

CONTROLLING THERMAL EXPANSION BY USE OF COMPOSITE MATERIALS

A. Kelly¹ and L N McCartney²

¹Department of Materials Science and Metallurgy, University of Cambridge, Cambridge UK

²National Physical Laboratory Teddington UK

ABSTRACT

The theory of the thermal expansivity of composite systems, both particulate and fibrous is reviewed. In the particulate case exact calculations and theoretical bounds are compared. The system SiC/Al is investigated in detail. For this and other particulate systems the range of values obtainable is limited to the range of values shown by the components. Examples of the use of particulates to obtain specific values for use in electronic applications are given. In order to obtain expansivities outside the values of the components it is necessary to use fibrous arrangements and laminates are shown to be particularly useful. The use of laminates containing fibres and matrix, both having positive expansivities, to obtain a negative expansivity is described in detail. An effective system requires control of the internal stresses within the composite because these limit the temperature range over which expansivity may be controlled.

1. INTRODUCTION

Thermal expansion of a monolithic solid is a third order effect. It arises from and is explained by knowledge of the anharmonic (cubic) terms in the governing equations for the oscillation of the component atomic nuclei in the material. It is an important fundamental parameter. The phenomenon is of great importance in engineering as thermal expansivity often limits the precision of devices and this limitation becomes more important as we move into the sphere of nano-materials and micro-electro-mechanical-systems (MEMS).

The range of experimental values for the linear expansivity (α) is relatively small – a factor of some 5000 times- between the lowest and the highest value. This may be compared with electrical resistance which varies by a factor of 10^{23} or with Youngs modulus (E) or thermal conductivity (both about 10^6 times). Normally α is positive and for metals values lie between $2 \cdot 10^{-6} \text{ K}^{-1}$ and $30 \cdot 10^{-6} \text{ K}^{-1}$.

In engineering practice uncontrolled thermal expansion is usually a nuisance and so precludes extreme precision of many devices. It is also a major factor in producing thermal shock. Very low expansivity is of particular importance in space applications of composites where extreme ranges of ambient temperature are difficult to avoid. e.g. [1]

In many applications in engineering the ideal material would be one showing zero expansion over a considerable range of temperature and with the concurrent ability to alter other thermomechanical properties e.g. Stiffness, dielectric constant etc.

The control and manipulation of values of the CTE are extremely important in the design of electronic packaging. Here there are advantages in producing a material with a CTE close to that of silicon, namely $4 \cdot 110^{-6} \text{ K}^{-1}$. Also there is the need to control interfacial stresses due to CTE mismatch in multilayer capacitors consisting (often) of alternate layers of Ag Pd and BaTiO₃. [2,3,4]

An excellent comprehensive summary of theoretical and experimental work on particle and fibre reinforced composites with special reference to metallic matrix composites has been given in the book by Taya and Arsenault [5]. The admirable survey of theory and experiment up to 1989 will not be repeated here. Taya and Arsenault also deal in passing with methods

of measuring CTE. Romeo and Fulla [6] have described the experimental precautions necessary to obtain accurate values of CTE in fibre composites.

In this review we shall first deal with particulate composites and then with those containing long fibres.

2.PARTICULATES

The reversible thermal expansion coefficient of arrays of particles in an elastic matrix when both phases are isotropic is well understood theoretically Arridge (7), has given an exact mathematical treatment for the thermal expansion coefficient of two particular regular arrays of spherical particles in a matrix without voids- both components being isotropic. The numerical examples given are appropriate to silicon carbide particles in aluminium. Aluminium is in fact closely isotropic.

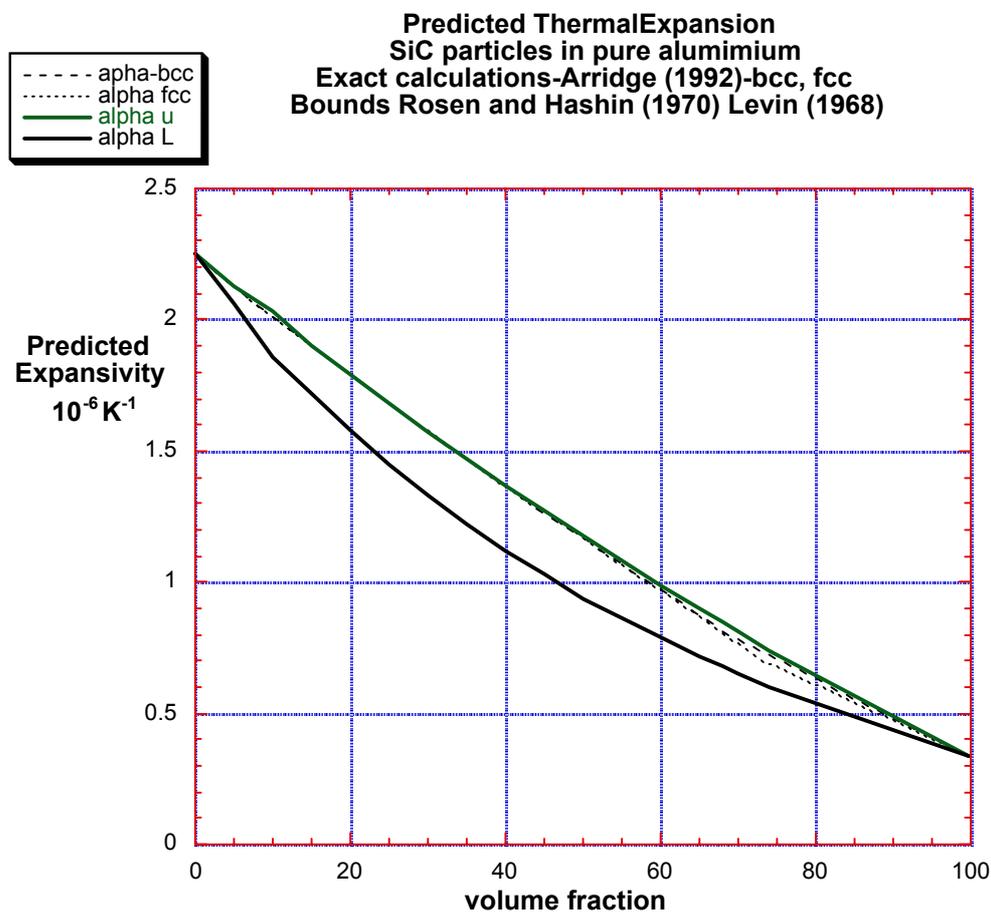


Fig 1. Predicted thermal expansion coefficients for a particulate array

. The result is shown in Fig 1 where the upper and lower bounds for a random array of spherical particles given by Rosen and Hashin [8] see also Levin [9] and evaluated for the SiC/Al system are plotted against volume fraction together with Arridge's exact theory for both a face centred and a body centred array of particles. Exact treatments require, of course, specification of the array. For these arrays the volume fraction cannot exceed 68% and 74%, respectively. The values for the exact calculation lie between the upper and lower bounds and, as may be seen from the figure, are barely distinguishable from the upper bound in this case.

We may conclude therefore that calculations of the CTE when both components are elastic is quite secure.

The internal stresses in a particulate composite also be estimated (with some precision) from Arridge's calculation. Using the values given by Arridge of α_{Al} of $22.5 \cdot 10^{-6} K^{-1}$, α_{SiC} of $3.3 \cdot 10^{-6} K^{-1}$, $E_{Al} = 72.5 GPa$, $\nu = 0.35$, $E_{SiC} = 483 GPa$, $\nu = 0.19$.

(There is an obvious mistake in the identification of these in the paper),

The values of the interfacial radial stress which is, in this case closely equal to the principal stress calculated by Arridge for the two distributions for volume fractions up to V_f of 50% are shown in the second and third columns of Table 1.

Table 1 Calculated values of interfacial Stress

Vf (%)	Stress-bcc MPa/ ⁰ K	Stress-fcc MPa/ ⁰ K	Stress Shell Model MPa/ ⁰ K	Stress MPa $\Delta T = 50^0$
10	1.56-1.62	1.57-1.61	1.59	79.50
15	1.44-1.55	1.42-1.54	1.40	70.
20	1.31-1.51	1.28-1.48	1.37	68.5
25	1.19-1.48	1.12-1.44	1.27	63.5
30	1.05-1.48	0.96-1.41	1.17	58.5
35	0.89-1.52	0.78-1.42	1.08	54
40	0.73-1.59	0.62-1.46	0.98	49
45	0.55-1.70	0.44-1.54	0.89	44.5
50	0.35-1.87	0.25-1.67	0.80	40

Also shown are approximations to the principal radial stress calculated from the spherical shell model Hashin [10]. The spherical shell model while exact for small values of volume fraction is less so as V_f increases. It provides an average stress which may be compared with the range of stresses predicted by the calculations for defined arrays. The largest predicted stresses appear at locations where the particles are closest to one another, hence along cube diagonals for the bcc and along face diagonals for the fcc case. The interesting fact emerges that the largest stresses, for both exact arrays change rather little as the volume fraction changes, being almost as large at 5% as at 50% in the fcc case. For both exact arrays the minimum stress decreases as V_f increases. This implies that the decrease in **mean** stress with increase in volume fraction shown by the shell model is probably correct. Of course it must be borne in mind that in all of these calculations the particles are assumed to be spheres which shape will minimise the stress. The mean stress for a temperature change of 50^0 calculated from the spherical shell model is shown in the final column of the table.

These internal stresses are very important clearly for a number of reasons. If the aim is to fabricate a composite having a specified value of CTE then in-elastic effects such as plastic yielding must be avoided, since if plastic flow occurs during a temperature excursion the CTE will not show reversible behaviour.

A second important reason is that resin matrix and metal matrix composites are both usually made by a process which involves cooling to room temperature –the temperature of employment- from some elevated temperature. If both components behave elastically during this change of temperature then internal stresses will arise at the boundaries between the constituents and elsewhere and these influence the yielding behaviour of the composite Ledbetter and Austin [11] studied.. internal strain in an SiC–Al particle reinforced composite by x-rays using the same values for the constants as Arridge.. $5 \mu m$ particles in Al 6061 with an estimated initial yield stress of 274 MPa were used. The intent was to measure the internal stresses attendant upon fabrication. They confirmed that the stress tensors were approximately hydrostatic, for a 30 volume % composite. being compressive within the

particles and tensile in the matrix...The final fabrication treatment will have resulted in a lowering of temperature from about 436K to 300C, so to a change of about 130⁰. They estimated an effective stress (von Mises) of 490MPa –higher than the assumed yield stress for the aluminium. Using Arridge’s figures we obtain a value of 152MPa for a value of ΔT of 130⁰. It is clearly well established that aluminium alloys which contain particles of SiC which are intended to lower the CTE while raising the Young modulus will function effectively over a temperature range of perhaps 100C but not a great deal more. Nonetheless they can be very useful by lowering the CTE while increasing the stiffness.

At the time of their writing – 2003 – electronic packaging materials based on particulates where the thermal expansion coefficient has been controlled are silicon carbide reinforced aluminium, beryllia particle reinforced beryllium and metal matrix composites such as invar/silver (silvar) and invar/copper (cuvar). see refs 2,3,4 The properties of some of these materials are shown in Table. 2. A particularly intriguing material appears in the final row..

Table 2 Particulate Systems for use in electronics

System	Density Mgm ⁻³	CTE 10 ⁻⁶ K ⁻¹	Young Modulus GPa	
BeO 40/ Al60	2.3	7.5	317	
SiC 40/ AL 60	2,9	12.1	134	
Invar65/ Ag 35	8.8	6.5	110	
NiTi 35/ Cu 65		4.1		

Mavoori and Jin [12] combined a NiTi alloy (Ni-44Ti) which can be produced in a form showing a negative expansivity of as much as $-2110^{-6} K^{-1}$, with copper, so as to obtain a composite with a CTE to exactly match that of silicon; copper being chosen as the matrix because of its high thermal conductivity Few details are given and it is not at all clear how stable the composite CTE is after repeated thermal cycling The negative CTE in Ni-44Ti seems to be due to the interaction of the volume change accompanying a change of crystal structure and the shape memory effect.

Gaohui Wu et al [13] have concentrated upon obtaining composites with large volume fractions of reinforcement. Using squeeze casting with AlSi alloys they obtained values of the CTE between 0 and 100C of 6.9, 7.8 and $9.710^{-6} K^{-1}$ with $V_f = 0.7, 0.7,$ and 0.6 using Al 20% Si in the first case and Al 12% Si in the latter two cases. These figures are quite consistent with Arridge’s calculations above.

The addition of β -eucryptite to an Al (6061) alloy to lower the CTE and in addition adding aluminium borate whiskers to increase the strength has been investigated by Wang et al [14]. The CTE of $11.10^{-6} K^{-1}$ with a combined volume fraction of eucryptite and borate is no lower than that predicted for 40 volume % of SiC particles.

Copper containing SiC particles has been studied recently by Shu and Tu. They obtained volume fractions up to 74% but none of the published curves, as I understand them, showed absence of hysteresis [15]

Fig 2 illustrates that there is still advantage to be sought in increasing the range of expansivities attainable by particulate composites

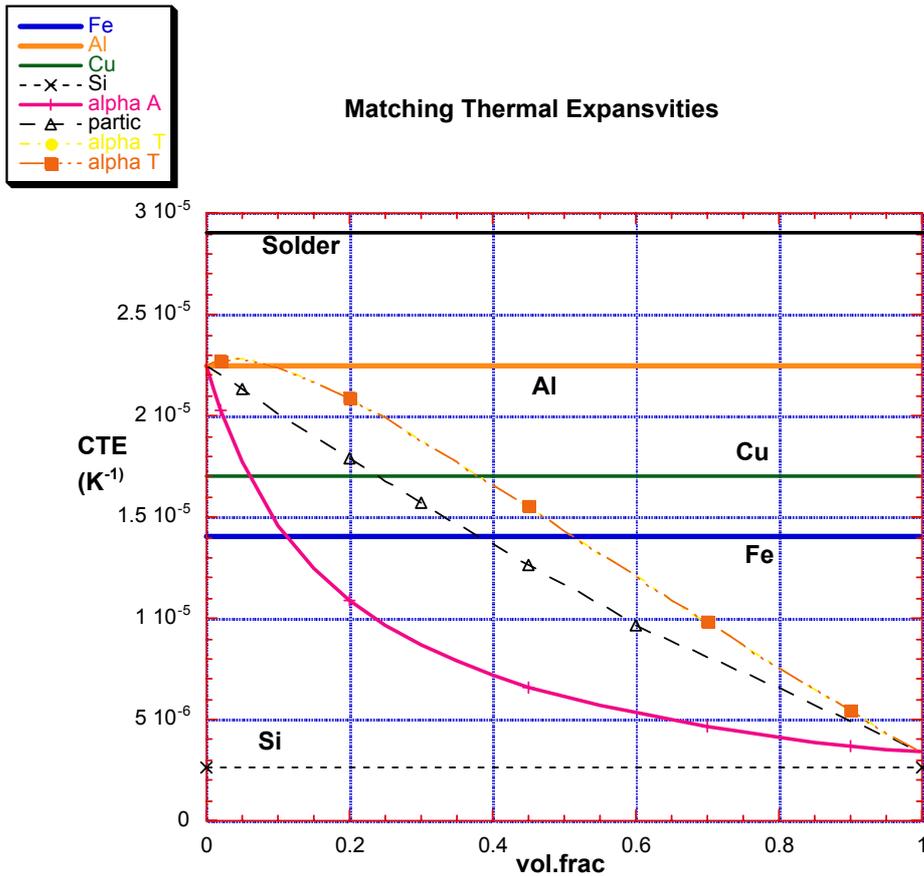


Fig 2 Comparison of values of CTE found in particulate AlSi with those of silicon and solder

3.UNIDIRECTIONAL FIBRE COMPOSITES

Calculation of the thermoelastic properties of aligned composites are described in detail in McCartney [16] and the relations given there are what we have used. The starting point is the axial concentric cylinder model of Rosen and Hashin-see Hashin [17] for a summary-supplemented by use of Christensen and Lo's [18] concentric cylinder model to find the transverse shear modulus. Details are given by McCartney and the results for the evaluation of CTEs validated by Li- as explained in McCartney [16].

Fig 3 illustrates a comparison between a particulate material and one containing long fibres of the same material in this case SiC in aluminium.

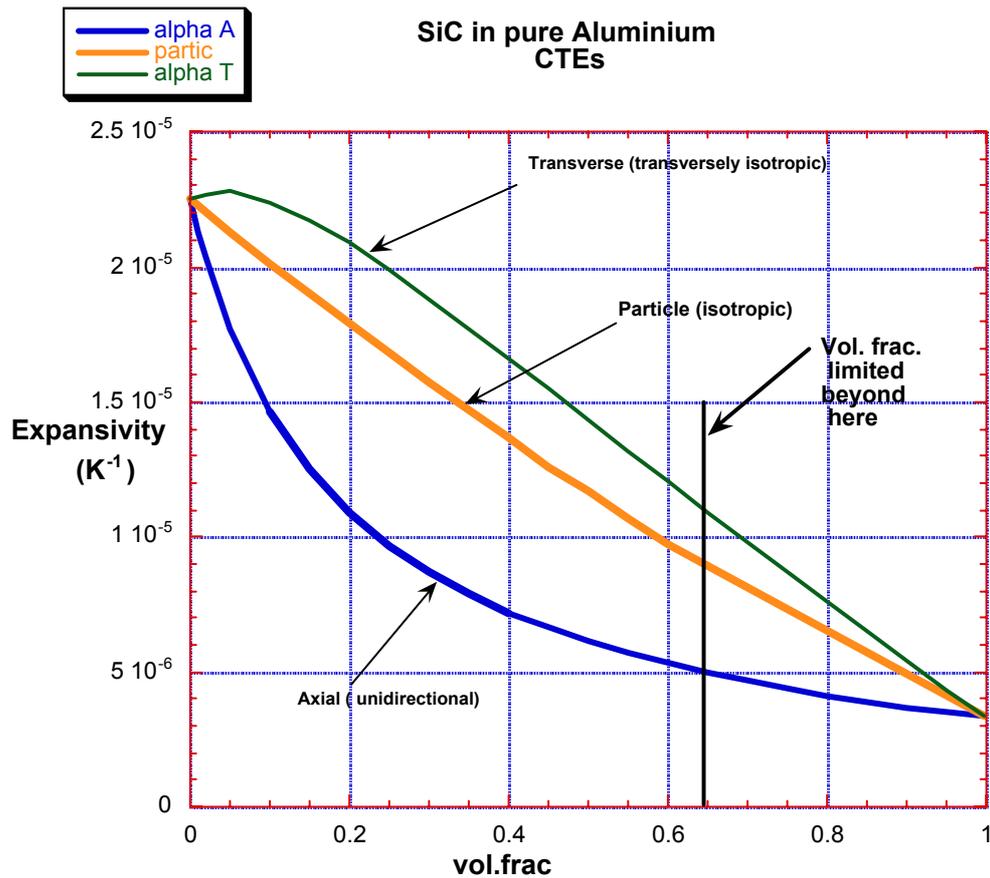


Fig 3 Predicted expansivities of particulate and (aligned fibre) AlSiC.

The values have been calculated as discussed above.

Where the aim is to decrease the expansivity in a single direction say from $22.5 \cdot 10^{-6} \text{ K}^{-1}$ to $10 \cdot 10^{-6} \text{ K}^{-1}$ this would be accomplished in the most expeditious manner by introducing about 24% of aligned fibres and in that direction. The elastic modulus would be increased from 70 GPa to 183 GPa. If an isotropic CTE in 3-D is required then 60 volume percent of particles are needed and the modulus, would be increased to 145 GPa in this case. Precise 3-D isotropy is not often required. In real practical applications, 2-D isotropy will suffice. In the SiCAl case a value of $10 \cdot 10^{-6} \text{ K}^{-1}$ - isotropic in the plane - would be found if a volume fraction of a little less than 70% were introduced. And in this case the isotropic stiffness, in the plane would be about 195 GPa - hence a little stiffer than that obtained with the particles.

If only 2-D isotropy is required this analysis implies that it is better to use aligned fibres than particles if decrease in CTE coupled with increase in stiffness were wanted. In this case it is worth noting that volume fractions up to 80% can be obtained with aligned fibres of a given diameter, while random particle arrangements of greater than about 60% are difficult to make in practice with particles of a single average size. Elliott Kelly and Windle [19] have considered how to obtain greater densities of packing. Larger densities of packing up to in fact greater than 90% is possible but only if a range of particle sizes is available with mean diameters of the populations differing by an order of magnitude.

These results emphasize the point that no value of the CTE shown by the composites so far discussed lies outside the range of values included between those of the two constituents. The only exception being that at small volume fractions the value of the transverse expansivity of the unidirectional composite shows a small increase above the value of the CTE of the matrix. As is well known, this arises because a stiff fibre prevents a compliant matrix of large

CTE from expanding in the fibre direction when the temperature is raised and so, due to the Poisson effect, the matrix is squeezed sideways. The effect is small and because the volume of reinforcement is also small the idea of using the effect to increase the value of CTE while at the same time increasing the lateral stiffness does not appear to be very fruitful. The concept of creating a material of large CTE coupled with a high stiffness –say a polymer CTE with a stiffness of several tens of GPa would have application in switchgear and so is worth exploring.

In order to obtain values of CTE outside the span of values covered by the values of the two constituents one must consider laminates. These we now consider and in particular how to obtain a negative CTE while using constituents each of which shows a positive CTE-hence clearly outside the relevant span. In addition we can obtain values of the CTE which exceed that of either constituent

4.LAMINATES

Balanced symmetric laminated fibre composites of the type designated $[\pm\theta]_{4s}$ made of glass fibres in a polypropylene matrix may show a negative expansion coefficients in the laminate plane, Ito et al [20].Landert et al [21] have pointed out that there is a necessary connection between the presence of a negative expansivity and the simultaneous appearance of a large value of the in-plane axial Poissons ratio.The physical reason for the latter is rather easy to see. Consider the fibres in the laminate to be represented by a capital X- somewhat elongated in the axial (i.e. vertical) direction on the page. If the composite is then stretched in this axial direction it is clear that the two sets of fibres will be encouraged to move into the same vertical direction by a “scissoring” motion –a larger than normal Poissons ratio in the axial direction is then expected and in deed observed. The conditions for a very large value are that the tensile modulus of the individual plies in the longitudinal direction i.e., parallel to the fibres, be very much larger than the shear modulus in that direction. Many fibre composites composed of stiff fibres in a resin matrix meet these conditions and large Poissons ratios are observed. [21]

Now consider the thermal expansion of the $[\pm\theta]_{4s}$ laminate. Provided the thermal expansivity of the fibre in its axial direction is a good deal smaller that that of the matrix then when the temperature is raised the matrix will be unable to expand in the longitudinal direction in each ply and will be forced to expand sideways resulting again in a scissoring action between the fibres forming the two arms of the X. However, now the X is encouraged to open in the vertical direction and to expand sideways. The result is a smaller than normal expansion coefficient in the axial (vertical) direction. It is, of course again necessary for the shear modulus in the axial direction of each ply in the composite to be much less than the tensile modulus in the direction parallel to the fibres.

Provided the above conditions are well satisfied, a negative expansivity may be observed in the axial direction of the laminate without its being necessary for either of the individual components of the composite (fibre or matrix) to itself show a negative expansivity. However, the necessary condition that the expansivity of the fibre in the axial direction be a good deal less than that of the matrix will naturally be more severely fulfilled if the fibre has itself a negative expansivity in the longitudinal direction, while that of the matrix is positive. Indeed, in the cases cited above of large Poissons ratios in carbon fibre epoxy composites there is also observed a negative expansivity in the plane of the laminate of the type which we are considering.

Figure 4 shows predicted and experimental values for the three CTEs of a balanced symmetric laminate of Kevlar fibres in epoxy resin

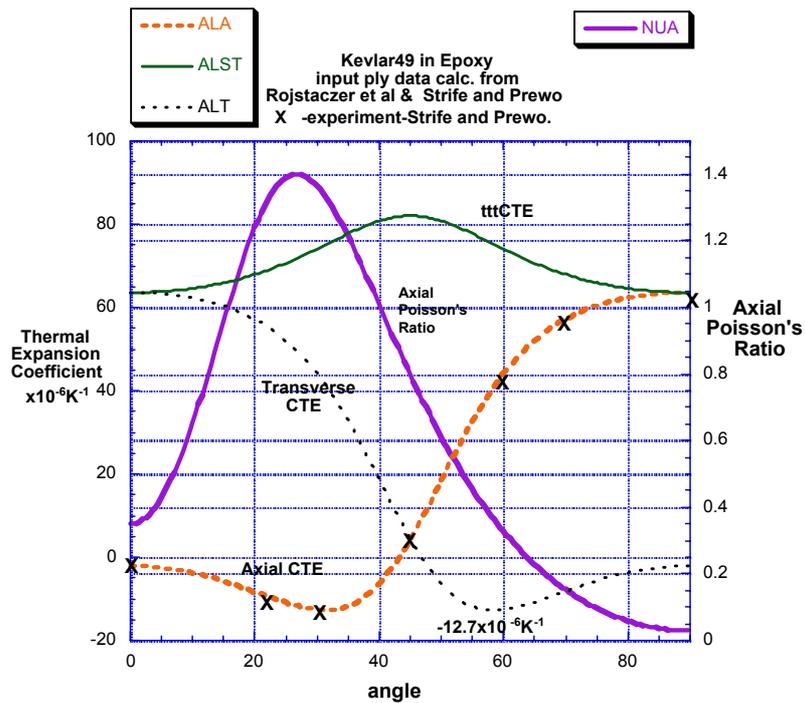


Fig 4 In-plane expansivity of Kevlar-epoxy from [22] and [23]

The range of values of the CTE of the two materials is between $62 \times 10^{-6} K^{-1}$ (resin) and a small negative value (fibre). The extreme values for the laminate consisting of a volume fraction of 50% kevlar 49 fibres are a maximum value for the through the thickness CTE of $83 \times 10^{-6} K^{-1}$ at an interfibre angle of 90° i.e. $\pm 45^\circ$ on the figure and a minimum which is a negative value of $12.7 \times 10^{-6} K^{-1}$

Table 3. Predicted expansivities of several systems

System (all at $V_f = 0.5$)	W wire in epoxy	W wire in PP	SCS 6 in epoxy	SCS 6 in PP	E glass in epoxy	Silenka glass in PP
Min. value of axial expansivity $\times 10^6 (K^{-1})$	-1.51	-5.54	-3.91	-7.97	5.69	-0.299
θ value for minimum ($^\circ$)	33	33	33	33	27	31
Max. value of Poisson's Ratio	1.93 at 24°	3.32 at 20°	1.90 at 24.5°	3.20 at 20°	0.73 at 32.5°	1.26 at 28°
E_A/E_T	20.0	54.6	19.5	53.5	4.09	10.3
E_A/μ_T	56.8	138	55.3	134	11.4	28.0
$(\alpha_T \alpha_A) \times 10^6 K^{-1}$	30.9	46	32.1	47.1	28.1	44.4

Provided the relative expansivities of fibre and matrix are as we have indicated and the relative shear and tensile moduli meet the required conditions, easily deduced from standard laminate theory -see [24], then negative expansivities will be observed in composite systems in which both fibre and matrix have positive expansivities. In order to illustrate this we have collected in Table 3 predicted values for a number of systems. using fibre materials which are isotropic in their properties Glass fibres are not very stiff so if one wishes to obtain a negative expansivity with these it will be necessary to couple the fibres with an extremely compliant matrix, such as polypropylene.

The system glass/polypropylene has been reinvestigated by Landert et al [21]. The material used for the laminates was a unidirectional prepreg tape provided by St Gobain Vetrotex (Chambéry, F). It was composed of 50 vol% of glass fibres in polypropylene confirmed by density measurements.

The experiments confirm that negative expansivities may be obtained over very small ranges of temperature and also show clearly that the material does not show stable behaviour when the temperature is changed for a number of reasons.. First the temperature range room temperature to 100C represents a very high temperature of the polypropylene matrix with respect to its melting temperature. (165 C) so 20⁰ C is 0.66 of the MP and 100 C 0.85 In much of the experimental regime the polypropylene matrix is above its quoted heat distortion temperature of 50⁰C and polypropylene has a glass transition temperature very close to room temperature.

Landert et al conclude that polypropylene is not a desirable matrix to use in a composite which is to be employed in a device to produce a negative thermal expansion coefficient or one designed to obtain a value of zero for that quantity, **at or around room temperature**. This is because its physical properties change quite markedly over the temperature range of interest and it is unable to withstand the internal stresses generated by a small temperature change without creeping and hence changing the expansivity.

Despite the difficulties shown by polypropylene as a matrix to be used at room temperature and slightly above the material does illustrate the advantage of an extremely low value of the small strain shear modulus which consequently enables one to obtain a negative or zero expansivity with a relatively compliant fibre such as glass. Other thermoplastic materials such as nylon or polystyrene or polyethylene will show the same disadvantages as polypropylene. Landert et al reason that an ideal material, could be a cross linked (or vulcanized) rubber of some type which is even more compliant than the semicrystalline or even the amorphous thermo-plastics but is much more resistant to creep—as any automobile tyre demonstrates!!.

To prove the point they made a specimen of a balanced laminate of the $[\pm\theta]_{4s}$ type consisting of rods (fibres) of invar in a polyurethane rubber matrix choosing invar which has a Young Modulus of 140 GPa and (uniquely among common metallic materials) a thermal expansion coefficient of $1.2 \cdot 10^{-6}/K$ compared with glass of $4.5 \cdot 10^{-6}/K$.

They constructed a specimen with square sectioned rods containing a nominal volume fraction of about 0.34., cured at 135⁰C and which may be used at temperatures up to 120⁰C A single specimen of the composite was prepared with the angle between the two sets of fibres of about 2×36^0 . The measured CTE of the rubber was $147 \cdot 10^{-6}/K$ —the third figure is probably not significant. On heating the composite showed no hysteresis and a reversible expansivity between room temperature and 100⁰ C. The measured expansivity in the axial direction was $-51 \cdot 10^{-6}/K$ and in the transverse direction $+81 \cdot 10^{-6}/K$. The experimental determination is sufficient to prove the point concerning the use of a cross linked rubber as the matrix. The predicted values are $-44 \cdot 10^{-6}/K$ and $93 \cdot 10^{-6}/K$ at the same angle.

The agreement is satisfactory given the relative uncertainty of the values for the very small strain elastic properties of the rubber. What is gratifying besides the vindication of the qualitative prediction is that the predicted value of the result shows that the computer

programs may be used with very large differences in the elastic moduli of the components of a composite. In this case the ratio of the moduli is a factor of 10^5 .

References

- 1 **Garibotti J F, Johnson R Jr and Cwiertyny A J** Material and Structure Approaches for large space structures. in Applications of Space Development XXXI International Astronautical Congress Tokyo (1980) Pergamon pp 191-212
- 2 **CHUNG D D L and Zweben Carl** Composites for Electronic Packaging and Thermal Management in Vol 6 of Comprehensive Composite Materials- Design and Applications A Kelly and C Zweben Edits Pergamon (2000), 701-726.
- 3 . **Chun-Hsueh and Ferber M K** Apparent coefficient of thermal expansion and residual stresses in multilayer capacitors. r Composites Part A 33,(2002) 1115-1121.
- 4 **C Zweben** Electronic Packaging and Production Volume 42 Number 9 September 2002 pp37-48
- 5 **Taya M and Arsenaul R J** Metal Matrix Composites Thermomechanical Behaviour (1989). Pergamon Press.
- 6 **Romeo G and Frulla G** Analytical and Experimental results of the coefficients of thermal expansion of high modulus graphite epoxy materials J Comp Materials 29 (1995) 751-765
- 7 **Arridge R G C** The thermal expansion and bulk modulus of composites consisting of arrays of spherical particles in a matrix with body or face centred cubic symmetry. Proc R Soc Lond A 438 (1992) 291-310
- 8 **Rosen B and Hashin Z** Effective thermal Expansion Coefficients and Specific Heats of Composite Materials Int J Engn Science 8 (1970) 157-173
- 9 **Levin V M** On the coefficients of thermal expansion of heterogeneous materials Mekhanika Tverdogo Tela 11 (1967) 88-94
- 10 Hashin Z The Elastic moduli of Heterogeneous materials J Appl Mech vol 29 Trans ASME 84 Series E (1962),143-150
- 11 **Ledbetter H M and Austin M W** Internal Strain(Stress) in an SiC-Al particle reinforced composite:an X-Ray diffraction Study Mater. Sci.and Eng 89 (1987) 53-61
- 12 **Mavoori , H and JIN S** Low Thermal Expansion Copper Composites via Negative CTE Metallic Elements JOM 50(6) (1998) 70-72
- 13 **Gaohui Wu ,qiang zhang,guoqin chen,longtao jiang, ziyang xiu** Properties of high reinforcement content aluminium matrix composite for electronic packages J, Mater Sc.: Mat in Electronics 14 (2003) 9-12
- 14 **Wang, L D Fei, W D Jiang, L S and Yao,C K** New Aluminium composite with lower coefficient of thermal expansion and higher strength J Mater Sci. 21 (2002) 737-738
- 15 **Shu K-M and Tu G C** The microstructure and the thermal expansion characteristics of Cu/SiC_p composites Mater Sci and Eng A349 (2003) 236-247
- 16 **McCartney L N** Physically based damage models for laminated composites Pro. Inst. Mech. Engrs 217 (2003) 163-199
- 17 **Hashin Z** Analysis of composite Materials – a survey J Appl Mechnics (1983) 481-505
- 18 **Christensen R M and Lo H K** Solutions for effective shear properties in three phase sphere and cylinder models. J Mech. Phys Solids 27, (1979)315 -330
- 19 **Elliott, J A Kelly A and Windle A H** Recursive Packing of dense particle mixtures Jour. Mater Sci. Letters 21, (2002)1249-1251.
- 20 **Ito, T . Sukanuma T, and Wakashima, K J. Mater. Sci. Lett. 18 (1999) 1363.**
- 21 **Landert M Kelly A Stearn RJ, Hine P J and Ward I M** *Negative Thermal Expansion of laminates J Mater Sci (2004) in press
- 22 **Strife J R and Prewo K M** Unidirectional and Bidirectional Kevlar/Epoxy Composites J. Comp Mater. 13, 264-277 (1979)
- 23 **S. Rojstaczer S Cohn D and Marom G** Thermal Expansion of Kevlar fibres and Composites J. Mater Sci. Letters 4, 1233-1236 (1985)
- 24 **A. Kelly, L.N. McCARTNEY and T.W. Clyne,** in Proceedings of the 10th European Conference on Composite Materials (ECCM-10), Brugge, June 2002, edited by H. Sol and J. Degrieck.