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The elastic properties in bulk and shear of a glass bead-reinforced epoxy resin composite

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A description is given of a new method for the measurement, using a single specimen, of the bulk, shear, and Young's moduli, and the thermal expansion coefficient of solid polymers. The method has been used to measure the bulk and shear moduli and expansion coefficient of a glass bead-filled epoxy resin over a particle concentration range of 0 to 40% volume. Results are compared with the theoretical predictions of Hill, Hashin and Shtrikman, Paul and others. In the glassy region the experimental data agree well with the Hashin and Shtrikman lower bound, but above T_g the material is reinforced much more than suggested by these theories. Some evidence is given for a difference in glass transition temperature between filled and unfilled materials.

1. Introduction

Measurements of the mechanical properties of polymers present many difficulties which arise mostly from their viscoelastic nature. This means that the materials possess properties which are often strongly dependent on temperature, frequency (or creep time) strain rate, strain, heating or cooling rate, thermal history, and stress history. Although most of these effects are well understood it makes the testing of such materials fairly difficult. Many of the discrepancies between literature values of mechanical properties for polymeric materials which are supposedly similar may well originate from one or more of the above sources. In polymer matrix composites the situation is more complex because there are problems of homogeneity, adhesion between phases, voidage, and phase geometry. For thermosets the concentration of curing agent, cure time, cure temperature, and even specimen size can all affect the final product. If the resulting composite is isotropic, only two viscoelastic functions are required to specify completely the mechanical behaviour, and for the reasons outlined above, it is most convenient, but rather rare, if the measurements are made on the same specimen. Most of the theoretical treatments of composite moduli are developed in terms of bulk and shear moduli, and the chief aim of this work was to test these predictions, both for bulk and shear moduli, using a new method which enables both these parameters, and also the Young's modulus and expansion coefficient to be determined on a single specimen.

1.2. Theoretical

The calculation of the various mechanical properties of composite materials has received considerable attention over recent years, and in particular the theory of the overall moduli of particulate composites is well developed. Rather less attention has been given to the calculation of thermal expansion coefficients of particulate composites, but exact theories now exist which relate the thermal expansion coefficient to the elastic moduli of the composite, and so the problem reduces to one of calculating the overall elastic moduli.

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1.2.1. *Calculation of the overall elastic moduli*

The earliest solutions to this problem follow the work of Einstein [1] and require that the filler particles are rigid, perfectly bonded, and spherical, and that the fillter concentration is low, and in general these treatments are not satisfactory for filler concentrations of more than 10 to 15 vol%. The various equations were originally used to calculate the viscosity of composites with Newtonian viscous matrices, but because of the similarity between the elastic and hydrodynamic equations it is common practice to use these equations for the calculation of shear modulus of elastic matrix composites (Neilsen [2]). The Einstein equation becomes

$$\frac{G}{G_1} = 1 + 2.5\phi_2$$

where G, G_1 are the overall and matrix shear moduli respectively, and ϕ_2 is the volume concentration of filler.

A second set of theoretical studies stems from the work of Bruggemann [3, 4], and includes the equations of Kerner [5] and van der Poel [6]. These methods take into account the stiffness of the filler, but again require low concentrations of perfectly bonded spherical particles. The equations due to Kerner are

$$\frac{G}{G_1} = \frac{\left[\dfrac{\phi_2 G_2}{(7-5\nu_1)G_1 + (8-10\nu_1)G_2} + \dfrac{\phi_1}{15(1-\nu_1)}\right]}{\left[\dfrac{\phi_2 G_1}{(7-5\nu_1)G_1 + (8-10\nu_1)G_2} + \dfrac{\phi_1}{15(1-\nu_1)}\right]}$$

$$\frac{K}{K_1} = \frac{\left[\dfrac{K_1\phi_1}{3K_1 + 4G_1} + \dfrac{K_2\phi_2}{3K_2 + 4G_1}\right]}{\left[\dfrac{\phi_1}{3K_1 + 4G_1} + \dfrac{\phi_2}{3K_2 + 4G_1}\right]}$$

where K, G, ν are respectively the bulk and shear moduli, and Poisson's ratio, and ϕ is the volume concentration. Subscript 1 refers to the matrix phase, 2 to the disperse phase, and quantities with no subscript refer to overall composite properties. This bulk modulus equation is identical to that of van der Poel.

More recent work follows the "self-consistent method" due to Hill [7] and Budiansky [8] which makes no assumption about concentration, but requires the particles to be ellipsoidal, and does not take into account the case where phase inversion does not occur. The results for G and K are

$$\frac{\phi_1 K_1}{K_1 + 4G/3} + \frac{\phi_2 K_2}{K_2 + 4G/3}$$

$$+\,5\left[\frac{\phi_1 G_2}{G - G_2} + \frac{\phi_2 G_1}{G - G_1}\right] + 2 = 0,$$

$$\frac{1}{K + 4G/3} = \frac{\phi_1}{K_1 + 4G/3} + \frac{\phi_2}{K_2 + 4G/3}.$$

The first equation may be solved by choosing a value for G and solving for ϕ_1, and then K may be calculated.

Methods which calculate bounds on the elastic constants using the energy principles of the theory of elasticity are those of Paul [9], Hashin and Shtrikman [10] and Walpole [11]. Generally these methods do not restrict the concentration or geometry of the particles, the sole limitation being that the composite must be macroscopically isotropic, and homogeneous. The Hashin–Shtrikman lower bound equations (HSLB) are

$$G = G_1 + \phi_2 \Bigg/ \left[\frac{1}{G_2 - G_1} + \frac{6(K_1 + 2G_1)\phi_1}{5G_1(3K_1 + 4G_1)}\right]$$

$$K = K_1 + \phi_2 \Bigg/ \left[\frac{1}{K_2 - K_1} + \frac{3\phi_1}{3K_1 + 4G_1}\right]$$

Upper bounds (HSUB) are obtained by interchanging 1 and 2 everywhere.

Probably the most commonly used of these equations are those of Kerner, Hashin and Shtrikman, and the SCM. In fact Kerner's equation, although derived by different methods, is identical to the bounds equations of Hashin and Shtrikman. If the particulate phase is stiffer than the matrix, the Kerner equation coincides with the HSLB, and if the matrix phase is stiffer the upper bound is obtained.

The Paul bounds are given by

$$1/[\phi_1/G_1 + \phi_2/G_2] \leqslant G \leqslant \phi_1 G_1 + \phi_2 G_2$$

$$1/[\phi_1/K_1 + \phi_2/K_2] \leqslant K \leqslant \phi_1 K_1 + \phi_2 K_2.$$

1.2.2. *Calculation of thermal expansion coefficient*

The problem of calculating thermal expansion coefficients of composites appears to have been neglected until the work of Turner [12] who gave the equation

$$\alpha = \frac{\alpha_1 K_1 \phi_1 + \alpha_2 K_2 \phi_2}{K_1 \phi_1 + K_2 \phi_2}$$

where α_1, α_2, α are the thermal expansion coefficients of the matrix, filler, and composite respectively. In this analysis the filler particles may be any size and shape, but the material is macroscopically isotropic, and perfect adhesion exists between phases. Later, Thomas, in a work quoted by Nielsen [2], proposed the relation

$$\alpha = \alpha_2^{\phi_2} \alpha_1^{\phi_1}$$

Kerner [5] derived the formula

$$\alpha = \alpha_1 \phi_1 + \alpha_2 \phi_2 - (\alpha_1 - \alpha_2) \phi_1 \phi_2$$
$$\left[\frac{1}{K_2} - \frac{1}{K_2}\right] \Bigg/ \left[\frac{\phi_1}{K_2} + \frac{\phi_2}{K_1} + \frac{3}{4G_1}\right].$$

This relation assumes perfect adhesion between phases, and spherical particles, and differs only slightly from the method of mixtures formula $\alpha = \alpha_1 \phi_1 + \alpha_2 \phi_2$.

Schapery [13] has used variational principles to derive exact bounds for α in terms of the composite moduli, and in the case of two-phase materials the bounds are equal. The expression for α is then

$$\frac{\alpha - 3\alpha_2}{3(\alpha_1 - \alpha_2)} = \frac{K_1(K_2 - K)}{K(K_2 - K_1)}$$

If only bounds on K are known, then only bounds on α may be calculated; the upper bound of K gives the lower bound of α and vice versa. The problem thus reduces to one of estimating K. If the Reuss equation for $K (1/K = \phi_1/K_1 + \phi_2/K_2)$ is used, the method of mixtures formula ($\alpha = \phi_1 \alpha_1 + \phi_2 \alpha_2$) is obtained, whereas if the Voigt value for K is used ($K = \phi_1 K_1 + \phi_2 K_2$) the resulting equation for α is the Turner equation. If the Kerner equation for K is substituted into the Schapery equation, then the resulting equation is Kerner's equation for α.

In a parallel treatment using the self-consistent method, Levin, quoted by Laws [14], has derived the same result as Schapery.

1.3. Experimental verifications

Measurements in shear of isotropic particulate-reinforced polymer matrix composites are fairly common in the literature. Speake, Arridge and Curtis [15] found the Hashin–Shtrikman lower bound (HSLB) in good agreement with shear modulus data for epoxy/glass beads for ϕ_2 up to 0.35. Lewis and Nielsen [16] have used a modified HSLB equation to describe the shear modulus of an epoxy resin/glass beads material for filler concentrations of up to 40 vol %, and Kolařík *et al.* [17] have used the same equation for polyhydroxymethyl methacrylate (PHEMA) glass beads for ϕ_2 up to 0.5.

Many workers prefer for experimental convenience to measure Young's modulus. Provided G_1, G_2, K_1, and K_2 are known it is possible to calculate $G(\phi)$ and $K(\phi)$ from the various theoretical predictions, and to calculate E of the composite from

$$E(\phi) = \frac{9K(\phi)G(\phi)}{3K(\phi) + G(\phi).}$$

This approach, which is only valid for isotropic composites has been used by several workers. Trachte and Dibenedetto [18] working on glass beads in polyphenylene oxide found good agreement with the HSLB up to $\phi_2 = 0.25$. Ishai and Cohen [19] reached a similar conclusion for an epoxy resin polymer, filled with natural silica, and the same matrix filled with air for ϕ_2 up to 0.3. Smith [20] has used his own data and those of Richard [21] for glass beads in a polyester matrix for ϕ_2 up to 0.5, and finds the HSLB satisfactory up to $\phi_2 = 0.35$. Above this the van der Poel equation is better, but both expressions give predicted values which fall below the experimentally determined ones. Nicolais and co-workers [22–25] have looked at several glass bead composites (ABS, polyhydroxymethyl-methacrylate, SAN, polystyrene, and polyphenyleneoxide) and in all cases the HSLB gave good agreement for ϕ_2 up to 0.4.

In most of the studies mentioned above, all the results are derived for systems where the matrix material is in its glassy state. Thus it seems that the HSLB is able to give accurate predictions of E and G at least up to filler concentrations of 40 vol % for a wide range of isotropic polymer matrix composites. Bulk modulus data are much rarer, and apart from the present study the only experimental data appear to be those of van der Wal *et al.* [26] who used sodium chloride particles in a polyurethane rubber matrix. For ϕ_2 up to 0.7, good agreement was found with the van der Poel equation, which has the same values as HSLB for bulk modulus. The lack of data for K is rather surprising, considering the fundamental importance of bulk modulus. One area where K is very important is in the calculation of the thermal expansion coefficient of the composite, and this subject, although treated well theoretically, is rather neglected as regards experimental work. It was for this reason that the present work was undertaken.

2. Materials and specimen preparation

The matrix material used in this study was an epoxy resin, diglycidyl ether of bisphenol A, (DGEBA), (CIBA–Geigy MY 750), cured by nadic methyl anhydride, (NMA), (CIBA–Geigy HY 906). Small amounts of triethylamine were used as accelerator. The glass beads were supplied by Plastichem Ltd., and were "A" glass microspheres, Plastichem grade 3000, which corresponds to a particle size range of 4 to 44 μm diameter; Plastichem state that 80% of the beads lie within this range, the average particle diameter being 30 μm. This corresponds to a screen size of 325. The spheres were supplied with a coating [Plastichem code (CPO2)], which is a silane coupling agent designed to provide good adhesion to epoxy resins.

The matrix material was composed of the following

100 parts by weight	DGEBA
90 parts by weight	NMA
2 parts by weight	triethylamine,

and the cure schedule adopted by 16 h at 100° C, followed by 1 h at 150° C and $\frac{1}{2}$ h at 200° C.

Specimen preparation is described in some detail in reference [27], and rather more briefly here. The methods used here all employ circular cylindrical specimens which were cast in a split mould in which a circular steel rod was centrally positioned. The split mould surfaces shape the outside surface of the specimen, whilst the inside surface is shaped by the steel rod. The beads were first added to the curing agent and were stirred continuously as the mixture was warmed to reduce its viscosity. The epoxy resin was then added and stirring continued for about 20 min until all the glass surfaces had been wetted. The mixture was heated further, and left to stand to allow small air bubbles to escape. After another period of stirring the accelerator was added, the mixture stirred again, and transferred to the heated mould. The mould was then transferred to the curing oven where it was left to rotate slowly about a horizontal axis to prevent sedimentation of the glass beads. End plugs for the specimens were fashioned from material from the same batch and given the same cure as the specimen. Bead concentrations of 0 to 40 vol % were used.

3. Measurement of mechanical properties

The main aim in devising the testing methods described here was to measure the bulk and shear mechanical properties at low strain on the same specimen. This dispenses with the problems associated with nonlinear viscoelasticity and those associated with differences between specimens. The measurements made are of creep compliance [$J(t)$ for shear, $B(t)$ for bulk] which is related to stress relaxation modulus by

$$\int_0^t J(\tau)G(t-\tau)\mathrm{d}\tau = t$$

$$\int_0^t G(\tau)J(t-\tau)\mathrm{d}\tau = t,$$

(and similarly for bulk). $G(t)$ may be calculated from $J(t)$ by Laplace transform methods if the analytical form of $J(t)$ is known, or otherwise by the numerical method of Hopkins and Hamming [28].

However the relaxed and unrelaxed compliances J_R and J_u are simply related to their modulus counterparts by

$$J_\mathrm{u} = 1/G_\mathrm{u}; \qquad J_\mathrm{R} = 1/G_\mathrm{R}$$

(and similarly for bulk). We follow usual practice and approximate the relaxed and unrelaxed compliances to the rubbery and glassy compliances respectively. Then, provided the transition region is avoided, the simple formulae may be used to relate compliance and modulus. Most of the theoretical predictions quoted in Section 2 are derived for the case of elastic matrix composites. The theory of viscoelastic matrix composites is not well-developed at present, and although some authors (Acierno, Nicolais, Vojta, and Janacek [25]); have tried using the appropriate viscoelastic functions in the existing equations for overall moduli, there is little formal justification for this procedure.

All the values of modulus quoted here are the gradients of stress–strain curves containing at least eight data points. In all the measurements the strain was kept very small, and in no case was nonlinearity of the stress–strain curve observed.

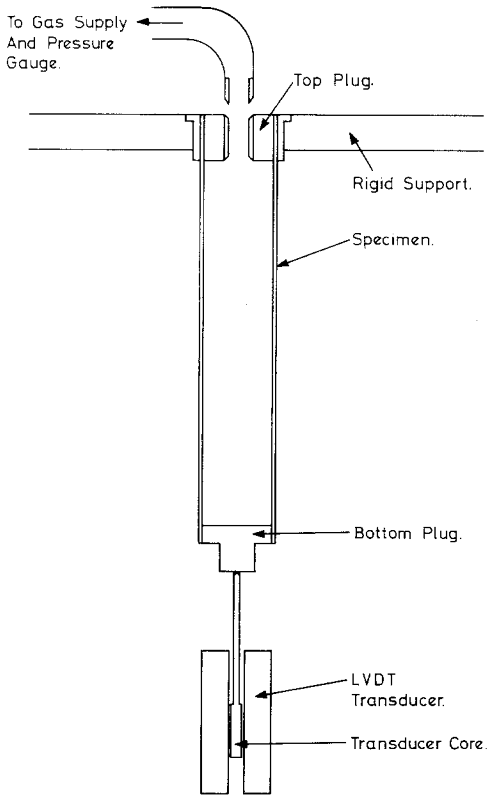

Figure 1 Apparatus for measurement of bulk compliance.

3.1. Bulk modulus

Bulk modulus was measured using a method based on that used by Mallock [29] for metals in 1904. The method has been modified and used for polymers by Arridge [30] and a more detailed study has been conducted by Crowson [27]. The experimental arrangement is shown in Fig. 1. The specimen is in the form of a thin-walled circular cylinder, with closed ends. When the specimen is subjected to a uniform internal pressure P, the bulk modulus may be expressed in terms of the axial strain by

$$K = \frac{Pr_i^2}{3(r_0^2 - r_i^2)e}$$

for the time independent case, where r_i = internal radius of the specimen, r_0 = external radius of the specimen, and e = axial strain. A compressed nitrogen cylinder equipped with a reducing valve provided the pressure, and a precision Bourdon gauge (Budenberg Ltd.) was used for pressure measurement. The axial strain was measured using a linear variable differential transformer (LVDT) (Electromechanisms Ltd.), which is sensitive to 1 μm. Using this method, values of K could be obtained for axial strains as low as 0.001%, but in general the axial strain level was kept below 0.01%, and an accuracy in K of about ± 5% could readily be achieved. Such small strain levels are particularly desirable for measurement of K, because in bulk deformation nonlinearity of the stress–strain curve occurs at low strains.

3.2. Shear modulus

The experimental arrangement could be modified easily to measure shear modulus. The pressure supply and transducer assembly were removed, and a light disc attached to the bottom end of the specimen. Cords were passed around the disc and over two fixed pulleys, and weights could be attached to pans on the ends of the cords. Using this arrangement a constant torque could be applied to the specimen. A small mirror was attached to the bottom of the specimen, and a ray of light was beamed on to the mirror, and the reflected ray followed on a moving light cell chart recorder (Sefram Graphispot). This system allowed an accuracy of about 1% in the measurement of angle of twist, and the total error in the measured shear modulus was about 5%. The maximum shear strain used in this study was less than 0.1%.

3.3. Young's modulus

Young's modulus could be measured on the same specimen with very little modification. The pressure supply system was disconnected, and a light cradle was attached to the bottom of the specimen. Weights could be put on to the cradle, which was balanced to ensure the load was applied axially. The displacement of the bottom end of the tube was measured using the same LVDT transducer as used for bulk modulus measurements, and an accuracy of 5% in E could be achieved for strains of less than 0.01%. The Young's modulus measurements did not form a major part of the work described here, but were used only to provide checks on the K and G data reported here.

3.4. Expansion coefficient

The linear thermal expansion coefficient was measured using the displacement measurement system described in 3.1. Temperature was varied using a coil-wound heater which enclosed the specimen. The heater was controlled by a Eurotherm temperature controller which could maintain temperature to better than 0.1° C. The expansion coefficient is given by

$$\alpha = \frac{1}{l_0}\frac{l_T - l_0}{T - T_0}$$

where l_0 = original specimen length at T_0, l_T = specimen length at T.

The procedure adopted was to change temperature in steps of 10° C, allowing 10 min between each reading. Readings were taken both for ascending and descending temperatures and graphs of $\Delta l (= l_T - l_0)$ against T were plotted. From such graphs the gradient was taken and

$$\alpha = \frac{\text{gradient}}{l_0}$$

The temperature range employed was sufficient to include the transition region, and by taking the gradient of the two tangents to the curve well below and well above T_g the values of glassy expansion coefficient (α_g) and rubbery expansion coefficient (α_r) could be measured. The point of intersection of the two tangents defines T_g.

4. Results and discussion

The results of the bulk and shear moduli against filler concentration are shown in Figs. 2 and 3 respectively. The data presented in these two graphs were obtained at room temperature (21° C). The data for the specimen containing 30 vol% beads show a considerable discrepancy from the trend of the rest of the results, and this is probably because this specimen had a much thinner wall. This means that the contribution of the uncertainty in wall thickness to the error in K and G is much larger, and so this discrepancy is within experimental error for that particular specimen. Errors in G and K for the other specimens are expected to be less than 5%.

Also shown in these graphs are the values predicted by the equations of Hill, Paul and Hashin and Shtrikman. The values used for calculation of these theoretical predictions are K_1 = 27.5 kbars, G_1 = 12.5 kbars, K_2 = 400 kbars, G_2 = 304 kbars. It should be noted that the data for the matrix material were obtained by measurement on an unfilled specimen. However the filler data are those of Lowrie [31] and refer to "E" glass. The filler in the present case is "A" glass, but no values for K and G have been found for this material in the literature. According to Ritter [32], the Young's moduli of "E" and "A" glass are 10.5 ×

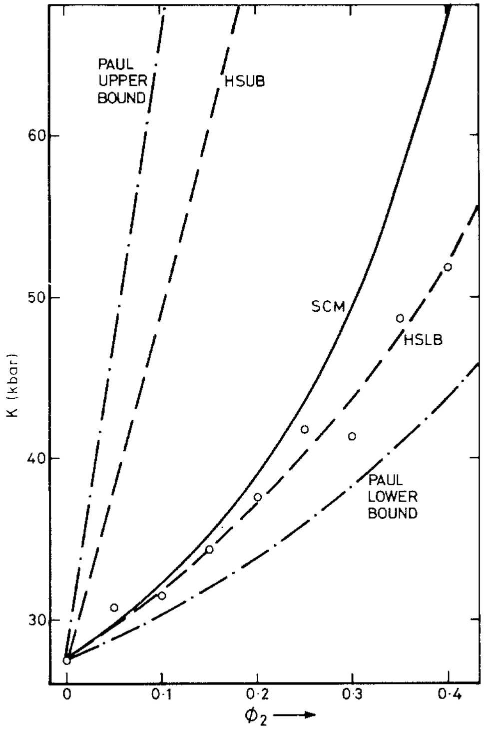

Figure 2 Bulk modulus versus volume fraction of beads at 21° C.

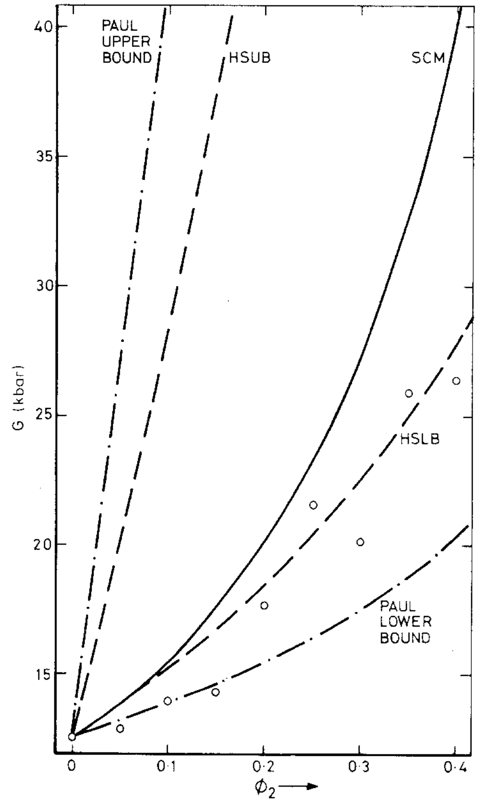

Figure 3 Shear modulus versus volume fraction of beads at 21° C.

10^6 and 11.0×10^6 psi respectively, and thus it seems reasonable to use the quoted values for "E" glass, since the difference between the two fillers will be apparent only at very high filler concentrations.

From Figs. 2 and 3 it is apparent that the best prediction, both for K and G is that of the Hashin and Shtrikman lower bound (HSLB) (or Kerner's equation for the case of a stiff filler). Paul's bounds are too widely spaced to be useful, and Hill's SCM equation predicts too much reinforcement at high filler concentration.

So far the discussion has been limited to glassy matrix composites, where viscoelastic effects are small. In addition measurements were made for one specimen (40 vol% filler) over a range of temperature including the transition region, and the results are shown in Figs. 4 and 5, in the form of graphs of reciprocal of compliance against temperature. The Hashin and Shtrikman equations are also included in these figures, but it should be noted that these equations were derived for elastic matrix composites, and so they are not expected to be valid in the transition region, where viscoelastic effects are prominent. The behaviour of the unfilled material in bulk and shear versus temperature is shown in Fig. 6, and it is obvious that the effect of the filler is to reduce the size of the relaxation both for bulk and shear deformations; that is to say that the reinforcing effect of the filler is greater above T_g than below. The Hashin–Shtrikman bounds shown in Figs. 4 and 5 were calculated from matrix data taken from Fig. 6, and the elastic constants of the filler material were assumed to be independent of temperature. This seems to be a fair assumption since the transition temperature of the filler material is well above the maximum temperature used here. From Figs. 4 and 5 it may be seen that the measured values of $1/B$ and $1/J$ in the rubbery region are about 3 times higher than the HSLB predictions. Similar observations have been made by other authors. Nicolais and co-workers [25] found that the HSLB could provide good agreement with their E and G data for polyhydroxyethylmethacrylate/glass beads below the matrix T_g, but that the prediction was only half the measured value above T_g. Speake *et al.* [15] found a similar effect for shear modulus of an epoxy resin/glass beads material, and Arridge [33] worked on an epoxy resin material unidirectionally reinforced with silica fibres, and found that simple fibre-reinforcement

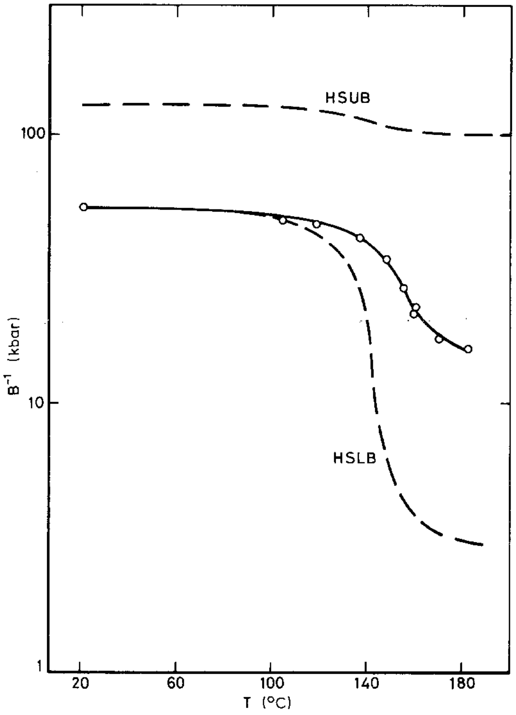

Figure 4 Reciprocal of bulk compliance versus temperature for the specimen containing 40 vol% filler.

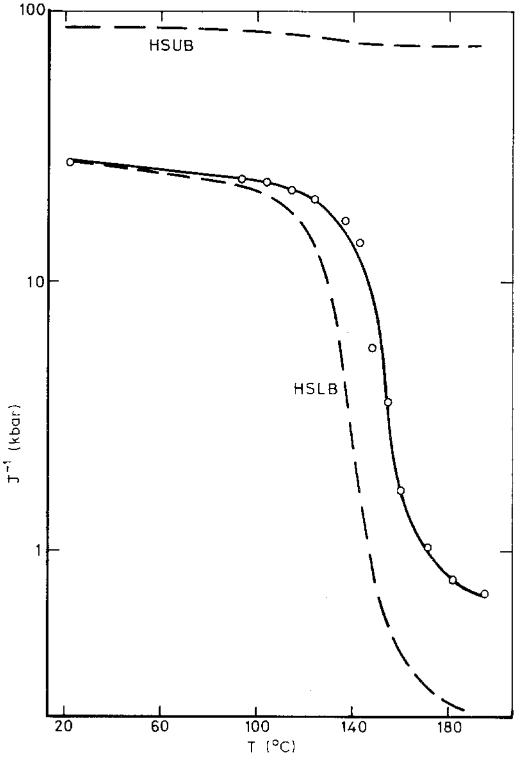

Figure 5 Reciprocal of shear compliance versus temperature for the specimen containing 40 vol% filler.

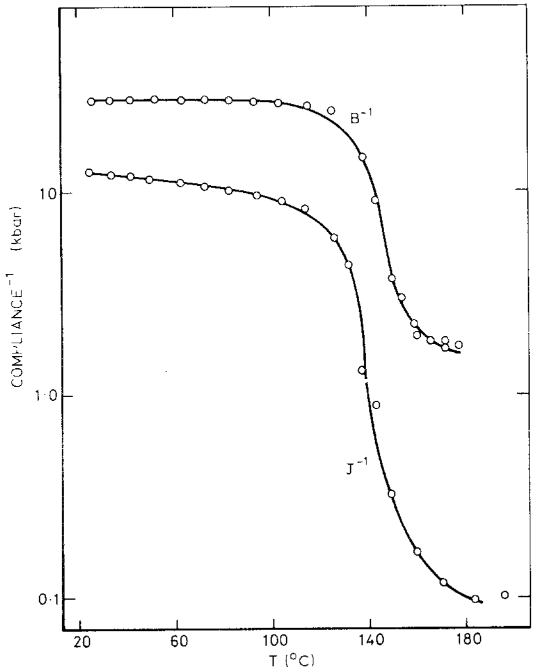

Figure 6 Reciprocal of bulk and shear compliance versus temperature for the unfilled specimen.

theories which gave good agreement below the matrix T_g were too low by factors of up to 3 above T_g. The only data available for K for a filled material above the matrix T_g, apart from the present study, again appear to be those of van der Wal *et al.* [26] who found that the HSLB agreed with experiment both in the glassy and rubbery regions of the composite. This result is contrary to that of present study and a possible reason for the discrepancy is suggested later.

The origin of the discrepancy between theory and experiment at temperatures above the matrix T_g has been discussed by Nielsen and Lewis [34] who take as their starting point the thermally-induced stress in the matrix due to the different thermal expansion coefficients of the two phases. If the specimen is fabricated above ambient temperature, then on cooling the two phases contract by different amounts. If $\alpha_1 < \alpha_2$ (as is usually the case) the matrix is put into a state of hydrostatic tension. Because of the non-linearity of the stress–strain curve the modulus now measured for a small strain deformation is different from that obtained when the material is in the unstressed state. If the superimposed stress is a hydrostatic tension then the modulus K will be lower than in the unfilled material. If the superimposed stress is shear then the situation is less simple. It is well known [35–38] that an applied hydrostatic pressure will increase the shear modulus by reducing the free volume and making it more difficult for molecular segments to move. Presumably a hydrostatic tension will increase the free volume and lower T_g which may lead to a decrease in G. Such an effect is predicted by Ferry and Stratton [39], although a competing mechanism has been proposed by Sternstein and Ho [40]. If, therefore, the effective matrix modulus could be inserted into the HSLB equation the predicted composite modulus would fall below experimental results. As the composite is heated to temperatures above T_g the thermally-induced stress is relieved, and the effective matrix modulus approaches that of the unfilled material. If this argument is correct, then the HSLB predictions would fall below experiment at all temperatures if the true matrix modulus could be used in the HSLB equations.

It is interesting to note that no discrepancy between theory and experiment was noticed for bulk modulus (van der Wal *et al.* [26]), or shear modulus (Schwarzl *et al.* [41]) of a polyurethane

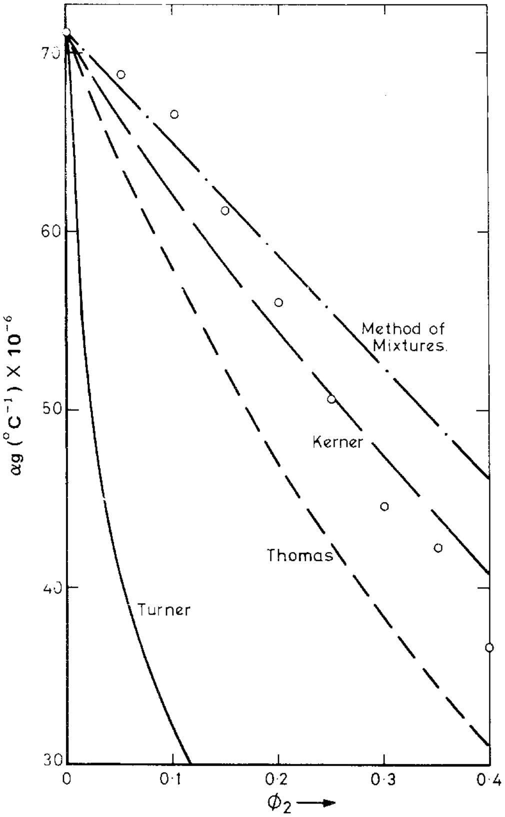

Figure 7 Glassy expansion coefficient versus volume fraction of beads at 21° C.

rubber filled with rock salt. The reason for this is probably that the expansion coefficients of the two materials are closer together than for the composite systems mentioned previously. ($\alpha_1/\alpha_2 \sim 6$ for polyurethane/salt, whereas $\alpha_1/\alpha_2 \sim 20$ for epoxy/glass). From Figs. 4 and 5 it may be seen that the discrepancy between HSLB and experiment is greater for bulk modulus than for shear modulus in the rubbery region

$$\left(\frac{K \text{ experimental}}{K \text{ predicted}} \sim 5; \quad \frac{G \text{ experimental}}{G \text{ predicted}} \sim 3\right).$$

The reason for this is unclear, but when the dependence of shear modulus on applied hydrostatic stress is better established it may be possible to make an explanation.

Figs. 7 and 8 show the variation of α_g and α_r (the glassy and rubbery expansion coefficients) on filler concentration, and the predictions of Kerner, Turner and Thomas are also included. The Kerner equation appears to give the best agreement both for α_g and α_r, and this equation is close to the method of mixtures equation

$$(\alpha = \alpha_1\phi_1 + \alpha_2\phi_2).$$

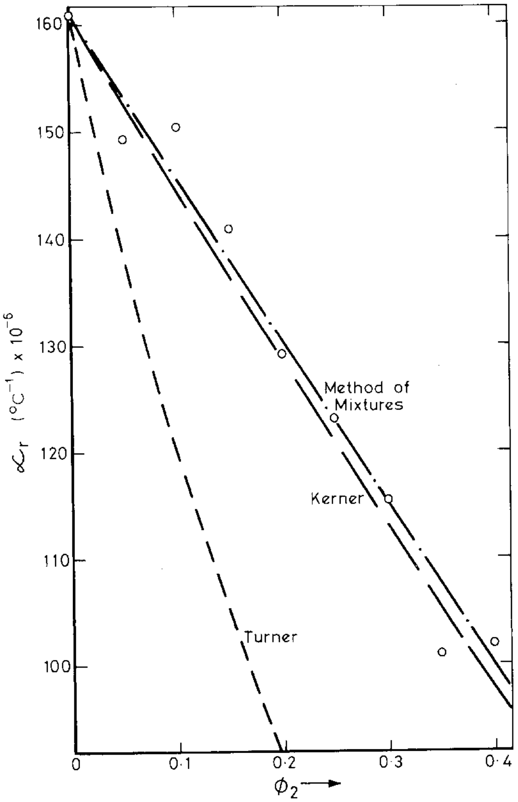

Figure 8 Rubbery expansion coefficient versus volume fraction of beads at 21° C.

TABLE I T_g values for different filler contents

ϕ_2	T_g (° C)	ϕ_2	T_g (° C)
0	139	0.25	142
0.05	143	0.30	147
0.10	146	0.35	144
0.15	144	0.44	139
0.20	145		

It is of some interest to compare values of T_g on the different specimens. Table I contains values obtained from thermal expansion data, and there seems to be no systematic variation of T_g with ϕ. Data are also available for the 0 and 40 vol% specimens from the plots of $1/B$ and $1/J$ against T in Figs. 6 and 7, and from these it seems that the T_g of the specimen containing 40 vol% filler is some 10° C above the T_g of the unfilled material. The reason for a difference between values derived from compliance measurements and values derived from α is unclear, but evidence for T_g shift due to filler has been found by several workers. Nicolais and co-workers [25, 42] have used differential scanning calorimetry (DSC) and differential thermal analysis (DTA) to study polyphenylene oxide/glass beads and polyhydroxyethylmethacrylate/glass beads, and noticed T_g increases of up to 9° C for $\phi_2 = 0.4$. This increase in T_g was seen both for the composite, and for a physical mixture of the two components, and the authors concluded that the T_g increase was due to changes in specific heat and thermal conductivity of the system, and not to changes in chain mobility or free volume.

Droste and Dibenedetto [43] used DTA and reported a 4° C increase in T_g of a phenoxy/glass bead polymer for $\phi_2 = 0.4$, whereas Landel and Smith [44] saw an increase in T_g of 20° C for a polyurethane rubber/ammonium perchlorate material at $\phi_2 = 0.5$. Nielsen *et al.* [45] observed T_g increases in a polystyrene/mica material, and in a later paper Nielsen [46] attributes the effect to the absorption of the matrix polymer on to the filler surfaces. This is expected to restrict the motion of the chain segments near the filler surface, and thus lead to an increase in T_g. A similar explanation was put forward by Iisaka and Shibayama [47] who worked on an epoxy resin filled with mica flake and/or glass beads. Lipatov *et al.* [48] studied the effect of filler on the shear relaxation time spectra of quartz powder in an epoxy resin matrix, and found that at high filler concentrations the spectrum is shifted to longer times. This observation is consistent with an increase in T_g with filler content, and they suggest that there are two competing mechanisms which tend to change T_g as ϕ_2 increases: one is the effect of immobilization of the polymer segments which are absorbed onto the filler surface, leading to an increase in T_g; the other effect is due to the non-deformability of the filler particles (which are rigid compared to the matrix), which means that most of the deformation will take place within the matrix phase, and so leads to a reduction in the average relaxation time i.e. a decrease in T_g. In most cases it would seem that the former effect is larger, and the result is an increase in T_g with filler. However there are cases in the literature [49] where T_g decreases with filler, and it may be that in these cases the latter effect dominates.

If the explanation of Lipatov *et al.* is correct there should be a dependence of composite modulus and T_g on particle size. For small particles the amount of interface for constant volume fraction increases, and thus the T_g shift should be larger because more of the polymer matrix would be absorbed and partly immobilized on the filler surface (if the former effect dominates). This appears to be a rather neglected area, and the only relevant work seems to be that of Alter [50], who suggested that composite modulus for constant ϕ increases linearly with the reciprocal of the particle diameter. No prediction was made for the dependence of T_g on particle size.

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