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Prediction of stress–strain relationships in polymer composites

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A unified theory is developed to predict the elastic moduli, yield stress, and stress–strain curve of polymer composites. In addition to the elastic moduli of filler and matrix, two more constants, related to the hole and activation volume, are needed as input parameters to describe the nonequilibrium mechanical properties of composites. This paper is a generalization of our earlier composite theory to incorporate the effect of structural relaxation. We have derived the compositional dependent relaxation time, and have applied it to understand the deformation kinetics, and to determine the compressive stress–strain behaviour as a function of the filler concentration, strain rate, and temperature. The type of stress applied to a system plays an important role in nonlinear deformations. We shall discuss uniaxial compression, which is not sensitive to cracks, and gives the characteristics of the pure material. As the volume fraction of filler increases, both the effective elastic modulus and yield stress increases. However, the system becomes more brittle at the same time.

(Keywords: filled polymers; Young's modulus; yield behaviour; stress–strain curve; relaxation time; activation volume)

INTRODUCTION

The importance of polymer composites arises largely from the fact that such low density materials can have unusually high elastic moduli and tensile strength[1–4]. For most part, the tensile properties have been quite adequately dealt with by utilizing the theory of elasticity. With the new demands for materials to survive in severe environment of high temperature, compression and strain rate, deformations from elasticity to viscoelasticity and plasticity do occur as the loading and environmental conditions vary. Models built on the basis of the theory of elasticity for the brittle tensile properties have to be modified, so that these three kinds of deformations can be described. In contrast to tension, a stress–strain curve measured in uniaxial compression is not significantly affected by cracks[1], and tends to be characteristic of the pure material.

The purpose of this paper is to seek a unified understanding and approach to the composite elastic modulus, yield stress, and stress–strain curve of polymers dispersed with particles in uniaxial compression. Previous works on amorphous polymers have shown that segmental mobility and structural relaxation play an important role in determining the mechanical properties[5–8], and the yield behaviour is closely related to the nonlinear viscoelastic phenomenon[9,10]. To extend these to the kinetics of deformation of composite systems, a pertinent rule of mixtures for the compositional dependent relaxation times has to be derived. This will provide the basis for calculating the compressive stress–strain behaviour of composite systems as a function of the filler concentration, strain rate and temperature.

COMPOSITE MODULUS

Consider the composite to be a disordered system of randomly distributed particles in a polymer matrix. The interaction between filler particles is treated by a mean field approximation, and the system as a whole is macroscopically homogeneous. Effective Young's modulus E_0 is given by[11,12]

$$E_0/E_2 = 1 + \tfrac{1}{3}\left(\frac{k_1/k_2 - 1}{D} + 2\,\frac{\mu_1/\mu_2 - 1}{G}\right)\Phi \qquad (1)$$

where E_2 refers to Young's modulus of the polymer, Φ is the volume fraction of filler, $k = E/3(1-2v)$ is the bulk modulus, $\mu = E/2(1+v)$ is the shear modulus, v is the Poisson ratio, and the subscripts 1 and 2 identify the filler and matrix;

$$D = 1 + (k_1/k_2 - 1)(1-\Phi)\frac{1+v_2}{3(1-v_2)} \qquad (2)$$

$$G = 1 + 2(\mu_1/\mu_2 - 1)(1-\Phi)\frac{4-5v_2}{15(1-v_2)} \qquad (3)$$

The use of the above equations is shown in *Figure 1* where the calculated and measured[13] Young's modulus of a crosslinked epoxy resin filled with silica (SiO_2) particles are compared. The elastic properties of the filler and matrix are[11]

$$\begin{aligned} &E_1 = 21.2E_2 && v_1 = 0.22 \\ &E_2 = 17\times 10^3\ \mathrm{kg\,cm^{-2}} && v_2 = 0.35 \end{aligned} \qquad (4)$$

In the rest of the paper, the composite system with the properties given by equation (4) will be used to illustrate the theoretical development. Glassy polymers are not in thermodynamic equilibrium. The change in the nonequilibrium glassy state and its relaxation define the viscoelastic response[5]. The relaxation modulus can, in general, be written as

$$E(t) = E_\infty + (E_0 - E_\infty)\Psi(t) \qquad (5)$$

where t is the time and E_0, mentioned in equation (1),

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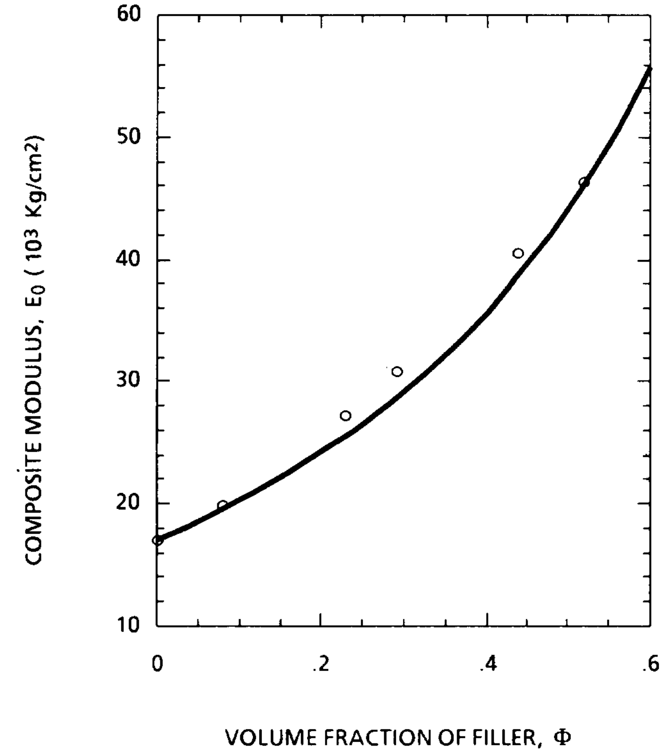

Figure 1 Effective Young's modulus for a filled epoxy. Circles are experimental data[13]

is the unrelaxed modulus which is much greater than the relaxed modulus (E_∞) in the glassy state. The normalized relaxation function has the form

$$\Psi(t) = \exp[-(t/\tau)^\beta] \qquad 0 < \beta \leqslant 1 \tag{6}$$

where τ is the effective relaxation time and β is a constant defining the shape of relaxation spectrum. The above equation has been successfully utilized in the past to describe the mechanical properties of amorphous and crosslinked polymers[5,14,15]. During the study, we have found the important differences[14,15] between Williams-Watts' equation for dielectric relaxation[16] and equation (6). Instead of being empirical constants, both τ and β are functionally related and molecularly interpreted[17]. In addition to temperature (T) and the nonequilibrium glassy state (δ), the origin of physical ageing, we now expect that τ is also a function of the filler concentration.

RELAXATION TIME

In order to understand the kinetic mechanism of deformation of a composite, one needs to know a pertinent rule of mixtures that defines the compositional dependent relaxation time. Consider the lattices for binary mixtures which consist of the number of lattice sites

$$N_j(t) = n_j(t) + x_j n_{xj} \quad (j = 1, 2) \tag{7}$$

where n_j and n_{xj} are the number of holes and polymer molecules, respectively, and x_j is the number of monomer segments for the jth material. Each lattice site occupies a single lattice cell with volume v_j. Blends of two-phase materials are generally expected to exhibit no volumetric deviation from an additive relationship:

$$V = v_1 N_1 + v_2 N_2 \equiv vN = v(n + xN) \tag{8}$$

This leads to the effective number of holes

$$n = (v_1 n_1/v) + (v_2 n_2/v)$$

and the free volume fraction of the blend

$$f = n/N = f_2 + (f_1 - f_2)\Phi \tag{9}$$

where the free volume fractions $f_j = n_j/N$, the volume concentrations $\Phi_j = v_j N_j/vN$ and $\Phi = \Phi_1 = 1 - \Phi_2$.

In a single phase material, the relaxation time is inversely proportional to the mobility of chain segments, and is related to the free volume fraction by the Doolittle equation[18]

$$\ln \tau_j = B_j/f_j \quad (j = 1, 2) \tag{10}$$

where B_j is a constant. Equations (9) and (10) give

$$\ln(\tau/\tau_2) = B/f - B_2/f_2$$
$$= [(B - B_2) - B_2(f_1/f_2 - 1)\Phi]/[f_2(1 - \Phi) + f_1\Phi] \tag{11}$$

When $\Phi \rightarrow 0$, τ/τ_2 approaches one. This requires $B = B_2$. Since β in equation (6) is inversely proportional to $B^{5,15}$, this suggests that the distribution of relaxation times may not be affected by the presence of fillers.

In the case of filled polymers, equation (11) can be further simplified by assuming the free volume of fillers (f_1) to be zero. Thus, we obtain

$$\log(\tau/\tau_2) \equiv (1/2.303)\ln(a_\phi) = C\Phi/(1 - \Phi) \tag{12}$$

where $C = B/2.303f_2$ and a_ϕ is the concentration dependent shift factor. The above equation is obtained by considering a disordered system which contains not only filler particles, but holes in a polymeric matrix. The volume of the system is close-packed and there is no interpenetrating of molecules and holes at the interface between filler and polymer. The composite relaxation time (τ) is determined by the motion of holes in a polymer matrix[17] constrained by the presence of fillers. Equation (12) reveals that a small increase in the filler concentration (Φ) can increase the effective relaxation time by an order of magnitude. The dependence of τ_2 on the physical ageing and temperature for amorphous and crosslinked polymers has already been reported elsewhere[5,15].

YIELD STRESS

The relaxation phenomenon discussed in the last section is within the linear viscoelastic range. At high stress levels, the contribution from the external work done on a hole lattice site has to be included in the analysis. By taking into account the long range cooperative interaction, the external work can, in general, be written as[5]

$$\Delta w = -\sigma_{ij}\Omega_{ij}(N/n) = -(\sigma_{ij}\Omega_{ij}/f_2) \tag{13}$$

where σ_{ij} and Ω_{ij} are the stress and activation volume components, respectively. For isotropic materials, the activation volume tensor has two independent components. These are the bulk activation volumes, which are equal to the lattice volume v, and the shear activation volume Ω_{12}. We have determined that $v/\Omega_{12} = 0.121$ for most polymers[5,19]. The ratio Ω_{ij}/f_2 in equation (13) represents the volume of polymer segments under deformation, and is between 1 and 2 orders of magnitude larger than the lattice volume. This is consistent with the previous studies[19,20].

In tension the composite exhibits brittle fractures[11,21,22], while in compression the filled polymer behaves as a ductile material[1,13] with a yield point and higher elongation to break. This can be treated as a relaxation phenomenon. The activation volume in uniaxial compression is found to be[19]

$$\Omega_{11} = \frac{2\Omega_{12}}{3}\left(1 - \frac{\upsilon}{2\Omega_{12}}\right) \tag{14}$$

which is smaller than that in tension or shear. When the magnitude of compressive stress is high, the effective relaxation time takes the form

$$\tau(T, \delta, \Phi, \sigma_{11}) = \tau_2(T, \delta)\alpha_\phi \alpha_\sigma \tag{15}$$

where the nonequilibrium glassy state $\delta = f_2(t) - f_2$, and the nonlinear stress dependent shift factor

$$a_\sigma = \exp\left(-\frac{|\sigma_{11}|\Omega_{11}}{2f_2\beta RT}\right) \tag{16}$$

Interestingly, we see a decrease in the effective relaxation time in uniaxial compression.

In the solid state deformation, the nonlinear viscoelastic effect is most clearly shown in the yield behaviour. The yield occurs when the product of the effective relaxation time and the applied strain rate ($\dot{e} = \dot{e}_{11}$) reaches a constant value[10,23]. Using equation (15) and replacing $|\sigma_{11}|$ by σ_y, we obtain the compressive yield stress:

$$\sigma_y = A + K\left(\log \dot{e} + \frac{C\Phi}{1 - \Phi}\right) \tag{17}$$

where A is a constant and $K = 4.606 f_2 \beta RT/\Omega_{11}$. A comparison of equation (17) and data at the room temperature (23°C), expressed in terms of the compressive yield stress *versus* strain rate at different filler contents, is shown in *Figure 2*. The slope gives the value of K, and reveals that the activation volume is not a function of Φ. The constant C defines the plots of yield stress *versus* filler concentration in *Figure 3*. These figures give

$$K = 105 \text{ kg cm}^{-2} \qquad C = 3.2 \tag{18}$$

for the silica filled epoxy. Experimental data used in *Figures 1–3* are taken from the same source[13]. Both equations (4) and (18) will be needed in calculating the stress–strain behaviour. The constant $A = 730 \text{ kg cm}^{-2}$, which can be extracted easily from *Figure 2*, will no longer be needed.

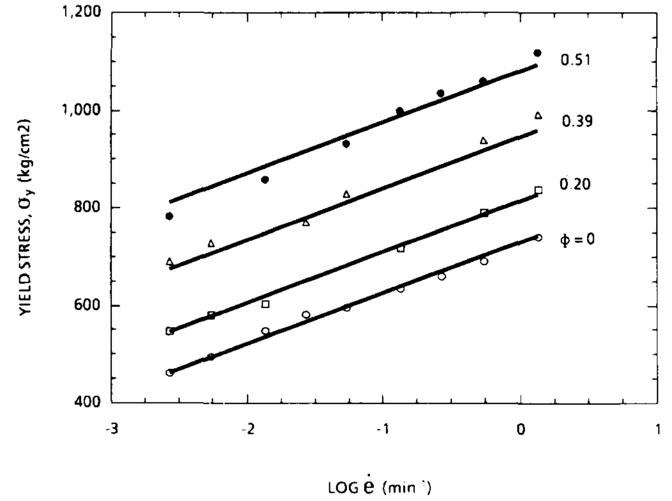

Figure 2 Comparison of the predicted (solid lines) and measured[13] (points) strain rate dependence of the compressive yield stress at different filler concentrations

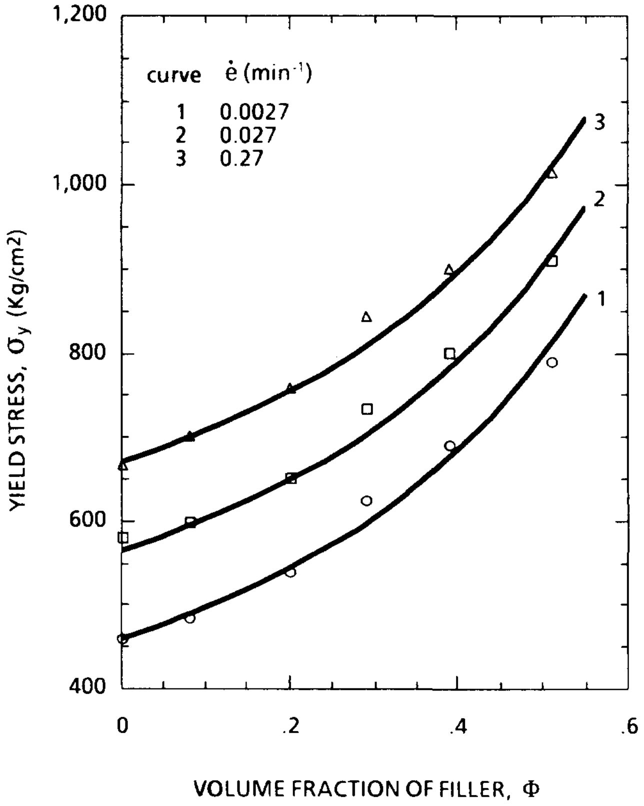

Figure 3 Compressive yield stress *versus* filler concentration at different strain rates. Points are experimental data[13]

STRESS–STRAIN BEHAVIOUR

The calculation is now being extended from the elastic modulus and yield stress to the stress–strain curve. The constitutive equation for stress and strain in uniaxial compression is given by the Boltzmann superposition integral:

$$\sigma(t) = \int_0^t E(t - s)\dot{e}(s)\,\mathrm{d}s \tag{19}$$

where E is the compressive relaxation modulus described by equations (5), (6), and (15). The subscript 11 for stress or strain has been dropped. The strain rate is usually kept constant in Instron measurements. Put $e = \dot{e}t$, and equation (19) becomes

$$\sigma(e) = \int_0^e E(e - e')\,\mathrm{d}e' \tag{20}$$

Substituting equations (5), (6) and (15) into equation (19), we get the compressive stress–strain relationship

$$\sigma(e) = E_0(\Phi)\int_0^e \exp\left\{-\left[\frac{e' \exp(2.303\sigma(e')/K)}{\dot{e}\tau_2 a_\phi(\Phi)}\right]^\beta\right\}\mathrm{d}e' \tag{21}$$

where the compositional dependent E_0 and a_ϕ are given by equations (1) and (12), respectively. In addition to equations (4) and (18), the parameters $\beta = 0.19$, and $\tau_2 = 0.711 \times 10^{13}$ s at 23°C are adopted in seeking the numerical solution of equation (21). As mentioned earlier,

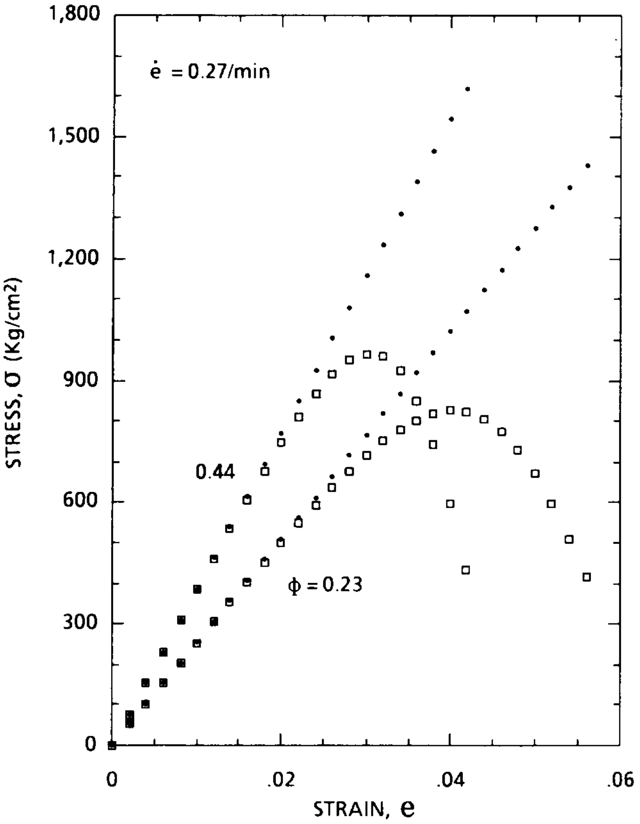

Figure 4 Effect of nonlinear stress on the compositional dependent stress–strain curves in uniaxial compression

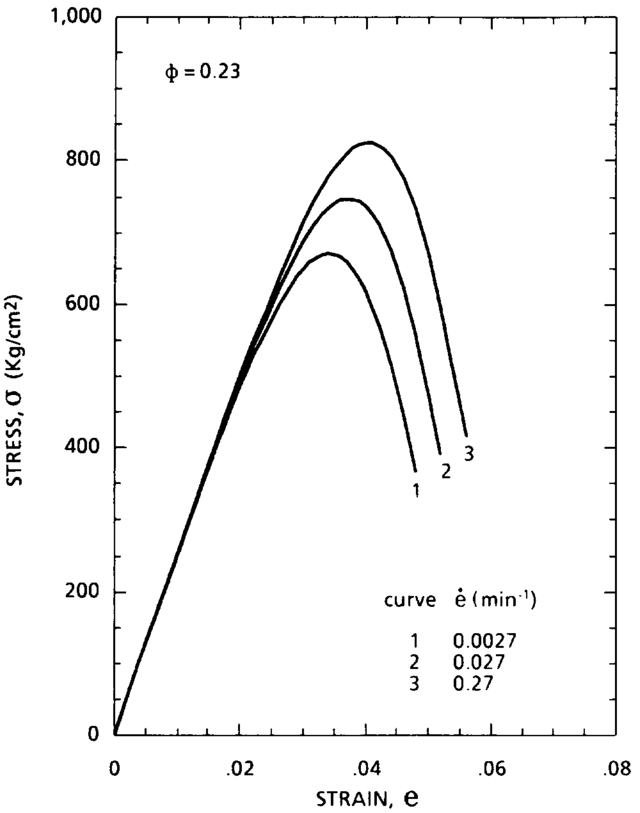

Figure 5 Dependence of the compressive stress–strain curves on strain rate

β for the composite system has the same value as that for epoxy resins[15].

The importance of incorporating the effect of nonlinear stress, equation (16), in the calculation of equation (21) is explained in *Figure 4*. The curves with square symbols include the nonlinear effect, while those with dots do not. The calculated nonlinear viscoelastic stress–strain properties shown in *Figure 4* resemble the corresponding measured curves[13]. The effect of strain rate is shown in *Figure 5*. The compressive stress–strain curves at different filler concentrations are plotted in *Figure 6*. The yield behaviour displayed here not only compares well with that in *Figure 3*, but exhibits the continuous change from elasticity to plasticity. As the volume fraction of filler increases, the yield stress of the composite system increases but, at the same time, the system becomes more brittle.

TEMPERATURE DEPENDENCE

Temperature has a great deal of effect on the mechanical properties of polymer matrix, but not on those of fillers. In order to calculate the stress–strain behaviour of a composite system, explicit temperature dependent expressions are required for the unrelaxed modulus, the constants C and K, and the polymer relaxation time τ_2. Young's modulus of epoxy resins[24] is scaled by $E_2(T) = E_2(23°\mathrm{C}) \times (296/T)$. As a crude first approximation, the free volume fraction below the glass transition temperature ($T_g = 115°\mathrm{C}$) may be treated as a constant. Therefore, C in equation (12) is independent of temperature. Because the activation volume is also unaffected by the change in temperature[5], equation (17) suggests that $K(T) = K(23°\mathrm{C}) \times (296/T)$. This is consistent with reported data[25]. In the glassy state, the temperature dependence of the relaxation time follows an Arrhenius type of equation

$$\tau_2(T) = \tau_2(23°\mathrm{C}) \exp\left[\frac{\Delta H}{R}(1/T - 1/296)\right] \qquad (22)$$

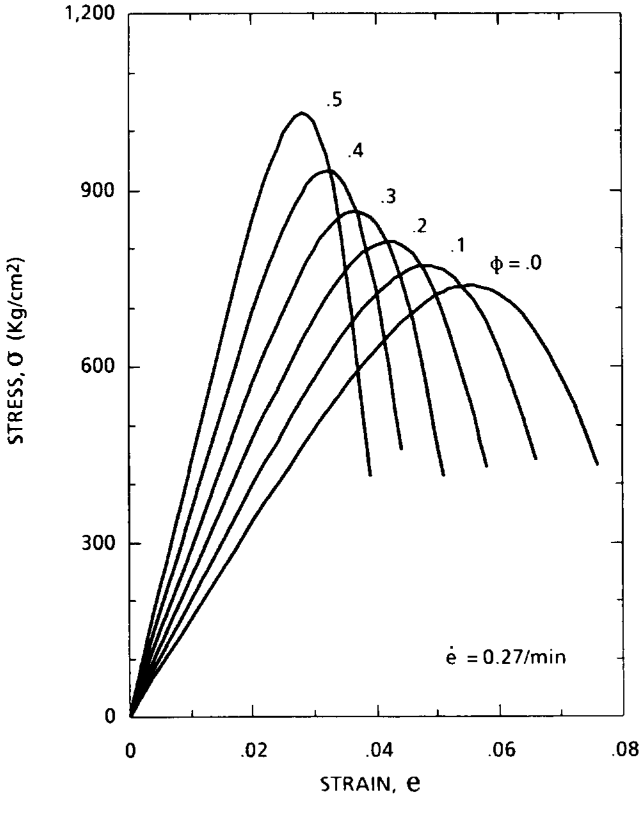

Figure 6 The compressive stress–strain curves at different filler concentrations

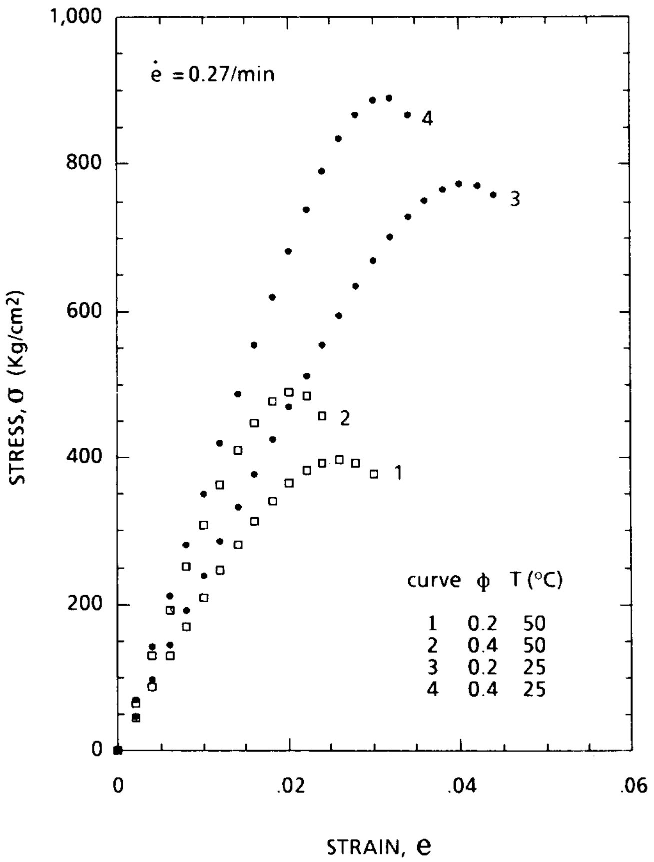

Figure 7 Effect of temperature on the compositional dependent stress–strain curves

where the activation energy $\Delta H = 84\,\text{kcal mol}^{-1}$ for epoxy resins[15,24], and R is the gas constant. The activation energy below T_g is significantly influenced by the physical ageing process[5,15].

By utilizing all these expressions in equation (21), the effect of temperature on the stress–strain relationships in the composite system is shown in *Figure 7*. Effective Young's modulus is not as strongly influenced by temperature as the viscoelastic and plastic responses are.

CONCLUSIONS

The effective Young's modulus, yield stress, and the stress–strain curve of polymers dispersed with particles in uniaxial compression have been calculated as a function of the filler concentration, strain rate, and temperature. In addition to the elastic moduli of filler and matrix, two more constants K and C, which relate to the activation volume and free volume fraction, respectively, are also needed as input parameters to describe the equilibrium and nonequilibrium mechanical properties.

The change in the physical mechanism of deformation from elasticity, viscoelasticity to plasticity depends on the time scales in which the composite system is measured and relaxed. We have derived the composite relaxation time by treating the composite as a disordered system of randomly distributed particles and holes in a polymeric matrix. The effective relaxation time increases with an increase in filler concentration, but decreases with an increase in uniaxial compression.

The type of stress applied to a system has little effect on the linear viscoelastic relaxation, but becomes very important as the stress level increases. The activation volume tensor is a key parameter. In the solid state deformation, the nonlinear viscoelastic effect is most clearly shown in the yield behaviour. Our analysis reveals that the compressive activation volume (Ω_{11}) is independent of the filler concentration. Since the filler and matrix are not mixed at molecular level, the relaxation spectrum (β) is also found to be independent of composition. This greatly simplifies the analysis. The theoretical prediction is in good agreement with the experiment. As the volume fraction of filler increases, both the effective elastic modulus and yield stress increase. However, the system becomes more brittle at the same time. Finally, through the mechanistic understanding of the structural relaxation and deformation kinetics, we have gained a solid basis to estimate the effect of temperature on the mechanical properties of polymer composites.

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