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The deformation of hybrid-particulate composites

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The deformation behaviour of a hybrid-particulate epoxy composite has been examined. The Young's modulus E and yield stress σ_y have been determined as a function of temperature and volume fraction of rigid glass spheres, for both a simple epoxy matrix and a two-phase epoxy toughened by the presence of rubber particles. In addition, the effect of improving the particle–matrix interface with a silane bonding agent has been studied. It is found that there is a steady increase in Young's modulus with the volume fraction of spheres for all systems. In contrast, the yield stress is only found to increase with the volume fraction of rigid particles when the epoxy matrix is not toughened with rubber. It is found that the yield stress is virtually independent of particle volume fraction when a rubber-modified epoxy matrix is employed. Finally, it is found that for all compositions tested the Young's modulus and yield stress increase with increasing temperature. The overall behaviour has been discussed in terms of existing theories concerning the deformation behaviour of amorphous polymers.

1. Introduction

It is now well established that there is a close relationship between the deformation and fracture behaviour of polymers [1]. Crack propagation in many polymers is known to be controlled by plastic deformation at the crack tip [1–3]. It is found that even such inherently brittle materials as epoxy resins are capable of undergoing a considerable amount of plastic deformation, especially when deformed in compression [4–6]. It was shown by Yamini and Young [6] that the plastic deformation mechanisms were essentially the same as those in glassy thermoplastics, being controlled by the geometry of the polymer molecules and apparently unaffected by the presence of cross-links.

Attempts to increase the resistance of epoxy resins to crack propagation have involved the dispersion of a second phase which can either be in the form of rubber particles [7–9] or brittle particles such as glass beads [10–12] and silica [13], the mechanism of toughening being different for the two types of particle. Very recently Maxwell *et al.* [14] have shown that hybrid-particulate composites, which contain both rubbery and rigid particles, allow the toughening mechanisms to be optimized, and the hybrid composites consequently have an improved resistance to crack propagation. Full details of the fracture behaviour of this hybrid-particulate composite are given in an earlier paper [15]. It is the purpose of this present paper to show how the presence of rubbery, brittle and mixtures of the two types of particles affects both the elastic and plastic deformation of an epoxy resin.

2. Experimental details

2.1. Materials

The epoxy resin used for this present study was derived from the reaction of bisphenol A and epichlorhydrin. It was largely composed of the diglcidyl ether of bisphenol A (DGEBA) with small quantities of higher molar mass polymers present, and the curing agent used was piperidine. The rubber employed was a carboxyl-terminated random copolymer of butadiene and acrylonitrile, CTBN (carboxyl content 2.37 wt %, acrylonitrile content 18 wt %, molar mass 3500 g mol^{-1}). Glass beads with particle sizes ranging from 10 to 100 μm and an average diameter of 50.3 μm were used as a rigid particulate filler. In some cases the beads were coated with a silane-based bonding agent, γ-glycidoxypropyltrimethoxysilane. It was applied by immersing the glass beads for 30 min in a 1 vol % solution in ethanol : water (95.5 by volume) and then drying the beads for 1 h at room temperature, 4 h at 40° C and finally for 1 h at 120° C. Three types of composite were fabricated: epoxy–glass, epoxy–glass–rubber and epoxy–glass(silane)–rubber, and details of the nominal compositions are given in Table I.

The composite samples were prepared by first adding the CTBN rubber (if required) to the DGEBA resin and mixing by hand for a few minutes. The mixture was then heated in a water bath to 65 ± 5° C and mixed for a further 5 min using an electric stirrer. It was then degassed in a vacuum oven at 60° C until most of the entrapped air had been removed. When the mixture had cooled to below 30° C the piperidine

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TABLE I Formulations of the hybrid composites

Material	Composition (phr)*
Epoxy Resin (DGEBA)	100
Piperidine	5
Rubber (CTBN)	0 or 15
Glass Beads[†]	0, 10, 25, 35, 50, 100, 200 or 300

*phr = Parts per hundred of resin by weight.

[†] Used either coated or uncoated with silane-based bonding agent.

curing agent was gently mixed in to minimize any air entrapment. This was followed by the glass beads (if required) which were gently stirred into the mixture. The glass-filled systems were allowed to stand at 120° C for 15 to 100 min (depending upon the glass content) to allow the viscosity of the mixture to increase in order to prevent the glass from settling out during moulding. The mixture was again gently stirred and then poured into preheated moulds and cured at 120° C. Two types of mould were employed, one which produced sheets 6 mm thick and another which gave cylindrical rods 5 mm in diameter. The total time allowed for curing at 120° C was 16 h, which in the case of the glass-filled systems included the standing time at 120° C. Finally, the cured composites were cooled slowly in the mould to room temperature.

The glass transition temperature of the composites was determined using differential scanning calorimetry. It was found to be 95 ± 2° C for all compositions, indicating that the presence of the glass spheres had not affected phase separation of the rubber. The exact volume fractions of glass were checked by burning off the resin and weighing the residues.

2.2. Young's modulus determination

The Young's modulus of each of the hybrid composites was determined as a function of temperature in three-point bending, using an Instron mechanical testing machine operated at a crosshead speed of $0.5\,\mathrm{mm\,min^{-1}}$. Specimens of each composition were cut from the 6 mm thick sheets into rectangular plates 80 mm by 15 mm and were tested as described in a previous publication [6]. The modulus of each specimen was measured by determining the variation of displacement at the centre of the specimen y as a function of applied load P, which was found to be approximately linear for all compositions tested. The ratio P/y is related to the Young's modulus E of the specimen [16] through the equation

$$P/Y = 4Ebh^3/L^3 \qquad (1)$$

for a rectangular cross-sectioned specimen of thickness h and breadth b, with a distance between the supports of L. Tests were carried out at a variety of different temperatures between − 70° and + 50° C in an Instron environmental chamber. The temperature was controlled by electric heating at elevated temperature and using liquid nitrogen at low temperatures, both to an accuracy of ± 2° C.

2.3. Yield stress measurement

Cylindrical specimens, 10 mm long and 5 mm diameter, were machined from the rods of the hybrid composites. They were deformed in uniaxial compression between polished lubricated steel dies in a compression rig in the environmental chamber of the Instron testing machine as described earlier [6]. The load P was converted into true stress σ_T using the initial cross-sectional area A_0 in the equation

$$\sigma_T = P(1 - e)/A_0 \qquad (2)$$

which is derived assuming constant volume deformation, e being the strain.

2.4. Optical microscopy

In order to examine the distribution of glass particles in the moulding and to check the composition of the composites, sections were obtained of a series of compositions. Specimens were sectioned, ground and polished and then examined in reflected light in a Zeiss optical microscope. Sections were also taken from specimens of the three systems deformed to just beyond yield in uniaxial compression. In this case they were carefully cut through the centre of the deformed cylinders parallel to the compression direction.

3. Results

3.1. Young's modulus measurements

The variation of the Young's moduli of the composites at different temperatures with volume fraction of glass beads, v_f(glass), is shown in Fig. 1. It can be seen that for the three systems, epoxy–glass, epoxy–glass–rubber and epoxy–glass(silane–rubber the value of Young's modulus increases with increasing v_f and decreasing temperature T. At any given temperature and volume fraction the epoxy–glass composites without any rubber phase have the highest modulus values (Fig. 1a), reflecting the flexibilizing effect of the rubber particles. The treatment of the glass spheres with silane bonding agent does not appear to have a significant effect upon the variation of E with v_f (Fig. 1c).

3.2. Yield stress measurements

It was found that all composite compositions were capable of undergoing plastic deformation when deformed in uniaxial compression. Fig. 2 shows a schematic compressive stress–strain curve for a typical composite, indicating the extrapolation procedure used to determine the true yield stress σ_y and the nominal yield strain e_y.

A series of stress–strain curves obtained at different temperatures for the three types of composites with v_f(glass $\sim 0{\cdot}17$ are given in Fig. 3. It can be seen that for all three systems there is an increase in yield stress with decreasing temperature. For convenience, all the stress–strain curves in Fig. 3 have only been plotted to a strain of about 15%, although many specimens were found to deform uniformly to strains in excess of 50%. It is quite remarkable that brittle polymers such as epoxy resins are capable of undergoing a considerable amount of post-yield deformation even when they are reinforced with rigid glass particles. However, similar behaviour has also been reported by Young and Beaumont [13] for a silica-filled epoxy resin.

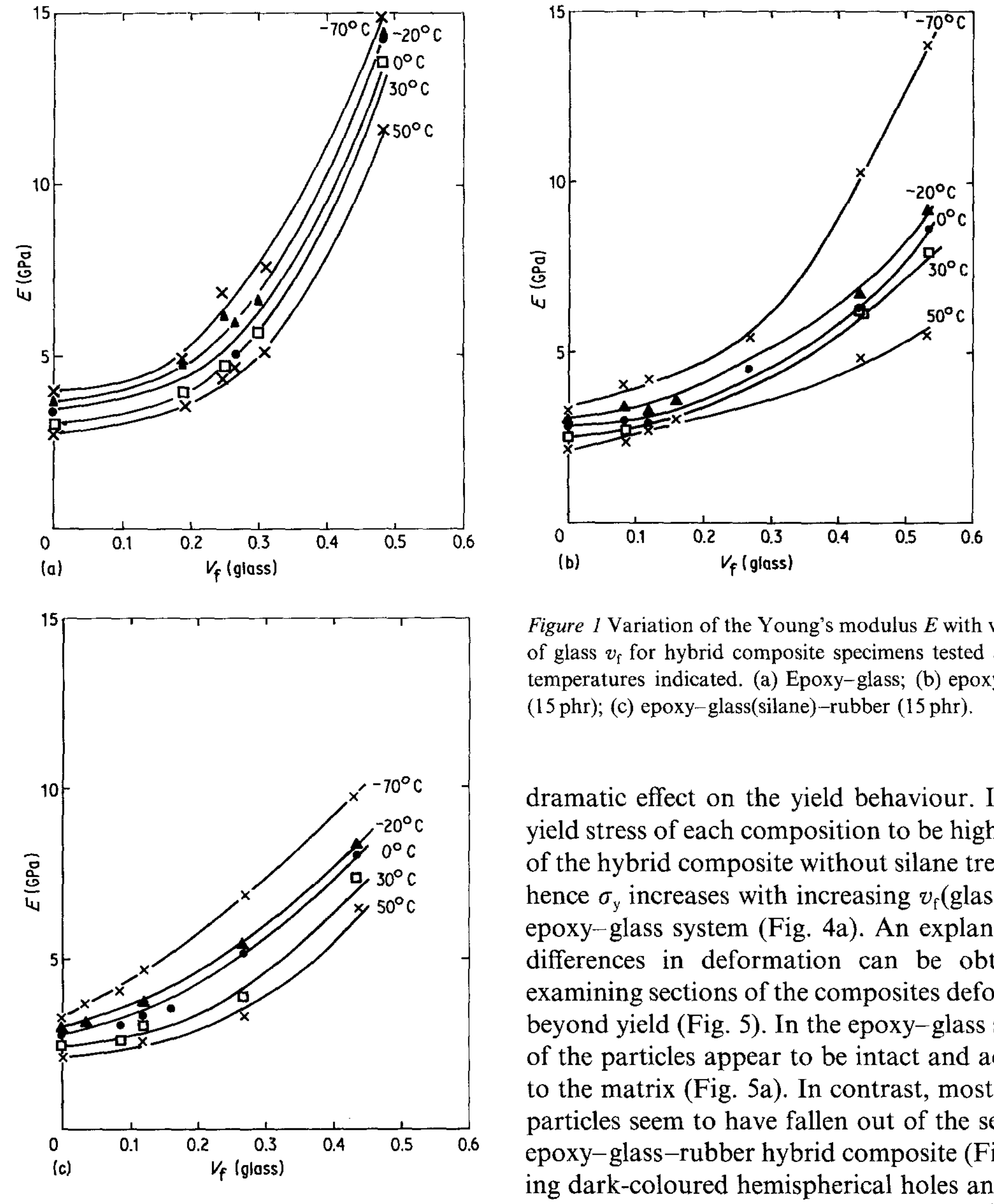


Figure 1 Variation of the Young's modulus E with volume fraction of glass v_f for hybrid composite specimens tested at the different temperatures indicated. (a) Epoxy–glass; (b) epoxy–glass–rubber (15 phr); (c) epoxy–glass(silane)–rubber (15 phr).

The variation of σ_y with v_f(glass) at different temperatures is presented in Fig. 4. It can be seen that for the epoxy–glass composite (Fig. 4a) the yield stress increases with an increasing volume fraction of glass. In contrast, σ_y does not increase with v_f for the epoxy–glass–rubber system (Fig. 4b) and even tends to fall at the highest volume fractions. However, the use of silane in the hybrid composite (Fig. 4c) has a dramatic effect on the yield behaviour. It causes the yield stress of each composition to be higher than that of the hybrid composite without silane treatment, and hence σ_y increases with increasing v_f(glass) as for the epoxy–glass system (Fig. 4a). An explanation of the differences in deformation can be obtained from examining sections of the composites deformed to just beyond yield (Fig. 5). In the epoxy–glass system most of the particles appear to be intact and adhering well to the matrix (Fig. 5a). In contrast, most of the glass particles seem to have fallen out of the section in the epoxy–glass–rubber hybrid composite (Fig. 5b), leaving dark-coloured hemispherical holes and indicating that interfacial debonding has occurred during deformation. However, for the epoxy–glass(silane)–rubber system (Fig. 5c) the glass particles can be seen in the section and few holes are present, indicating the improvement in particle–matrix adhesion caused by the use of the silane bonding agent. Clearly, there must be a correlation between the debonding in the epoxy–glass–rubber composite and the tendency of σ_y not to increase as v_f(glass) increases (Fig. 4b). It appears that it may be the extra constraint caused by the presence of well-bonded glass particles which causes the increase in σ_y observed in Figs. 4a and c.

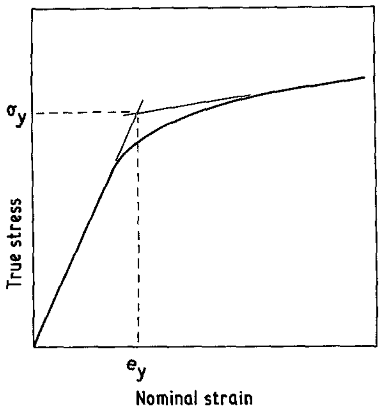


Figure 2 Schematic plot of variation of stress with strain for the hybrid particulate composites deformed in uniaxial compression. The extrapolation procedure used to determined σ_y is indicated.

4. Discussion

4.1. Young's modulus

The dependence of the Young's modulus upon temperature and glass particle volume fraction shown in Fig. 1 appears to be similar for the three systems. Now several theories have been developed to explain the variation of E upon v_f for particulate composites [17] and the data in Fig. 1 have been fitted to one of them. Ishai and Cohen [17] modelled such composites as an array of cubic particles surrounded by a shell of matrix. If the cube boundary is subjected to a uniform displacement then the theory produces a lower bound given by

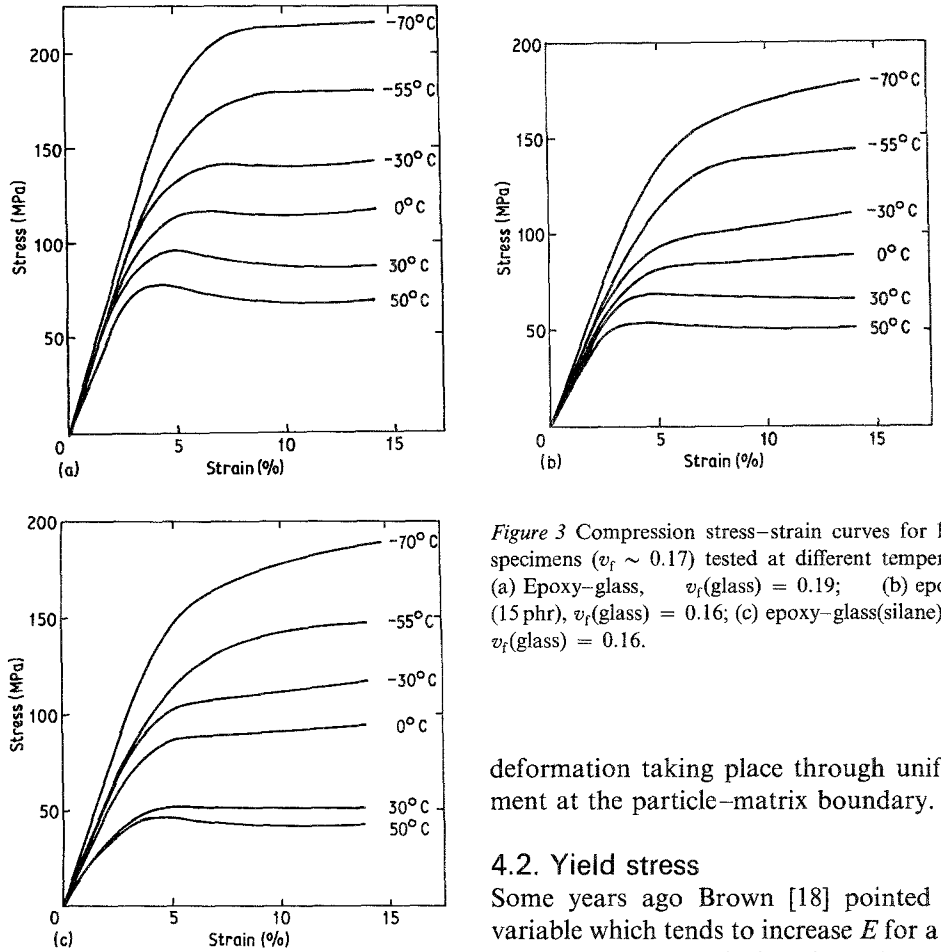


Figure 3 Compression stress–strain curves for hybrid composite specimens ($v_f \sim 0.17$) tested at different temperatures indicated. (a) Epoxy–glass, v_f(glass) = 0.19; (b) epoxy–glass–rubber (15 phr), v_f(glass) = 0.16; (c) epoxy–glass(silane)–rubber (15 phr), v_f(glass) = 0.16.

$$\frac{E_c}{E_0} = 1 + \frac{v_f}{m/(m-1) - Sv_f^{1/3}} \tag{3}$$

where E_c and E_0 are the composite and matrix moduli and $m = E_p/E_0$, the modular ratio, where E_p is the modulus of the particles. An alternative upper bound equation is produced if the cube boundary is subjected to a uniform stress, and this is

$$\frac{E_c}{E_0} = \frac{1 + (m-1)v_f^{2/3}}{1 + (m-1)(v_f^{2/3} - v_f)} \tag{4}$$

The ratio E_c/E_0 has been calculated from the data in Fig. 1 and is replotted for all three systems in Fig. 6. Equations 3 and 4 have also been plotted in Fig. 6 assuming that E_p = 73 GPa [11] and taking E_0 as the value of the matrix modulus when $v_f = 0$. Since E_0 varies with temperature and E_p is not so sensitive to temperature the bounds defined by Equations 3 and 4 vary with temperature. However, within the error in the measured values of E this is not significant and the bounds are represented by shaded regions.

It can be seen that for the epoxy–glass systems (Fig. 6a) the data fall close to the lower bound except at high volume fractions, where they tend to rise above the upper bound. The behaviour for the two hybrid systems containing rubber in the matrix (Figs. 6b and c) is similar except that all the data fall closer to the lower bound. It appears that the theory of Ishai and Cohen [17] is successful in explaining the behaviour of the hybrid particulate composites with deformation taking place through uniform displacement at the particle–matrix boundary.

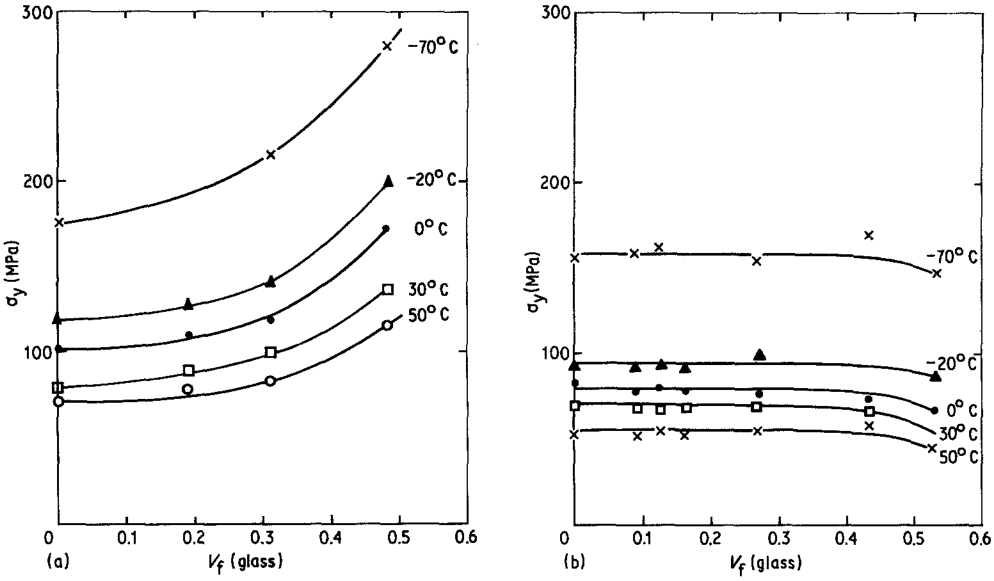
4.2. Yield stress

Some years ago Brown [18] pointed out that any variable which tends to increase E for a glass polymer also increases σ_y such that the ratio σ_y/E is generally in the range 1/60 to 1/30. This behaviour has been found to hold for both thermoplastics [18] and thermosetting polymers such as epoxy resins [6]. It is therefore of interest to determine the effect of adding rigid and soft particles to an epoxy resin upon its yield behaviour at different temperatures.

As far as temperature changes are concerned the behaviour appears to be conventional. The yield stresses of all compositions increase as the temperature of testing is reduced (Figs. 3 and 4) although not as rapidly as the dependence of the Young's modulus upon temperature shown in Fig. 1. However, there are certain anomalies in the dependence of σ_y upon v_f for the epoxy–glass–rubber system. It can be seen from Fig. 4b that the yield stress does not increase as v_f increases, and it even drops below the matrix value at the highest glass particle volume fractions. In contrast, the Young's modulus of the system increases steadily as v_f is increased. Hence σ_y/E changes from about 1/25 at the lowest volume fractions to less than 1/100 at the highest values of v_f. It is clear that the breakdown of the interface in the epoxy–glass–rubber system during plastic deformation that can be seen in Fig. 5 has the effect of depressing the yield stress of the composite. On the other hand, since E is measured at lower strains the interface is not disrupted and the Young's modulus increases with increasing v_f as with the other systems.

4.3. Yield theories

It has been possible to explain the yield behaviour of a large number of glassy thermoplastics and epoxy resins in terms of molecular theories of yielding



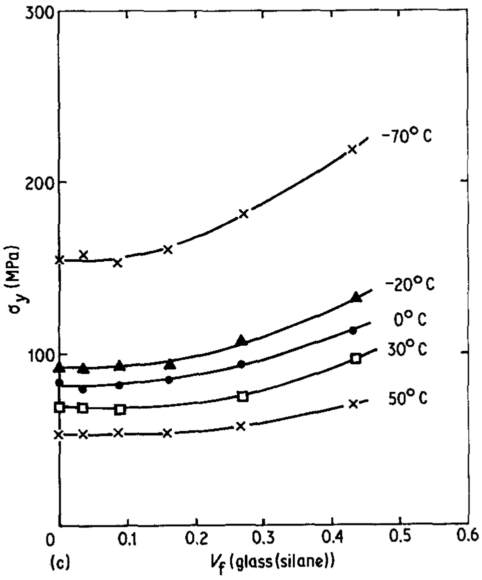


Figure 4 Variation of the yield stress σ_y with volume fraction of glass v_f for hybrid composites tested at different temperatures indicated. (a) Epoxy–glass; (b) epoxy–glass–rubber (15 phr); (c) epoxy–glass(silane)–rubber (15 phr).

[19–23]. Although these theories have been developed for single-phase amorphous polymers it is of interest to see how far they can be used to account for the observations in this present study. In addition, various parameters are derived from the theories which can be correlated with molecular structure of the polymer.

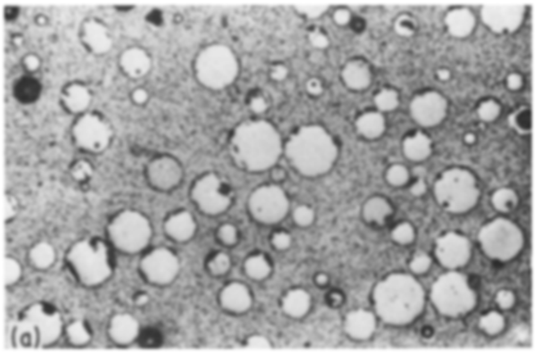
4.3.1. Argon's theory

Argon [21] and Argon and Bessonov [22, 23] proposed that yield in glassy polymers occurs by the thermally-activated production of local molecular kinks which can be modelled as wedge disclinations. They showed that using this model a relationship between the shear yield stress τ and the shear modulus μ is given by

$$(\tau/\mu)^{5/6} = A - B(T/\mu) \qquad (5)$$

where T is the thermodynamic temperature. A and B are constants and are given by

$$A = \left(\frac{0.077}{1 - \nu}\right)^{5/6} \qquad (6)$$



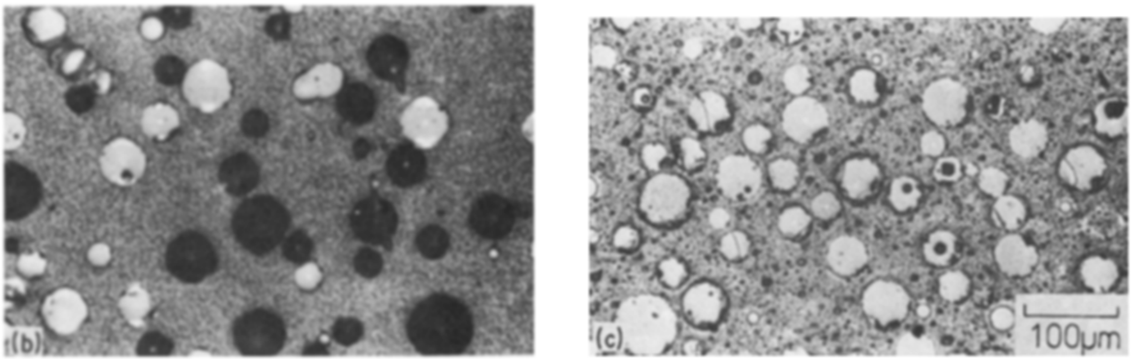


Figure 5 Optical micrographs (all at the same magnification) of sections of the hybrid composites ($v_f \sim 0.27$) deformed in uniaxial compression. The compression direction is vertical. (a) Epoxy–glass; (b) epoxy–glass–rubber; (c) epoxy–glass(silane)–rubber.

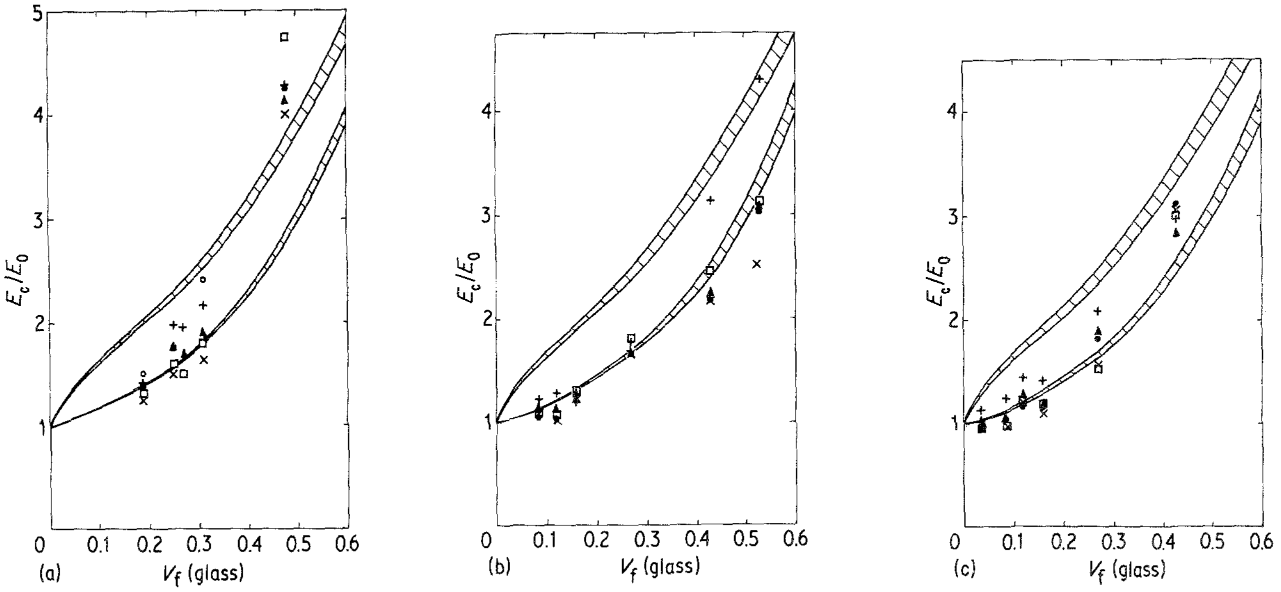


Figure 6 Variation of E_c/E_0 with v_f for the hybrid composites measured at different temperatures: (×) −70° C, (▲) −20° C, (●, ○) 0° C, (□) 30° C, (+) 50° C. The lower and upper bounds are given by Equations 3 and 4 respectively. (a) Epoxy–glass; (b) epoxy–glass–rubber (15 phr); (c) epoxy–glass(silane)–rubber (15 phr).

and

$$B = A\left[\frac{16(1-v)k}{3\pi\omega^2 a^3}\ln(\dot{\gamma}_0)/\dot{\gamma})\right] \qquad (7)$$

where γ is Poisson's ratio, k Boltzmann's constant, ω the net angle of rotation of the molecular segment between the initial conformation and the activated conformation, and a the mean molecular radius. The shear strain rate is given by $\dot{\gamma}$, and the pre-exponential frequency factor $\dot{\gamma}_0$ is usually taken as about $10^{13}\,\text{sec}^{-1}$. Equations 5 to 7 predict that plots of $(\tau/\mu)^{5/6}$ against (τ/μ) should be linear and, since $v \sim 0.3$ for most glassy polymers, it is expected that they should all have a common intercept of $A \sim 0.16$ as $T \rightarrow 0$.

In order to fit the experimental data to the theoretical equations it is necessary to convert the E and σ_y values from Section 3 into shear moduli and shear yield stresses [23] using the equations

$$\mu(T) = E(T)/2(1 + v) \qquad (8)$$

$$\tau(T) = \sigma_y(T)/3^{\frac{1}{2}} \qquad (9)$$

Both $E(T)$ and $\sigma_y(T)$ ought to be measured at the same strain rate but they have instead been determined at a similar crosshead speed. However, it is not envisaged that this will produce significant error in the calculation of the various parameters.

It was found that all the data in Figs. 1 and 4 could be fitted to Equation 5, and straight lines were obtained when $(\tau/\mu)^{5/6}$ was plotted against T/μ. Fig. 7 shows typical plots for the three systems for specimens which have a glass particle volume fraction of 0.27. The parameters A and B can be determined from the intercepts and slopes of such plots and they are listed in Table II for all the specimens tested.

The usefulness of the Argon theory is that the values of A and B can be used to generate molecular parameters. This has been done successfully for single-phase polymers such as thermoplastics 21 and epoxy resins [6]. It is questionable, however, as to how meaningful these molecular parameters will be for a multi-phase system. Nevertheless, an attempt has been made to calculate them from the values of A and B in Table II.

The mean molecular radius a can be determined by rearrangement of Equation 7 [21] as

$$a^3 = \frac{A}{B}\,\frac{16(1-v)k}{3\pi\omega^2}\ln(\dot{\gamma}_0/\dot{\gamma}) \qquad (10)$$

The calculated values of a are listed in Table II setting ω equal to 2 [21] and $\dot{\gamma}$ as $4 \times 10^{-4}\,\text{sec}^{-1}$. It can be seen that although there is a certain amount of spread in the values of a they generally fall within the range of 0.4 ± 0.1 nm which is typical of many glassy polymers [21]. No systematic variation of a with particle volume fraction can be seen with the exception that

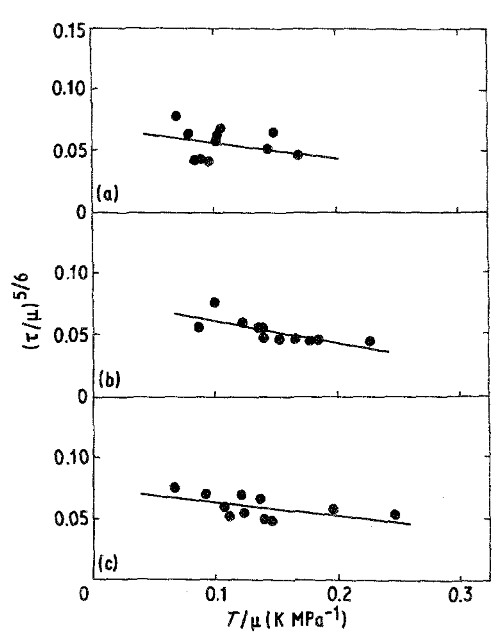


Figure 7 Variation of $(\tau/\mu)^{5/6}$ with T/μ for samples of the hybrid particulate composites ($v_f \sim 0.27$). The straight lines have been plotted according to Argon's theory. (a) Epoxy–glass; (b) epoxy–glass–rubber; (c) epoxy–glass(silane)–rubber.

TABLE II Values of the various parameters derived from Argon's and Bowden's theories of plastic deformation in glassy polymers

System	v_f	A	B (MPa K^{-1})	a (nm)	z^* (nm)	b (nm)
epoxy–glass	0	0.134	0.238	0.432	0.926	0.40
	0.19	0.078	0.068	0.577	1.379	0.35
	0.25	0.065	0.218	0.350	0.866	0.26
	0.27	0.063	0.201	0.353	0.879	0.26
	0.31	0.066	0.102	0.452	1.117	0.23
	0.48	0.058	0.318	0.297	0.752	0.14
epoxy–glass–rubber	0	0.131	0.185	0.467	1.005	0.45
	0.08	0.110	0.158	0.464	1.035	0.39
	0.12	0.099	0.114	0.499	1.136	0.39
	0.16	0.100	0.168	0.440	0.999	0.33
	0.27	0.078	0.181	0.397	0.947	0.25
	0.43	0.049	0.094	0.423	1.107	0.18
	0.53	0.040	0.174	0.321	0.875	–
epoxy–glass(silane)–rubber	0	0.131	0.185	0.467	1.005	0.45
	0.04	0.100	0.093	0.537	1.202	0.43
	0.08	0.097	0.078	0.563	1.288	0.40
	0.12	0.090	0.105	0.499	1.157	0.35
	0.16	0.095	0.127	0.476	1.093	0.35
	0.27	0.069	0.092	0.477	1.167	0.27
	0.43	0.071	0.289	0.328	0.797	0.19

for the three systems, the highest volume fraction composites tend to have the lowest values of a.

The other parameter that can be determined from Argon's theory is z^* which is the critical separation at yield of a pair of kinks (wedge disclinations) in the polymer molecule. It is given at absolute zero [21] by

$$\left(\frac{z^*}{a}\right)_{T=0} = \left[\frac{45}{8(1-v)}\right]^{1/6} A^{-1/5} \qquad (11)$$

It is not thought that the value of z^* varies significantly with temperature. The values of z^* are also given in Table II and it can be seen that they lie mostly in the range 1 ± 0.2 nm. Again there is no systematic variation with volume fraction, with the exception that for the three composite systems the highest volume fractions have the lowest values of z^*.

4.3.2. Bowden's theory

Bowden and co-workers [19, 20] developed an alternative model to explain the yield behaviour of glassy polymers which is based on the assumption that the critical step in the yield process is the thermally activated nucleation under stress of small disc-shaped sheared regions. The strain fields around such regions are assumed to be analogous to those of dislocation loops with a Burgers vector b equal to the shear displacement.

The energy U of a dislocation loop of Burgers vector b and radius R in a solid with shear modulus μ and under an applied stress τ is given approximately [19] by

$$U = 2\pi R\left(\frac{\mu b^2}{4\pi}\right)\ln\left(\frac{2R}{r_0}\right) - \pi R^2 \tau b \qquad (12)$$

where r_0 is the dislocation core radius. The energy of the loop increases as R increases until it reaches a maximum value of U_c at R_c which is given [19] by

$$U_c = \left(\frac{\mu b^2 R_c}{4}\right)\left[\ln\left(\frac{2R_c}{r_0}\right) - 1\right]$$

at

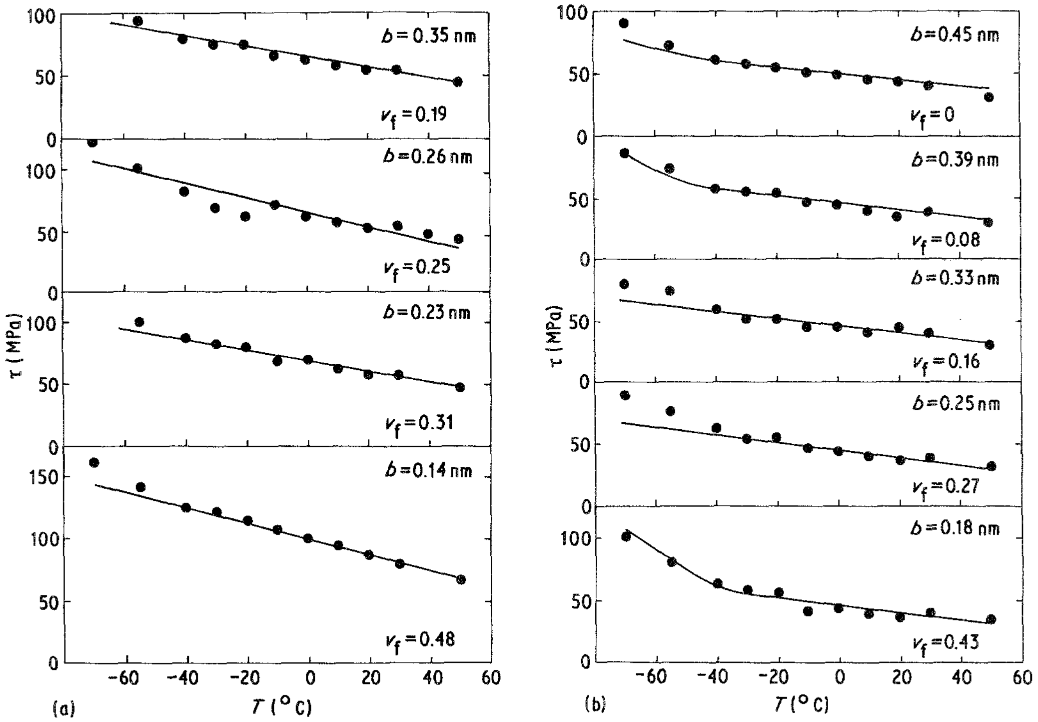
$$R_c = \left(\frac{\mu b}{4\pi\tau}\right)\left[\ln\left(\frac{2R_c}{r_0}\right) - 1\right] \qquad (13)$$

It is possible to eliminate the core radius r_0 by assuming that at absolute zero τ reaches a critical value of $\mu/3^{1/2}\pi$ [19] and this means that $r_0 = b3^{1/2}/e$ ($\simeq b$). It is expected [19] that yielding will occur when U_c reaches $50kT$ which is the energy available from thermal fluctuations. This value of U_c allows Equation 13 to be solved by choosing suitable values of b along with the experimental values of μ to predict the variation of τ with temperature. This has been done in Fig. 8 where the solid lines represent the predicted variation of τ with temperature using values of μ derived from Fig. 1 using Equation 8. The experimental points are determined from Fig. 4 using Equation 9. Values of b have been chosen to achieve the best fit between the theoretical predictions and the experimental data and they are listed in Table II. It can be seen that the Bowden theory gives good agreement between the theoretical predictions and the experimental data over the entire range of temperature. Also it is clear that there is a systematic decrease in b as the volume fraction of particles increases for all three systems.

It is possible to expand and generalize Bowden's theory so that the relationship between μ and τ can be represented by a power law relation [24] of the form

$$\frac{T_0\tau}{T\tau_0} = \left(\frac{T_0\mu}{T\mu_0}\right)^n \qquad (14)$$

where τ_0 and μ_0 are the values of shear yield stress and modulus at some references temperature T_0 (normally taken as ambient temperature) and n is a temperature-independent exponent. It was shown by Kitigawa [24] that a relationship of the form of Equation 14 held for most polymers over a wide range of temperature. He found that n had a unique value of 1.63 for amorphous



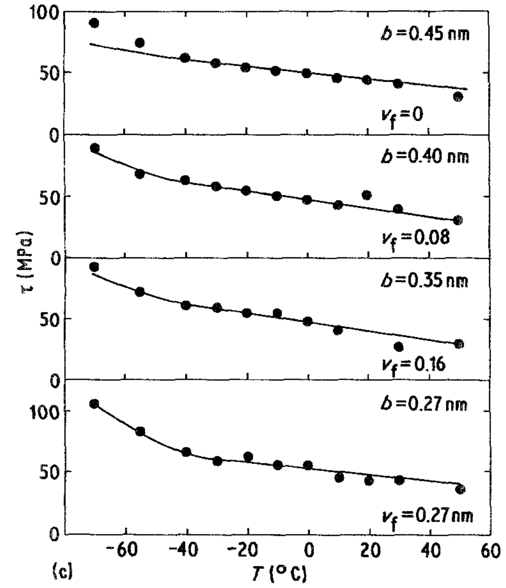


Figure 8 Variation of τ with testing temperature T for the hybrid composites. The curves were predicted from the modulus measurements using the Bowden theory with the values of Burgers vector b indicated. (a) Epoxy–glass; (b) epoxy–glass–rubber (15 phr); (c) epoxy–glass(silane)–rubber (15 phr).

polymers and was between 0.8 and 0.9 for semi-crystalline polymers over a wide range of temperature. It has also been found to be 1.63 for epoxy resins [6]. The modulus and yield data for the three type of composite from Figs. 1 and 4 have also been plotted according to Equation 14 [25]. It has again been found that the data fall on a straight line of slope of about 1.63, in line with other amorphous polymers. The presence of the glass and rubber particles appears to have no effect upon the exponent n.

4.3.3. Comparison of the theories

It is important at this point to compare the usefulness and applicability of the two theories used in this present study to model the yield behaviour of hybrid particulate composites. Although the data can be fitted to the theoretical equations it is vital to know if the fit is fortuitous, or if it can give insight into the underlying deformation mechanisms.

Turning first of all to Argon's theory (Section 4.3.1), it can be seen from Table II that although the value of A falls steadily from 0.13 to about 0.05 as the volume fraction of glass particles increases, the value of B shows no systematic variation with v_f. Although the values of these constants are obtained from fitting the experimental data to Equation 5, they are simply related to the mechanical behaviour of the composite. For instance, inspection of Equation 5 shows that A is effectively the yield strain of the composite at $T = 0$. It is clear therefore that the fall in A with increasing v_f is due to the addition of glass particles causing a large reduction in the yield strain of the material. It is therefore of considerable interest to note that the values of the molecular parameters z^* (~ 10 nm) and a (~ 0.4 nm) generated from A and B through Equations 10 and 11 are similar to values generated for other epoxies [6] and do not change signficantly with v_f for the hybrid epoxy composites. This implies that in the composites studied the yield process is governed principally by the deformation of the epoxy resin matrix in all three systems. The presence of glass and rubber particles controls the value of the yield stress and strain but does not affect the underlying deformation mechanism, which is shear yielding in the epoxy resin matrix.

It can be seen from Fig. 8 that there is excellent correlation between the experimental data and the variation of yield stress with temperature predicted theoretically using the theory of Bowden. This gives considerable confidence in the applicability of the theory to the hybrid particulate composites. However, it can be seen from Table II that there is a rather disturbing systematic decrease in the value of the molecular parameter b with v_f. The Burgers vector b is the only fitting parameter in Bowden's theory, and this makes the theory particularly attractive and easy to use. Examination of the theory of Bowden [19] shows that b is related to the yield strain of the material as $T \rightarrow 0$ (in a similar way to Argon's parameter A). It is clear that the reduction in yield strain induced by the incorporation of glass particles has a profound effect upon the value of b generated. This is rather unfortunate as b is supposed to be a parameter related to the molecular structure. It is unlikely that the presence of glass particles will affect the molecular structure and so one must question the generality of Bowden's theory in the light of the successful way in which Argon's parameter for the composites can be related to the molecular structure of the epoxy matrix.

5. Conclusions

It has been found that the deformation behaviour of hybrid-particulate epoxy composites can be explained satisfactorily in terms of existing theories of deformation of amorphous polymers. In particular it is found that

1. The variation of the Young's modulus with particle volume fraction can be accounted for by the theory of Ishai and Cohen [17] assuming that there is uniform displacement at the particle–matrix interface.
2. The composites are capable of undergoing a considerable amount of plastic deformation even at very low temperatures with high volume fractions of particles. The behaviour can be explained in terms of both the Argon [21] and Bowden [19] theories of plastic deformation. However, the Argon theory would appear to be somewhat more satisfactory as the parameters produced can be related directly to the structure of the epoxy matrix and are virtually independent of particle volume fraction.

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