JOURNAL OF MATERIALS SCIENCE **26** (1991) 1–5

A creep apparatus to explore the quenching and ageing phenomena of PVC films

H. H. D. LEE*, F. J. McGARRY
Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA

A creep apparatus has been constructed for an *in situ* determination of length and length change. Using this apparatus, the creep behaviour of PVC thin films associated with quenching and ageing was studied. The more severe the quench through the glass transition temperature (T_g), the greater is the instantaneous elastic deformation and the subsequent creep behaviour. As ageing proceeds, the quenched films gradually lose the ductility incurred by quenching. These results agree well with the well-known phenomena of physical ageing. Thus, the changes reflecting molecular mobilities due to quenching and ageing can be properly monitored by such a creep apparatus.

1. Introduction

Quenching and ageing are phenomena being universally observed in wide varieties of pure materials and alloys such as glasses, metallic glasses, and glassy polymers. By quenching these amorphous materials from the molten or rubbery state to the glassy state, free volume [1–5] is introduced and trapped in the glassy matrices. As a result, the quenched materials are characterized by ductility, lower modulus of elasticity, high flow stress, superior fatigue resistance, higher electrical resistivity and superior corrosion resistance [5–10]. These properties, however, gradually diminish with time; this phenomenon is known as physical ageing.

Typically, changes in physical properties (especially, molecular mobilities) associated with quenching and ageing are studied by monitoring the creep behaviour or stress relaxation of the glassy materials. In this connection, thin-film specimens are preferred because faster cooling rates throughout the specimens can be achieved, so the corresponding response ascribable to quenching can be more distinct. However, thin-film specimens are rather difficult to hold in the clamps normally designed for bulk samples; thus, sample slippage inevitably occurs during testing. This is a serious problem because the determination of strain or stress on an Instron is always based on the relative movement of two clamps. In addition to sample slippage, it has been experienced that the rubber coating on the inside surface of the clamps could creep even more than the sample itself. Furthermore, using the Instron for such time-consuming experiments is economically unpractical. Thus, there is a strong need to construct a simple yet delicate apparatus for conducting creep or stress-relaxation study. This paper reports the construction of a creep apparatus.

An ideal creep apparatus should be able to monitor not only instantaneous elastic deformation but also subsequent creep. Because both essentially involve a determination of length, the use of a mechanical extensometer as a basic component seems logical. While there is no problem to use an extensometer with high sensitivity (for instance, 5 μm), it is rather difficult to widen the range of linearity to at least 5 cm without sacrificing sensitivity. This shortcoming thus eliminates it from the application concerned. To resolve these problems, an optical determination of strain has been employed for constructing a creep apparatus. The construction details and the creep measurements illustrating the phenomena associated with quenching and ageing are reported.

2. Experimental details

2.1. Construction of the creep apparatus

Fig. 1 illustrates the constructed creep apparatus. The key components of this set-up include a stretching unit, a cathetometer, and/or an environmental chamber.

The stretching unit comprised a pair of sample holders, a guiding frame, and weights. The sample holders were specially designed to prevent any possible sample slippage during measurement. This was achieved by adhering the paper side of a 220 sandpaper to the surface of an aluminium sheet 0.05 cm thick. A pair of the sandpaper-adhered aluminium sheets were then joined to the tips of the Mueller clip. The rough surface of the sandpaper thus provides a firm holding of the thin-film specimen. With these specially modified Mueller clips, mounting a sample on the stretching unit becomes easy and fast. This is

---

* *Present address*: General Motors Research Laboratories, Warren, Michigan 48090-9055, USA.

0022–2461/91 $03.00 + .12

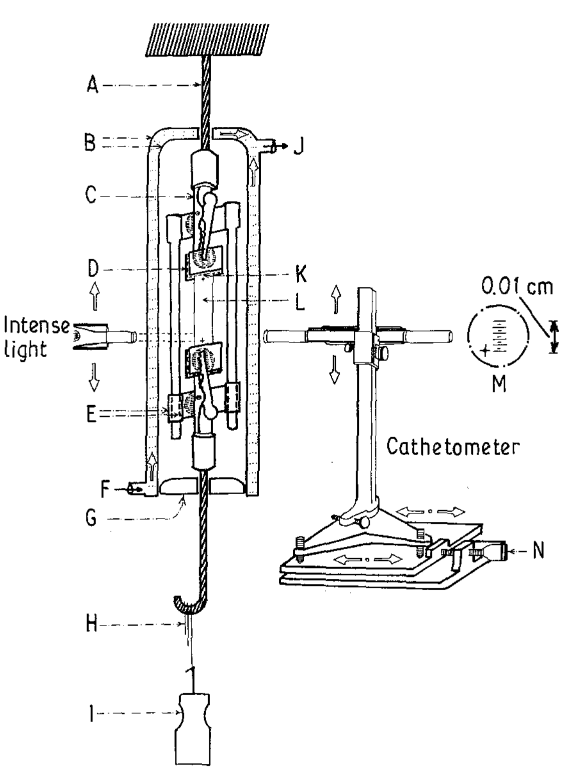

Figure 1 A diagrammatic view of the creep apparatus and its notes. A, no. 13 copper wire; B, Pyrex glass; C, Mueller clip; D, aluminium sheet (0.05 cm thick); E, Pyrex tubing and rod; F, inlet of water from a constant-temperature bath; G, rubber stopper; H, fine weights; I, coarse weights; J, outlet of water to a constant-temperature bath; K, no. 220 sandpaper; L, sample with two targets; M, fine focus (resolution 5 μm); N, coarse focus adjuster.

crucial because the mechanical properties of quenched glassy materials are sensitive to ageing time.

To guide the sample movement properly during testing, two pairs of Pyrex tubing (3 cm long) and Pyrex rod (20 cm long) were epoxy-bonded to the top and the bottom sample holders, respectively. Special care was taken to align both pairs of tubing and rod. This sliding frame thus provides rigid and smooth guidance to the dislocation of the sample under an external stress.

In order to ensure precision of measurement, the cathetometer was carefully levelled. Further, two targets were marked at both ends of the sample, and the distance between the targets as monitored by the microscope of the cathetometer was then determined. This *in situ* measurement thus gives absolute accuracy in length determination. The cathetometer used in this study reads to 5 μm. If the length of a sample is 4 cm, then the detectable strain almost reaches 0.0001 cm cm^{-1} (or 0.01%).

In cases where it is not possible to conduct the creep testing in a temperature-controlled room, an environmental chamber can be used to enclose the creep tester. The chamber can be made of Pyrex glass with circulating water to a constant-temperature bath, so that a constant temperature can be maintained.

2.2. Sample preparation

The study of quenching and ageing phenomena was emphasized on polyvinyl chloride, which was supplied in a powder form (Geon 121, Goodrich Co; synthesized by emulsion polymerization) with a spherical size of ~600 nm. Tetrahydrofuran (THF) was used as solvent for thin-film casting. The film thickness was 0.11 mm, which allowed higher quenching rates to be achieved throughout the specimens. The cast films were subjected to vacuum at 60 °C for 72 h, then exposed to a series of annealing cycles (3 min each at 140 °C) until no weight loss occurred. Finally, creep specimens with dimensions 50 mm long and 5 mm wide were cut from the annealed film using a surgical blade.

2.3. Annealing and quenching of thin films

During annealing and quenching, the specimens were wrapped in aluminium foil (0.02 mm thick) and then copper sheet (0.13 mm thick) to maintain good shape for creep testing. The annealing temperatures were in the range 94 to 153 °C at atmospheric pressure. The annealing times necessary for the specimens to reach equilibrium structures were 3 to 6 min, as determined from dilatometry [5]. Then, these annealed specimens were rapidly immersed into ice–water. While annealing and quenching proceeded, a thermocouple was inserted into the sandwich structure to monitor temperature change with time. The idealized cooling rate was estimated to be 450 °C sec^{-1}.

The processes of annealing and quenching always introduce buckling to the thin-film specimens which would cause great error in strain calculation. To resolve this problem, the sample was sandwiched using two pieces of a microscope slide and then squeezed by two clamps at both ends of the microscope slide, and the specimen was flattened. Thus, accurate measurement of the initial length is possible.

3. Results and discussion

3.1. Reliability of the creep apparatus

To test the reliability of this apparatus, a piece of aluminium foil (50 mm × 13.4 mm × 0.02 mm) was mounted on the stretching unit. The load was 680 g, which created a 24.82 MN m^{-2} (3600 p.s.i.) stress to the aluminium specimen. Fig. 2 shows the creep curve of this aluminium foil for a period of 44 h at room temperature (21 to 23 °C). Except for the instantaneous elastic deformation, no other response was detected. This observation agrees well with the expected physical response of aluminium foil under a stress less than its yield stress, that is, no creep should occur. If the thickness measurement of 0.02 mm was assumed accurate enough, the tension modulus calculated from the stress (24.82 MN m^{-2}) and the instantaneous elastic deformation (0.028%) would be 8.86×10^4 MN m^{-2} (12.9×10^6 p.s.i.) which approaches the reference value of 10×10^6 p.s.i.

Following the success with aluminium foil, the creep behaviour of PVC was subsequently investigated. In this case, two PVC specimens with dimensions of 50 mm × 5 mm × 0.11 mm were annealed at 98 °C to reach equilibrium and then slowly cooled at a rate of 0.5 °C min^{-1}. The stress applied to the films was

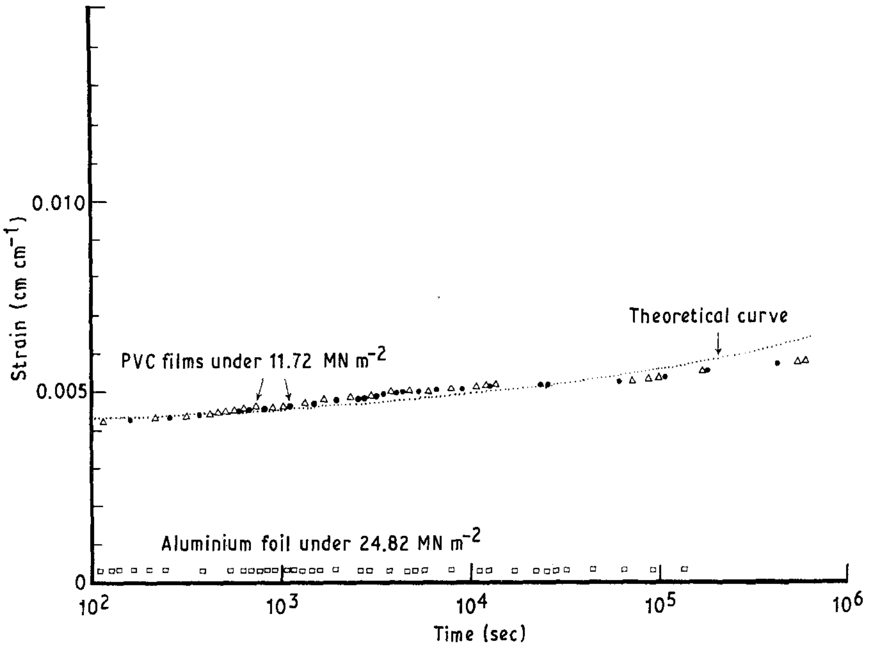

Figure 2 Creep behaviour of an aluminium foil and aged PVC films.

11.72 MN m^{-2} (1700 p.s.i.), which fell in the linear region of PVC according to the work of Onaran and Findley [11]. The creep curves of both specimens are shown in Fig. 2. It is clear that no difference can be perceived from both curves, confirming apparatus reliability as well as experimental reproducibility.

The experimental data obtained for the PVC specimens were curve-fitted into an empirical equation derived by Findley and Peterson [12]. The final equation has the form

$$\varepsilon(t) = 0.0039 + 1.31 \times 10^{-4} \times (t)^{0.221} \qquad (1)$$

where 0.0039 is the time-independent strain or instantaneous elastic deformation, 1.31×10^{-4} the coefficient of time-dependent term, t the testing time, and 0.221 a constant for the time factor. Without considering the effects of ageing, this equation describes long-term creep behaviour less accurately than the short-term behaviour.

3.2. Thermoreversible nature of quenching and ageing

In order to demonstrate the thermoreversible nature of quenching and ageing, two specimens were repeatedly subjected to various thermal histories. The creep results are depicted in Fig. 3. Tests on two samples which were quenched from 96 to 0 °C ice–water and aged 9, 10, and 11 min prior to loading at 11.72 MN m^{-2} showed identical creep behaviour. As compared with the air-cooled sample (test 2, Sample 1), a great difference in creep was seen. Such different creep behaviour can be ascribed to the fact that the ice–water quenching freezes more excess free volume in the sample than the slow air-cooling, as monitored by a hydrostatic weighing method [5]. The higher free volume content of the quenched samples confers much greater molecular mobility which results in a larger initial extension and a faster creep rate. On the other hand, the denser structure of the slowly-cooled sample is characterized by a lower instantaneous strain and less subsequent creep.

Following the sequence of the tests, Sample 1 displayed ductile, brittle, then ductile behaviour. More importantly, the molecular mobilities not only properly responded according to the thermal change but also precisely resumed their original state. This clearly confirms that previous thermal histories and thus mechanical properties can be erased by a subsequent thermal treatment. Thus, this creep apparatus clearly demonstrates the thermoreversible nature of quenching and ageing on PVC.

3.3. Effects of quenching on creep behaviour

To reveal the influence of initial annealing temperature (T_0) on molecular mobility, creep behaviour was studied on a sample being repeatedly quenched from various T_0 (106, 118, 123, 133, 143, 153, 96, and 153 °C in sequence) to 0 °C but having the same ageing interval (10 min) prior to loading.

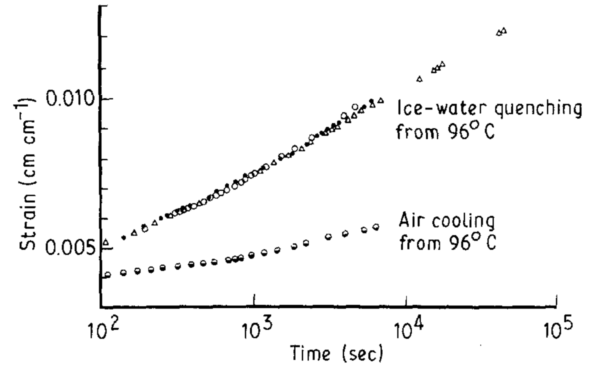

Figure 3 Creep behaviour of PVC films, showing thermoreversibility between quenching and ageing. Sample 1: (○) test 1, ice–water quenching and 9 min ageing*; (◒) test 2, air cooling and 11 min ageing; (●) test 3, as test 1, but 11 min ageing*. Sample 2: (△) test 4, as test 3 of sample 1. Ageing time at room temperature prior to 11.72 MN m^{-2} loading.

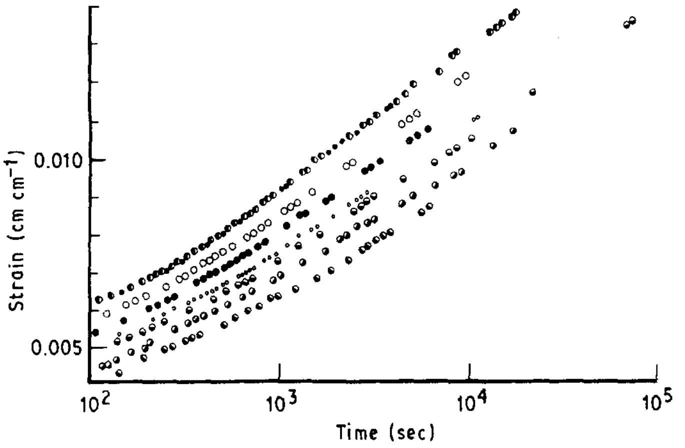

Figure 4 Quenching effects on creep behaviour of a PVC film being repeatedly quenched from various T_0 to ice–water and aged 10 min prior to 11.72 MN m^{-2} loading. T_0 (°C) in testing sequence: (◕) 106, (◒) 118, (○) 123, (●) 133, (◯) 143, (◐) 153, (◔) 96, (•) 153.

The results are shown in Fig. 4. Two tests of quenching from 153 °C have an identical creep curves, confirming the above thermoreversibility as well as apparatus reliability. The quench from 153 to 0 °C produces the least dense structure and the highest creep, whereas the quench from 96 to 0 °C gives the most dense structure, leading to the slowest creep behaviour. This phenomenon is understandable because the initial annealing temperature (T_0) dictates the state of conformational structures, from which the quenching takes place. For a higher T_0, greater excess free volume or molecular mobility is most likely to be frozen into the glassy matrix if quenching is properly executed. Thus, molecular mobility is predetermined by the initial annealing temperature.

In essence, quenching from various temperatures above T_g to ice–water clearly produces different levels of instantaneous elastic deformation if the ageing interval prior to loading is held constant. The different levels of instantaneous elastic deformation subsequently lead to different creep rates.

3.4. Effects of ageing on creep behaviour

By ageing the quenched sample at room temperature for various intervals prior to loading, the concept of molecular mobility being dominated by the trapped excess free volume can be revealed. For this purpose, a sample was repeatedly quenched from the equilibrium state at 96 °C to ice–water and then aged at room temperature for 18, 36, 9, 153, 214, and 10 min in sequence prior to being subjected to a stress of 11.72 MN m^{-2}.

Under no stress, length shrinkage of the quenched sample has been observed in the tests at 153 and 214 min ageing intervals. Presumably the shrinkage is uniform in all three dimensions and volume contraction can be derived accordingly. The calculated results together with the measured volume contraction (from a hydrostatic weighing method [5]) are listed in Table I for comparison. The calculated value of 0.077% is in good agreement with the measured value of 0.079%. Although a more accurate and direct volume measurement (for instance, by a hydrostatic weighing method or volume dilatometry) is necessary to describe precisely the volume contraction during ageing, these preliminary results in length or volume shrinkage do indicate the diminishing of excess free volume in the glassy matrix as a consequence of molecules seeking an equilibrium state at the final temperature.

TABLE I Volume contractions due to ageing

Quenching conditions (°C)	Interval of ageing time, $\log(t_2/t_1)$	Calculated volume contraction (%)	Measured volume contraction (%)
96 to 0	1.86	0.077	–
	2.13	0.077	–
94 to 0	1.86	–	0.079

The influence of ageing on reducing molecular mobility is illustrated in Fig. 5. Different periods of ageing times prior to loading do produce different levels of instantaneous elastic deformation. Along with the observed length and volume shrinkage under no stress, these experimental results corroborate the statement suggested by Matsuoka *et al.* [13], that the instantaneous elastic deformation could be associated with an estimated fractional free volume.

The different levels of instantaneous elastic deformation further lead to different creep rates. For instance, nearly a 50% difference in the modulus or the compliance of the PVC can be seen at 5000 sec creep for a difference in ageing interval of 205 min between test 5 (214 min ageing) and test 3 (9 min ageing). Thus,

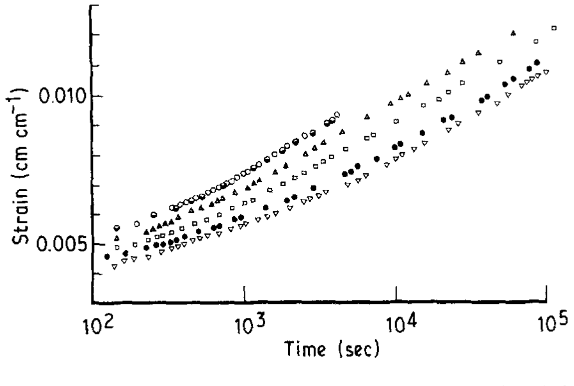

Figure 5 Ageing effects on creep behaviour of a PVC film being repeatedly quenched from 96 °C to ice–water, but with various ageing intervals prior to 11.72 MN m^{-2} loading. Ageing times (min) in testing sequence: (△) 18, (□) 36, (○) 9, (●) 153, (▽) 214, (◒) 10.

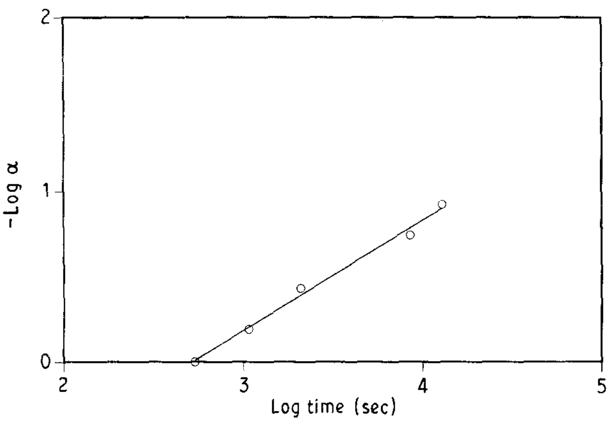

Figure 6 A linear relationship of log α–log time characterizing the ageing effects on the creep behaviour of PVC.

a negligible amount of volume contraction can give rise to a significant change in molecular mobility.

The creep curves of Fig. 5 can be superimposed on a reference curve (for instance, test 3), according to the Boltzmann superposition principle. However, discrepancy has been seen in the portions of curves that represent the long-term creep, where the testing times (under stress) are longer than the previous ageing times (prior to loading). The reason is that the process of ageing also takes place while the specimen is undergoing the creep process. So, the materials are eventually stiffened as the testing time exceeds the previous ageing time. This phenomenon is similar to that observed for the slowly-cooled PVC films (Fig. 2). Nevertheless, the valid regions (short-term creep portions) can be superimposed fairly well by a shift along the logarithmic time axis with a shift rate of μ, defined as [2]

$$\mu = -\mathrm{d}\log\alpha/\mathrm{d}\log t_e \qquad (2)$$

where, α is the shift factor and t_e is the ageing time. The shifted results are plotted in Fig. 6. Accordingly, the ageing effects on creep behaviour shown in Fig. 5 can be represented by $0.67\log(t_e/t_r)$, where t_r is an arbitrary reference ageing time, 9 min in this instance. Nearly, a linear-shift relationship is associated with the effects of ageing on creep behaviour.

4. Conclusion

Based on an optical determination of length and strain, a simple yet delicate apparatus has been constructed to monitor the creep behaviour of PVC thin films. Experimental results prove that this apparatus can precisely reflect the phenomena associated with quenching and ageing.

It has been observed that previous thermal histories and mechanical properties of PVC can be erased by subsequent thermal treatment, reflecting the thermoreversible nature of quenching and ageing. Quenching from a higher initial temperature leads to a larger instantaneous elastic deformation and faster subsequent creep. Thus, the more severe the quench through the glass transition temperature, the greater is the molecular mobility. As ageing continues, the molecular mobility incurred by quenching becomes more and more sluggish. In this regard, the effects of ageing on short-term creep behaviour appear to be in a linear relationship within the experimental observation period, and all reflect that quenching and ageing greatly affect the macroscopic properties of PVC.

Acknowledgements

The authors thank the National Aeronautics and Space Administration Headquarters for a grant of OSP 88726 (Washington, D.C., Materials Processing in Space Division), and Professor S. Backer for the use of the cathetometer.

References

1. A. J. KOVACS, R. A. STRATTON and J. D. FERRY, *J. Phys. Chem.* **67** (1963) 152.
2. L. C. E. STRUIK, in "Physical Aging in Amorphous Polymers and Other Materials" (Elsevier, 1978).
3. S. E. B. PETRIE, *Amer. Chem. Soc. Polym. Chem. Polym. Prepr.* **15** (1974) 336.
4. D. G. LEGRAND, *J. Appl. Polym. Sci.* **13** (1969) 2129.
5. H. D. LEE, PhD thesis, Massachusetts Institute of Technology (1983).
6. T. R. ANANTHATAMAN and C. SURYANARAYANA, *J. Mater. Sci.* **6** (1971) 1111.
7. H. JONES, in "Rapidly Quenched Metals", edited by N. J. Grant (Massachusetts Institute of Technology Press, 1976) p. 1.
8. H. A. DAVIES, in "Rapidly Quenched Metals III", edited by B. Cantor (Chameleon Press, London, 1978) p. 1.
9. H. WARLIMONT, *Phys. Technol.* **11** (1978) 28.
10. P. CHAUDHARI, B. C. GIESEEN and D. TURNBULL, *Sci. Amer.* **98** (April, 1980).
11. K. ONARAN and W. N. FINDLEY, *Trans. Soc. Rheol.* **9** (1965) 299.
12. W. N. FINDLEY and D. B. PETERSON, *Proc. ASTM* **58** (1958) 841.
13. S. MATSUOKA, H. E. BAIR, S. BEARDER, H. E. KERN and J. T. RYAN, *Polym. Engng Sci.* **18** (1978) 1073.

Received 25 August 1989
and accepted 19 February 1990