

Stress-strain behaviour of physically ageing polymers

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Equations are derived to predict the effects of physical ageing on the Young's modulus, yield stress, yield strain and stress-strain relationship of glassy polymers in uniaxial compression. The stress-strain behaviour of a quenched and annealed polymer depends on the timescales in which the amorphous solid is aged, relaxed and measured. The mechanical properties of polystyrene are calculated as a function of annealing time, annealing temperature and strain rate. The calculation reveals that both Young's modulus and yield stress increase with ageing, but the yield strain decreases only slightly. As ageing continues, polymers become more brittle. In the glass transition region, the effects of physical ageing on Young's modulus and yield stress diminish after a critical ageing time. The critical time is a function of annealing temperature, and is related to how the non-equilibrium glassy state approaches equilibrium.

(Keywords: Young's modulus; yield stress; yield strain; stress-strain relationship; physical ageing; glassy polymers; modelling)

INTRODUCTION

The yield behaviour of polymers has been studied extensively in the literature as a function of strain rate and temperature¹⁻⁶. Since glasses are not in thermodynamic equilibrium, the slow variation in structure as a function of time affects the mechanical properties of polymers. This is known as the physical ageing phenomenon⁷. The effect of physical ageing on stress-strain relationships has been observed^{8,9}, but has not been analysed theoretically. On the basis of our dynamic theory of glasses¹⁰, the dependence of yield stress on the aged time of polymeric glasses¹¹ and on the composition of compatible blends¹², and the stress-strain curve of particulate composites¹³ have been quantitatively analysed.

In this paper, the same concept is extended to the understanding of the stress-strain behaviour of quenched and annealed polymers. The stress-strain behaviour is controlled by the timescales in which an amorphous solid is aged, relaxed and measured. We shall consider that polymer is quenched isobarically from liquid to glass for annealing before it is quenched again to room temperature for assessing the stress-strain behaviour. The material presented in this paper is organized under four sections. We start with the essential features of our dynamic theory of glasses. New equations will then be presented to calculate and to discuss the effects of physical ageing on Young's modulus, yield stress and stress-strain relationships.

NON-EQUILIBRIUM GLASSY STATE

Amorphous solids are not in thermodynamic equilibrium. The departures from equilibrium for the holes (free volumes) and bond rotations during vitrification and physical ageing have been treated as a stochastic process.

We have reported that the conformational activation energy controlling the rotational relaxation of bonds is between one and two orders of magnitude lower than the hole activation energy¹⁰. As a result, the conformer relaxes much faster than the hole. Since the mechanical properties of glasses vary slowly in time, the dominant contribution to the structural relaxation and physical ageing is from holes. Consider a lattice consisting of n holes and n_x polymer molecules of x monomer segments each. The total number of lattice sites (N) and volume (V) are written in the forms:

$$N(t) = n(t) + xn_x \quad \text{and} \quad V = vN \quad (1)$$

In the model, each lattice site occupies a single lattice cell of volume v . It is important to mention that $n(t)$ consists of both equilibrium and non-equilibrium contributions in the glassy state. For temperatures (T) above the glass transition temperature (T_g), the non-equilibrium part of n goes to zero. The change of $n(t)$ below T_g defines the glassy state. Minimizing the excess Gibbs free energy due to hole introduction with respect to the hole number, the temperature dependence of equilibrium hole fraction, $\bar{f} = \bar{n}/N$, is given by¹⁴:

$$\bar{f}(T) = f_r \exp \left[-\frac{\varepsilon}{R} \left(\frac{1}{T} - \frac{1}{T_r} \right) \right] \quad (2)$$

where ε is the mean hole energy, R is the gas constant and the subscript r refers to the condition at $T = T_r$, which is a fixed quantity near T_g (see equation (11) later). The hole energy characterizes the intermolecular interaction.

The glassy-state relaxation is a result of the local configurational rearrangements of molecular segments, and the dynamics of holes provide a quantitative description of the segmental mobility. We have analysed the hole dynamics and fluctuations on a fractal lattice¹⁰, and have addressed important questions in the structural

relaxation and physical ageing. Integrating the hole density distribution function over space, the non-equilibrium hole fraction, $\delta(t) = f(t) - \bar{f}$, is obtained for a system started from equilibrium:

$$\delta(T, t_a) = -\frac{\varepsilon}{R} \int_0^{t_a} \frac{q\bar{f}}{T^2} \Psi(t_a - t') dt' \quad (3)$$

where t_a is the ageing time and $q < 0$ is the cooling rate. Different paths of time integration describe different thermal history behaviours of the structural relaxation and recovery kinetics. When further analysis of the hole dynamics is carried out¹⁰, we have derived the relaxation function:

$$\Psi(t) = \exp[-(t/\tau)^\beta] \quad 0 < \beta \leq 1 \quad (4)$$

where $\tau = \tau_r a$ is the relaxation time, and the shift factor:

$$a(T, \delta) = \left(\frac{\bar{f} + \delta}{f_r} \right)^{-1/[\beta(\bar{f} + \delta)]} \quad (5)$$

At $T = T_r$, we have $\delta = 0$, $\bar{f} = f_r$ and $\tau = \tau_r$, which require $a = 1$. In the vicinity of T_g , equation (5) becomes:

$$\ln a(T, \delta) = 2.303 \log a(T, \delta) \approx \frac{1}{\beta} \left(\frac{1}{\bar{f} + \delta} - \frac{1}{f_r} \right)$$

as $\frac{\bar{f} + \delta}{f_r} \rightarrow 1$ (6)

which may be called the 'generalized' Doolittle equation. When $T \geq T_g$, we have $\delta = 0$ and equation (6) reduces to the exact form of Doolittle's equation¹⁵.

There are important differences between the Kohlrausch-Williams-Watts (KWW) equation and equations (4) and (5). KWW treats β and τ as empirical parameters, which must alter continuously through the glass transition region in order to fit the relaxation data. Since τ is a time-dependent quantity for $T < T_g$, the accurate way of determining β from relaxation data is by treating t/τ as an independent master variable plotted in the transient or dynamic master curves. On the basis of our extensive studies^{10,11,16} of volume and viscoelastic relaxations, β is found to be a constant through the glass transition region and τ can be a function of temperature, ageing time, non-linear stresses, and the structure and composition of materials.

YOUNG'S MODULUS

Since all physical properties of glasses vary slowly in time, the system is in a quasi-equilibrium state. The contribution from the hole fraction to the bulk modulus (k) can therefore be written approximately by¹⁶:

$$k_{\text{hole}} \approx \frac{RT}{v(\bar{f} + \delta)} \quad (7)$$

Consider that polymer is cooled from liquid to glass and is then isothermally annealed. Using equations (6) and (7), the change in the bulk modulus is:

$$(k_2 - k_1)_{\text{hole}} = \beta \frac{RT_a}{v} [\ln a(T_a, t_2) - \ln a(T_a, t_1)]$$

$$\equiv \beta \frac{RT_a}{v} \Delta \ln a \quad (8)$$

for polymer aged from $t_a = t_1$ to t_2 at the annealing

temperature $T = T_a$. We have assumed here that the compressibility of the lattice, expressed in terms of v and xn_x in equation (1), does not contribute to the physical ageing. For isotropic glasses, Young's modulus is $E_0 = 3(1 - 2\nu)k$, where ν is the Poisson ratio. Following equation (8), we obtain:

$$\Delta E_0 \equiv E_0(t_2) - E_0(t_1) = 3\beta(1 - 2\nu) \frac{RT_a}{v} \Delta \ln a \quad (9)$$

In accordance with equations (2)–(6) and (9), the effects of the ageing time and temperature on the change in Young's modulus of a quenched and annealed polystyrene (PS) is calculated in Figure 1. The increase in Young's modulus is a result of volume relaxation. The shape of the curves depends on how long it takes for δ to approach equilibrium at different annealing temperatures. We have $\nu = 1/3$ for amorphous solids, and have chosen $t_1 = 1$ h. The input hole parameters for PS are^{10,14}:

$$\varepsilon = 3.58 \text{ kcal mol}^{-1} \quad \beta = 0.48 \quad \tau_r = 30 \text{ min}$$

$$f_r = 0.032 \quad (10)$$

which describes the glass transition and volume relaxation of PS. The hole energy ε is related to T_r by¹⁴:

$$\varepsilon/RT_r = \gamma \quad (11)$$

where γ is a function of the lattice coordinate number. For linear PS, we have $\gamma = 4.86$ and $T_r = 370.5$ K. When $T < T_r - 10$ K, equation (9) and Figure 1 reveal that the ageing rate of ΔE_0 is proportional to:

$$\frac{RT_a}{v} = \frac{1}{\gamma} \left(\frac{T_a}{T_r} \right) \left(\frac{\varepsilon}{v} \right) \sim \frac{\varepsilon}{v} \quad (12)$$

The hole energy density, ε/v , is a key parameter in describing the temperature dependence of the yield stress¹¹:

$$\frac{d\sigma_y}{dT} = -0.194 \frac{\varepsilon}{vT_r} \quad (\text{in uniaxial compression}) \quad (13)$$

From the σ_y versus T data¹⁷, one gets $\varepsilon/v = 309.4 \text{ cal cm}^{-3}$ for PS, which is larger than $190.6 \text{ cal cm}^{-3}$ for poly-

$\Delta E_0, 10^3 \text{ kg/cm}^2$

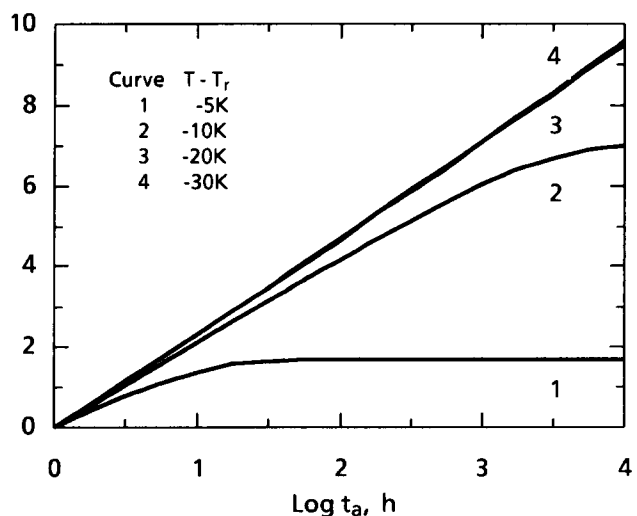


Figure 1 Effect of annealing time (t_a) on the change in Young's modulus of a polystyrene glass. Curves represent the different annealing temperatures (T_a)

carbonate (PC)¹¹. Therefore, physical ageing has a stronger effect on Young's modulus of PS than on that of PC. This finding is consistent with the data reported in the literature^{8,9,11}. Because it takes much less time for ε/v , versus $\Delta E_0(t_a)$, to be measured, the hole energy density could provide a useful indication of how the ageing affects Young's modulus of linear polymers, which have β close to 1/2 (ref. 10).

Struik has introduced an exponent μ in the glassy state to characterize the physical ageing observed in his isothermal creep experiments⁷:

$$a(T, t_a) \sim t_a^\mu \quad (14)$$

The ageing exponent μ is not treated as an experimental constant here, but is calculated directly from equations (5) and (10). It is equal to 0.84 at $T_a = T_r - 20$ K. Equations (9) and (14) yield:

$$E(t_2) - E(t_1) \simeq 6.91\beta\mu(1-2\nu) \frac{RT_a}{v} \log\left(\frac{t_2}{t_1}\right) \quad (15)$$

which approximates the curves 3 and 4 shown in Figure 1. This logarithmic variation in the glassy state is well exhibited in the reported data⁸.

When the shift factor, equation (14), is substituted into equation (4), we obtained:

$$-\ln \Psi \sim \left(\frac{t}{a}\right)^\beta \sim t^{(1-\mu)\beta} \sim \begin{cases} t^{0.0786} & T < T_r - 20 \text{ K} \\ t^{0.48} & T > T_r \end{cases}$$

which illustrates the drastic change of the 'effective' stretched exponential (the KWW exponent) with temperature in the vicinity of the glass transition. The ageing exponent μ changes with temperature, but β remains constant.

YIELD STRESS

In the solid-state deformation, the non-linear viscoelastic effect is most clearly shown in the yield behaviour. The yield occurs when the product of the non-linear relaxation time and the applied strain rate reaches a constant value^{2,3}:

$$\dot{\varepsilon} \tau_{\text{non-linear}} \sim \text{constant} \quad (16)$$

The non-linear relaxation time has been derived^{11,16} to be:

$$\tau_{\text{non-linear}}(T, \delta, \sigma_{11}) = \tau \exp\left(-\frac{\Delta w}{2\beta RT}\right) \quad (17)$$

where the linear relaxation time τ has been mentioned earlier. Equation (17) can also be interpreted in terms of the relaxation of the local configurational rearrangement of molecular segments in ref. 18. At high stress levels, the contribution from the external work done on a lattice cell has to be included in the non-linear viscoelastic analysis. By taking into account the long-range cooperative interaction, the external work done by σ_y acting on a hole cell during yielding is:

$$\Delta w = -\sigma_y \Omega_{11} \frac{N}{n} = -\frac{\sigma_y \Omega_{11}}{f} \quad (18)$$

where Ω_{11} is the activation volume in uniaxial compression. The ratio Ω_{11}/f represents the volume of the polymer segment, which has to move as a whole in order

for plastic yield to occur. Using equations (16)–(18), we obtain the compressive yield stress:

$$\sigma_y = A + K[\log \dot{\varepsilon} + \log a(T, \delta)] \quad (19)$$

where A is a constant and $K \sim \beta f RT / \Omega_{11}$. When the strain rate is kept constant, the change in the yield stress is related directly to the change in the shift factor:

$$\Delta \sigma_y / K = \Delta \log a(T, t_a) \quad (20)$$

This equation is used in the calculation of the dependence of $\Delta \sigma_y$ on the ageing time and temperature for PS glass. In Figure 2, we see that $\Delta \sigma_y$ increases linearly with $\log t_a$ in the glassy state. However, there is no such simple relationship in the glass transition region. This theoretical prediction is consistent with experimental observation¹⁹. The diminishing effect of physical ageing is a result of the vanishing δ as a function of t_a .

In the rest of the paper, we consider that PS is quenched from liquid (T at $t'=0 \geq T_r + 10$ K and $q \rightarrow -\infty$ in equation (3)) to T_a where the sample is annealed (t_a) before it is quenched again to room temperature (23°C) for assessing the stress-strain behaviour. Calculation has revealed that the effect of physical ageing is essentially due to the isothermal annealing step at T_a . The compressive yield stress versus strain rate at different ageing times is shown in Figure 3, where $K = 90 \text{ kg cm}^{-2}$ is chosen in accordance with the data of a well aged PS measured at room temperature (23°C). At $T_a = T_r - 20$ K, Figure 3 can be described by:

$$\frac{\Delta \sigma_y}{K} \simeq \log\left(\frac{\dot{\varepsilon}_2}{\dot{\varepsilon}_1}\right) + \mu \log\left(\frac{t_2}{t_1}\right) \quad (21)$$

which approximates equation (19). A similar logarithmic variation with ageing time appears as in the case of equation (15), but the variation is not characterized by the same constant. Equation (21) provides a good description to the published data²⁰.

STRESS-STRAIN RELATIONSHIP

The non-linear relaxation modulus $E(t)$ of a quenched and annealed glass changes not only with the ageing time

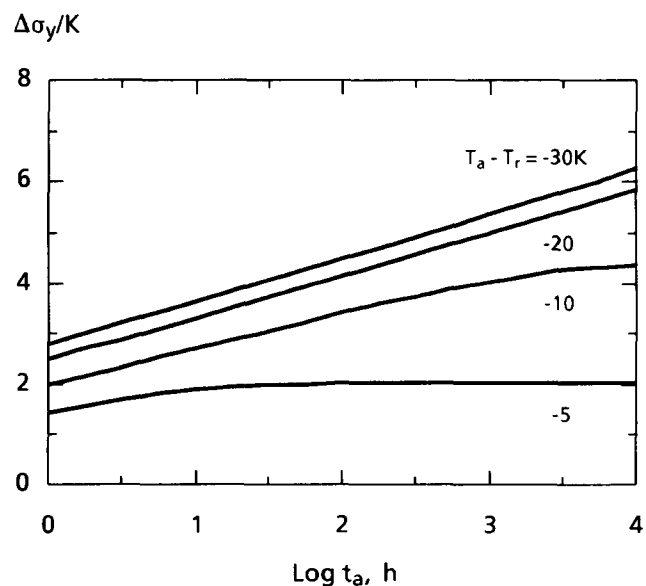


Figure 2 Effect of annealing time on the change in compressive yield stress of PS. Curves represent the different annealing temperatures (T_a)

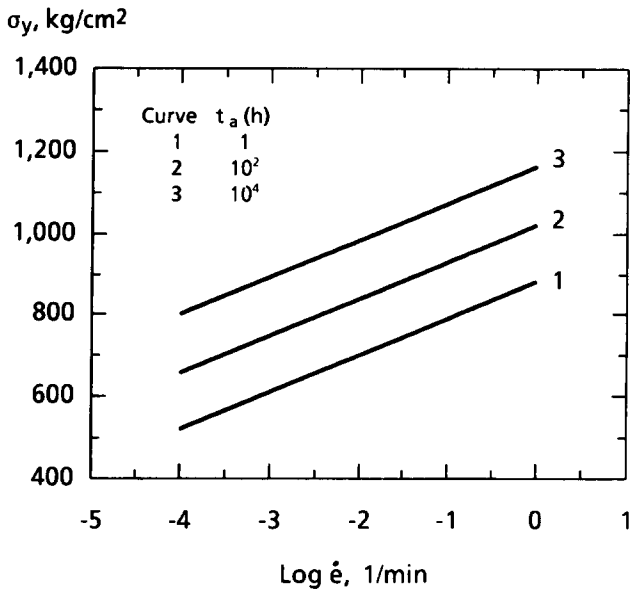


Figure 3 The dependence of the compressive yield stress of PS on the annealing time and strain rate. The annealing temperature is $T_a = T_r - 20$ K

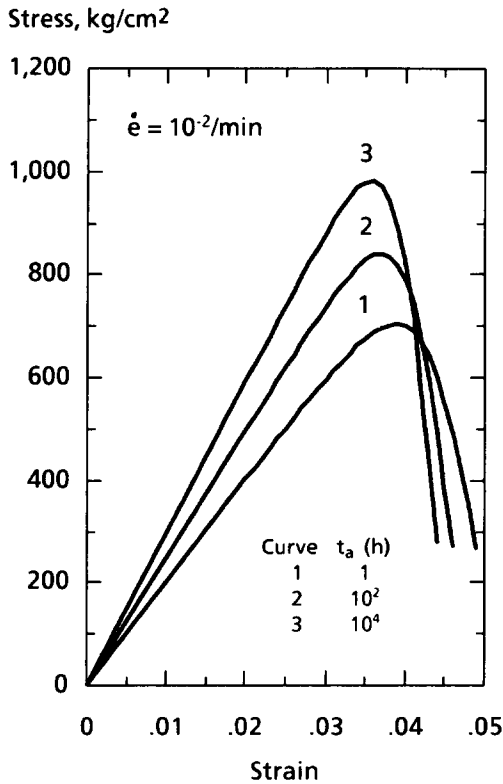


Figure 4 Effect of annealing time on the stress-strain curves of PS in uniaxial compression. The annealing temperature is $T_a = T_r - 20$ K

(t_a) but also with the load time (t). In general, both t_a and t are coupled non-linearly²¹. The load time ($t = e/\dot{\epsilon}$) in Instron measurements is always many orders of magnitude smaller than the ageing time ($\log(e/\dot{\epsilon}) \ll \log t_a$). Therefore, the effect of the two times can be decoupled, and the stress-dependent relaxation modulus is:

$$E(t, \sigma) = E_0(t_a) \exp\{-[t/\tau_{\text{non-linear}}(\sigma)]^\beta\} \quad (22)$$

in accordance with equation (4), where E_0 and $\tau_{\text{non-linear}}$ have already been mentioned in equations (9) and (17),

respectively. The constitutive equation for stress and strain in uniaxial compression is given by the Boltzmann superposition integral:

$$\sigma(t) = \int_0^t E(t-s, \sigma) \dot{\epsilon}(s) ds \quad (23)$$

The subscript 11 for stress or strain has been dropped. The strain rate is usually kept constant in Instron measurements. Substituting equations (17) and (22) into equation (23) and putting $e = \dot{\epsilon}t$, we get the explicit stress-strain relationship:

$$\sigma(e) = E_0(t_a) \int_0^e \exp\left[-\left(\frac{e' \exp[2.303\sigma(e')/K]}{\dot{\epsilon}\tau(T, t_a)}\right)^\beta\right] de' \quad (24)$$

where the dependence of relaxation time on physical ageing can be determined from:

$$\tau(t_2) = \tau(t_1) \times 10^{\Delta \log a} \quad (25)$$

In addition to those predetermined material parameters (equation (11), ν and K), $E_0 = 29.6 \times 10^3$ kg cm⁻² and $\tau = 2 \times 10^{14}$ min at 23°C for a well aged ($t_a = 10^4$ h at $T_a = T_r - 20$ K) PS are adopted in seeking the numerical solution of equation (24). The calculated effect of physical ageing on the compressive stress-strain behaviour is shown in Figure 4. Curve 3 compares well with the reported data²². The trend shown in Figure 4 is also consistent with experimental observation^{8,9}. The effect of strain rate is shown in Figure 5. Both the strain rate and physical ageing have a similar effect on the yield stress; however, they have completely different influences on Young's modulus and yield strain (e_y). Figure 4 reveals that e_y changes only slightly from 3.9% for curve 1 to 3.6% for curve 3. As the ageing time increases, both Young's modulus and yield stress increase but, at the

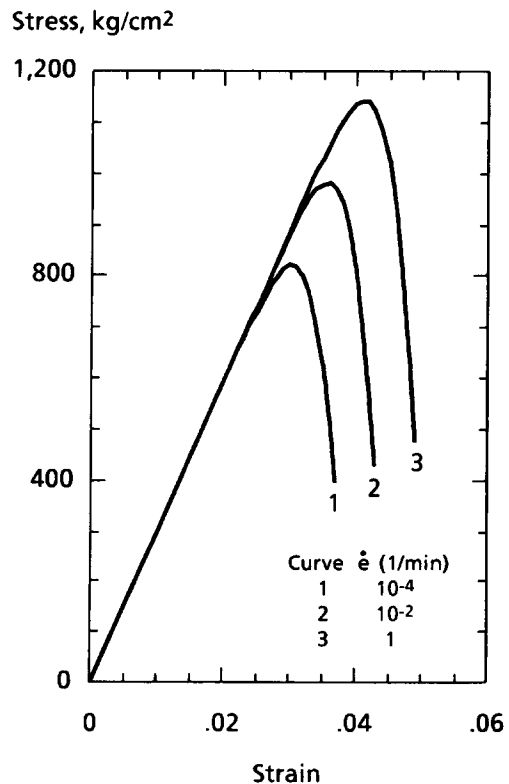


Figure 5 Dependence of the compressive yield stress of PS on strain rate. The sample has been well aged ($t_a = 10^4$ h at $T_a = T_r - 20$ K)

same time, the aged polymer becomes more brittle. Comparing Figure 5 with curve 3 in Figure 3, we get an exact agreement in the yield stresses as a function of the strain rate calculated from equations (24) and (19), respectively.

CONCLUSIONS

The yield stress and strain, Young's modulus and the stress-strain behaviour of quenched and annealed polymeric glasses in uniaxial compression have been calculated as a function of the annealing time, annealing temperature and strain rate. Equations are derived that link the mechanical properties of polymers to the non-equilibrium state and the glassy-state relaxation, which control the non-linear viscoelastic nature of plastic deformation. In the glassy state, we see a simple linear relationship between the increase in yield stress, or Young's modulus, and logarithmic ageing time. However, in the glass transition region, the effects of physical ageing diminish after a critical ageing time, which is a function of annealing temperature. The critical ageing time depends on how long it takes for the non-equilibrium glassy state to approach equilibrium. Although both Young's modulus and yield stress increase with ageing, the yield strain decreases slightly. As ageing continues, polymers become more brittle. The change in the physical mechanism of deformation from ductile to brittle depends

on the timescales in which the amorphous solid is aged, relaxed and measured.

REFERENCES

- 1 Howard, R. H. (Ed.) 'Physics of Glassy Polymers', Wiley, New York, 1973
- 2 Ward, I. M. 'Mechanical Properties of Solid Polymers', 2nd Edn., Wiley, New York, 1983
- 3 Eyring, H. *J. Chem. Phys.* 1936, **4**, 283
- 4 Robertson, R. E. *J. Chem. Phys.* 1966, **44**, 3950
- 5 Argon, A. S. *Phil. Mag.* 1973, **28**, 839
- 6 Landel, R. F. and Peng, S. T. *J. Rheol.* 1986, **30**, 741
- 7 Struik, L. C. E. 'Physical Aging in Amorphous Polymers and Other Materials', Elsevier, Amsterdam, 1978
- 8 Ott, H. J. *Colloid Polym. Sci.* 1980, **258**, 995
- 9 Bauwens-Crowet, C., Bauwens, J.-C. and Homes, G. *J. Mater. Sci.* 1979, **14**, 1817
- 10 Chow, T. S. *Macromolecules* 1989, **22**, 701; *Phys. Rev. (A)* 1991, **44**, 6916; *Macromolecules* 1992, **25**, 440
- 11 Chow, T. S. *J. Polym. Sci. (B)* 1987, **25**, 137
- 12 Chow, T. S. *Macromolecules* 1990, **23**, 4648
- 13 Chow, T. S. *Polymer* 1991, **32**, 29
- 14 Chow, T. S. *Macromolecules* 1989, **22**, 698
- 15 Doolittle, A. K. *J. Appl. Phys.* 1951, **22**, 1471
- 16 Chow, T. S. *Polym. Eng. Sci.* 1984, **24**, 915; *J. Rheol.* 1986, **30**, 729
- 17 Cavrot, J. P., Haussy, J., Lefebvre, J. M. and Escaig, B. *Mater. Sci. Eng.* 1978, **26**, 95
- 18 Chow, T. S. *Adv. Polym. Sci.* 1992, **103**, 149
- 19 G'Sell, C. and McKenna, G. B. *Polymer* 1992, **33**, 2103
- 20 Matsuoka, S. *Polym. J.* 1985, **17**, 321
- 21 Chow, T. S. *J. Mater. Sci.* 1990, **25**, 957
- 22 Howard, R. N., Murphy, B. M. and White, E. F. *J. Polym. Sci. (A-2)* 1971, **9**, 801