the Tg appeared to have moved to higher temperature [7]. A mT-TM scan gave a non-reversing dimension change curve that contained the distortions. The reversing dimension change curve showed a distinct Tg inflection with linear regions either side of Tg that was used to calculate the linear CTE [9]. A new sample of the same epoxy–amine was used to perform a mT-TM scan with heating–cooling-heating–cooling programme so that changes in the resin were able to be compared between reversing and non-reversing dimension change in a first heating and second heating, and also in the complementary cooling situation [8]. These measurements were repeated for the epoxy–glass fibre and epoxy–carbon fibre, vinyl ester–glass and unsaturated polyester–glass composites.

Information about thermal ageing, post-cure and relaxations is observed [10, 11] when a material is heated in a first scan. These phenomena are separated using mT-TM where the linear CTE and glass transition inflection are observed in the reversing dimension change, and recovery from thermal ageing, relaxations and post-cure are observed in the non-reversing dimension change [12]. These non-reversing events will not be present in a subsequent cooling scan or a second heating scan. However, the elimination of ageing and completion of cure will be expected to change the linear CTE and Tg in the cooling or second heating scans. Thus, parameters for the original and the fully cured relaxed material are made available from the repeated scans.

Relief of internal stress may occur on first heating, since such stress can be relaxed upon heating above the Tg.

Internal stresses often arise from cure processes—an example is the differential shrinkage of the resin during cure in a bed of fibres that have no shrinkage but immobilize some of the resin by adsorption [11]. Examples that demonstrate these variables have been chosen from epoxy–amine resin recently cured without post-cure, epoxy–amine glass fibre composite with post-cure but with relaxation approaching equilibrium, and advanced epoxy carbon fibre aerospace composite fully cured and equilibrated.

The aim was to characterize various thermoset resins, including epoxy, vinyl ester, unsaturated polyester, in glass and carbon fibre composites, using mT-TM. An objective was to use multiple heating and cooling scans to confirm reversing and non-reversing character of events. Lissajous figures were used to evaluate the linearity and steady state of the modulation response. The mT-TM technique is important because it is a bridge between DSC and other force-related TM techniques. Unlike other TM techniques, mT-TM does not disturb the test specimen, other than by temperature change since the probe rests upon the specimen with only contact force. DSC is based upon heat capacity whilst mT-TM is based upon thermal expansion coefficient, both thermodynamic quantities. Since its introduction [8, 9], mT-TM has received little attention in the literature whilst it can be applied to measurement of Tg and the underlying thermal expansion independent of thermal relaxations, creep and other kinetic changes to materials under investigation.

Experimental

The epoxy resin with and without chopped glass fibres was diglycidylether of bisphenol-A (DEGEBA) cured with diethylene triamine (DETA), 0.5 v/v glass fibres; this epoxy composite was prepared by manual lay-up on an aluminium sheet pre-treated with mould release agent, with consolidation using a grooved roller and cured under ambient temperature for 10 h, then post-cured at 373 K for 1 h. The epoxy resin used with carbon fibres was tetraglycidyl diamino diphenyl methane (TGDDM) cured with diphenylsulfone diamine (DDS), 0.5 v/v woven carbon fibres; this composite was prepared in an autoclave by the Aerospace Composites Laboratory, RMIT University. The vinyl ester resin was a bisphenol-A diglycidyl dimethacrylate with styene reactive monomer and 0.4 v/v glass fibres. The unsaturated polyester was a poly(propylene phthalate-co-maleate) with styrene reactive monomer and 0.4 v/v glass fibre; the vinyl ester and unsaturated polyester composites were prepared using the same method as for the epoxy glass fibre composite.

Static force thermomechanometry (sf-TM) and its modulated hybrid were performed with a force of 0.01 N

with heating and cooling from 300 to 470 K at 2 K min^{-1}. Scans were performed on first heating and cooling, followed by a second heating and cooling in some cases using TA Instruments Q400EM Thermomechanical Analysis (TMA). mT-TM resolved dimension changes that were in-phase (reversing) and out-of-phase (non-reversing) with the modulated temperature programme [12–15]. Specimens with a height of ~2 mm were heated from 353 to 423 K at a rate of 0.5 K min^{-1}. A sinusoidal modulation with an amplitude of 2 K and a period of 180 s was superimposed on the temperature ramp. The temperature range was chosen to bridge the Tg range of the resins and the relatively slow temperature ramp rate was required because of the sample size, sensor mass and high temperature amplitude that must approach thermal equilibrium. A high temperature amplitude was required to provide a dimension change magnitude that could be measured with precision. The conditions were selected after testing other ramp rates, temperature amplitudes and periods. A cooling ramp, followed by a second heating and second cooling ramp, was performed on each material.

mf-TM was performed using a Perkin-Elmer DMA 8000 in single cantilever mode (span 12 mm) with a frequency of 1 Hz, a deformation of 10 μm and heating from 353 to 423 K at a heating rate of 2 K min^{-1}. Specimen dimensions were accurately measured using test pieces 20 × 8 × 1.2 mm.

Results and discussion

A recently cured epoxy–amine exhibited a sf-TM curve with several distortions and the location of Tg unclear. A second scan gave a better-defined sf-TM curve with a distinct Tg inflection much as expected for this type of experiment, though the Tg appeared to have moved to higher temperature. A mT-TM scan gave a non-revering dimension change curve that contained the distortions. The reversing dimension change curve showed a distinct Tg inflection with linear regions either side of Tg that were used to calculate the linear CTE. A new sample of the same epoxy–amine was used to perform a mT-TM scan with heating–cooling-heating–cooling programme so that changes in the resin were able to be compared between reversing and non-reversing dimension change in a first heating and second heating, and in the complementary cooling situation. These measurements were repeated for the epoxy–glass fibre and epoxy–carbon fibre composites.

Figure 1 shows a continuous heating sf-TM scan of the epoxy–glass composite under a contact maintaining force. The first heating scan shows a negative coefficient of thermal expansion before Tg, that then leads to expansion after Tg. A relaxation expansion occurred just before Tg.
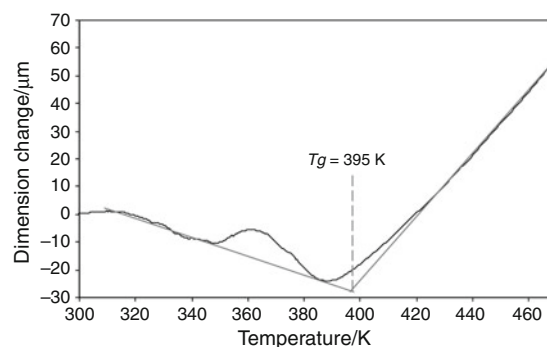

Fig. 1 Epoxy–glass fibre linear coefficient of thermal expansion measured using sf-TM, showing Tg
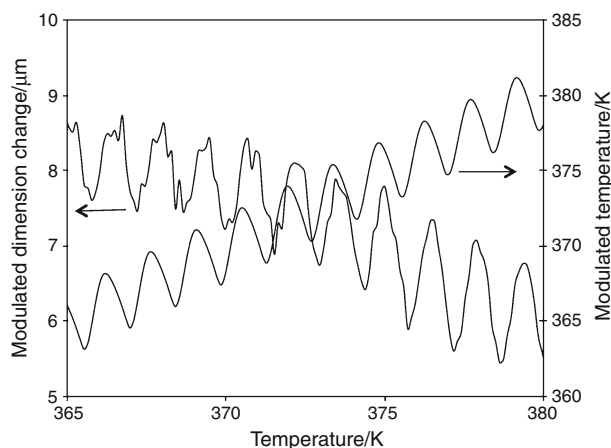

Fig. 2 Expanded mf-TM curve of epoxy–glass fibre showing modulated temperature and modulated dimension change

The Tg is accurately depicted though there is uncertainty in the gradient of the curve at temperatures lower than Tg and the true CTE is not expected to be negative. Other thermal events such as stress relief and post-cure must be added to the CTE.

Figure 2 demonstrates the sinusoidal modulated temperatures and consequential modulated dimension change that is lagging, that is showing a positive phase angle. The modulated temperature curves are smooth and follow exactly the programme, whilst the modulated dimension changes exhibit deviations from the sinusoidal cycles, the most obvious being the phase lag [9, 12] though some irregular response or noise is evident. The deviations have been observed to be greater for highly filled and cross-linked polymers than for amorphous thermoplastics [14]. The deviations in the modulated dimension change response are reflected in Lissajous figures where lack of overlay of successive cycles was observed.

The modulations shown in Fig. 2 lead to reasonably uniform curves in Fig. 3a. The total dimension change curve in Fig. 3a shows similar shrinkage to the curve in
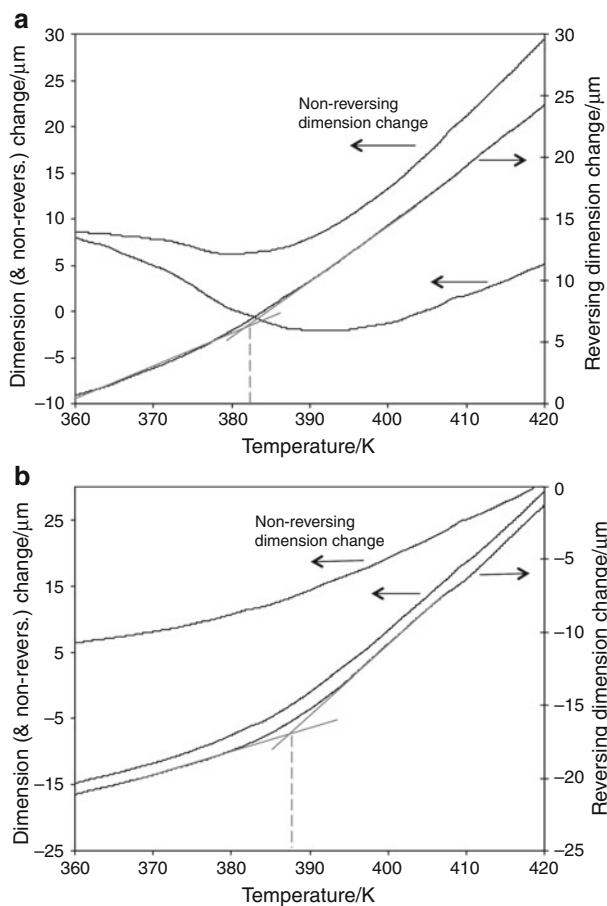
Fig. 3 Epoxy–glass fibre mT-TM curves showing dimension change and the reversing and non-reversing resolved dimension changes, **a** first heating cycle, **b** cooling cycle (construction lines indicate Tg)

Fig. 4 Epoxy–glass fibre mT-TM curves showing dimension change and the reversing and non-reversing resolved dimension changes for second heating ramp (construction lines indicate Tg)

Fig. 1. This shrinkage behaviour is paralleled by the non-reversing dimension change curve, indicating that the changes leading to shrinkage are due to a non-equilibrium structure formed during cure in the presence of a high volume fraction of glass fibres that absorb and limited mobility in the resin during cure. Thermal ageing usually leads to a volumetric expansion or enthalpy endotherm associated with Tg [3]. Most of the changes observed in Fig. 3a are revealed in the total and non-reversing dimension change curves. The reversing curve has been resolved from extraneous events and shows a continuous volume expansion with temperature, with an inflection followed by an increase gradient after Tg. The coefficients of linear thermal expansion and the Tg can be precisely measured from the reversing dimension change curve [12].

Following from the heating scan, a cooling scan was performed (Fig. 3b). The cooling scan starts in the rubbery region where structural equilibration is rapid. In Fig. 3b the total and reversing curves are parallel and close so that most of the structural change is reversing. The glass transition region from the reversing curve is similar to that
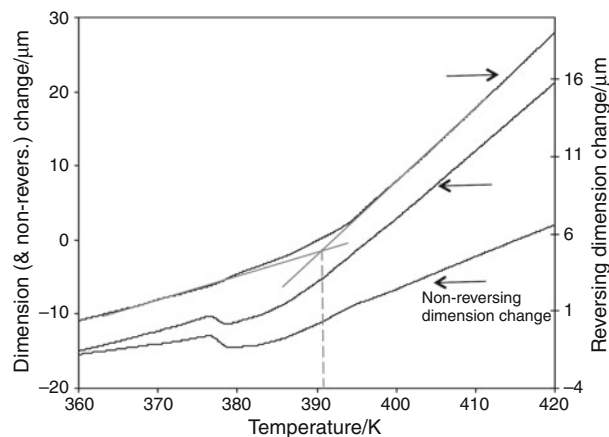
from Fig. 3a, except that the value of Tg has moved to higher temperature. The high temperature (423 K) and relatively long time for the scan (0.5 K min^{-1}) has allowed the epoxy resin to undergo further cure. The composite used for these experiments was post-cured only at 373 K. An advantage of mT-TM is that it can be performed under heating or cooling programmes [8]. Scans over a relatively higher temperature range such as those used in this article allow efficient temperature modulation without external cooling, other than an aluminium block for heat dissipation. Our Q400EM operates from a cooling bath that can be used with any added coolant, but for long scans, the coolant must be periodically replenished, which is a problem if liquid nitrogen needed to be used.

Second heating and cooling scans were performed on the epoxy–glass composite, though only the second heating scan is shown (Fig. 4). The reversing curve in Fig. 4 is similar to those in Fig. 3, though Tg has been shifted to a still higher temperature than that in the cooling curve of Fig. 3b. Though the previous scan was a cooling scan, the resin has been subjected to an overall longer time at elevated temperatures. The total and non-reversing curves show an unexpected relaxation in the temperature region before Tg. Each curve exhibits a positive slope, linear CTE, before the Tg in contrast to the first heating scan.

Lissajous figures are used for assessing the relation between temperature and dimension modulations. Traditionally, Lissajous figures are formed by the interaction of two impulses of different frequencies and/or amplitudes and phases. The major axis of the ellipse represents energy storage whilst the width represents energy dissipation [8, 9, 12]. Lissajous figures for the epoxy–glass composite are shown in Fig. 5. Figure 5a shows the differential temperature–dimension interaction for the first heating ramp where the modulations do not display steady state. The first
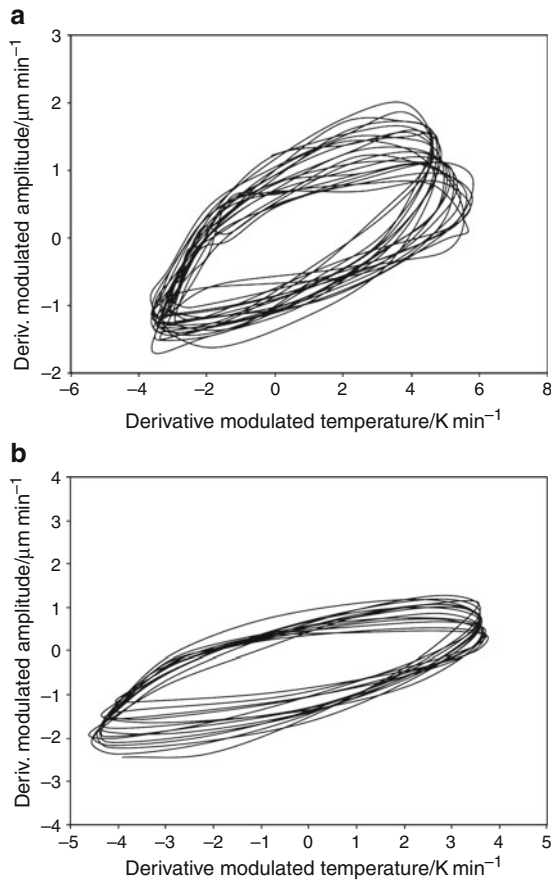
a

b

Fig. 5 Epoxy–glass fibre mT-TM Lissajous figures showing overlay of repetitive cycles and phase angle direction
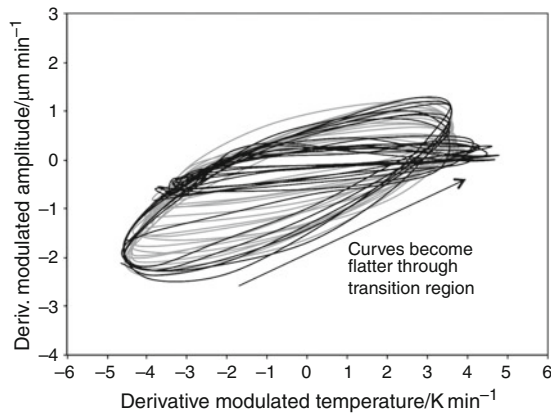

Fig. 6 Epoxy–glass fibre mT-TM Lissajous figures showing overlay of repetitive cycles and phase angle direction over a heating cycle with red showing linear region Pre-Tg, and blue showing linear region post-Tg

cooling cycle shown in Fig. 5b displays reasonable overlay of repeating cycles, similar to Lissajous figures obtained from modulated DSC data.

A Lissajous figure for a complete heating scan is shown in Fig. 6. The cycles in Fig. 6 appear to be widespread until
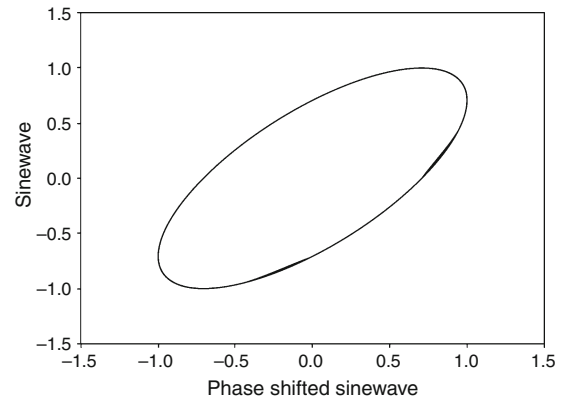

Fig. 7 Calculated Lissajous figure with amplitudes set to 1.0, and using a similar phase angle to the mT-TM data
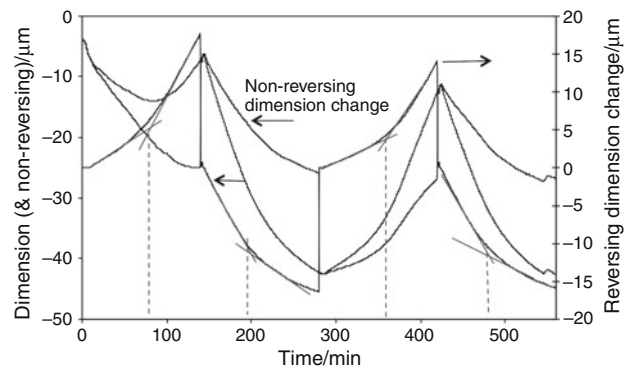

Fig. 8 Unsaturated polyester resin–glass fibre mT-TM showing repeated heating–cooling scans against time (construction lines show linear coefficient of thermal expansion tangents and Tg)

the regions before, during and after Tg are highlighted. The cycles shown with tilted ellipse are for the linear portion of the glassy state that display a larger phase angle, whilst the flattened cycles shown in black are for the linear portion of the rubbery sate. The grey-coloured cycles represent migration between the glassy and rubbery state regions during the transition region.

Figure 7 displays a calculated Lissajous figure with similar parameters to the glassy state first heating data. The figure was calculated to show many cycles, though with this theoretical data the cycles are exactly superimposed upon each other, in contrast to the experimental data.

A full first and second heating–cooling time data set for the cured glass fibre-filled unsaturated polyester resin is shown in Fig. 8 for the total, reversing and non-reversing dimension changes. Tangents are shown on each of the reversing curves to highlight the linear regions and the Tg at the intersections. Multiple scans are useful to compare changes to a material between the first and second heating scans, and better equilibrated results are obtained using the cooling scans since the Tg is approached from the rubbery

regions where relaxation times are rapid relative to the scan time. The first heating scan begins with contraction of the total and non-reversing dimension changes with the total dimension change increasing after Tg, whilst the non-reversing dimension change continued to contract.

Each of the following cooling cycles shows dimension contraction as expected. The second heating scan shows expansion for each of the three curves. Only the reversing dimension change curves show distinct linear regions with an inflection at Tg. The mT-TM technique is useful for extracting thermal expansion coefficient information and Tg measurement with minimal disturbance of the material, in contrast to modulated force measurement [4]. The material must be heated; however, there is no force to distort the material and no concern about operating within a linear viscoelastic region since no deformation is applied. The criteria of linear thermal response and steady-state conditions required for mT-DSC are applicable in the mT-TM measurement conditions.

The data for the first heating cycle is isolated in Fig. 9 where tangents are shown for the linear sections of the reversing curve, and the Tg is identified at 389 K. The Tg is due to polystyrene segments that are crosslinked by maleate units along the polyester chain. The total dimension change has an unexpected curve shape with a minimum indicating a contraction before Tg; however, this shape is due to the superposition of the reversing and non-reversing components. The non-reversing dimension change shows a continual shrinkage, maybe due to further cure or molecular relaxation. The reversing dimension change shows the expected thermal expansion before Tg that increases after Tg, and the Tg is precisely defined by the intersection of the two tangents to the linear regions.

The epoxy–graphite composite shown in Fig. 10 differed from the results described to this point. The temperature modulation was performed with the same scan programme as for the other composites presented. A modulated dimension change was obtained, though when resolved a continuously increasing reversing dimension change was obtained with a zero non-reversing dimension change. A glass transition was not revealed. The epoxy-graphite was a much more tightly packed composite than those with glass fibres, with finely woven graphite cloth.

A mf-TM experiment (Fig. 11) demonstrated that the Tg was detectable and in a temperature range of about 393–413 K [16]. Figure 11 shows that mf-TM is more sensitive for detection of transitions than mT-TM, as expected because the instrument will apply as much force as necessary and available to obtain the set deformation, whereas mT-TM thermal force is small and relies upon detection of a small thermal expansion that will be limited by crosslink density and filler composition.

The vinyl ester glass fibre composite results for mT-TM scans are shown in Fig. 12. Most of the dimension change upon first heating (Fig. 12a) is non-reversing as shown by the closely overlapped total and non-reversing dimension change curves. Tg occurred between 373 and 378 K, which

Fig. 10 Epoxy–graphite mT-TM curves showing lack of non-reversing response with Tg undetected
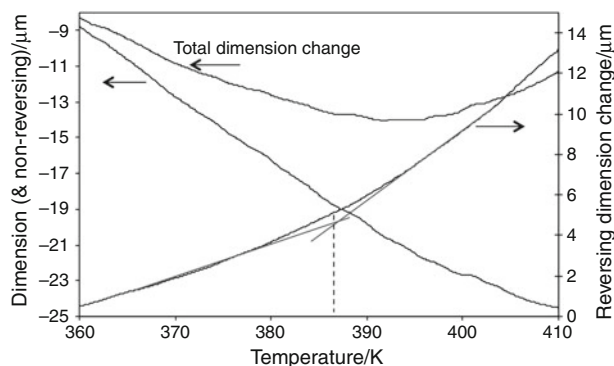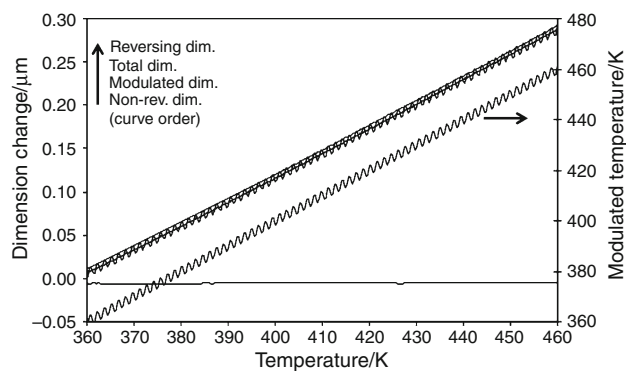
Fig. 9 Unsaturated polyester resin–glass fibre mT-TM curves showing dimension change and the reversing and non-reversing resolved dimension changes for second heating ramp (construction lines indicate Tg)
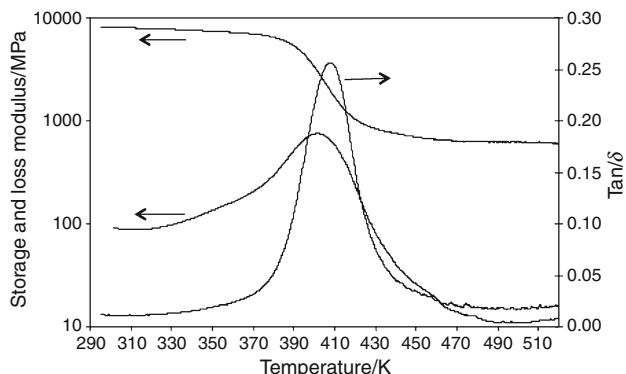
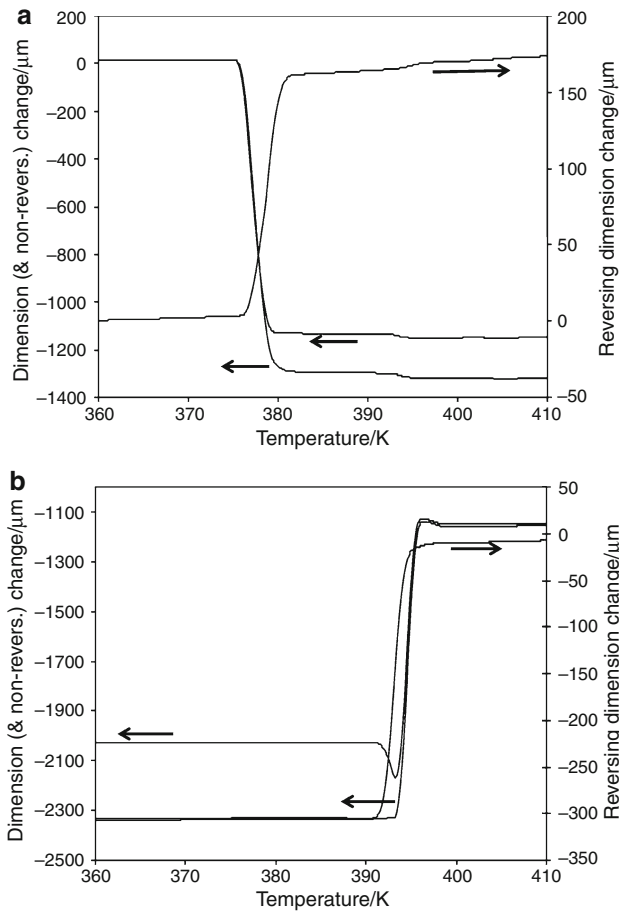Fig. 11 Epoxy–graphite composite mf-TM scan I single cantilever mode at 1 Hz and 2 K min^{-1} using a Perkin-Elmer DMA 8000 instrument

Fig. 12 Vinyl ester–glass fibre mT-TM showing a step-inflection in each curve, **a** first heating cycle, **b** first cooling cycle

Fig. 13 Vinyl ester–glass fibre mT-TM showing a step-inflection in each curve for this second heating cycle

reflects the crosslinking by polystyrene units with methacrylate terminal units on the vinyl ester structure. In this case Tg is accompanied by a sharp dimensional decrease after a nearly constant glassy state thermal expansion region. A further small transition occurred at 393 K. The reversing dimension change curve is the opposite with a sharp, though much smaller, increase at Tg and an increase at the 393 K transition.

The step change in dimension is not a function of internal stress or cure related change because the first cooling curve (Fig. 12b) shows the same step change in reverse. The cooling step change temperature increased to 393 K, the same temperature of the small inflection in the first heating curve. In the cooling cycle the total and reversing curves parallel each other until below Tg where further relaxation is reversing. The reversing curve exhibited relaxation at a lower temperature of about 2 K compared with the total and non-reversing curves in the cooling cycle.

The vinyl ester was similar in structure to the unsaturated polyester in that both are cured with styrene polymerisation. The vinyl ester was end linked and each vinyl
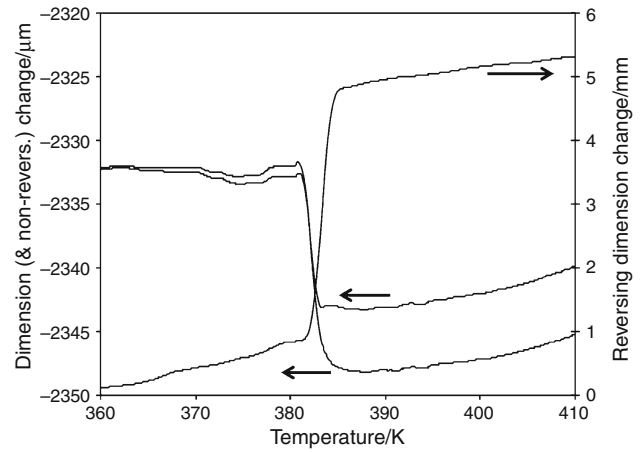
ester pre-polymer was tetra-functional. The unsaturated polyester contained di-functional branch points randomly along the polyester chain due to maleate units. The sharp change in dimension is not understood or apparent from comparison of the two resin systems.

A second heating cycle for the vinyl ester composite is shown in Fig. 13. The changes in each dimension change curve were similar in appearance to those of the first heating cycle except they were of much lower magnitude. Tg in the second heating curves occurred at 383 K, a slightly higher temperature than for the first heating curve but lower than for the cooling curve. Some baseline irregularities are visible in the total and non-reversing curve, whilst the reversing curve in Fig. 13 (similar to Fig. 12) was smooth throughout.

Conclusion

The reversing and non-reversing contributions to the coefficient of linear thermal expansion have been resolved using mT-TM for thermoset composites including epoxy, vinyl ester and unsaturated polyester. The reversing curves enabled the measurement of the expansion coefficients of the glassy and rubbery phases and the Tg, independent of other thermal events. The non-reversing curve revealed changes including further cure, relaxations and stress relief during heating. The non-reversing changes, such as residual cure and thermal relaxations, may contribute to changes in the reversing properties and such changes are revealed by a second scan. Measurements conducted upon cooling were informative since the glass transition region was approached from the rubbery state where equilibrium was occurring much faster, and appropriate for measurement of Tg. Without modulated temperature measurement of linear coefficient of thermal expansion and Tg were obscured by

the other events. The modulated temperature technique enabled us to obtain the measurements at low scan rates or over long times where the response of differential scanning calorimetry would not be detected. Response of mT-TM, where there is minimal interference with the test specimen, lacked sensitivity for detection of Tg in a high modulus epoxy carbon fibre composite where mf-TM was required. The nature of mT-TM is that the probe does not disturb the test specimen, and therefore it rests upon the specimen and senses dimension changes caused by temperature change.

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