JOURNAL OF MATERIALS SCIENCE **39** (2004) 3563 – 3567

Negative thermal expansion of laminates

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Measurements have been carried out on the in-plane and through the thickness thermal expansion coefficients of glass polypropylene fibre composites of 50% volume fraction between room temperature and 120°C. Only in the temperature range 20° to 75°C are reproducible results obtained. It is confirmed that in-plane negative values may be obtained in specific directions. The physical reason for this and its connection with the necessary appearance of a large Poisson ratio is pointed out. The expansivity of the matrix material depends strongly on temperature. Very good agreement between the experimental values and those predicted from the properties of the two constituents is found provided that the value for the expansivity of the polyoropylene is that within the temperature range considered. It is shown that the polypropylene matrix does not provide a matrix which is stable enough in its properties to enable the system to yield consistent negative values of expansivity. An alternative system is proposed and a single experiment confirms that a negative value of the thermal expansivity of as large as -50×10^{-6} K^{-1} may be obtained. © *2004 Kluwer Academic Publishers*

1. Introduction

That balanced symmetric laminated fibre composites of the type designated $[\pm\theta]_{4s}$ made of glass fibres in a polypropylene matrix may show negative expansion coefficients in the laminate plane has been pointed out by Ito *et al.* [1] who extol the virtues of the system for its being composed of relatively cheap and easily available materials. These authors, in a later paper [2], present results to show that the matrix creeps and that the measured expansivities depend quite strongly on the temperature of measurement. As part of a program to explore the expansivities of composite materials we have repeated the experiments.

Wakashima *et al.* [3] state very clearly the algebraic conditions necessary to obtain a negative expansivity in terms of standard laminate theory (e.g., Chou [4]). They do not emphasize the physical reason for the negative value nor the very necessary connection between the presence of a negative expansivity and the simultaneous appearance of a large value of axial Poissons ratio which we now explain.

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 [5, 6].

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 these 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

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0022–2461

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.

Provided the relative expansivities of fibre and matrix are as we have said and the relative shear and tensile moduli meet the conditions, then negative expansivities will be observed in composite systems with isotropic fibre and isotropic matrix—e.g., tungsten wire in epoxy resin. 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 question then arises whether the matrix is sufficiently stable when the temperature is raised and it is subject, as it must be, to the large shear stresses occasioned by a negative expansivity when the temperature is changed more than a few degrees.

2. Experimental details

The material used for the laminates was a unidirectional prepreg tape with a thickness of 0.26 ± 0.02 mm and a width of 72 mm provided by St. Gobain Vetrotex (Chambéry, F). It was composed of 50 vol% of glass fibres and 50 vol% polypropylene confirmed by density measurements. This specific prepreg was not commercially available.

The laminates were composed of 12 plies pressed at 6.2 bar for 4 min cooled, and then cut with a diamond saw to 25 × 5 × 3 mm. This procedure was carried out accurately in order to obtain samples with a variation in length of only ±0.3 mm and with faces as parallel as possible. After cutting samples were dried for 15 min with hot air (60–70°C) and subsequently stored in sealed containers. A longer exposure at a higher temperature as has been done by Ito *et al.* [2] was not sought in order to avoid an anticipation of material changes such as for example relaxation. The measurements were carried out with a dilatometer Netzsch DIL402C in a protective atmosphere of Argon.

For the measurement of α_x (axial CTE) a Netzsch Al_2O_3 cylindrical standard of 25 mm length, the same length as the samples was used The calibration run of the through thickness measurements (α_z) was carried out with a shorter Al_2O_3 standard (5.29 mm) from Goodfellow, in order to be as close as possible to the sample thickness of about 3 mm. In all the measurements (standard and samples) two Alumina platelets were placed at the two edges of the specimen to align the latter properly and to distribute the applied force of the push rod (30 cN) uniformly over its cross-section.

Since the thermal conductivities of glass fibres and polypropylene are very low, glass fibres: 13 $Wm^{-1}\,K^{-1}$, PP: 0.2 $Wm^{-1}\,K^{-1}$, [7], the heating rate was chosen as slow as possible, in order to minimize the temperature lag (between set temperature and actual sample temperature). However, the minimum heating rate of 0.5 K^{-1} rather than 0.1 K^{-1} has been selected as a measurement with the former setting would have been too time consuming.

3. Results

TABLE I CTE values obtained from measurements below 90°C

CTE (10^{-6}/K)	0°	±10°	±20°	±30°	±40°	±90°
Axial (α_x)						
1. Heating	8.1	3.4	−0.8	−6.4	4.5	70.6
1. Cooling	10.2	6.3	2.7	−3.5	7.9	74.1
2. Heating	9.7	6	2	−4.7	6.9	72.2
2. Cooling	10.1	6.2	2.4	−3.3	7.8	73.2
3. Heating	9.8	5.9	2	−4.1	7.1	72.2
3. Cooling	10	6.3	2.8	−3.1	7.9	72.8
Average	9.65	5.68	1.85	−4.17	7.0	72.5
Average neglecting1,1	9.9	6.1	2.3	−3.8	7.4	72.6

The coefficient of thermal expansion (CTE) of different angle-plies was measured over the range of temperature: 20–120°C. In all cases the expansion on heating and contraction on cooling shows a hysteresis which is more marked the larger the temperature excursion. In the initial experiments we found a marked difference in behaviour between specimens heated only to 80° to 90° and those heated to higher temperatures. In fact the apparent value of the expansivity could change sign between these two regimes. The reasons for these difficulties (lack of reproducibility) are discussed in detail below. Because of them we therefore present here only the measured values obtained in the low temperature range. These are given in Table I and an average is presented for each of the laminates. Because of the hysteresis (small in this case) we present two averages and regard the second one in the table, which is obtained by omitting the values for the first heating cycle, as the more accurate. The heating and cooling cycles do show after the first one that the measured expansivities are reversible and therefore represent measurement of a genuine thermal expansion coefficient even if only over a small temperature range. Similar anomalous behaviour in the first cycle of thermal expansion measurements has been noted before by for example Rojstaczer *et al.* for Kevlar-epoxy laminates.

Values for the through thickness expansivity are presented in Table II. The values at 0 and ±90° result from the same measurement. It is to be noted that the measured value of the in-plane axial expansivity at ±90 is not the same as the through thickness value—the latter being the larger. This is due to the fact that the individual plies are not transversely isotropic. This was ascertained from ultrasonic measurement—the ultrasonic measurements on these specimens will be reported elsewhere.

TABLE II CTE values—through the thickness

CTE (10^{-6}/K)	0°	±10°	±20°	±30°	±40°	±90°
Through-thickness (α_y)						
Heating	72.4	63.6	86	80.1	94.1	72.4
Cooling	86.1	79.6	90.2	86.4	100.7	86.1
Average	79.2	71.6	88.1	83.3	97.4	79.2

TABLE III Properties of fibre, matrix and unidirectional composite

Material	E_{axial} (GPa)	$E_{\text{transverse}}$ (GPa)	ν_{axia}	$\nu_{\text{transverse}}$	G_{axia} (GPa)	α_{axia}	$\alpha_{\text{transverse}}$
Fibre	73	73	0.2	0.2	30.4	$5 \times 10^{-6}\ \text{K}^{-1}$	$5 \times 10^{-6}\ \text{K}^{-1}$
Matrix	1.3	1.3	0.3	0.3	0.5	$135 \times 10^{-6}\ \text{K}^{-1}$	$135 \times 10^{-6}\ \text{K}^{-1}$
Comp	37	3.6	0.24	0.35	1.43	$7.3 \times 10^{-6}\ \text{K}^{-1}$	$75.8 \times 10^{-6}\ \text{K}^{-1}$

E = Young's modulus, G = shear modulus, ν = Poissons's ratio, α = expansivity.

4. Discussion

We can predict the values of the elastic properties of the laminates from measurements of the properties of the individual constituents. We have done this using published values of the properties of the glass fibre and of the polypropylene produced by Shell. We have used published values appropriate to room tempearture for the expansivity of the glass but for polypropylene we have used the value of the expansivity appropriate to a temperature of 20 to 80°C Ogorkiewicz [9].

The values used for the two components are shown in Table III.

We utilise the very well validated NPL program PLYPROPS for predicting composite properties from those of the constituents [10] see this reference for details. The values of the engineering elastic constants are given in the row marked comp in Table III. The predicted values of the axial expansivity is 7.3×10^{-6}/K and of the transverse expansivity is 75.8×10^{-6}/K in quite good agreement with the measured values of 9.9×10^{-6} and 72.6×10^{-6}/K. The program PLYPROPS assumes transverse isotropy. The predicted values for the whole range of angles is presented in Fig. 1, together with the experimental points. The qualitative agreement for the in-plane properties is good reproducing the form of the run of the experimental points and in particular a minimum negative value of -3.1×10^{-6}/K at 31.5° compared with a measured average value of -3.8×10^{-6}/K at 30°. Also using the predicted elastic constants there is predicted a pronounced maximum in the through the thickness value of the expansivity namely 95×10^{-6}/K and quite good qualitative agreement with the form of the ttt curve. It is to be noted carefully that if we use the same elastic properties in our predictive program as are given in Table III but take the value of the expansivity for the matrix at **room temperature** of 90×10^{-6}/K, then the observed negative expansivity shown in Fig. 1 is not predicted. This is completely in line with the physical reasoning for the cause of a the negative expansivity given above- namely the difference between the axial expansivity of the fibre and the (isotropic) expansivity of the matrix is not large enough. It may be thought amusing that in order to obtain a negative value of the expansivity it is necessary to **increase** the expansivity of the matrix.

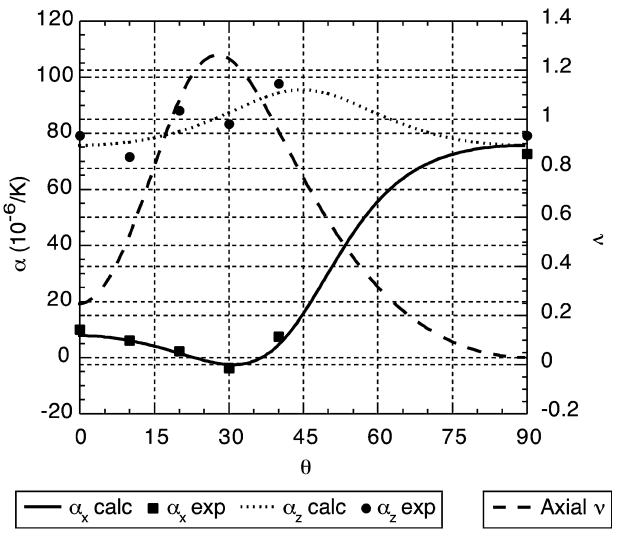

Figure 1 Predicted and experimentally determined values of the thermal expansivity in plane and through the thickness. The curve showing the large value of axial Poissons ratio is included by way of illustration.

These 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 temperaure is changed. There are a number of reasons for this. First we note that we are working in a temperature range which represents a very high temperature of the polypropylene matrix with respect to its melting temperature (165°C) −20°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 50°C (see e.g., Muzzy [11]).

Secondly we are experimenting with a matrix (polypropylene) which has a glass transition temperature very close to room temperature—quoted values are around −0°C e.g., Cowey [12] and hence that we are using a matrix in a temperature range where the physical properties including the elastic properties and the thermal expansion coefficient depend very sensitively on the exact value of the temperature. The glass transition in a thermoplastic partially crystalline polymer such as polypropylene is not at all a sharp transition and the value of the glass transition temperature itself depends quite sensitively on the degree of crystallinity.

In addition there are within the **composite** internal stresses due to (1) the difference in physical properties of fibre and matrix, (2) due to the processing and subsequent cooling when the laminates are made and (3) due to the interlaminar stresses arising from the difference in orientation of the component plies. These are not easy to quantify except for the last one. It is this interlaminar stress which is in fact responsible for the negative expansivity shown at angles of between 30 and 40. An accurate expression for it has been given by Kelly *et al.* [13]. The value depends, of course, on the difference in temperature over which the expansivity is to be measured and on the thermoelastic constants. Using the values of these given above we have calculated the interlaminar shear stress for a temperature difference of 50° when θ is around 30°. The estimated value is between 8 and 12 MPa which is of the same order as the quoted yield strength of polypropylene at 50°C of some 20 MPa [9].

We conclude that polypropylene is not a desirable matrix to use in a composite which is to be employed in a device either to produce a negative thermal expansion coefficient or 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.

5. An alternative system?

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 relativlely compliant fibre such as glass. One may then ask whether there are extremely compliant materials to be used as the matrix which are much more resistant to creep and show greater thermal stability than does polypropylene. Another thermoplastic material with the relevant thermal properties would be Peek but this is too stiff. Other thermoplastic materials such as nylon or polystyrene or polyethylene will show the same disadvantages as polypropylene. An ideal material, however 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 we have made a specimen of a balanced laminate of the $[\pm\theta]_{4s}$ type consisting of rods (fibres) of invar in a polyurethane rubber matrix. We chose invar for its similarity to glass in that it is only a little stiffer (118 GPa our measured value) compared to 70 GPa for glass and has (uniquely among common metallic materials) a thermal expansion coefficient of 1–2 × 10^{-6}/K compared with glass of 4–5 × 10^{-6}/K. We constructed a specimen with square sectioned rods of thickness 500 μm with gaps of 400 μm in one direction and 300 μm in the perpendicular direction to yield a specimen containing a nominal volume fraction of about 0.34. The spacing was not exact and we can state that the volume fraction was between 25 and 35%. The rubber was a urethane rubber of the type Monothane A60 obtained from Chemical Innovations Ltd of Preston Lancs. Monothane is "heat-pour-cure" elastomer of the polyester/polyether type containing no isocyanates. It was cured at 135°C and may be used at temperatures upto 120°C.

A single specimen of the composite was prepared with the angle between the two sets of fibres of about 2 × 36°. We measured the thermal expansion of the rubber to be 147 × 10^{-6}/K—the third figure is probably not significant. We measured the dimensions of the sample with a Laser Micrometer-heating the specimen by placing it upon an electrically heated hot plate. For a specimen with highly conducting fibres such as invar we have previously found this method to be satisfactory. On heating the composite showed no hysteresis and we were able to obtain reversible expansivity between room temperatrure and 100°C see Fig. 2. We reversed the temperature three times and obtained reproducible results.

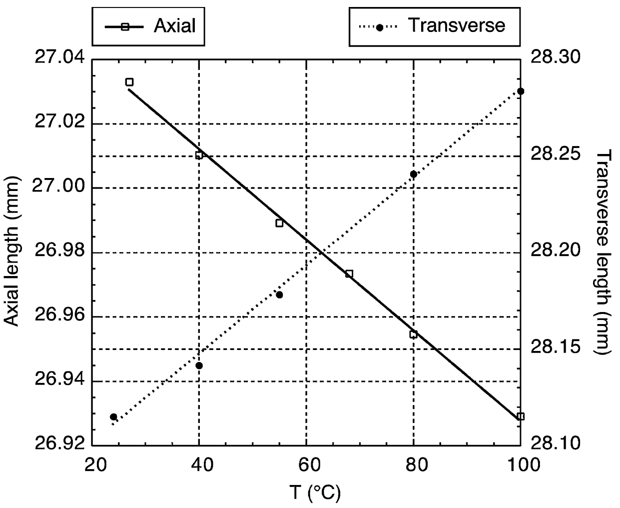

Figure 2 Change of length as a function of temperature of a specimen of a composite containing approximately 35% by volume of invar rods in urethane rubber matrix—axial and transverse directions.

The measured expansivity in the axial direction was -51×10^{-6}/K and in the transverse direction $+81 \times 10^{-6}$/K. The experimental determination is sufficient to prove the point concerning the use of a cross linked rubber as the matrix. We may attempt to predict the value to be expected. Taking the modulus of invar as 118 GPa and its Poissons ratio as 0.22 and the thermal expansivity as 2.25 × 10^{-6}/K (measured) together with the Handbook values for the urethane rubber—a tensile modulus of 1 Mpa together with a Poissons ratio of 0.495 and our measured value for the expansivity of 140 × 10^{-6}/K we predict a value of the axial expansivity of -42×10^{-6}/K together with a transverse value of 90 × 10^{-6}/K when the value of θ is 35°. If we use, in these estimates the commonly accepted (Handbook value) for the Young modulus of invar of 145 GPa then the predicted values become -44×10^{-6}/K and 93 × 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 LAMPROPS and PLYPROPS 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.

6. Conclusions

These experiments confirm that negative thermal expansion coefficients may be obtained in the plane of a suitable laminated composite provided a material with the correct thermoelastic properties is used, but that to obtain reproducible values a rubber material provides a superior matrix to that of a soft thermoplastic.

Acknowledgements

The work described here on polypropylene formed the Diploma Thesis of Martin Landert submitted to the Department of Materials Science of ETH Zurich. M.L. and A.K. are grateful to Professors M. O. Speidel, T. W. Clyne and I. M. Ward for their interest in the work.

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Received 29 December 2003
and accepted 10 February 2004