JOURNAL OF MATERIALS SCIENCE 8 (1973) 301–311

Review: The thermal expansion of composites based on polymers

L. HOLLIDAY, J. ROBINSON
Department of Polymer Science, Brunel University, Middlesex, UK

In the past 25 years, several approaches have been made to the theoretical study of thermal expansion of composites. These approaches range from the empirical, to sophisticated analyses based on applied mechanics. The alternatives are discussed in the following paper, after which the available experimental data are examined in the light of current theory. The approach of Kerner and similar workers shows reasonable success for those systems where the dispersed particles can be treated as spheres, but this case is of limited technological interest. On the other hand, the equation due to Turner most closely represents those systems in which the fillers are fibrous or plate-like in nature. Apart from particle shape, it appears that any general theory must take into account a number of physicochemical variables which have hitherto been omitted.

Attention is drawn to the possible relationship which exists between bulk modulus or Young's modulus, and thermal expansion. This has been pointed out earlier by Barker.

1. Introduction

Composites of which the matrix is a polymer are of great technological importance, obvious examples being GRP and carbon black reinforced rubbers. The essence of the science of composites can be expressed as follows:
If P_i is a given physical property, e.g. coefficient of thermal expansion or Young's modulus, and P_{mi}, P_{pi} and P_{ci} are the specific values of that property for matrix, filler and composite respectively, the science of composites then concerns the rules which relate P_{ci} as $f(P_{mi}, P_{pi})$ and the other variables of the system.

Usually these relationships are complex, although a few simple properties are additive on a volume basis and the linear mixture equation (LME) applies, i.e.

$$P_{ci} = V_m P_m + (1 - V_m) P_{pi} \qquad (1)$$

Here V_m is the volume fraction of the matrix phase, the equation representing a two-phase system. This relationship is often called the mixture rule, or the law of the mixtures, but it is neither a rule nor a law. Nevertheless it provides a useful baseline and will be called the LME in the text.

In this paper we discuss the theoretical background to the thermal expansion behaviour of composites based on polymers, and summarize previous experimental work. We adopt the convention throughout, that α represents the linear coefficient, and γ the cubical coefficient of expansion. This point is to be particularly emphasized, since considerable confusion exists in the literature where α sometimes represents the linear, and sometimes, the cubical coefficient. Whilst in an isotropic composite (with which we are largely concerned)

$$\gamma = 3\alpha \qquad (2)$$

in a fibrous composite which is uniaxially aligned, and isotropic in the two transverse directions,

$$\gamma = \alpha_{\parallel} + 2\alpha_{\perp} \qquad (3)$$

The question is, what is the relationship between γ_c, γ_m and γ_p? Polymers have a much higher coefficient of expansion than the inorganic materials, such as inorganic glass, with which they are combined, i.e. in this case $\gamma_m > \gamma_p$ and we have an opportunity to reduce the high expansion of polymers. Since polymers show viscoelastic behaviour, it is not evident whether the coefficient of expansion of composites is a time-dependent property or not.

The thermal expansion behaviour of composites has received a certain amount of theoretical study by Kerner and other workers, but there has been little systematic experimental work, and no serious attempt to check these theories on a variety of systems. Thermal expansion involves the transmission of stresses across an interface, and should thus throw light on the adhesion between the phases. In addition, the thermal expansion behaviour is closely related to the elastic properties of the phases, as Barker and others have shown. It is possible that the measurement of this simple property may enable an estimate to be made of Young's or bulk modulus of the composite, the latter being difficult to measure by simple experimental methods.

2. The status of existing theory

Consider a random two-phase composite which is isotropic. Each phase is assumed homogeneous and isotropic, and linearly elastic over a small range of volumetric strains. One phase, subscript p, is dispersed in a polymer phase, subscript m, and $\gamma_m > \gamma_p$. The composite has the cubical coefficient of expansion γ_c. No limitation is placed on the size, size distribution, shape or other aspect of the particle geometry at this stage, other than that the composite itself is isotropic.

Such a composite will be prepared at a temperature above ambient, whether thermoplastic or thermoset. In the process of cooling, each phase will shrink, but the shrinkage of the matrix will be restrained by the particles, thus setting up compressive stresses across the interface, see [1]. In time these stresses may be relieved or reduced by non-elastic deformations in the matrix.

When the composite is heated, the matrix will wish to expand more than the particles, and if the interface is capable of transmitting the stresses which are set up, the expansion of the matrix will be reduced. In the theoretical treatments to be described, it is invariably assumed that the adhesion at the interface is adequate to withstand these thermal stresses. (To provide background for this assumption, we calculate that the thermal stress for a system of polyethylene with an inorganic filler can amount to 7×10^5 N m^{-2} °C^{-1} based on Equation 10 in [7].)

There are enough experimental data scattered throughout the literature to check the validity of current theory, and this is discussed below. Meanwhile we begin by considering two situations which give useful guidelines, and then consider the existing theories in two classes.

2.1. There is no adhesion between the phases

If there is no adhesion between the two phases, if $\gamma_m > \gamma_p$ and if there are no residual compressive stresses across the interface, then on heating the composite the matrix will expand away from the particles. In this case $\gamma_c = \gamma_m$ and is independent of composition. This is shown as line AB in Fig. 1. This line, which in any case is largely hypothetical terminates at a point where the polymer ceases to be the continuous phase because of the increase in volume fraction of the other phase.

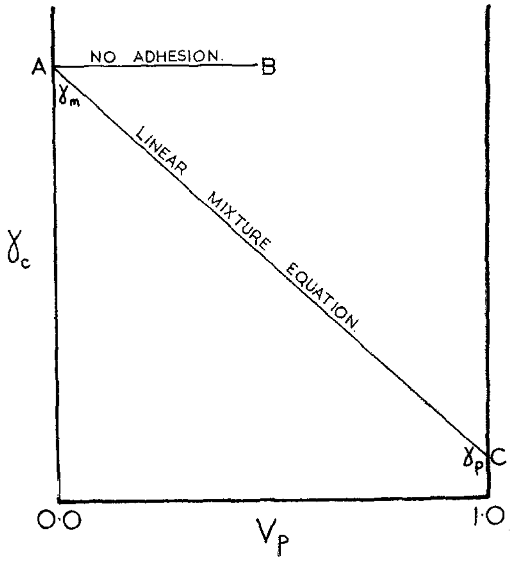

Figure 1 Two hypothetical cases of thermal expansion behaviour.

2.2. The matrix phase behaves as a liquid

The line AC shows the linear mixture equation (Equation 1 above). This can be rewritten

$$\gamma_c = \gamma_p + V_m(\gamma_m - \gamma_p) \qquad (4)$$

This line, of slope $\gamma_m - \gamma_p$, applies if the matrix behaves as a liquid, since its validity depends upon each phase expanding unhampered by the other. It will also apply fortuitously if, in the general function

$$\gamma_c = f(V_m, \gamma_m, \gamma_p \ldots) \qquad (5)$$

the derivative

$$\frac{d\gamma_c}{dV} = \gamma_m - \gamma_p$$

for a particular combination of properties. Although the linear mixture equation has no general significance, it is not uncommon to encounter systems where it applies, e.g. natural rubber filled with sodium chloride particles [2].

2.3. Theoretical equations for spherical and other particles

A dispersion of spheres has a relatively small effect on the thermal expansion of a polymer matrix as will be shown later. It has attracted the greatest theoretical interest since it presents an easier problem than an arrangement of fibres or platelets.

Alternative equations are now shown and are discussed briefly below. These assume perfect adhesion.

2.4. List of equations

Special case of spherical particles:

Kerner

$$\gamma_c = V_m\gamma_m + V_p\gamma_p - (\gamma_m - \gamma_p)V_mV_p\,\theta \quad (6)$$

Where

$$\theta = \frac{(1/K_m) - (1/K_p)}{(V_p/K_m) + (V_m/K_p) + (3/4G_m)}$$

*Blackburn**

$$\gamma_c = \gamma_p + \frac{3/2(1-\nu_p)\,V_m(\gamma_m-\gamma_p)}{\frac{1}{2}(1+\nu_p) + V_m(1-2\nu_p) + (1-2\nu_m)\,E_p/E_m\,V_p} \quad (7)$$

Wang and Kwei

$$\gamma_c = \gamma_m - V_p\,\theta\,(\gamma_m - \gamma_p) \quad (8)$$

where

$$\theta = \frac{(3E_p/E_m)V_p}{(E_p/E_m)(2V_p(1-2\nu_m)+(1+\nu_m))+2V_m(1-2\nu_p)}$$

Tummala and Friedberg

$$\gamma_c = \gamma_m - V_p(\gamma_m - \gamma_p)\,\theta \quad (9)$$

where

$$\theta = \frac{(1+\nu_m)/2E_m}{(1+\nu_m)/2E_m + (1-2\nu_p)/E_p}$$

General equations:

Turner

$$\gamma_c = \frac{\gamma_m V_m K_m + \gamma_p V_p K_p}{V_m K_m + V_p K_p} \quad (10)$$

$$\text{or} \quad \gamma_c = \frac{\gamma_m V_m E_m + \gamma_p V_p E_p}{V_m E_m + V_p E_p} \text{ if } \nu_m = \nu_p$$

Thomas

$$\gamma_c^a = V_m\gamma_m^a + V_p\gamma_p^a \quad (11)$$

where "a" may vary from -1 to $+1$

or $\ln\gamma_c = V_m \ln\gamma_m + V_p \ln\gamma_p$

if "a" is small

Cribb

$$\gamma_c = \theta_1\gamma_m + \theta_2\gamma_p \quad (12)$$

where

$$\theta_1 = \frac{K_m(K_c - K_p)}{K_c(K_m - K_p)}\quad \theta_2 = \frac{K_p(K_m - K_c)}{K_c(K_m - K_p)}$$

In these equations K represents bulk modulus, E Young's modulus, G shear modulus and ν Poisson's ratio. The other symbols are indicated in the text.

2.4.1. *The dispersed phase is made up of spherical particles*

(a) *The equation of Kerner*

Kerner [3] made the first sophisticated analysis of the thermoelastic properties of composites. The composite is assumed to be macroscopically isotropic and homogeneous, and it is assumed that the dispersed phase is in the form of grains suspended in, and bonded to, a uniform medium. The grains are distributed spatially at random, and they are spherical. The model considers an average grain surrounded by an average shell of suspending medium. Beyond this, there is the average medium with properties identical to those of the composite.

Examination of the Kerner equation shows that the third item, i.e. $(\gamma_m - \gamma_p)\,V_m\,V_p\theta$, can be considered to represent the deviation from the LME. This term disappears if $\gamma_m = \gamma_p$ or $K_m = K_p$. Furthermore, having fixed the properties of the constituent phases, the coefficient of expansion of the composite is regarded as being solely a function of the volume fraction. Any effect of particle size is neglected.

(b) *The equation of Blackburn*

Arthur and Coulson [4] refer to an equation of

---

*Corrected – this equation is quoted incorrectly in Reference 4.

Blackburn which was derived for the case of spherical particles in a matrix at low concentrations. They applied it to uranium dioxide/stainless steel cermets, where it agrees with experiment up to 10% volume of UO_2, after which it gradually diverges. This is attributed to poor adhesion in this particular case.

(c) *The equation of Wang and Kwei*

In a recent publication, Wang and Kwei [5] have investigated the thermal expansion of filled polymers. The model is similar to that used by Hashin [6] for evaluating the elastic constants of heterogeneous materials, and considers the composite to be an assemblage of tiny spherical composites each made up of a filler particle surrounded by a shell of polymer.

In the original paper, the equation is set out in terms of the linear coefficient of expansion, but for the sake of consistency we use the cubical coefficient above.

(d) *The equation of Tummala and Friedberg*

Tummala and Friedberg (7) have considered the thermal expansion of dilute binary composites where the dispersed particles are treated as elastic spheres. Examination shows that the term θ is a constant for a given system since it is not a function of the volume fraction of either phase. This gives a straight line, emphasizing that it can only be valid over a limited range. Where $E_p \gg E_m$ θ will not deviate greatly from unity, in which case the equation approaches closely to the LME.

2.4.2. *No restriction is placed on the shape of the suspended particle*

This represents the most general case and, although it cannot be treated satisfactorily at the moment, it has been considered by three workers.

(a) *The equation of Thomas*

In 1960, Thomas [8] put forward an empirical equation which is given in the above list. The exponent "a" may vary from −1 to +1, depending on the particular system. At these limits, the equation takes the following forms:

$$a = -1 \qquad \frac{1}{\gamma_c} = \frac{V_m}{\gamma_m} + \frac{V_p}{\gamma_p}$$

$$a = +1 \qquad \gamma_c = V_m \gamma_m + V_p \gamma_p$$

These are formally analogous to the Reuss and Voigt bounds for bulk moduli, and represent such wide extremes that most data can be accommodated within them. The empirical nature of the equation makes it suitable for most filled systems by the correct use of the adjustable constant.

(b) *The equation of Turner*

The earliest paper on the subject with which the authors are familiar is that of Turner [9].

The Turner equation is identical with the LME if $K_p = K_m$ (this is an unlikely situation for the case of an inorganic filter in a polymer matrix).

The basic assumptions behind the equation are that "each component in the mixture is constrained to change dimensions with temperature changes at the same rate as the aggregate (composite), and that shear deformation is negligible."

The assumption, that each material behaves like the composite is equivalent to an assumption of uniform strain. The derivation of the equation is straightforward and is based on the assumption of substantial residual microstresses resulting from the restraint of each phase on cooling. The equation satisfies the requirements:

$$V_m = 0 \qquad \gamma_c = \gamma_p$$

$$V_m = 1 \qquad \gamma_c = \gamma_m$$

An important weakness of this equation is that it states that γ_c, the coefficient of expansion of the composite, is a unique function of the volume fraction of the disperse phase (or matrix, since $V_p + V_m = 1$). Turner realized that this simplification runs counter to the experimental observation that particle shape and size can have an effect on the coefficient of expansion.

Kingery has shown [10] that the Turner equation applies to at least two ceramic systems Al/SiO_2 and W/MgO, where the samples were prepared by pressing and sintering the mixed powders. Nevertheless, this sort of agreement is the exception rather than the rule.

(c) *The equation of Cribb*

Cribb [11] adopted an approach in which no limitations are made on the shape or size of the particles. The phases are assumed to be homogeneous, isotropic and linearly elastic. The simplicity of his approach is attractive, but it converts the problem of calculating γ_c to the related question of calculating the bulk modulus of a composite in the general case. It will be seen from the list of equations that to use this equation in practice requires a knowledge of K_c or an ability to calculate K_c from the properties and volume fractions of the individual components. On the other hand, as pointed out by Cribb, it enables one to calculate K_c given a measured value of γ_c and knowing the required constants of the constituent phases. This appears to be a valuable feature.

In his paper, Cribb suggests that the bounds of Reuss and Voigt may be used to calculate K_c, but these are too far to be generally useful (see Fig. 2). As an alternative, the bounds derived by Hill [12] may be used. In Fig. 2 these are shown as the Cribb-Hill bounds. Furthermore, if the particles can be regarded as spheres, the equation of Kerner [2] may be used to calculate K_c. This takes the form:

$$K_c = \frac{(K_m V_m)/(3K_m + 4G_m) + (K_p V_p)/(3K_p + 4G_m)}{V_m/(3K_m + 4G_m) + V_p/(3K_p + 4G_m)} \quad \ldots\ldots (13)$$

A somewhat similar approach by Hobbs [11] requires the bulk modulus of a composite containing pores in place of aggregate particles. In view of this difficulty it will not be discussed further here.

3. Discussion

3.1. Thermal expansion behaviour

The foregoing summarizes the methods available for predicting the coefficient of expansion of an isotropic composite. The equations are plotted in Fig. 2 for the following hypothetical case, which is close to the nylon-silica system:

assumed that

$\gamma_m = 20 \times 10^{-5}\ {}^\circ C^{-1}$, $\gamma_p = 1 \times 10^{-5}\ {}^\circ C^{-1}$

$K_m = 4 \times 10^4$ bar, $K_p = 4 \times 10^5$ bar

ν_m 0.33, ν_p 0.17

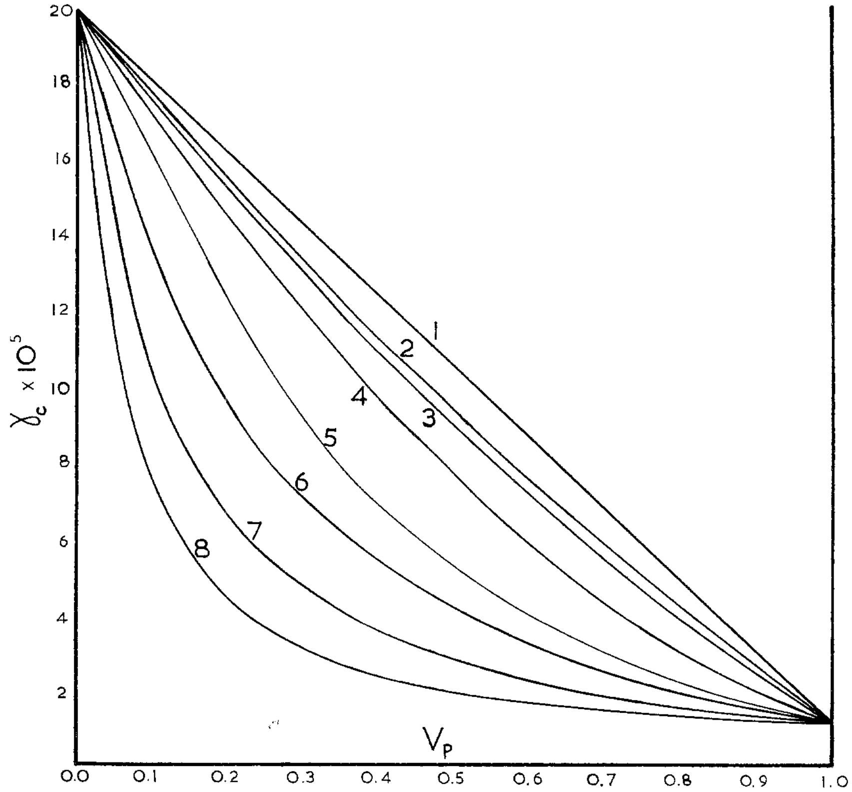

Figure 2 Theoretical graphs of γ_c versus V_p for a hypothetical composite.

Key: 1. Linear Mixture Equation, Tummala, Cribb (Ruess bound)
2. Cribb (Hill bound)
3. Kerner, Wang and Kwei
4. Thomas (a = 0.5)
5. Thomas (a = 0.1)
6. Cribb (Hill bound), Blackburn
7. Turner (using K), Cribb (Voigt bound)
8. Turner (using E), Thomas (a = 1.0).

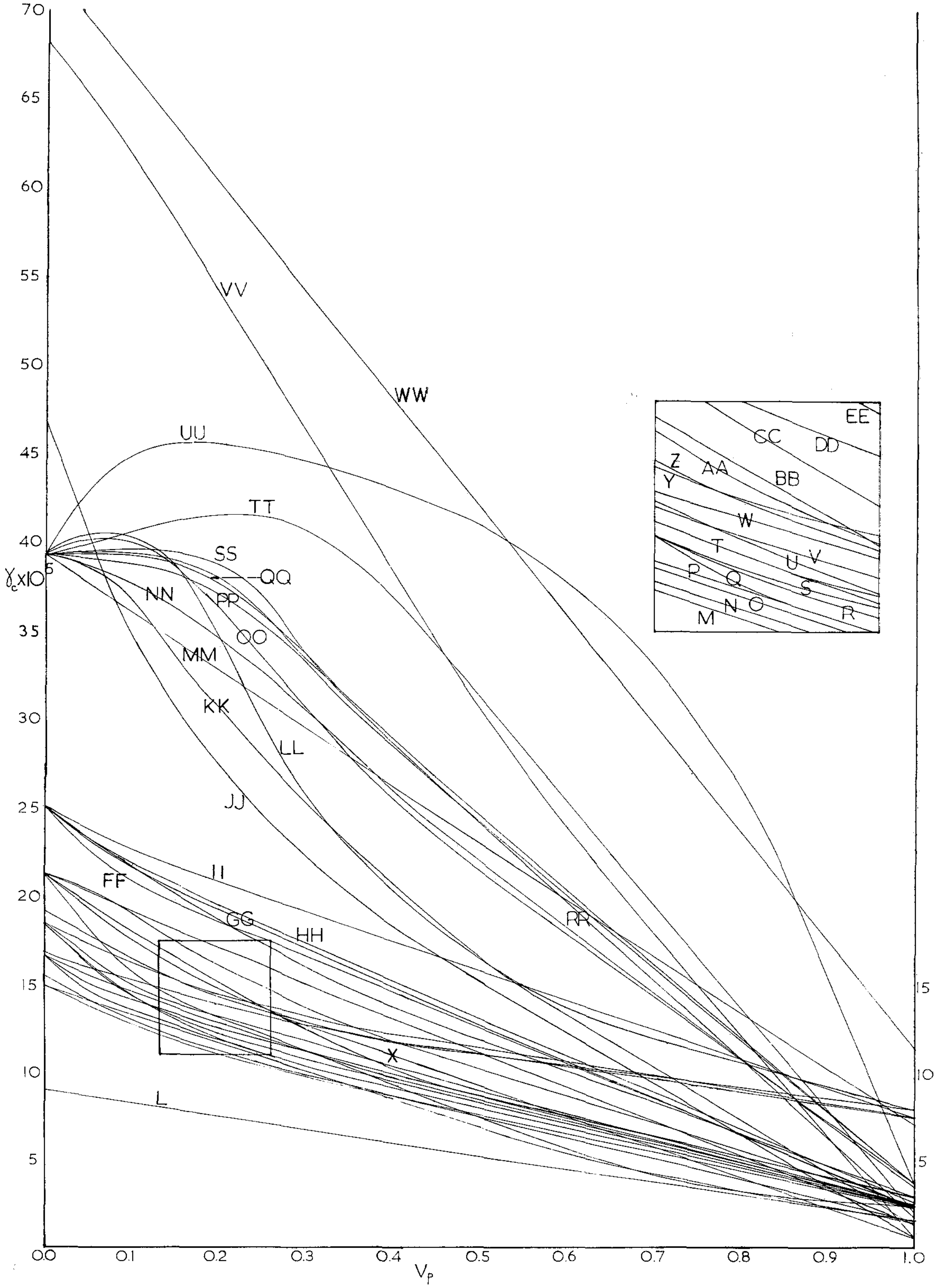

Figure 3a Coefficient of cubical expansion versus volume fraction for a range of composites containing particulate fillers. (See Table 3a for materials)

calculated from

E_m 4×10^4bar, E_p 8×10^5bar
G_m 1.5×10^4bar, G_p 3.4×10^5bar

Predictions for composites containing spherical particles are shown as curves 1, 3 and 6, which represents rather a wide spread. The general equations are bounded by curves 1 and 8, which is an even wider spread. How do these curves compare with experiment?

There is enough information scattered in the literature to enable us to gain some idea of the thermal expansion behaviour of a range of composites. The results are shown in Figs. 3a and b, the key to which is shown in Tables IA and B. For convenience the curves have been extrapolated to $V_p = 1.0$ but in general, results were only available up to $V_p = 0.5$. The main source of information is [13], but some unpublished results are also included [14]. It will be seen that the polymers quoted cover a wide range of coefficients from Styrocast polyester resin ($\gamma_m = 9 \times 10^{-5}\ ^\circ C^{-1}$) to polyurethane rubber ($\gamma_m = 72 \times 10^{-5}\ ^\circ C^{-1}$). Similarly, the fillers cover a wide range of expansivities, from glass ($0.5 \times 10^{-5}\ ^\circ C^{-1}$) to sodium chloride ($14 \times 10^{-5}\ ^\circ C^{-1}$). Although little information is available on this point, there is a wide range of shapes and sizes of fillers included. Since Figs. 3a and b are complicated, the data have been normalized and plotted in a block-diagrammatic form in Fig. 4.

The existing data can be further analysed as follows:

The various equations of Kerner etc. discussed earlier are of the following general form:

$$\gamma_c = f(\gamma_m, \gamma_p, V_m, X_m, X_p, X_c) \qquad (14)$$

Where X represents one or more of the elastic constants – bulk modulus, Young's modulus and Poisson's ratio. The differential $(d\gamma_c/dV_m)$ $V_m \rightarrow 1$

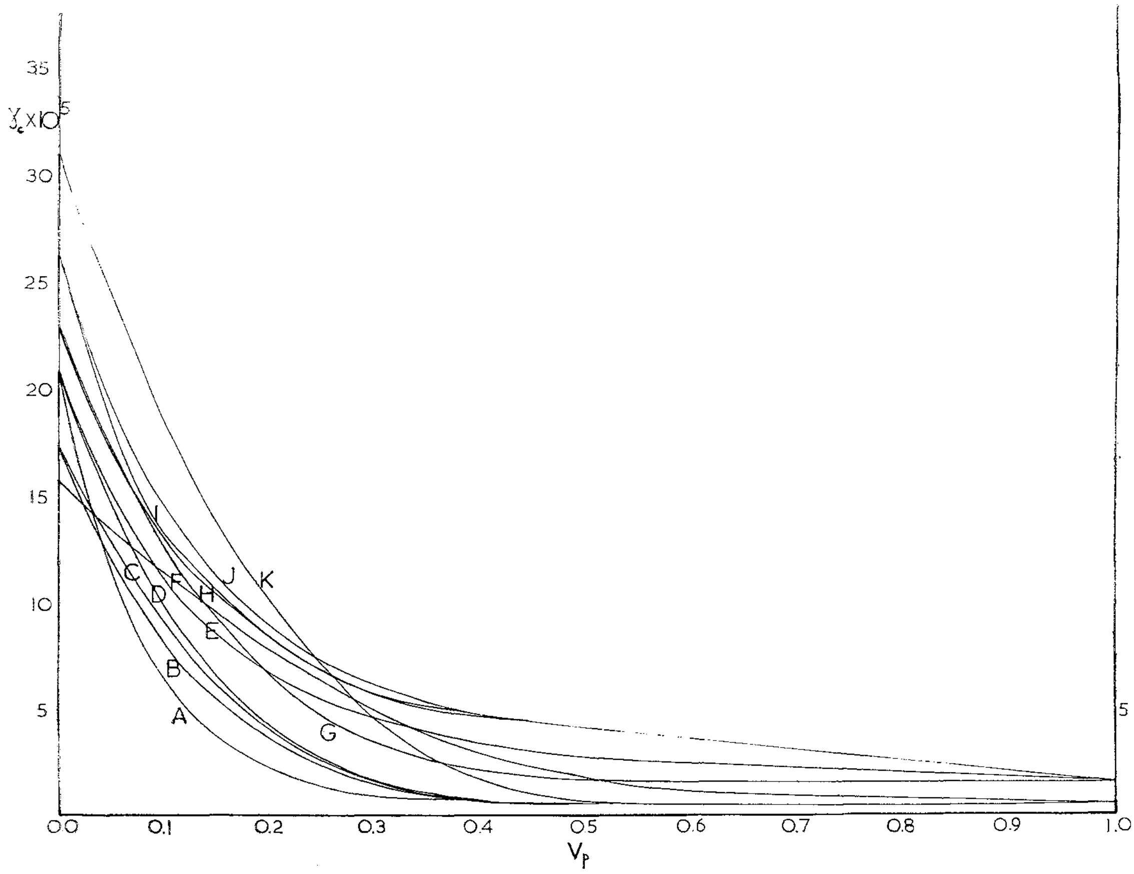

Figure 3b Coefficient of cubical expansion versus volume fraction for a range of composites containing fibrous fillers. (See Table 3b for materials).

TABLE 1A Materials code for Fig. 3a

Code	Matrix material	Filler
L	Polyester resin	Quartz powder
M	Phenolic resin	Aluminium oxide
N	Phenolic resin	Channel black
O	Epon 828	Quartz powder
P	Epon 828	Titanium dioxide
Q	Polyester resin	Calcium carbonate
R	Polyester resin	Lithium aluminium silicate
S	Epon 828	Calcium carbonate
T	Epon 828	Lithium aluminium silicate
T^1	Epon 828	Aluminium oxide
U	Epon 815	Quartz powder
V	Polyester resin	Titanium dioxide
W	Epon 828	Aluminium powder
X	Polyester resin	Aluminium oxide
Y	Polyester resin	Aluminium powder
Z	Epoxy resin	Glass powder
AA	Polymethylmethacrylate	Calcium carbonate
BB	PMMA	Aluminium oxide
CC	PMMA	Zinc oxide
DD	PMMA	Silica
EE	50:50 Epon 828-polyamide resin	Lithium aluminium silicate
FF	50:50 Epon 828-polyamide resin	Titanium dioxide
GG	50:50 Epon 828-polyamide resin	Aluminium oxide
HH	50:50 Epon 828-polyamide resin	Calcium carbonate
II	50:50 Epon 828-polyamide resin	Aluminium powder
JJ	Polypropylene	Glass powder
KK	Polytetrafluorethylene	Litharge
LL	PTFE	Boron carbide
MM	PTFE	Calcium boride
NN	PTFE	Iron powder
OO	PTFE	Calcium carbonate
PP	PTFE	Iron oxide (Fe_2O_3)
QQ	PTFE	Quartz powder
RR	PTFE	Cobalt/iron alloy
SS	PTFE	Titanium dioxide
TT	PTFE	Barium titanate
UU	PTFE	Mica powder
VV	Polyethylene (LD)	Glass powder
WW	Polyurethane rubber	Sodium chloride

In order to analyse this data, we adopt the approach that the slope of γ_c against V_m curve is a measure of the "interaction" between the two phases, and that this can be compared as follows. The data is normalized by dividing the initial slope of the curve ($1.0 > V_m > 0.8$) by the slope of the corresponding LME and the resulting parameter

$$(d\gamma_c/dV_m)/(\gamma_m - \gamma_p) \tag{15}$$

represents the slope of the curve at a low filler concentration, *and this slope is a way of characterizing a composite.* Examination of Fig. 3 shows that $(d\gamma_c/dV_m)\ V_m \rightarrow 1$ may be positive or negative, and if positive it may be greater or less than $(\gamma_m - \gamma_p)$ which is the slope of the LME.

TABLE 1B Materials code for Fig. 3b

Code	Matrix material	Filler
A	Polycarbonate	Glass fibre
B	Epon resin	Glass fabric
C	Polyester resin	Glass fabric
D	SAN	Glass fibre
E	SAN	Glass fibre
F	Phenolic resin	Glass mat.
G	Nylon 6	Glass fibre
H	ABS	Glass fibre
I	Polystyrene	Glass fibre
J	HIPS	Glass fibre
K	Nylon 6	Glass fibre

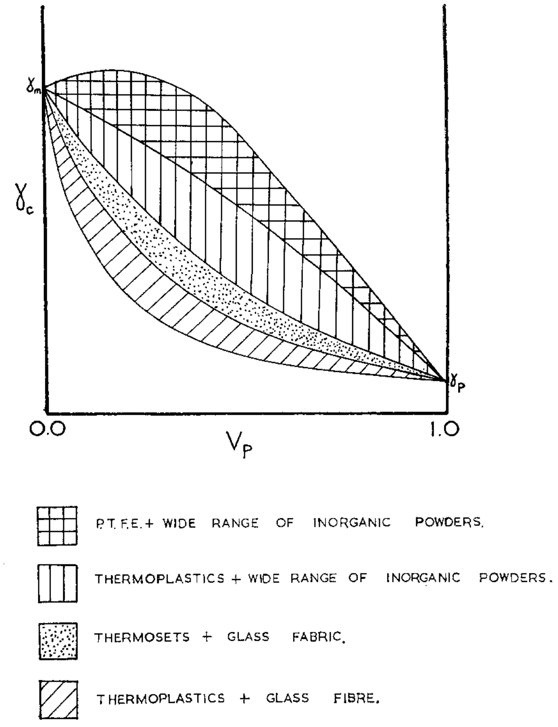

Figure 4 Normalized block diagrammatic form of Figs. 3a and 3b.

for the available data is listed in Table II. From Fig. 2, it will be seen that according to Kerner's equation (valid for spherical particles) the ratio is = 1.3 whilst according to the Turner equation the ratio is + 4.7 for one hypothetical system. The experimental data summarized in Table II shows that this ratio varies from − 0.64 to + 4.6, a very wide spread. These extremes are given by the systems mica powder, in PTFE and glass fibres in polycarbonate. A comparison of theory with experiment shows the inadequacies involved in the theoretical predictions, although Turner's equation agrees quite well with the fibre-filled composites.

Too much reliance should not be placed on the parameter listed in Table II, because all the data

TABLE II Summary of available data on thermal expansion behaviour of polymer-based composites

Matrix material	Filler	Slope of LME line S(LME)	Slope of exp. line S(EXP)	$\frac{S\text{(EXP)}}{S\text{(LME)}}$
	Fibre			
Polycarbonate	Glass	− 0.41	− 1.9	4.6
SAN	Glass	− 0.41	− 1.7	4.1
Nylon 6	Glass	− 0.52	− 2.0	3.8
HIPS	Glass	− 0.52	− 1.8	3.5
Nylon 6	Glass	− 0.62	− 2.2	3.5
ABS	Glass	− 0.47	− 1.6	3.4
SAN	Glass	− 0.41	− 1.4	3.4
Polystyrene	Glass	− 0.40	− 1.2	3.0
Polystyrene	Glass	− 0.41	− 1.2	2.9
	Fabric			
Epon resin	Glass	− 0.36	− 1.5	4.2
Polyester resin	Glass	− 0.36	− 1.4	3.9
Phenolic resin	Glass	− 0.30	− 0.77	2.5
	Metal oxide powders			
Polyethylene	Ferric iron	− 0.84	− 3.3	3.9
Polyethylene	Scandium	− 0.87	− 2.7	3.1
Polyethylene	Germanium	− 0.86	− 2.6	3.0
Polyester resin	Titanium	− 0.32	− 0.53	1.7
Phenolic resin	Aluminium	− 0.26	− 0.45	1.7
PMMA	Aluminium	− 0.37	− 0.55	1.5
Epon 828 resin	Titanium	− 0.29	− 0.40	1.4
Epon 828/polyamide resin	Titanium	− 0.46	− 0.65	1.4
PMMA	Zinc	− 0.37	− 0.48	1.3
Epon 828 resin	Aluminium	− 0.29	− 0.37	1.3
Epon 828/polyamide resin	Aluminium	− 0.46	− 0.59	1.3
Polyester resin	Aluminium	− 0.33	− 0.41	1.2
PTFE	Ferric iron	− 0.72	− 0.20	0.28
PTFE	Titanium	− 0.72	− 0.02	0.02
	Other powders			
PMMA	Calcium carbonate	− 0.26	− 0.61	2.3
Polypropylene	Glass powder	− 0.93	− 2.0	2.2
Polyester	Calcium carbonate	− 0.32	− 0.67	2.1
Polyester	Aluminium powder	− 0.22	− 0.41	1.9
Polyester	Lithium aluminium silicate	− 0.31	− 0.60	1.9
Epon 815	Quartz powder	− 0.39	− 0.64	1.6
Phenolic resin	Channel black	− 0.28	− 0.43	1.5
Epon 828	Calcium carbonate	− 0.28	− 0.42	1.5
Epoxy resin	Glass powder	− 0.37	− 0.52	1.4
Epon 828	Aluminium powder	− 0.18	− 0.26	1.4
Epon 828	Lithium aluminium silicate	− 0.28	− 0.38	1.4
Epon 828/polyamide resin	Lithium aluminium silicate	− 0.45	− 0.57	1.3
Epon 828/polyamide resin	Calcium carbonate	− 0.45	− 0.57	1.3

Table II contd.

TABLE II continued

Matrix material	Filler	Slope of LME line S(LME)	Slope of exp. line S(EXP)	$\frac{S(\text{EXP})}{S(\text{LME})}$
Epon 828/polyamide resin	Aluminium powder	− 0.35	− 0.42	1.2
Epon 828	Quartz powder	− 0.27	− 0.32	1.2
Styocast resin	Quartz powder	− 0.15	− 0.16	1.1
Polyethylene†	Glass powder	− 1.36	− 1.5	1.1
Polyurethane rubber	Sodium chloride	− 1.22	− 1.4	1.1
PMMA	Silica	− 0.39	− 0.40	1.0
PTFE	Calcium boride	− 0.64	− 0.66	1.0
PTFE	Powdered iron	− 0.72	− 0.46	0.64
PTFE	Quartz powder	− 0.76	− 0.15	0.20
PTFE	Cobalt/iron alloy	− 0.72	− 0.11	0.17
PTFE	Chalk	− 0.62	+ 0.08	− 0.01
PTFE	Boron carbide powder	− 0.76	+ 0.12	− 0.02
PTFE	Barium titanate powder	− 0.74	+ 0.23	− 0.31
PTFE	Mica powder	− 0.72	+ 0.46	− 0.64

Information from [13] apart from † which comes from [14].

used are not equally reliable. Nevertheless the following points can be made.

(a) It is possible to reduce markedly the thermal expansion of isotropic plastics by the use of the correct filler. The greatest effect is caused by glass fibres and fabrics.

(b) Generally speaking, powders show a smaller effect but there is a considerable spread in the results.

(c) The behaviour of PTFE is strikingly unusual.

(d) The thermal expansion of composites in which the filler is fibrous is closely predicted by Turner's equation.

(e) Several equations especially those of Kerner, and Wang and Kwei apply quite well to those matrices containing spherical filler particles.

There are indications that the existing theoretical approaches summarized above and exemplified by Fig. 2 ignore idiosyncratic features of real systems, such as particle size and shape, interfacial area, polarity of polymer and particles etc. This is seen by comparing Figure 2 with Figure 4. The best approach will take account of the physicochemical and shape factors involved.

3.2. Thermal expansion and elastic constants

In two papers [15] Barker demonstrated an approximate relationship between elastic moduli and thermal expansivities. Apart from a small number of exceptions, the following equation is valid:

$$E\alpha^2 \simeq 15 \text{ Nm}^{-2}\,^\circ\text{C}^{-2} \qquad (16)$$

The probable error bounds lie at $E\alpha^2$ values of 7.5 and 24 Nm^{-2} °C^{-2}, the materials which conform to this equation being called "main sequence" substances. In this equation, α is the coefficient of linear expansion. Among the numerous examples plotted by Barker are 24 plastics, six of which are composites. For an isotropic and homogeneous solid it should be possible to write:

$$E\gamma^2 \simeq 135 \quad \text{Nm}^{-2}\,^\circ\text{C}^{-2} \qquad (16\text{a})$$

since $\gamma = 3\alpha$ under these circumstances. Furthermore since

$$K = \frac{E}{3(1 - 2\nu)}$$

for isotropic solids, the following approximate relationship will apply:

$$3K(1 - 2\nu)\gamma^2 \simeq 135 \text{ Nm}^{-2}\,^\circ\text{C}^{-2} \qquad (17)$$

and if ν is a constant for the materials under consideration, then $K\gamma^2$ = constant, an equation analogous to Equation 16. This possibility is suggested in Barker's second paper. It is also possible to calculate K_c from γ_c according to Cribb's equation, given basic data on the components.

Finally, there is evidence in the literature [16, 17] of a relationship between bulk modulus and hardness, so conceivably there is a relationship between hardness and coefficient of expansion for the composites under discussion.

References

1. K. L. LOEWENSTEIN. in "Composite Materials". Ed. L. Holliday (Elsevier, Amsterdam, 1966) p. 156 *et seq.*
2. C. W. VAN DER WAL, H. W. BREE, and F. R. SCHWARZE, *J. Appl. Polymer Sci.* **9** (1965) 2143.
3. E. H. KERNER, *Proc. Phys. Soc.* **B69** (1956) 808.
4. G. ARTHUR and J. A. COULSON, *J. Nuclear Matls.* **13** (1964) 242.
5. T. T. WANG and T. K. KWEI, *J. Polymer Sci.* **A2** 7 (1969) 889.
6. Z. HASHIN, *J. Appl. Mech.* **29** (1962) 943.
7. R. R. TUMMALA and A. L. FRIEDBERG, *J. Appl. Phys.* **41** (1970) 5104.
8. J. P. THOMAS, General Dynamics Corporation, Fort Worth Rep. No. FGT 2713 of 22 December 1960.
9. P. S. TURNER, *J. Res. Nat. Bur. Stand.* **37** (1946) 239.
10. W. D. KINGERY, *J. Amer. Ceram. Soc.* **40** (1957) 351.
11. J. L. CRIBB, *Nature* **220** (1968) 576. D. W. HOBBS, *ibid* **222** (1969) 849.
12. R. HILL, *Proc. Phys. Soc.* **A65,** (1952) 349, see also Z. HASHIN, *Appl. Mech. Rev.* 17 January 1964.
13. A. GOLDSMITH, T. E. WATERMAN, and H. J. HIRSCHHORN, "Handbook of Thermophysical Properties of Solid Materials" (Pergamon Press, Oxford). K. WILMES, *Kunstoffe* **58** (1968) 9.
14. L. HOLLIDAY and R. CAROLL, unpublished data.
15. R. E. BARKER JUN, *J. Apppl. Phys.* **34** (1963) 107. *Idem, ibid,* **38** (1967) 4234.
16. J. N. PLENDL and P. J. GIELISSE, *Phys. Rev.* **125** (1962) 828.
    J. N. PLENDL, S. S. MITRA, and P. J. GIELISSE, *Phys. Stat. Sol.* **12** (1965) 367.
17. L. HOLLIDAY and W. A. HOLMES-WALKER, *J. Appl. Polymer Sci.* **16** (1972) 139.

Received 15 February and accepted 18 May 1972.