JOURNAL OF MATERIALS SCIENCE 8 (1973) 863–870

Creep and recovery of polycarbonate

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The creep behaviour of polycarbonate was investigated at high stresses in tension and compression. The creep curve was separated into a recoverable strain and persistent strain. The equation describing the recoverable strain was directly related to the kinetics of the recovery curve. The concept of an internal stress was useful in describing the recoverable part of the creep and recovery.

The persistent strain-rate was related to the failure of the material by accelerated creep. Measurements of the temperature during creep showed that heating was not responsible for the occurrence of the material softening which lead to accelerated creep.

It was found that the strain behaviour during loading and unloading was asymmetrical in that the instantaneous loading strain was less than the instantaneous unloading strain.

1. Introduction

This paper has two objectives (1) to determine the relationship between creep and recovery in polycarbonate in the non-linear region of viscoelasticity, and (2) to determine the conditions under which its creep behaviour becomes unstable.

There are many experimental and theoretical investigations on the non-linear behaviour of glassy polymers. Sherby and Dorn [1] studied the kinetics of tensile creep in PMMA as influenced by temperature and stress. Yannas and co-workers [2-4] have used creep and other measurements to determine the limit of linear viscoelastic behaviour in PC. Bauwens and co-workers [5-7] have studied yield behaviour in PC. Matz *et al* [8] have studied the relationship between stress and time to fail in creep. Stratonova [9] has outlined a method for predicting the deformation behaviour under step loading from constant-stress creep curves. Robertson [10] has shown how the total strain in PC can be divided into recoverable and non-recoverable components. Higuchi and Imai [11] measured the temperature change during the yielding of PC.

In this paper, the creep and recovery of PC was studied at room temperature at stresses near the yield point in both tension and compression. These constant-load tests showed that the differences between tension and compression tests were not caused by the changes in stress during deformation but by the intrinsic behaviour of the material. The temperature changes during creep and recovery were also measured. These temperature changes indicated that heating was not responsible for creep failure. The creep and recovery curves for the recoverable and persistent strain components were obtained. It was also found that the instantaneous unloading strain was greater than the instantaneous loading strain.

2. Experimental procedure

2.1. Material

The material used for tensile specimens was General Electric Lexan polycarbonate sheet 0.030 in. thick. Tensile specimens were machined to a 0.500 in. gauge length and 0.200 in. width. Machining marks were removed by light polishing. For the compression tests $\frac{1}{2}$ in. Lexan rod was used. The rod was cut to 0.550 in. lengths on a lathe; then the ends were metallographically polished to a 0.1 µm finish. A metal holder was used during the polishing operations which kept the ends parallel to about 0.0001 in.

2.2. Tensile testing

Tensile creep was performed under dead-weight loading. The weights were raised and lowered by a hand-actuated jack. The lower grips themselves weighed 0.2 lb; so this load was present during recovery. The loads are known to approximately ± 0.1 lb.

Strain was measured with a clip-on strain-gauge extensometer and continuously recorded on a strip-chart recorder. The minimum strain which could be measured was 3×10^{-4}, and the recorded strain was accurate to better than 1% of full scale reading. Strain-rates were calculated by picking three points off of the recording, fitting a parabola to the points, and using the calculated slope of the parabola at the centre point. This gives more consistent results than drawing tangents to the creep curves.

2.3. Compression

The compression work was performed on an MTS Systems closed-loop testing machine. This is a feedback-controlled hydraulically-activated machine with great flexibility. The polished samples were lubricated with a teflon film lubricant and placed between the parallel faces of tool steel anvils. A preload of 50 lb was used to seat the samples. The samples were generally loaded in 0.1 sec and held constant for a certain time of creep. Then the load was decreased to 50 lb and the rate of strain recovery was observed. The displacement of the hydraulic piston was used to measure the strain. Long-time recovery was monitored by daily measurements of sample length with a micrometer.

2.4. Temperature tests

For measurements of temperature changes during creep, a hole was drilled more than half way into some compression specimens. The resultant hole was always somewhat larger than the 0.016 in. nominal diameter of the drill. A thermocouple, using 0.005 in. copper and constantin wires, was inserted into the hole and taped into place. The thermocouple was connected directly to a recorder with a full scale sensitivity of 1.0 mV and had a response time of less than 0.1 sec. The same type of temperature response was observed when the thermocouple was taped to the side of the specimen; the magnitude of the response was greater when the thermocouple was in the hole. The creep behaviour was slightly effected by the presence of the 0.016 in. hole. The small deformation bands which were visible near the hole occurred after a strain of about 9%.

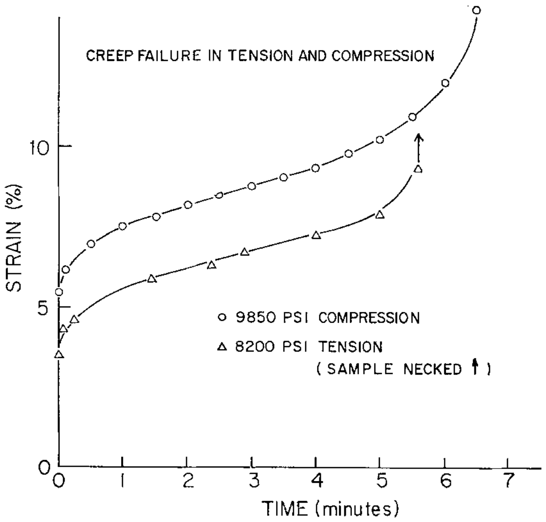

Figure 1 Creep curves in tension and compression.

3. Experimental results

3.1. Creep curves in tension and compression

Typical creep curves at constant load for compression and tension are shown in Fig. 1. The important feature, as previously pointed out by Ender and Andrews [12], is that the creep-rate decelerates to a minimum value and then accelerates rapidly. Since very large deformations are produced during the accelerated creep, it is useful to consider that creep failure begins at the time and strain where accelerated creep begins.

The compression and tension creep curves have the same general shape, but exhibit certain differences. Under constant load (Fig. 1), the compression creep-curve accelerates less rapidly than the tension curve, simply because the stress is decreasing during compression and increasing during tension. A more fundamental difference between tension and compression is in the stress required to produce creep failure at a given time. As shown in Fig. 1, creep failure or accelerated creep began at about 4 min for both the tension and compression curves but the stress for the tension curve was much lower than for the compression curve, 8200 psi versus 9850 psi. This effect is well known and is connected with the effect of the hydrostatic component of the stress on yielding in polymers as shown by Mears *et al* [13] and by Rabinowitz and Ward [14]. It is to be noted that although the total creep strain at creep failure is greater for compression than for tension, 9.2% versus 7.2%, the amount of time-dependent creep strain is nearly the same up to the point of creep failure. The difference is partially accounted

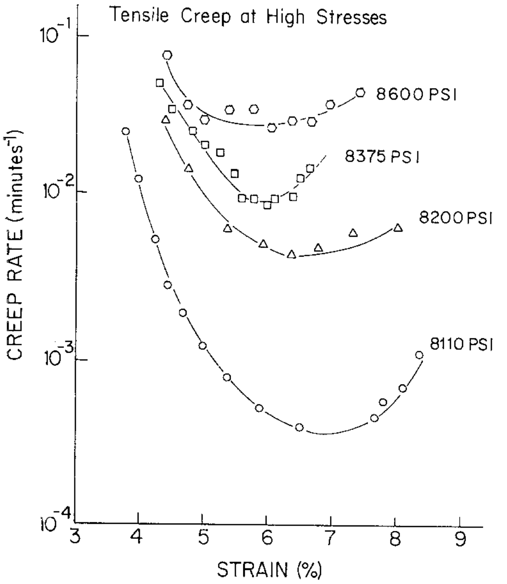

Figure 2 Creep-rate versus strain for tension.

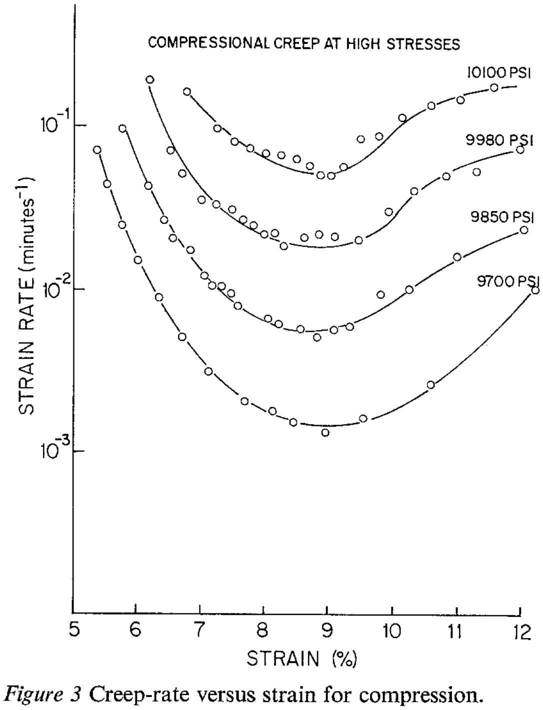

Figure 3 Creep-rate versus strain for compression.

for by the greater elastic strain at the higher stress in compression.

The effect of stress on the creep curves is shown in Figs. 2 and 3, where in accordance with the suggestion by Sherby and Dorn [1], log $\dot{\epsilon}$ is plotted against ϵ. The minimum in the creep-rate or the beginning of accelerated creep occurs at total strain of 9.0% for compression regardless of stress whereas the minimum varies from 6 to 7% while going from higher to lower stress in tension. As the stress is lowered in tension, there is an increase in crazing which may cause some of the difference between tension and compression. The shape of the curve of log $\dot{\epsilon}$ versus ϵ for PC is very similar to that found by Sherby and Dorn for PMMA; however, they did not show any data beyond the minimum in the curve.

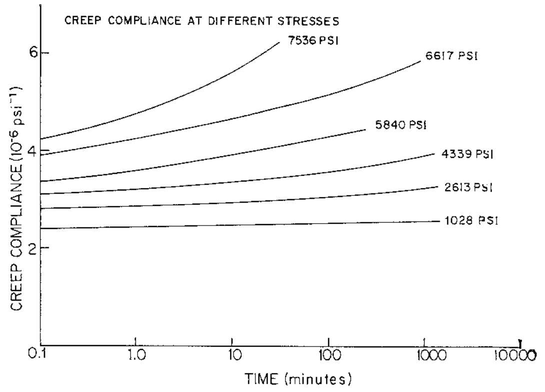

Figure 4 Creep compliance versus time for compression.

Samples tested at lower stresses in tension are plotted in Fig. 4 as creep compliance versus log time in order to show that the non-linear region of viscoelastic behaviour is involved. Fig. 4 also shows that, in the earliest regions of creep, strain is a linear function of log *t*. This observation will be important in relating creep and recovery since the recovery curves also show the same relationship during the initial part of the recovery curves.

3.2. Creep and recovery curves

Typical creep and recovery curves are shown for tension and compression in Figs. 5 and 6. Qualitatively, the tension and compression curves have the same form. It is useful to describe the creep and recovery curves in terms of the following empirical components of the total strain, ϵ: ϵ_L is the instantaneously measured strain upon loading; ϵ_C is the time dependent creep strain; ϵ_u is the instantaneously measured strain during unloading; ϵ_R is the time dependent recovery strain; and ϵ_P is the persistent strain after a long recovery time. The demarcation

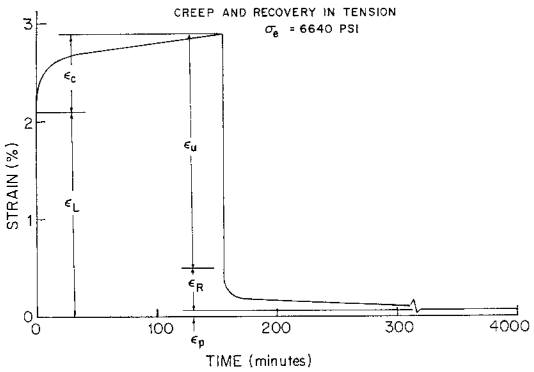

Figure 5 Creep and recovery curves in tension.

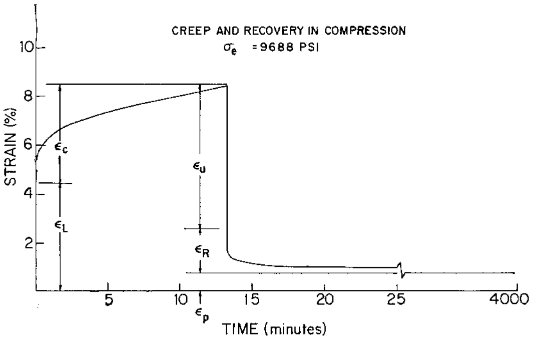

Figure 6 Creep and recovery curves in compression.

between ϵ_L and ϵ_c and between ϵ_u and ϵ_R is somewhat arbitrary since it depends on the rapidity with which the load can be applied or removed and how rapidly the strain can be measured. If ϵ_L and ϵ_u were purely elastic strains, then it would be expected that they would be equal. However, as shown in Figs. 5 and 6, ϵ_u was always equal or greater than ϵ_L; this difference cannot be attributed to any difference in the speed with which the strain is measured during loading and unloading. The so-called persistent strain has not been designated as a permanent strain because it is only permanent in the time scale of our experiments and at room temperature. The longest recovery time was about a month and generally was on the order of 3 to 4 days. However, the changes in strain observed between 4 days and 30 days is smaller than our experimental error. Thus, the recovery-rate rapidly decays within a few hours to a negligible value, so that the demarcation between ϵ_R and ϵ_p is fairly sharp.

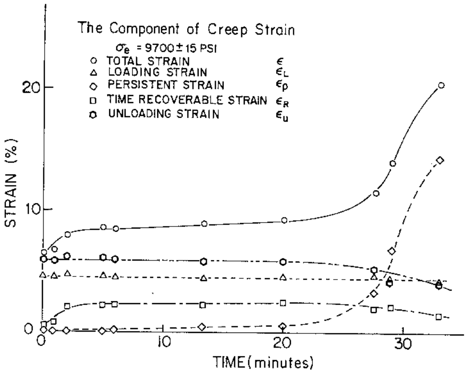

Figure 7 Creep curves for various components of the strain in compression.

3.3. Change in components of strain with time

The way that the various strain components change with time is shown in Fig. 7. These data were obtained by using a series of specimens, each of which was kept in compression for a different time at the same load and then was recovered. The composite creep curve for the total strain from the different specimens coincided with the individual creep curve from a single specimen as is expected. One should think of Fig. 7 as the complete time curves for the various strain components of creep and recovery. Obviously, ϵ_L should be independent of time. ϵ_u, except for the very short times and very long times, is also constant, but larger than ϵ_L. The decrease in ϵ_u after long times is understandable because the true stress changes significantly after large total strains. However, the nearly constant difference ($\epsilon_u - \epsilon_L$), over most of the test is not readily explainable, and will be a subject of the discussion. ϵ_R rapidly approaches a maximum value which is attained about half-way through the test, and decreases as the true stress decreases. ϵ_p is zero at zero time and does not become significant until the creep-rate has nearly reached its minimum value. The final part of the creep curve parallels the behaviour of ϵ_p. Thus, it appears that creep failure is associated with the onset of the persistent component of strain, ϵ_p. The general behaviour shown in Fig. 7 for the various components of the creep strain was exhibited at all stress values. As shown in Fig. 8, the magnitude of the difference between ϵ_u and ϵ_L increased rapidly with stress. ϵ_R increased slightly with stress.

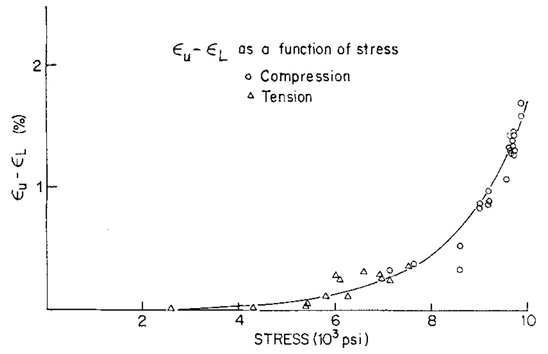

Figure 8 Difference between the strain on loading and the strain during unloading versus stress.

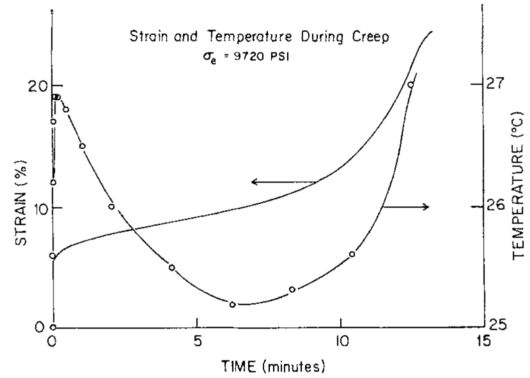

Figure 9 Change in temperature with time during compressive creep and simultaneous measurement of creep strain.

3.4. Temperature and strain versus time

The temperature of the specimen and the creep strain in compression were measured simultaneously as a function of time as shown in Fig. 9. Ambient temperature was 25° C. There was a rapid increase in temperature during loading which reached a maximum of 2° C a few minutes after loading. As the creep-rate diminished, the temperature decreased when the rate of conduction loss exceeded the rate of heat generation by deformation. When the creep-rate reached its minimum values, the specimen temperature was very close to ambient. As the creep-rate began to accelerate, the temperature began to rise again. These results show that the onset of accelerated creep or creep failure is not determined by the temperature rise that occurs during the initial part of the creep deformation. This observation is in agreement with Higuchi and Imai [11] concerning the small direct effect of temperature on fatigue failure in PC. The magnitude of the temperature changes increased with stress since higher creep-rates occur at greater stresses.

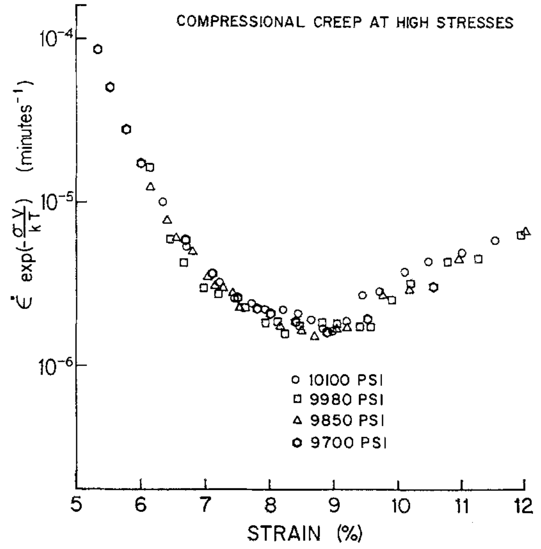

Figure 10 Synthesis of creep data in Fig. 3 using an activation volume of 5700 Å^3.

4. Discussion

4.1. Equation for creep

Let us first consider how the creep curves may be represented quantitatively. Sherby and Dorn's creep results with PMMA were similar to our compression creep curves as shown in Fig. 3 in that (1) the minimum creep-rate occurred at the same strain independent of stress and (2) a vertical shift of the curves using a single parameter, called the activation volume, brought all the curves into coincidence. Thus, using a value of 5700 Å^3 for the activation volume, the data of Fig. 3 can be reduced to the single curve shown in Fig. 10. The tensile data cannot be reduced as nicely because the strain at the minimum creep-rate was not independent of stress. This difference in behaviour between tension and compression for PC may be attributed to the fact that crazing takes place in tension in addition to shear flow while shear flow is the only deformation mechanism in compression. The activation volume of 5700 Å^3 that fits our compressive creep-data is very close to activation volumes which have been obtained from the measurement of the strain-rate sensivitity of the yield point [5]. This fact suggests that the deformation mechanism during the yielding in a constant strain-rate test is the same as that during creep.

Following the suggestion of Sherby and Dorn, the creep data in Fig. 10 can be represented by a general equation of the form

$$\dot{\epsilon} = f_1(T) f_2(\sigma/T) f_3(\epsilon) \quad (1)$$

where $f_1(T)$, $f_2(\sigma/T)$, and $f_3(\epsilon)$ are separate functions of the variables T, σ, and ϵ. According to the data of Sherby and Dorn $f_1(T)$ has the form expected for a thermally activated process

$$f_1(T) = \text{constant}\ x\ e^{-Q/kT}. \quad (2)$$

Sherby and Dorn in agreement with our results (Fig. 10) found that $f_2(\sigma/T)$ could be fitted by an exponential. We would like to modify the simple exponential form originally used by Sherby and Dorn by taking into account the effect of the hydrostatic component of the stress as suggested by Ward [15]. Thus,

$$f_2(\sigma/T) = e^{\sigma_H v_p/kT} e^{\sigma v_s/kT} \quad (3)$$

where v_p and v_s are the pressure and shear activation volumes respectively. Since, for a uniaxial stress, $\sigma_H = \sigma/3$ the activation volume of 5700 Å, shown in Fig. 10, should be equal to $({}^{v}{}_{p}/3 + v_s)$. Ward [15] has shown that v_p is much smaller than v_s so that the measured activation volume is mostly v_s.

4.2. Dividing strain into components

The form of the function $f_3(\epsilon)$ will now be explored by dividing the creep strain into its recoverable and persistent components. The time-dependent creep strain, ϵ_c, has a recoverable component which we will call $\epsilon_R(c)$ and the persistent component, ϵ_p, which is measured from the recovery curve (Figs. 5 and 6). $\epsilon_R(c)$ can now be derived in terms of the measured components of strain from the creep and recovery curves. The total strain may be represented in terms of its creep or recovery components

$$\epsilon = \epsilon_L + \epsilon_c = \epsilon_L + \epsilon_R(c) + \epsilon_p \quad (4a)$$

$$\epsilon = \epsilon_u + \epsilon_R + \epsilon_p\,. \quad (4b)$$

By combining the above equations, the recoverable component of the creep curve is given by

$$\epsilon_R(c) = (\epsilon_u - \epsilon_L) + \epsilon_R\,. \quad (5)$$

Since $(\epsilon_u - \epsilon_L)$ and $\dot{\epsilon}_R$ are known (Fig. 7), ln $\dot{\epsilon}_R(c)$ can be plotted versus ϵ as shown in Fig. 11. Again using the data in Fig. 7, the curve of ln$\dot{\epsilon}_p$ versus ϵ was obtained. Thus, the entire creep-rate is equal to $(\dot{\epsilon}_R(c) + \dot{\epsilon}_p)$. It is noted that the initial part of the creep process involves mostly $\dot{\epsilon}_R(c)$ and the later part mostly $\dot{\epsilon}_p$. Note also that, for the very initial part of the creep curve, the log of the creep-rate diminishes linearly with strain so that in Equation 1 the initial part of the creep curve can be represented by

$$f_3(\epsilon) = \text{constant}\ x\ e^{-a\epsilon_R(c)}\,. \quad (6)$$

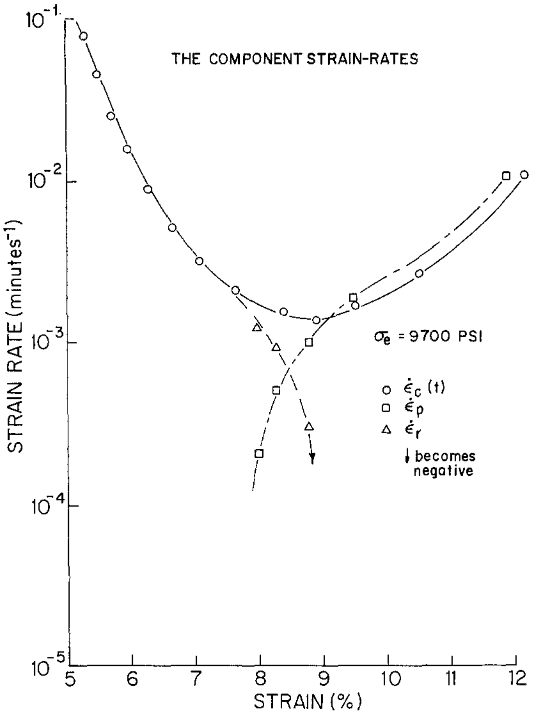

Figure 11 Creep-rate of various components of strain vesus total strain in compression.

It does not seem that, over the entire creep curve, $f_3(\epsilon)$ can be simply represented by separate functions for $\epsilon_R(c)$ and ϵ_p. Experimental work, which is still going on, indicates that there is an interaction between the recoverable and the persistent components of the strain.

4.3. Creep, recovery, and internal stress

Let us consider how the kinetics of recovery, $\dot{\epsilon}_R$, are related to the kinetics of the recoverable part of the creep strain, $\dot{\epsilon}_R(c)$. Equation 5 shows that the functional forms of $\dot{\epsilon}_R(c)$ and $\dot{\epsilon}_R$ should be the same since $(\epsilon_u - \epsilon_L)$ is nearly independent of time (Fig. 7). The functional form of the recovery rate as determined experimentally

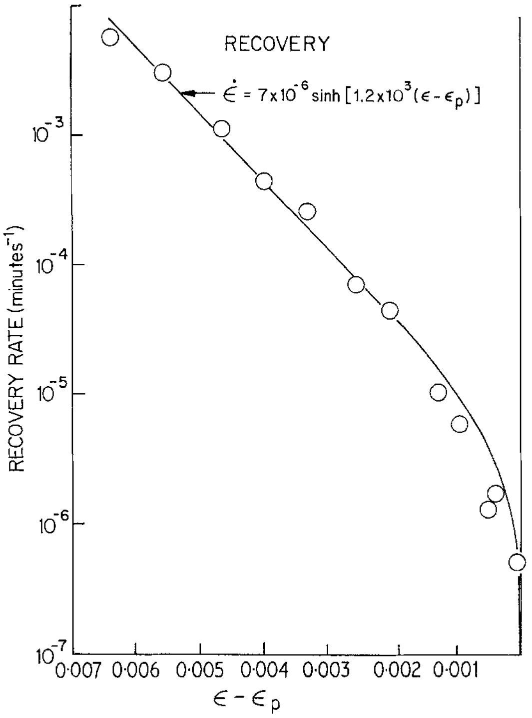

Figure 12 Rate of strain recovery versus amount of recoverable strain.

is shown in Fig. 12 and is very well represented by the equation

$$\dot{\epsilon}_R = \text{constant } x \sinh C\,(\epsilon - \epsilon_p) \qquad (7)$$

where C is a constant; ϵ is the total strain in the specimen; $(\epsilon - \epsilon_p)$ is the amount of strain that is yet to be recovered. Now let us see how the Creep Equations 1, 2, 3, and 6 lead to Equation 7. Since we are relating recovery to the recoverable part of the creep curve only the initial part of the creep curve as represented by Equation 6 should be considered. Substituting Equations 2, 3 and 6 into Equation 1 gives

$$\dot{\epsilon} = \text{constant } x\ e^{-Q/kT}\, e^{\sigma_H v_p/kT}\, e^{\sigma v_s/kT}\, e^{-a\,\epsilon_R(c)}\,. \qquad (8)$$

Equation 8 may be given the following form

$$\dot{\epsilon} = \text{constant } x\ e^{-Q/kT}\, e^{\sigma_H v_p/kT}\, e^{(\sigma-\sigma_{\text{int}})v_s/kT} \qquad (9)$$

where $a\epsilon_R(c) = \sigma_{\text{int}}\, v_s/kT$. σ_{int} has the character of an internal stress which opposes the applied stress. Since σ_{int} increases with strain, then the effective stress $\sigma - \sigma_{\text{int}}$ decreases with strain and therefore the creep-rate diminishes in accordance with the observations. The suggestion that the diminishing creep-rate at the beginning of the creep curve was related to the build up on an internal stress, was previously made by Gurevich [16] and Stratonova [9] in the case of polymers. This same concept of an internal stress decreasing the creep-rate in metals had been proposed by Nowick and Machlin [17] and is now generally accepted as the primary reason for transient creep in crystalline solids. It is now proposed that the purely exponential form of the creep-rate in Equations 8 and 9 be changed to the hyperbolic sine form as follows:

$$\dot{\epsilon} = \text{constant } x\ e^{-Q/kT}\, e^{\sigma_H v_p/kT} \sinh[(\sigma - \sigma_{\text{int}})v_s/kT]\,. \qquad (10)$$

The reasons for favouring Equation 10 over Equation 9 are the following: (1) since our investigation has been concerned only with large stress both Equations 9 and 10 fit the data equally well; (2) Equation 10 arises naturally from the theory of thermal activation as proposed by Eyring [18] and used by Bauwens-Crowet *et al* [5] for polymers; (3) at low stresses it reduces to the linear theory of viscoelasticity; (4) when the sign of the stress is reversed the sign of the strain-rate reverses, and (5) it nicely correlates with recovery data represented by Equation 7. Recovery occurs when the applied stress is reduced to zero and thus Equation 10 becomes

$$\dot{\epsilon} = \text{constant } x\ e^{-Q/kT} \sinh[-\sigma_{\text{int}}\, v_s/kT]\,. \qquad (11)$$

Since σ_{int}, as given above, is proportional to the amount of strain that is to be recovered, Equation 11 agrees exactly with the experimental recovery data as described by Equation 7. Thus, it is seen that the driving force for recovery is the internal stress, σ_{int}.

An insight into the possible physical origin of the internal stress comes from the observation of Sherby and Dorn that the function $f_3(\epsilon)$ is independent of temperature. If the recoverable strain were associated with a decrease in entropy, then for small strains the internal stress would be given by

$$\sigma_{\text{int}} = \text{constant } x\ kT\epsilon_R \qquad (12)$$

because the entropy modulus of elasticity is proportional to T. Substituting Equation 12 in Equation 9 would then lead to the observation of Sherby and Dorn concerning $f_3(\epsilon)$ being independent of T. Observed decreases in temperature during unloading have also suggested that some entropy elasticity is involved. We plan to learn more about the physical nature of the internal stress by measuring the temperature changes associated with the recoverable creep and recovery both in tension and compression.

4.4. Predicting time for creep failure

It is of practical importance to be able to predict how long it will take a material to fail in creep at a given stress and temperature. If creep failure occurs when the creep-rate reaches its minimum value, then it is natural to suggest, that failure occurs when the creep strain is equal to that value at the minimum creep rate. Time to creep failure would be given by

$$t_F = \int_0^{\epsilon_{\min}} \frac{d\epsilon}{\dot{\epsilon}} \qquad (13)$$

where $\epsilon_{\min}$ is the creep strain at the minimum creep-rate. In the regime of high stresses, Equation 8 should be applied to Equation 13.

$$t_F = \text{constant } e^{Q/kT} \, e^{-\sigma v/kT} \int_0^{\epsilon_{\min}} \frac{d\epsilon}{f(\epsilon)} \qquad (14)$$

For the case of uniaxial compression the parameters v, $\epsilon_{\min}$ and $f(\epsilon)$ for evaluating Equation 14 at room temperature, would be obtained directly from Fig. 10.

4.5. The asymmetry in the loading and unloading strains

The final point of discussion concerns the observation that $\epsilon_u \geqslant \epsilon_L$. These results cannot be derived from Equations 10 and 11. It is not suggested that there is a difference in the unrelaxed modulus during loading and unloading. What is observed is that there is an increment of recoverable strain which occurs very rapidly during unloading so that experimentally it appears to be instantaneous. The interesting point is that the same amount of rapid strain does not occur during loading. At the present time our only explanation is based on an inherent asymmetry in the barrier for thermal activation. It is suggested that even at zero stress and strain the activation energy for a unit of flow to go from the unstrained to the strained state is greater than for the flow process in the reverse direction. A similar suggestion was made by Matz *et al* [8] in order to explain their experiments on the delay time for creep failure.

4.6. Final remarks

The kinetics of creep and recovery are complex. Our creep Equation 10 is not perfect nor complete, but we consider it to be a further step in describing non-linear viscoelasticity and directly relating creep and recovery curves. We have not presented a theory for the persistent part of the creep strain. However, the method of dividing the strain into components is expected to be a fruitful approach toward improving our understanding of the non-linear viscoelastic behaviour of polymers.

Acknowledgement

Mr Raymond de la Veaux was very helpful during the operation of the MTS-machine. The work was supported by the Advanced Research Projects Agency of the Department of Defense, the National Science Foundation, and by the Army Research Office, Durham.

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Received 10 October and accepted 26 October 1972.