JOURNAL OF MATERIALS SCIENCE 13 (1978) 467–472

High temperature creep of polyvinyl chloride

JAMES P. STEPHENS*, AZIZ AHMADIEH†, AMIYA K. MUKHERJEE
Materials and Devices Research Group and Department of Mechanical Engineering, University of California, Davis, California, USA

The creep behaviour of polyvinyl chloride (PVC) has been studied in the temperature range 280 to 340° F under constant stress varying from 3.4 to 22.7 p.s.i. It is shown that the steady-state creep rate is an exponential function of stress as suggested by Norton but the exponent decreases with temperature. The activation energy for creep is determined using an activated-state rate process and it is found to be a decreasing function of stress with a higher value at temperatures 320° F and above. It is shown that the time dependent strain can be represented by

$$\gamma = \gamma_0 + \dot{\gamma}_s t + \gamma_T \left[1 - \exp\left(-K\dot{\gamma}_s t\right)\right]$$

where γ_0 is the instantaneous strain on stressing, $\dot{\gamma}_s$ the secondary creep rate, γ_T transient strain, and K is a constant. Scanning electron micrograph studies of the fracture surface and the change in activation energy apparently support the probability of two different deformation mechanisms i.e., domain flow and chain segmental or molecular flow at temperatures below and above 320° F, respectively.

1. Introduction

The mechanical behaviour of materials under applied stress has been studied extensively and generally creep experiments have been used to analyse and predict the behaviour of materials at high temperature. Andrade [1, 2] was a pioneer investigator of the creep of metals and later, Norton [3] presented a creep law which was subsequently applied to polystyrene and other materials by Marin and Pao [4]. Other investigators such as Nadai [5] and Nutting [6] proposed equations which have been modified by various workers to describe the specific behaviour of materials under isothermal conditions.

The rheological behaviour of polymers is particularly difficult to model since most polymers exhibit viscoelastic behaviour at ambient temperature. In addition, polymers often undergo thermal instability and a number of transitions may occur in their mechanical properties. Transition of viscoelastic behaviour to rubber-like elasticity at temperatures above the glass transition temperature T_g, and viscous flow at temperatures higher than melting points are two of such transitions. The earlier work of Eyring [7] in 1943 describing molecular flow as an activated-state rate process was specifically formulated to apply to the elastic-viscous nature of polymers. Williams *et al.* [8] later introduced a creep law describing the viscosity of a polymer by expressing the temperature in terms of its T_g.

Although recent literature contains numerous creep and stress relaxation studies of polyvinyl chloride [9–11], there is an apparent absence of high temperature polymer creep data. In this investigation we were interested in studying the rheological behaviour of straight uncompounded PVC in a temperature range where rubber-like elasticity is observed. The glass transition temperature of the specimens was of the order of 180° F. The study was mainly directed; (i) to analyse the creep data with Norton's creep law, (ii) to determine the activation energy for creep based on an activated-state rate process, (iii) to determine

---

*Now at Signetics Corporation, Sunnyvale, California, USA.

†Permanent address: Department of Materials Science and Engineering, Pahlavi University, Shiraz, Iran.

the effectiveness of utilizing the steady-state strain rate to predict the creep behaviour of PVC by generating a universal curve for the creep process that would accommodate different test stresses and temperatures, and (iv) to identify the probable deformation mechanisms.

2. Experimental procedure

The creep experiments were conducted in torsion, using hollow thin-walled cylindrical specimens which were $1\frac{1}{2}$ in. long, $\frac{3}{4}$ in. in external diameter and 1/16 in. in wall thickness. To eliminate variation in composition and manufacturing history, all of the specimens were cut from the same rod and no thermal conditioning was used prior to testing.

Creep tests were performed in air in an environmental furnace chamber in conjunction with the creep testing machine. Shear strain was calculated from the angular rotation of a steel marker that could be viewed from outside through the pyrex-glass window of the environmental chamber. The specimen was kept at the test temperature for about 2h before loading to allow the parts to reach a steady-state temperature. The temperature of the furnace was held constant by a proportional bandwidth controller to better than ±2° F of the reported values. Stresses were maintained constant to ±0.2% and strains to ±0.0001.

Creep behaviour was examined at temperatures ranging from 280 to 340° F at stress levels of 3.4 to 22.7 p.s.i. The tests were run until a steady-state creep was established. The microstructure of the fractured specimens was viewed in a Cambridge Scanning Electron microscope at magnifications up to 2000 x.

3. Experimental results

Typical creep curves are shown in Fig. 1. All the creep curves obtained in the temperature range of 280 to 340° F and the stress range of 3.4 to 22 p.s.i. showed the usual trend of shear strain versus time relation, with a primary stage of decreasing creep rate followed by a steady-state stage. It was found that the strain rate $\dot{\gamma}_s$ during steady-state followed a relation of the form

$$\dot{\gamma}_s \propto \tau^n \qquad (1)$$

as suggested by Norton [3], where τ is the shear stress. The stress exponent n was found to decrease with increase in temperature. The steady-state creep rate $\dot{\gamma}_s$ versus the stress τ is plotted in Fig. 2 where n, the stress dependence of $\dot{\gamma}_s$, and variations of n with temperature are determined from best fitted straight lines. The value of exponent n varies from 3.7 at 280° F to 2.4 at 340° F and is apparently independent of stress.

Assuming that creep is a thermally activated process, the steady-state rate can be described in terms of the temperature and stress as

$$\dot{\gamma}_s = \frac{d\gamma_s}{dt} = A(\tau/G)^n \exp(-Q_c/RT) \qquad (2)$$

where A is a structure dependent constant, G is the shear modulus, Q_c is the apparent activation energy for creep, R is the gas constant, and T is the absolute temperature. Because of the inclusion of G, T, and n in Equation 2, the apparent acti-

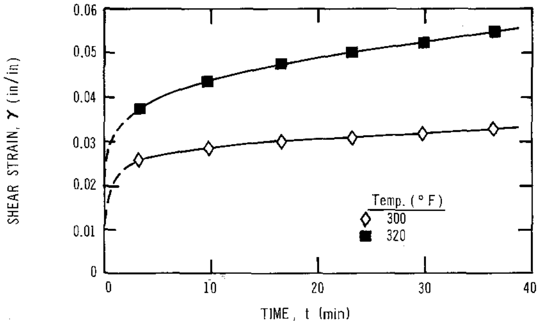

Figure 1 Typical creep curves for PVC.

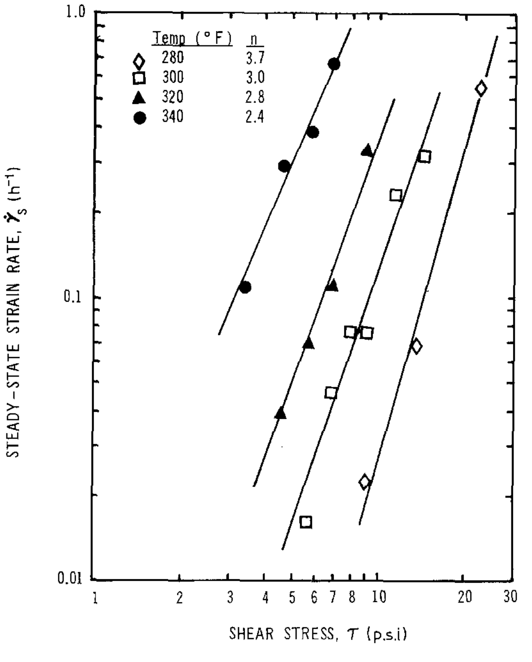

Figure 2 Effect of temperature on the stress exponent of steady-state creep rate for PVC.

vation energy for creep

$$Q_c = \left[\frac{\partial \ln \dot{\gamma}_s}{\partial(-1/RT)}\right]_{\tau = \text{constant}} \simeq \left[\frac{\Delta \ln \dot{\gamma}_s}{\Delta(-1/RT)}\right]_{\tau = \text{constant}}$$

is always slightly different from the activation enthalpy of the process. It is therefore convenient to define [22] a true activation enthalpy for creep, H_c, which does not contain terms arising from either G, T, or n

$$H_c = Q_c - RT\left[(n-1)T/G\left(-\frac{\partial G}{\partial T}\right) - 1\right] \quad (3)$$

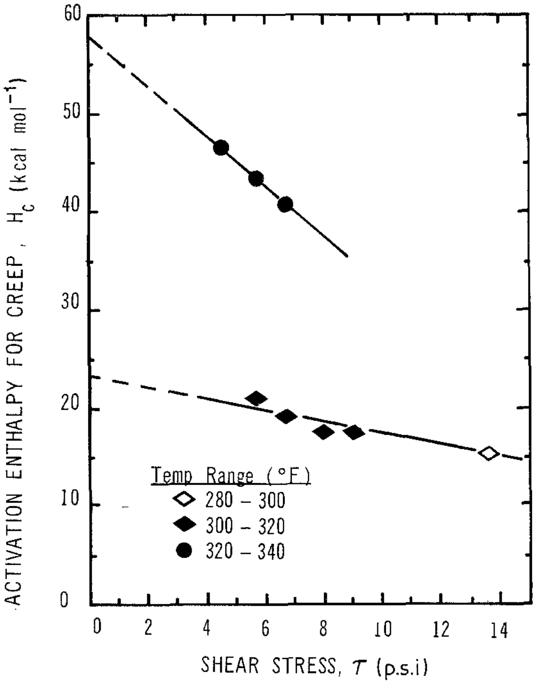

Figure 3 Stress dependence of activation enthalpies for two different creep temperature ranges.

Fig. 3 shows H_c versus applied stress indicating that activation enthalpy is a decreasing function of stress. It is also interesting to note that there is a definite change in the stress dependence of the activation enthalpy when the temperature is raised to 320° F or above. H_c decreases more rapidly with stress at higher temperatures.

The micrographs presented in Figs. 4 to 6 demonstrate certain aspects of the deformation process. Figs. 4 and 5 show typical fracture surfaces of specimens tested to failure at 280 and 340° F, respectively. The difference in fracture surface topographies in these figures suggest the possibility of different deformation mechanisms which are operative at these two different temperatures. An etched sample which had been used as a test specimen is shown in Fig. 6 where it appears to have crystallized to a great extent. A similarly etched sample with no thermal conditioning or testing did not reveal any crystallite boundary structure indicating the typically amorphous structure of the samples as they were received.

4. Discussion

The experimental data documented in the preceding section clearly support the power dependence of the steady-state creep rate on the

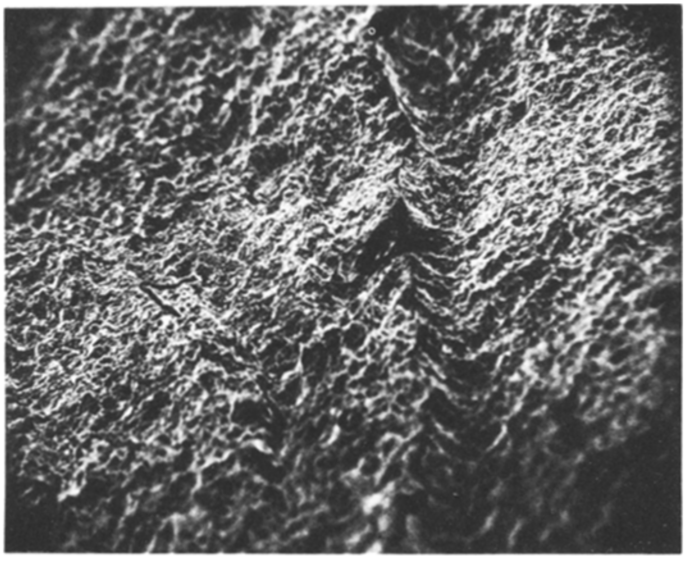

Figure 4 Scanning electron micrograph of PVC creep fracture surface for 280° F test (X 193).

Figure 5 Scanning electron micrograph of PVC creep fracture for 340° F test (X 13).

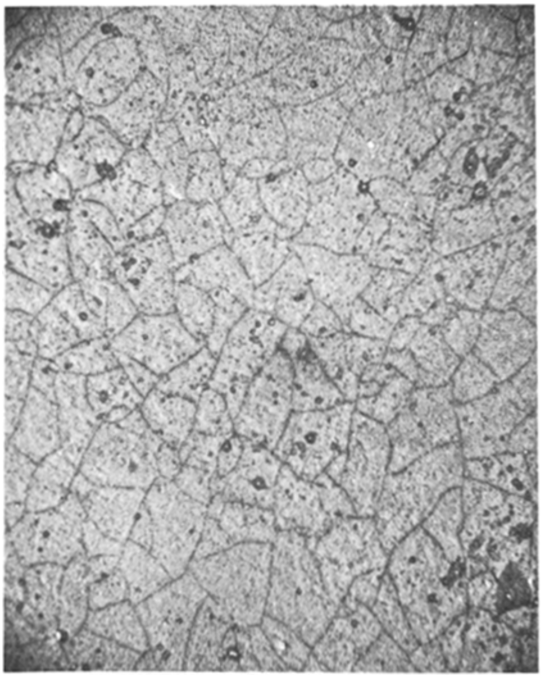

Figure 6 Scanning electron micrograph of polished and etched PVC sample which has crystallized (X 85).

creep stress as shown in Equation 2. The stress exponent and the activation energy could then be calculated as shown in Figs. 2 and 3.

Although the forms of creep curves for PVC are typical of most materials, the stress dependence of the activation energy with its change at higher temperatures and temperature dependence of the stress exponent *n* are somehow unusual and atypical [22] of pure metals and alloys. However, these results agree quite well with the findings of earlier investigations such as Regel *et al.* [12], where they found that the activation energy for creep of polymers was approximately between 25 and 50 kcal mol^{-1}. Dyson [9] has also shown that there is no unique activation energy for the tensile creep of plasticized PVC. Recently, Collins and Krier [13] proposed a change in flow mechanism from a low energy of activation at low temperatures to a higher activation energy at around 374° F. In both cases, the activation energy was seen to decrease as the shear rate increased.

Despite the complications of the stress dependence of the activation energy and the probability that a change in deformation mechanism occurs at temperatures higher than 320° F, it will be shown that an appropriate equation for the rate constant using molecular kinetics could well define the creep behaviour of PVC over large stress–temperature variations. Assuming that a single mechanism controls transient creep and it obeys the laws of unimolecular kinetics, the rate constant can be given in terms of the temperature and stress as $K\dot{\gamma}_s$, where $\dot{\gamma}_s$ is the steady-state creep rate and K is a constant

$$\frac{d}{dt}(\dot{\gamma}-\dot{\gamma}_s) = -K\dot{\gamma}_s(\dot{\gamma}-\dot{\gamma}_s) \qquad (4)$$

as shown by Amin *et al.* [14]. Integrating above twice, one obtains

$$\gamma = \gamma_0 + \dot{\gamma}_s t + [(\dot{\gamma}_i-\dot{\gamma}_s)/(K\dot{\gamma}_s)] \\ [1-\exp(-K\dot{\gamma}_s t)] \qquad (5)$$

where $\dot{\gamma}_i$ is the initial creep rate at $t = 0$, γ_0 is the initial strain upon stressing, and

$$(\dot{\gamma}_i-\dot{\gamma}_s)/(K\dot{\gamma}_s) = \gamma_T$$

is the total transient strain. In addition, if one assumes that the transient and steady-state stages of creep have the same energy of activation and the same kinetics of reaction, then it follows that $\dot{\gamma}_i = \beta\dot{\gamma}_s$, where β is a constant. Therefore, the total transient strain

$$\gamma_T = (\dot{\gamma}_i-\dot{\gamma}_s)/(K\dot{\gamma}_s) = (\beta-1)/K \qquad (6)$$

where β and K are constants independent of stress and temperature which means γ_T must also be a constant and independent of temperature and stress.

The value of $\gamma_T = 0.146$ was determined from experimental data for the total transient creep strain. The rate constant K was determined at one-half of the total transient strain γ_T, where from Equation 5 one obtains $K = [(\ln 2)/(\dot{\gamma}_s t)]$. The calculated value of K was 300. Hence for the specific case for PVC Equation 5 reduces to

$$\gamma - \gamma_0 = \dot{\gamma}_s t + 0.146\,\{1 - \exp(-300\,\dot{\gamma}_s t)\} \tag{7}$$

which should give a universal expression correlating the effect of time, stress and temperature on the time-dependent creep strain. It should be noted that the effects of stress τ and temperature T are implicitly contained in $\dot{\gamma}_s$ through Equation 2. The stress dependence of the creep rate n and the activation energy Q_c (or more rigorously the true enthalpy of activation H_c) which are needed to evaluate $\dot{\gamma}_s$ are obtainable from Figs. 2 and 3 over the temperature and stress ranges that were investigated.

The validity of Equation 7 is shown by the creep curve depicted in Fig. 7 for the experimental data on PVC tested. Although the data covered a wide range of stress–temperature combinations, the creep curve of Fig. 7 reveals that regardless of temperature and stress, the data fall well onto a single curve which agrees reasonably (within 10% error) with the solid theoretical curve of Equation 7. Based on the belief that some crystallization of PVC took place during the time of testing as shown in Fig. 6, the accuracy of Fig. 7 is in apparent agreement with Sato *et al.* [15] results. They found that data obtained for specimens with a high fraction of PVC did not form a single master curve but gave a domain in time–temperature regions where crystallization took place.

A review of the experimental data and particularly the drastic change in the stress dependence of activation energy and its value, and close examination of the electron micrographs of the fracture surface suggest a possible change in the deformation mechanism when temperature is raised to above about 320° F. There are several theories describing the plastic deformation of polymers and a complete and satisfactory analysis of the deformation mechanism cannot be made here on the basis of the present data. However, an attempt will be made to demonstrate that the low temperature deformation may be consistent with domain flow which then changes to molecular flow at higher temperatures as described by Collins and Krier [13].

Although most theories [12, 16–18] do not account for the low values of the activation energy of creep, it is widely accepted that polymer chain segmental mobility is a primary factor controlling viscous flow within polymeric materials [16]. The low temperature deformation of PVC cannot be ascribed to the kinetic theory of Regel *et al.* [12] because of the extremely small activation energies that were experimentally obtained.

A possible simple explanation for the behaviour may lie in the presentation of Collins and Krier [13]. They suggested that a considerable amount of secondary bonding can exist between chains at

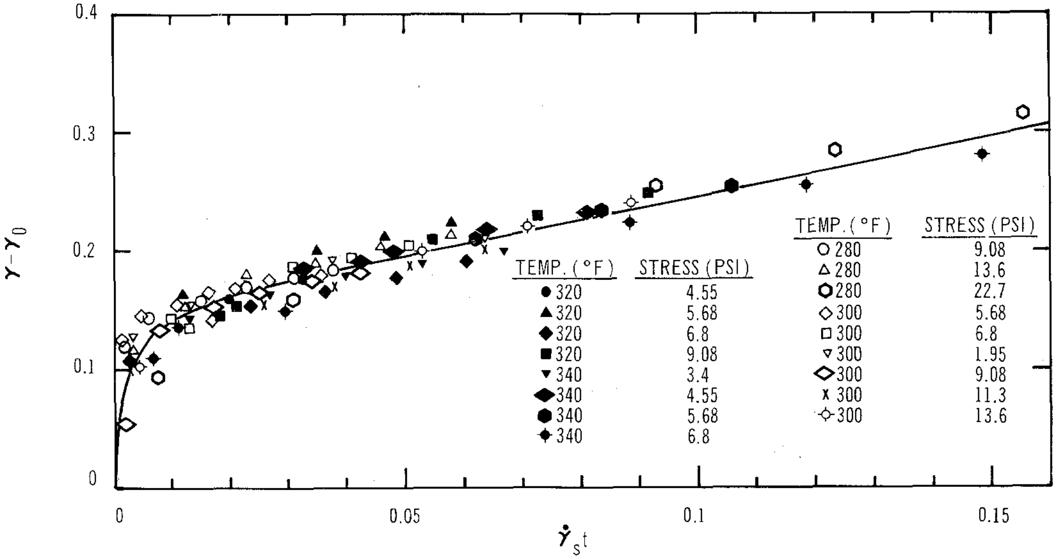

Figure 7 Master curve for creep of PVC. The solid line corresponds to Equation 7.

low temperatures resulting in domain flow caused by movement of some segments in favourable positions. At higher temperatures, the kinetic energy of the segments is sufficient to overcome the secondary bonding forces and chain segmental or complete molecular movement is the dominating mechanism. This is in agreement with Brody's observations [19] with the exception that he considered the change in mechanism to be stress dependent. Tobolsky *et al.* [16] concluded from his experimental work that the heat of activation for viscous flow is just the heat required for a segment of 20 to 25 atoms for paraffin and polyester chains, which is in accord with chain segmental movement discussed here.

The electron micrograph evidence tends to support the suggestion of a change in the mechanism of deformation at around 320° F. The smoothness of the surface topography at higher temperatures appears to indicate a more ductile fracture, such as molecular movement rather than breaking of the chains. It appears that the samples which were amorphous when received, underwent some crystallization during the warm-up as shown in Fig. 6. This is not in contradiction with the findings of Utsuo and Stein [20] that PVC crystallizes upon a central structure at above 100° C or the results of McKinney and Faltz [21] that there is an indication of an annealing process developing a small amount of crystallinity in PVC. Thus the probability that a PVC crystallite network existed above the glass transition temperature and prevented molecular flow below the crystallite melting point does not seem unreasonable.

5. Conclusions

The following conclusions are drawn from the present work:

(a) The steady-state strain rate is dependent upon a power of the stress as implied by Norton, but the stress exponent is temperature dependent, varying from 2.4 to 3.7 over the 60° F temperature range investigated.

(b) The activation energy for creep was found to be a function of stress and the calculated values were comparatively low with respect to the dissociation energies of the primary covalent bonds in PVC.

(c) A universal creep curve for PVC can be adequately described by an equation relating time dependent strain to the steady-state strain rate multiplied by time.

(d) A possible change in deformation mechanism takes place at around 320° F which may be a transition from domain to molecular flow.

References

1. E. M. ANDRADE, *Proc. Roy. Soc.*, 84 (1970) 1.
2. *Idem, ibid* A90 (1914) 329.
3. F. H. NORTON, "Creep of Steel at High Temperatures", (McGraw–Hill, New York, 1929) p. 219.
4. J. MARIN and Y. H. PAO, *Proc. ASTM* 51 (1951) 1277.
5. A. NADAI, "Timoshenko 60th Anniversary Volume", (Macmillan, New York, 1938) p. 63.
6. P. NUTTING, *Proc. ASTM* 21 (1921) 1162.
7. A. TOBOLSKY, R. POWELL and H. EYRING, "The Chemistry of Large Molecules", (Interscience, New York, 1943) p. 17.
8. M. L. WILLIAMS, R. F. LANDEL and J. D. FERRY, *J. Amer. Chem. Soc.* 77 (1955) 3701.
9. A. DYSON, *J. Polymer Sci.* 7 (1951) 147.
10. I. J. GRUNTFEST, E. M. YOUNG Jr., and W. KOOCH, *J. Appl. Phys.* 28 (1957) 1106.
11. W. N. FINDLEY, A. M. REED and P. STERN, *Modern Plastics* 45 (1968) 141.
12. V. R. REGEI, A. I. SLUTSKER and E. E. TOMASHEVSKII, *Soviet Physics USPekhi,* 15 (1972) 45.
13. E. A. COLLINS and C. A. KRIER, *Trans. Soc. Rheology* 11 (1967) 225.
14. K. E. AMIN, A. K. MUKHERJEE and J. E. DORN, *J. Mech. Phys. Solids* 18 (1970) 413.
15. Y. SATO, M. HOSODA and M. SAKURAI, *Zairyo,* 16 (1967) 472.
16. C. E. ROGERS, J. R. SEMANCIK, and S. KAPUR, "Structure and Properties of Polymer Films", edited by R. W. Lenz and R. S. Stein, (Plenum Press, New York, 1973) p. 297.
17. A. Z. GOLIK and YU. F. ZABASHTA, *Mekh. Polim.* 7 (1971) 969.
18. D. McCOMMOND and P. BENHAM, *Plastics and Polymers,* 39 (1971) 130.
19. H. BRODY, *Plastics and Polymers* 37 (1969) 21.
20. UTSUO and STEIN, *J. Polymer Sci.* 349 (1965) 49.
21. P. V. McKINNEY and C. R. FOLTZ, *J. Appl. Polymer Sci.* 11 (1967) 1189.
22. A. K. MUKHERJEE, "Treatise on Materials Science and Technology", Vol. 6, edited by R. Arsenault (Academic Press, New York, 1965) p. 163.

Received 25 February and accepted 25 July 1977.