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The mechanism of creep behaviour in glassy polymers

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A model is presented to describe the creep behaviour of glassy polymers below the glass transition temperature. It consists of a Hookean spring in series with a non-Newtonian dashpot having an entropy spring in parallel. The shape of the response of this spring is deduced from a master curve, giving the extension as a function of logarithm of time, built from creep data, reported here and obtained on polycarbonate over a wide range of times and temperatures. The model takes into account a number of aspects of creep behaviour and predicts a threshold stress beneath which delayed yielding no longer occurs. Torsional creep data, obtained on polyvinylchloride by Mallon and Benham are found to be in excellent agreement with the proposed model.

1. Introduction

Our intention in this paper is to give an interpretation of the mechanism of creep of glassy polymers, valid in the linear as well as in the non-linear region of viscoelasticity over a wide range of temperatures. The proposed creep mechanism is based on tensile creep data at various temperatures obtained on polycarbonate (PC), which complete the study of Mindel and Brown [1], restricted to high stresses at room temperature. The investigated range is located below and not too close to the glass temperature T_g and therefore differs from the one considered by Matz *et al.* [2], who have given an interpretation of the creep behaviour of PC near T_g. Careful examination of our data has led us to ascertain that:

(a) the value of ϵ_0, the instantaneously measured strain upon loading at small stresses, is independent of temperature in the range considered (−20 to 80° C). (This is in agreement with the data of Yannas and Lunn [3]);

(b) the shape of the curve giving the extension as a function of log t (t denoting time) is the same at any level of applied stress σ or temperature T.

The model proposed here was inspired by that of Haward and Thackray [4] and is shown to be capable of accounting for these experimental facts and for a number of different aspects of creep behaviour given in the literature, e.g.:

(a) some entropy elasticity is involved and creep strain is not completely recoverable [1, 5];

(b) the creep-rate depends on the following variables: T, σ/T, and the total strain, by means of separate functions of these variables [1, 5];

(c) a threshold value of the applied stress exists beneath which delayed yielding no more occurs in glassy polymers [2];

(d) the level of the stress related to what is often called "the transition between linear and non-linear viscoelasticity" decreases as the temperature approaches the vicinity of T_g [3].

Mallon and Benham's data [6] on torsional creep of polyvinylchloride (PVC) were used to test the proposed model.

2. Experimental

The material and the specimens were the same as those used in previous investigations related to tension, tensile creep and impact tests [7, 8]. Tensile creep tests were performed under dead-weight loading inside an environmental chamber provided with windows and capable of maintaining a constant temperature to within ± 0.5° C.

The extension was obtained with a dial gauge, a method which allows one to measure accurately the extension variations with time over a wide range of times and temperatures, but which is not accurate enough to determine the absolute value of the extension. Photographs of the dial gauges were taken automatically at times varying in a

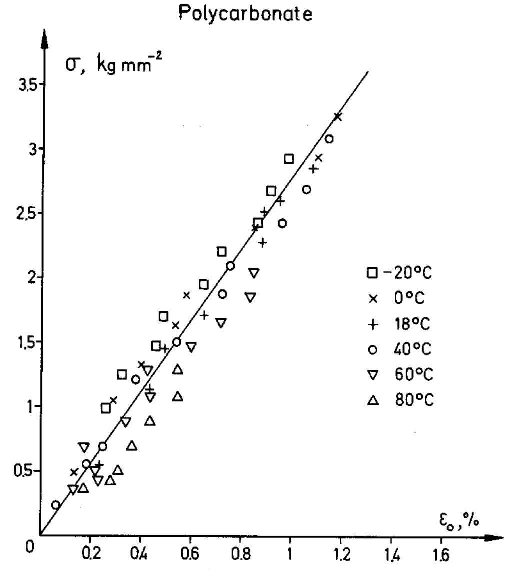

Figure 1 A plot of the applied stress as a function of the instantaneous strain upon loading in the linear range and at various temperatures.

geometric progression (base 2), from $t_1 = 4$ sec after the beginning of loading.

Determination of the value of the extension e_1 at t_1 was made by considering that loading is only a tensile test at a rather high speed. This speed is estimated at 5 cm min^{-1}. Tensile tests were performed at this speed on analogous specimens mounted in the same grips and at the same temperatures as in the creep tests. e_1 is deduced from these tensile curves (corrected for the deformation of the tensile machine) as a function of σ and temperature T. The results are in agreement with values of e_1 derived from the proposed model, as will be shown in Section 3.5. As the extension measurements are made by grip separation, both in creep and tensile tests, strain within the gauge length l_0 must be calculated from:

$$\epsilon = \frac{e}{k\,l_0} \tag{1}$$

where e denotes the extension at a given time and k a correction factor estimated at 1.52.

For creep tests performed at small stresses (linear behaviour) from −20 to 40° C, the instantaneous extension upon loading, e_0, was recorded using strain gauge extensometers of the Baldwin type. For tests conducted at higher temperatures, e_0 was measured using a cathetometer by evaluating the increase of distance between two marks painted on the specimen (in this case the test-pieces consisted of strips 25 mm wide, 2 mm thick, machined to a 200 mm gauge length). Above room temperature, every test was performed after the specimen had remained at the required temperature 16 h. All stresses considered in this paper are engineering stresses.

3. Results

3.1. Instantaneous strains ϵ_0 upon loading at small stresses

At temperatures varying from −20 to 80° C, the applied stress σ is plotted versus ϵ_0 in Fig. 1, where it can be seen that a proportional dependence may be assumed. The following formula may be adopted for a first approximation:

$$\sigma = E_0 \epsilon_0 \tag{2}$$

where E_0 denotes an elasticity modulus which is independent of T. E_0 was found equal to 280 kg mm^{-2}.

3.2. Variation of the extension e with log t

Extension e was plotted against log t for each creep test. The shape of these curves suggested that they may be superimposed.

3.3. Master curve

To generate a master curve from our data, we have adopted the following procedure. A given curve $e = f(\log t)$ is taken as reference (we chose the curve related to $\sigma = 4.69$ kg mm^{-2} *at* 40° C). Each $e = f(\log t)$ curve is then brought into coincidence with the reference curve without paying attention to differences between the absolute value of the total extension, but considering the horizontal shift factors that are necessary to make the curves coincide. A master curve is thus obtained which accurately fits the data, as can be seen from Figs. 2 and 3 where the data are plotted, respectively related to 40° C and various temperatures.

It should be pointed out that three curves related to $T = 80°$ C and low values of σ/T (lower than 10^{-2} kg mm^{-2} K^{-1}) are not superposable in their entirity; only the parts corresponding to small times coincide. This range of experimental conditions must, therefore, be considered as the limit of applicability of the proposed model.

3.4. Variation of the shift factor as a function of σ/T

Let t_r be a given time on the reference curve chosen equal to 100 min and t the corresponding

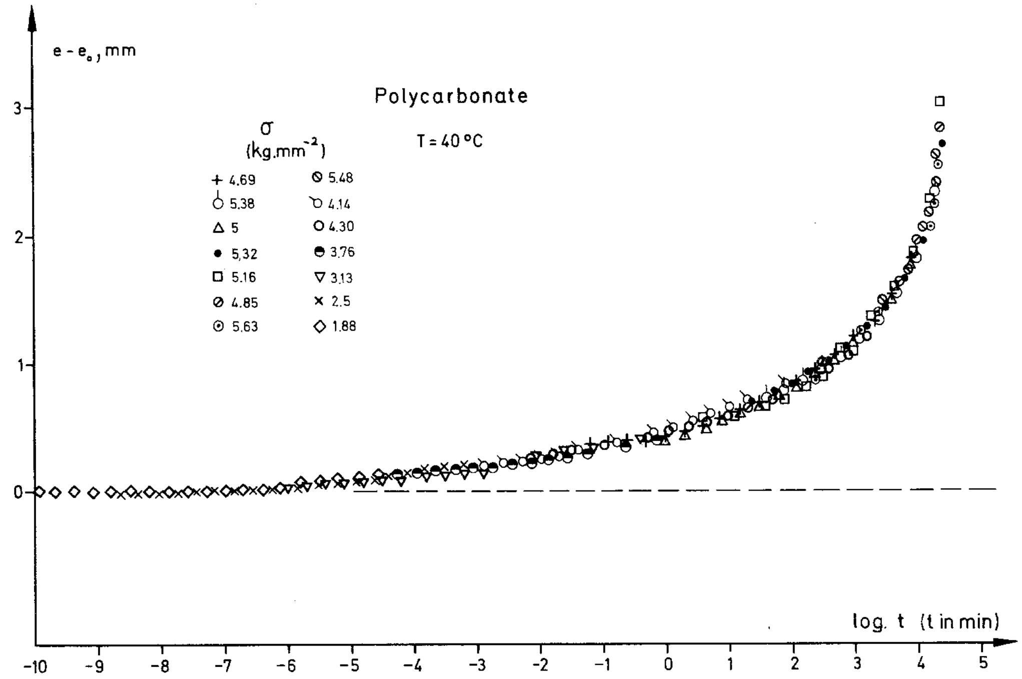

Figure 2 Master curve obtained at 40° C and reduced to $\sigma = 4.69\,\mathrm{kg\,mm^{-2}}$, giving the time dependent part of the extension: $(e - e_0)$ as a function of log t.

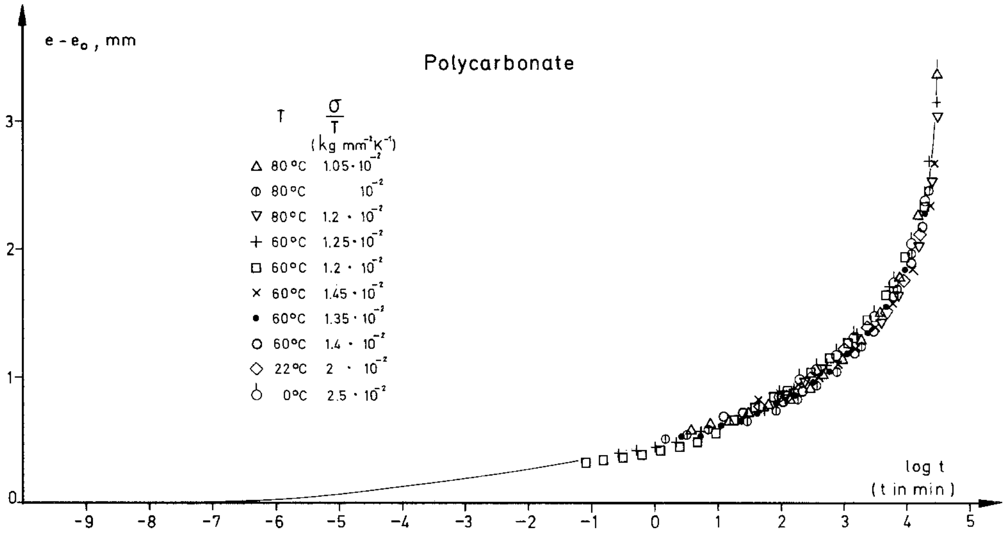

Figure 3 Examples of the coincidence of the creep data obtained at various temperatures with the master curve given in Fig. 2.

time on a partial curve (times are said to correspond when related to superposed data). σ/T (the ratio of stress to absolute temperature) is plotted as a function of log (t_r/t) in Fig. 4. Through the data we have drawn a set of parallel straight lines (one straight line for each temperature) having a slope equal to $2.3 \times A$.

The horizontal distance s between two straight lines related to temperatures T_1 and T_2 respectively is calculated from the following relation:

$$s = \frac{2 \times 2.3 \times Q}{(1/T_1) - (1/T_2)}. \tag{3}$$

The values of A and Q (recalled in Table I) are taken from a previous note [8], showing that the tensile yield behaviour of PC in tension as well as

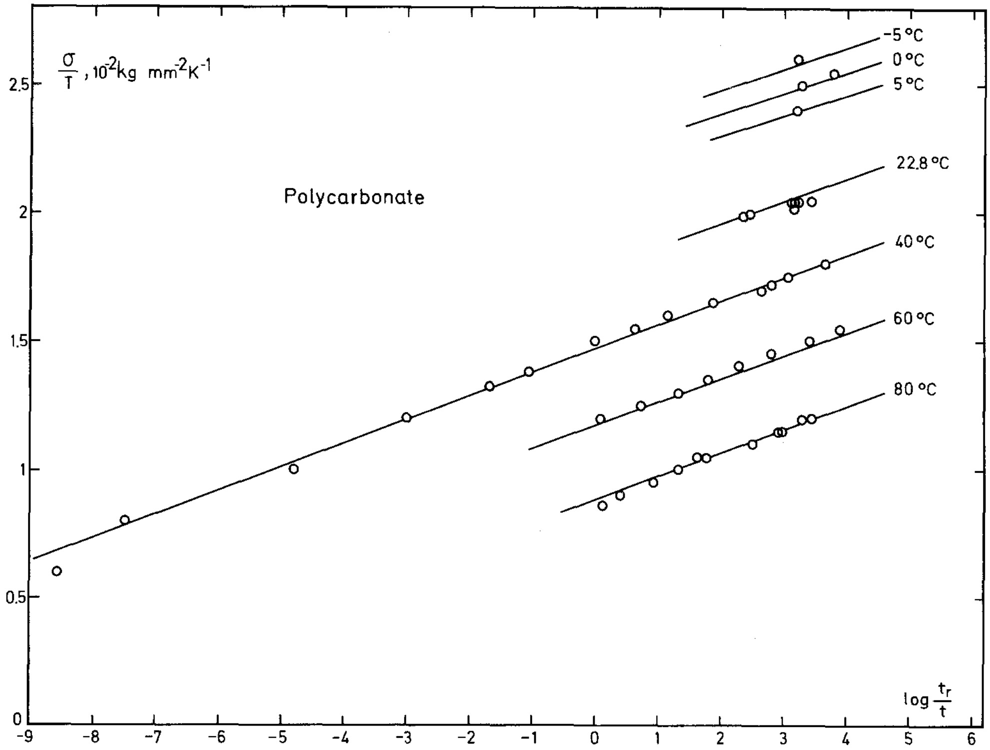

Figure 4 A plot of the ratio of the applied stress to temperature against the shift related to the superposition of the data on the master curve. The set of parallel straight lines is calculated from Equation 3 and Table I (t_r is a reference time related to the master curve and chosen equal to 100 min).

in creep, may be described by an Eyring type equation:

$$\frac{\sigma}{T} = A\left(\ln 2\,C\dot{\epsilon} + \frac{Q}{RT}\right), \tag{4}$$

where Q denotes the activation energy of the yield process, $\dot{\epsilon}$ is the strain-rate, A and C are constants, and R is the universal gas content.

In the previous note [8], the yield point was chosen as the inflexion of the creep curve (i.e. the curve giving e versus t). On a plot giving e versus $\log t$, the yield point is located at Y (Fig. 7). From Equation 4, the non-Newtonian viscosity at this point is expressed by:

$$\eta = 2\,C\sigma \exp\left[\frac{1}{T}\left(\frac{Q}{R} - \frac{\sigma}{A}\right)\right]. \tag{5}$$

The satisfactory fit of the data to Equation 4 suggests that η may not only represent the viscosity at the yield point but also at any point of the creep curve.

3.5 Evaluation of ϵ_1, the strain at t_1 = 4 sec for each creep test

The master curve admits a horizontal asymptote at short times intersecting the vertical axis at the extension e_0. Let

$$\Delta e_1 = e_1 - e_0 \tag{6}$$

denote the difference in extension, measured on the master curve between a point, related to a given value of σ/T and $t_1 = 4$ sec and the level of the asymptote. Therefore, Equations 1, 2 and 6 lead to Equation 7 which must be used to obtain the accurate value of ϵ_1:

$$\epsilon_1 = \frac{\sigma}{E_0} + \frac{\Delta e_1}{kl_0} \tag{7}$$

where Δe_1 depends on σ/T.

At a given temperature, ϵ_1 thus evaluated as a function of σ, may be compared to the total strain from a tensile test conducted at 5 cm min^{-1} at the

TABLE I Constants related to PC

E_0 (kg mm^{-2})	A (kg mm^{-2} K^{-1})	Q (kcal mol^{-1})	C (sec)	σ_c/T (kg mm^{-2} K^{-1})
280	3.96 10^{-4}	85	1.4 10^{-43}	7 × 10^{-3}

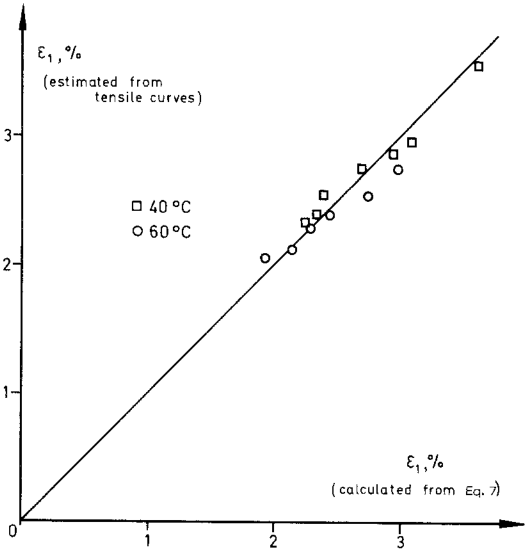

Figure 5 Comparison of ϵ_1, the total strain at 4 sec, evaluated from tensile curves and calculated from Equation 7.

same temperature. Examples at 40 and 60° C are given in Fig. 5 where a good agreement between both types of estimation may be verified, indicating that the superposition principle and Equation 7 may be considered valid. This fact implies that the value of the total strain related to a given point of the creep curve depends on σ and σ/T. In this respect our observations are not in agreement with those of Mindel and Brown [1] who consider that the strain corresponding to the minimum of the creep rate (i.e. what we have defined as the yield point), is a constant. It must, however, be pointed out that the value of the stress related to their tests did not vary more than 5%, and that those tests were all conducted at room temperature.

3. Proposed model

We propose a rheological model based on our experimental results which is intended to provide the formalism of the creep behaviour of glassy polymers. We have sought the simplest system where:

(a) the same viscous process is responsible for the time dependency of the creep strain, at any value of the applied stress or the temperature (with T never greater than 353 K);

(b) some entropy elasticity is involved in creep strain (as already suggested by Sherby and Dorn [5] and Mindel and Brown [1] which absorbs a part of the applied stress and accounts for the strain-rate variation in a creep test;

(c) the variation of ϵ_0 is proportional to the applied stress σ.

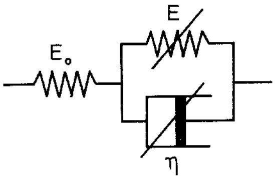

Figure 6 Simple three-element system representing the proposed model. η denotes an Eyring dashpot and E an entropy spring.

The simple three-element model of Fig. 6, involving a Hookean spring E_0, a non-Newtonian dashpot η, an entropy non-Hookean spring E, fulfils these conditions. This model differs from the one proposed by Haward and Thackray [4] by the

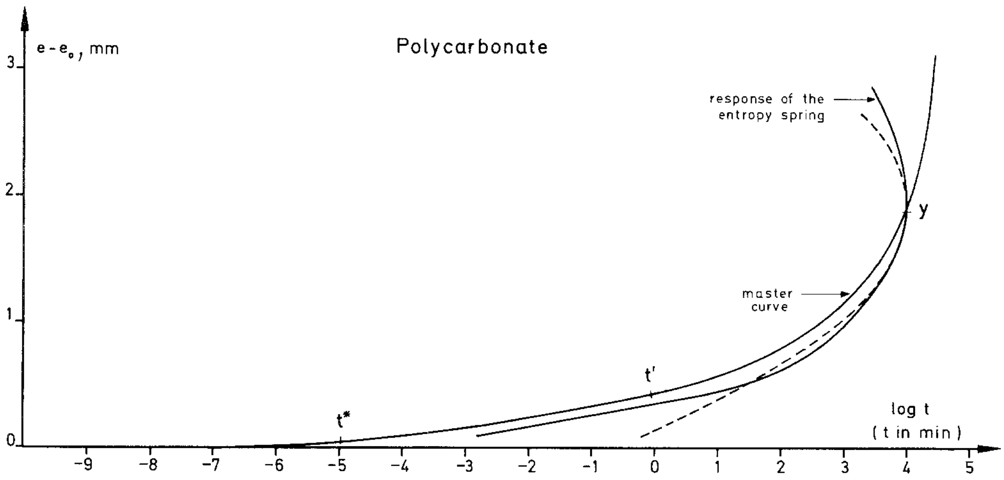

Figure 7 Response of the entropy spring calculated from Equation 8 and the master curve; a dashed parabola is given for comparison.

nature of the spring E (they used as E a rubber elasticity spring which gives a good model to describe isothermal stress–strain curves at large plastic deformations but fails to explain creep behaviour at extensions of less than 5%, which is the range of strains we have considered).

Let us suppose that up to a time t' (Fig. 7) related to the reference test, the response of the entropy spring is still Hookean with a modulus equal to E proportional to the absolute temperature. In this case, the response of the model is given by:

$$\epsilon - \epsilon_0 = \frac{AT}{E}\left(\ln t + \ln\frac{E}{AT} + \frac{\sigma}{AT} - \frac{Q}{RT} - \ln 2C\right) \tag{8}$$

for

$$t' \geqslant t \gg t^* = \frac{2ACT}{E}\exp\left(\frac{Q}{RT} - \frac{\sigma}{AT}\right)$$

and ϵ denoting the total strain at time t. If $\log t'$ and $\log t^*$ are respectively taken equal to 0 and -5 (see Fig. 7) and the value of E/T may be deduced from the master curve. For times larger than t' the response of the entropy modulus is no longer Hookean; let us express it by:

$$\sigma_1 = f(\epsilon - \epsilon_0),$$

whereas

$$\sigma_2 = A\left(\ln 2C\dot{\epsilon} + \frac{Q}{RT}\right) \tag{10}$$

will give the response of the dashpot η.

According to our model, we can write:

$$\begin{aligned}\sigma_1 &= \sigma - \sigma_2\\ &= \sigma - AT\ln 2C - AT\ln\left(\frac{\mathrm{d}(\epsilon-\epsilon_0)}{\mathrm{d}t}\right) - A\frac{Q}{R},\end{aligned} \tag{11}$$

which may be written:

$$\begin{aligned}-\log\dot{\epsilon} &= \log t - \log\frac{\mathrm{d}\epsilon}{\mathrm{d}\log t}\\ &= \frac{f(\epsilon-\epsilon_0)}{2.3AT} - \frac{\sigma}{2.3AT} + \frac{Q}{2.3RT} + \log 2C\end{aligned} \tag{12}$$

At a given temperature T, $f(\epsilon - \epsilon_0)$ may be deduced from the master curve (reduced to T) using Equation 11; such a construction is given in Fig. 7. A dashed parabola is drawn on the same graph for comparison, indicating that the response of the entropy spring may perhaps be of this type.

Such a result is similar to that of Mindel and Brown [1] who presented the variation of the logarithm of the creep-rate as a function of the logarithm of strain, a type of plot which may also be expressed by Equation 12. Up to a strain equal to about 8% in tension and 11% in compression, parabolas are a good approximation of these curves.

A parabolic response of the entropy spring could, perhaps, be explained by considering that the polymer contains a given number of elements capable of being deformed elastically with a constant modulus E and a given number of elements which will flow with a viscosity η, and that, as a function of time, the former will diminish and the last increase. The expression of strain derived from this assumption is given in the Appendix.

5. Testing of the model

Mallon and Benham [6] have performed accurate measurements in simple shear creep on PVC at 21° C. They presented a family of curves related to various stresses τ and giving the total strain γ versus $\log t$. The curve corresponding to the lowest stress admits a horizontal asymptote; from the strain level of this, we have calculated the value of G_0 reported in Table II. For each curve, $\gamma_0 = \tau/G_0$ is evaluated. The master curve is then built by the superposition of curves giving $\gamma - \gamma_0$ as a function of $\log t$. This master curve, reduced to $\tau = 0.689$ kg mm^{-2}, is represented in Fig. 8 together with the plot of τ/T versus $\log(t_r/t)$ (where $t_r = 10^3$ sec). It can be seen from the graph that the data are nicely superposable with a linear dependence of τ on the

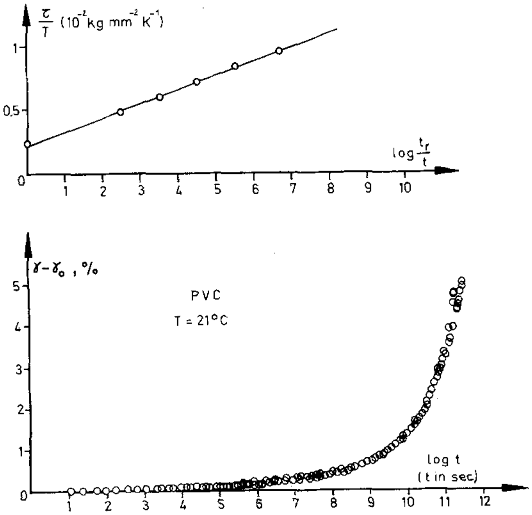

Figure 8 Master curve, reduced to $\tau = 0.689$ kg mm^{-2}, obtained from superposition of the data of Mallon and Benham [6] on PVC; and plot of τ/T versus the shift factor of the data ($t_r = 10^3$ sec).

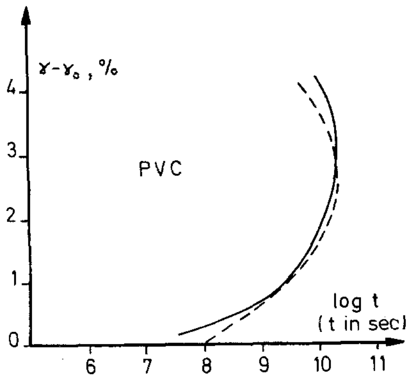

Figure 9 Response of the entropy spring calculated from the master curve of Fig. 8; a dashed parabola is given for comparison.

shift factor and, therefore, that they constitute a convincing test for the model. The response of the entropy spring compared to a dashed parabola is given in Fig. 9.

Let 2.3 A_T denote the slope of the straight line representing τ/t versus $\log(t_r/t)$. The constant A, appearing in Equation 4, may be evaluated from A_T using the following equation, derived from a yield criterion previously established [9, 10] and based on the Eyring theory:

$$A = \frac{\sqrt{3}(1+a)A_T}{2a} \qquad (13)$$

where a denotes the ratio of the yield stress in compression to the yield stress in tension. Using a value of this ratio equal to 1.3, calculated for PVC [10] as a function of the engineering yield stresses, the constant A, evaluated from Equation 13, is found to agree with the value calculated from tensile experiments [7]; both are given in Table II.

The activation energy Q cannot be known from the data of Mallon and Benham which are all obtained at room temperature; we have, therefore, taken $Q = 70.5\,\mathrm{kcal\,mol^{-1}}$ from our previous results [7] in order to evaluate the constant C quoted in Table II.

6. Discussion

An important consequence of the proposed model is that deformation at the yield point has merely the appearance of purely viscous flow. It entails, in fact, an entropy elastic component requiring a constant part σ_c/T of the ratio σ/T. This influences the value of the constant C which was previously deduced from a graph giving σ/T versus $\log \dot{\epsilon}_y$ ($\dot{\epsilon}_y$ denoting the strain-rate at yield). According to our model, C must be calculated from a $(\sigma - \sigma_c)/T$ versus $\log \dot{\epsilon}_y$ plot, or from the measured value of t^* using Equation 8; both methods give a new value of C quoted in Tables I and II.

The proposed model implies a threshold value of σ/T beneath which yielding can no longer occur. The critical value σ_c/T found for PVC (Table II) lies near the level at which, for this material, the tensile yield stress becomes independent of strain-rate at 50 and 60° C [11]. This result is satisfactory, as it has been shown previously that creep and tensile yield behaviours are similar [8]. From our data on PC (Table I), we have found a value of σ_c/T which agrees on the one hand, with that derived from the results of Matz *et al.* [2] at 90° C:

$$\frac{\sigma}{T} = 8.3 \times 10^{-3}\,\mathrm{kg\,mm^{-2}\,K^{-1}}$$

for which the delay time becomes infinitely large; and, on the other hand, with the level of σ/T at which the tensile yield stress becomes independent of strain-rate [11].

In the case of PC, however, we must point out, that at 80° C for values of σ/T lower than $9.5\ 10^{-3}$ $\mathrm{kg\,mm^{2}\,K^{-1}}$, the creep curves giving e versus $\log t$ cease to be superposable up to the yield point. This may be due to some rearrangements in the material occurring when this polymer is maintained at 80° C for long times and which are reflected in the yielding properties [12]. We plan to investigate this point further, but the important

TABLE II Constants related to PVC

G_0 (kg mm^{-2})	A (kg mm^{-2} K^{-1})	Q (kcal mol^{-1})	C (sec)	σ_c/T (kg mm^{-2} K^{-1})
120	7.4×10^{-4} (calculated from Equation 13 – torsional creep data [6]). 7×10^{-4} (tensile data [7])	70.5 (tensile data [7])	3.4×10^{-41}	7×10^{-3}

thing is that the model predicts the existence of a threshold stress depending on T and that the value found for it is quite plausible.

From Equation 12, an expression of the creep-rate may be deduced, which has the classical form [1, 5]:

$$\dot{\epsilon} = f_1(\epsilon)\cdot f_2\left(\frac{\sigma}{T}\right)\cdot f_3(T) \qquad (14)$$

where $f_1(\epsilon)$, $f_2(\sigma/T)$, $f_3(T)$ are separate functions of the variables ϵ, σ/T and T.

Another consequence of the model is that perfect linear viscoelasticity only exists for extremely low values of the applied stress implying a Newtonian behaviour of the dashpot η. At short times, in a creep test, if viscoelasticity appears to be linear, it is only because the major part of the deformation is related to the Hookean spring.

The decrease, as a function of T, of the stress threshold above which creep deviates from linear behaviour by more than a given value [3] may easily be explained by the model: in isochronous experiments at various temperatures, the stress required to produce a given value of the extension of the dashpot, diminishes when T increases.

It has been shown previously [13] that the effect of deformation prior to yielding must be taken into account in the calculation of the true tensile yield stress. This is equally valid for the stress related to any value of the extension of the dashpot [14]. Therefore, the engineering stress σ, must be replaced by $\sigma(1 + \epsilon)$ where ϵ is the value of the total strain at a given time t. This correction has not been considered here, because we wished to compare our results with previous data related to engineering stresses, but is easily done if desired. It hardly affects the value of Q and C and gives a value of A which is no more than 6% higher than the one given in Table I.

The shape of the response of the entropy spring, graphically given in Figs. 7 and 9, shows that creep extensions exceeding the value related to the vertex of the curve may not be entirely recoverable. This remark indicates that the model takes into account a persistent component of the strain, as observed by Mindel and Brown [1].

7. Conclusions

The proposed model, although very simple, gives a satisfactory fit to the data, over a wide range of times and temperatures. Valid in the non-linear as well as in the linear region of viscoelasticity, it implies a stress threshold beneath which delayed yielding can no more occur.

This model considers that the viscous part of the creep extension may be represented by a single non-Newtonian dashpot, obeying an Eyring-type equation. As such an equation may easily be expressed as a function of a number of different cases of testing conditions, the applicability of the model is not restricted to creep, but can be enlarged to other types of tests.

The theoretical considerations presented to explain the shape of the response of the entropy spring, are only suggestions, but may perhaps constitute a first step towards understanding non-linear behaviour of glassy polymers.

Appendix

A parabolic response of the entropy spring may derive from the following assumption.

Let us consider that after loading at $t = 0$, the material is composed of purely elastic deformation units related to a constant modulus E (E being proportional to T); and let us assume that, as a function of time, a fraction α of these elastic units transforms into flow units having a non-Newtonian viscosity η. Moreover, let us stipulate that creep consists of increasing the elastic extension of the remaining $(1-\alpha)$ fraction of elastic units, following the rule:

$$\sigma_1 = E(1-\alpha)(\epsilon-\epsilon_0).$$

Now, if Γ_0 denotes the elementary shear related to the flow process, one obtains:

$$\epsilon-\epsilon_0 = K\alpha\Gamma_0$$

where K is a constant. Therefore,

$$\sigma_1 = E\left[(\epsilon-\epsilon_0)-\frac{(\epsilon-\epsilon_0)^2}{K\Gamma_0}\right].$$

This parabolic response of the entropy spring together with the model leads to the following expression of the strain-rate:

$$\log\dot{\epsilon} = \frac{1}{2.3\,AT}\left[\sigma - E(\epsilon-\epsilon_0)+\frac{E}{K\Gamma_0}(\epsilon-\epsilon_0)^2\right] - \frac{Q}{2.3\,RT} - \log 2\,C$$

which may explain Equation 12.

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