Physical ageing in rigid chain polymers

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Torsional and tensile creep properties of a cellulose acetate butyrate ester and the polyimide Kapton-H were studied in order to reveal physical ageing in these rigid chain polymers. The measured shift rates, μ, were 0.75 and 0.5 for cellulose and polyimide respectively, which indicates that physical ageing also occurs in polymers with stiff chains. These values, compared with those already known for most thermoplastics ($\mu \sim 1$), suggest that physical ageing is slowed down by the rigidity of the main chain.

Keywords Physical ageing; cellulose; polyimide; creep compliance

INTRODUCTION

The post-yield behaviour of glassy polymers is controlled by the strain-hardening process. If strain hardening sets in soon after yield the polymer will extend uniformly and no neck will form. Based on the assumption that yielding consists of straightening the polymer chains out of points of entanglement, Thackray[1] proposed a mechanical model tailored to predict the engineering stress–strain curve of a polymer. In this model a rubber elasticity spring with an ultimate limiting network strain was inserted to account for large deformations beyond the yield point (strain softening was not taken into account). The limiting network strain depends on *n*, the number of statistical links between points of entanglement. Since the strain-hardening function depends on *n*, which in turn depends on the polymer conformation in the glass, Haward[2] concluded that the chain structure is of paramount importance.

Thus polymers with a long natural hinge length (the distance between points of rotation) should strain-harden quickly and extend uniformly. Indeed, polymers like cellulose esters, polyimides, polybutyl isocyanates (1-nylon) and others extend in tension uniformly, with no appreciable stress drop or none at all. Haward, assuming that the molecular movements activated by the stress during the deformation become thermally activated above T_g, tried to establish a correlation between the mechanical behaviour and the change in specific heat at T_g. The above-mentioned polymers are then expected to exhibit a small C_p increase and indeed ΔC_p is small or undetectable in the range of thermal stability. This would indicate that the number of accessible conformations is quite limited even at high temperature. All this suggests that physical ageing, a phenomenon that has been shown to take place in a large variety of materials, might be of little importance or absent at all. In fact, the increase in C_p at T_g is accompanied by a parallel increase in free volume whose gradual reduction brings about ageing. To substantiate the relation between ΔC_p and ageing, Haward quoted[2] the results obtained with some polyesters in which the decrease in annealing rate, detected by d.s.c., was paralleled by a decrease in ΔC_p and natural draw ratio.

In order to investigate the effect of chain rigidity on physical ageing, a number of isothermal creep experiments have been performed on acetate butyrate cellulose ester (CAB) and the polyimide Kapton-H. The results of these tests will be described in this paper.

EXPERIMENTAL

The tensile and torsional creep tests were made with the instruments described in appendix A5 of ref. 3. The specific heat was determined with a DuPont DSC model 910. The stress–strain tests were made with a floor Instron machine.

RESULTS AND DISCUSSION

The results of small strain creep tests of CAB are presented in *Figures 1* and *2*. At each temperature the

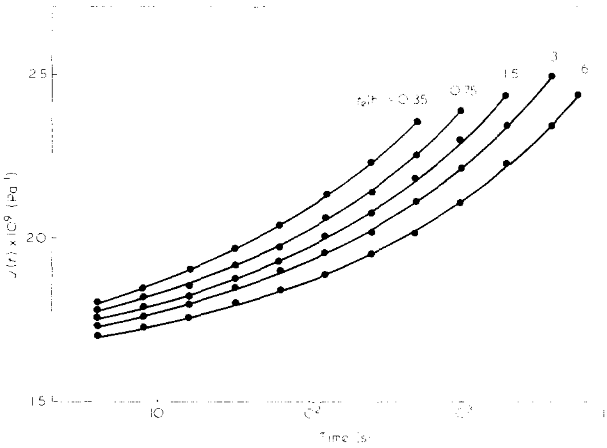

Figure 1 Small strain shear creep compliance of CAB at different elapsed times, t_e, after a quench from above T_g to 20°C (maximum shear strain, 3 x 10^{-3})

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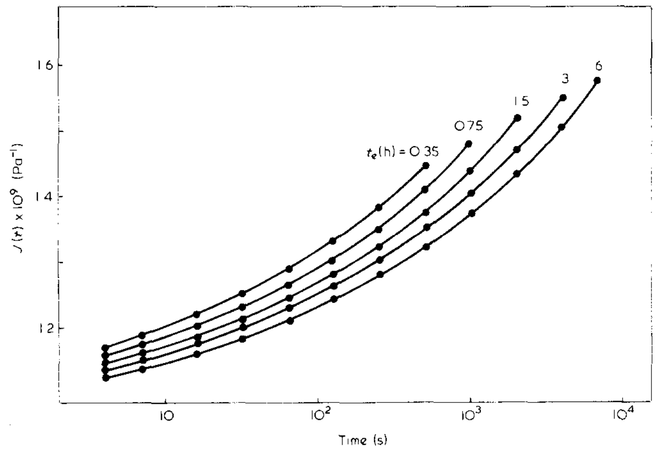

Figure 2 As for *Figure 1*, but now at −40°C

creep properties were measured at different times, t_e, after quenching from above T_g down to the selected temperature. The individual curves can be horizontally shifted to form a single master curve. The horizontal shift needed for the superposition, a, plotted against t_e yields the ageing shift rate

$$\mu = \mathrm{d}(\log a)/\mathrm{d}(\log t_e)$$

The maximum value of μ obtained in the explored temperature range was 0.75, smaller than the value of about 1 found for most amorphous polymers[3] (*Figure 3a*).

The proposed relation[2] between ΔC_p and natural draw ratio has already been mentioned and both quantities were determined for CAB. ΔC_p was similar to that of PS or PMMA, about 0.065 cal g^{-1}K^{-1}. CAB showed a well defined yield point in tension (*Figure 4*) with a stress drop of about 10%; nevertheless it extended uniformly without necking up to failure (draw ratio of about 2). That cellulose esters yield with a stress drop but do not neck, which is in disagreement with the principle of Considere, has been already reported[1,4]. What is worth noting here is the lack of correlation between ΔC_p and natural draw ratio (c.f.2).

For the polyimide Kapton-H the situation is somehow different. This polymer is characterized by the stiff monomeric unit:

It extends uniformly, without any drop in stress, and after yield the stress goes up steeply owing to a very strong strain hardening (*Figure 5*). Moreover, the polymer does not have a glass transition and does not show any modulus fall up to 400°C[5]. Thus the normal procedure to study physical ageing, a quench from above T_g, could not be used. A different approach was then devised. It has been shown[3] that if the linear viscoelastic range is exceeded in a mechanical test the net result is that the previous ageing is erased, at least in part, and the material starts ageing again. In other words a high stress pulse can simulate a quench. We applied this technique to a film of Kapton and monitored the creep behaviour at different elapsed times after removing the high stress.* The results of these tests are shown in *Figure 6*. It can be seen that there is a regular shift to the right, towards longer times, which resembles that normally observed during physical ageing after a quench. Also this process, as outlined above, is characterized by a double logarithmic shift rate (*Figure 7a*), but the value of μ instead of being constant decreases with time (from ~1 to ~0.5) which indicates that ageing slows down. The same trend was observed when the effects of high stresses on PVC were studied[3]. In *Figure 8* are shown the results of a different test. A sample of Kapton was kept

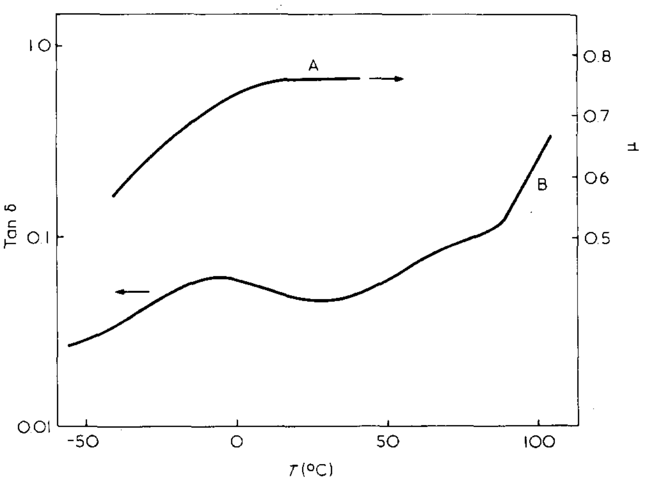

Figure 3 Shift rate as a function of temperature for CAB (curve A); loss factor for CAB at 1 Hz (curve B)

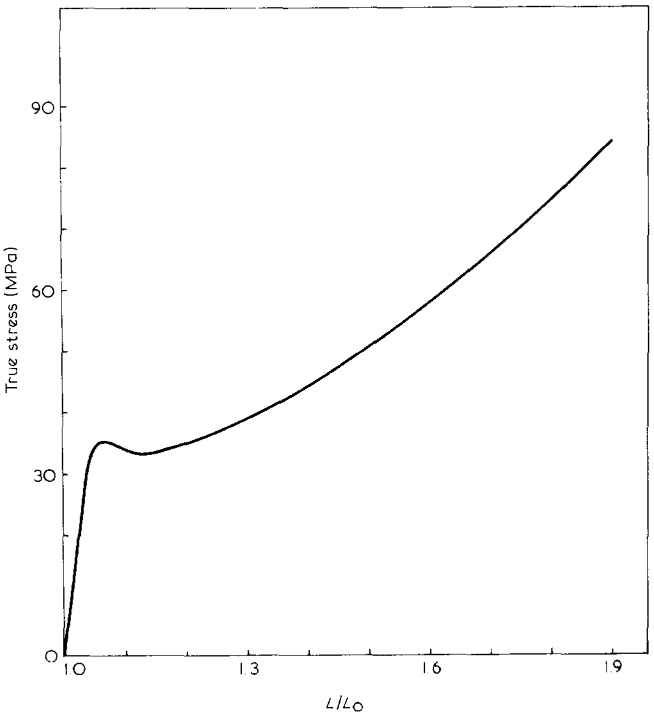

Figure 4 Stress–strain curve of CAB in tension (T = 23°C, $\dot{\varepsilon}$ = 0.063 min^{-1})

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* The duration of the stress pulse was found not to influence ageing. This is consistent with the finding that the falling edge of the stress also has the effect of de-ageing the material. However, in order to allow most of the deformation to be recovered, the duration of the stress pulse was shorter than the subsequent recovery before measuring creep properties. The intensity of the high stress was 10 times the stress used to measure the small strain compliance.

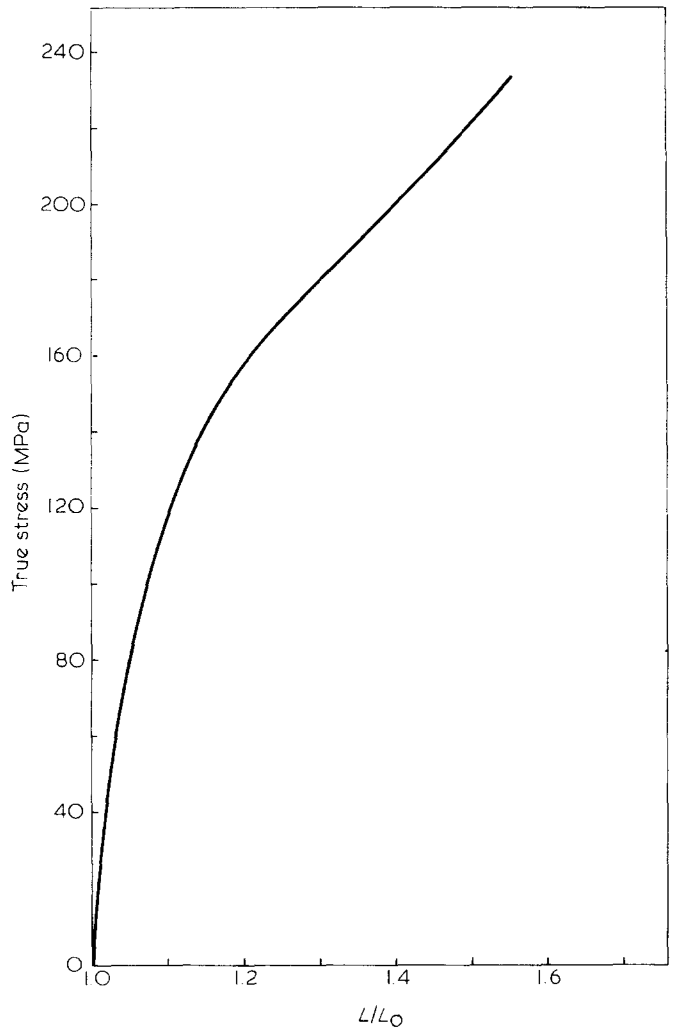

Figure 5 Stress–strain curve of Kapton-H in tension (T=23°C, $\dot{\varepsilon}$ = 0.05 min^{-1})

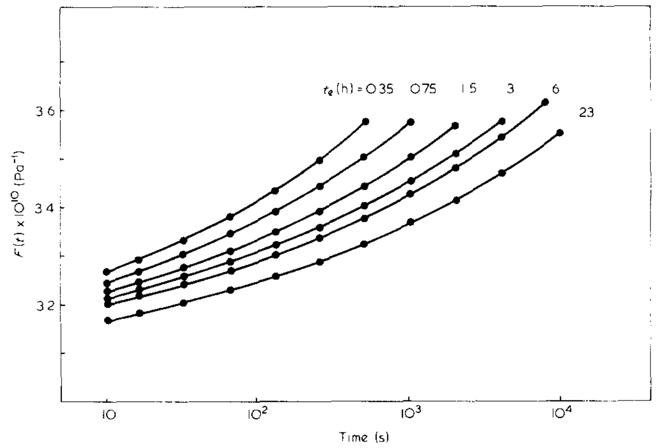

Figure 6 Small strain tensile creep compliance of Kapton-H at different elapsed times, t_e after the removal of a high stress. The pulse duration was 300 s and the magnitude 34 MPa. The stress for measuring the creep compliance was 3.7 MPa

overnight at 100°C (the highest temperature possible with our tensile tester) and then rapidly cooled at 30°C. The successive measurements followed the usual schedule. In this case, too, the regular shift of the creep curves indicates ageing, occurring this time at constant rate (μ=0.5).

All these results clearly indicate that physical ageing does occur in polymers with stiff chains or polymers in which a clearly defined T_g does not exist. Our point of view is that physical ageing may be slowed down by the rigidity of the polymer chains, as suggested by the low values of μ for cellulose and Kapton, but not hampered. The annealing process and therefore ageing is a very complex one, not being attributable to a single and simple origin, except the spontaneous reduction in free energy. It has been proposed[3] that the major driving force for physical ageing is volume contraction and this seems to be the most straightforward explanation, but there is no doubt that other factors may play a role; for instance, formation of nodular or mesomorphic structures, or redistribution of rotational isomers. However, the finding that physical

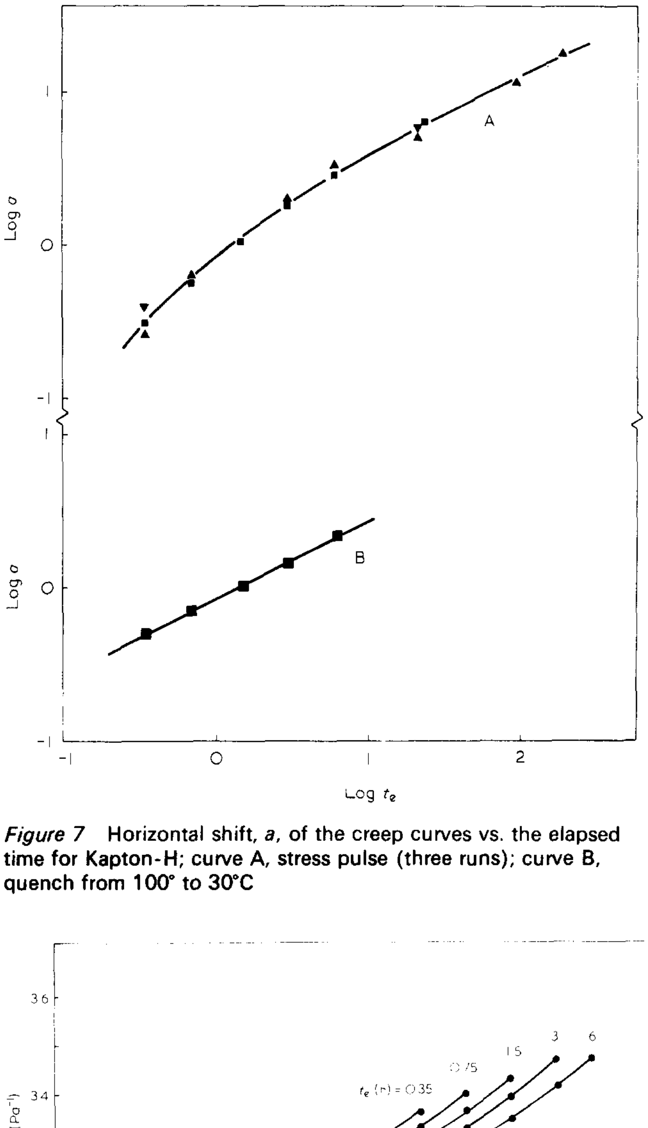

Figure 7 Horizontal shift, a, of the creep curves vs. the elapsed time for Kapton-H; curve A, stress pulse (three runs); curve B, quench from 100° to 30°C

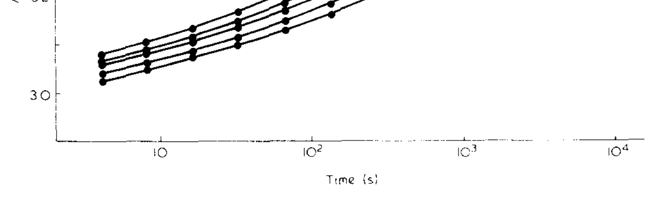

Figure 8 Small strain tensile creep compliance of Kapton-H at different elapsed times, t_e after a quench from 100° to 30°C

ageing almost ceases at temperatures below the β transition indicates that short-range mobility is a prerequisite for large-scale movements or all kinds of processes from which physical ageing can originate. Struik has pointed out that volume contraction and therefore ageing require the persistence of a certain amount of segmental mobility in the glass and a comparison between the loss factor and the shift rate confirms this also for the cellulose ester (*Figure 3*).

Dynamic mechanical studies[5] have shown that there are for polyimides intense relaxation processes at low temperature. This has also been found for other polymers with stiff chains like aromatic polyamides. Moreover, new relaxation phenomena, absent in the usual thermoplastics, have been found (β^*).

That ageing is present in rigid chain polymers is not surprising. In fact ageing can be absent only when the polymer structure has attained its thermodynamic equilibrium or when it is completely frozen in. Neither of these two conditions are realistic and physical ageing is just the outcome of a non-equilibrium state. But the rate at which ageing occurs seems to depend on chemical structure as well as on temperature. Since physical ageing changes the overall behaviour of a polymer, it can be detected in several ways, but care must be taken as not all techniques have the same sensitivity or act without interfering with the process itself. For instance, d.s.c. measurements are unable to detect subtle changes otherwise clearly revealed by low-frequency dynamic mechanical tests. More important, a d.s.c. run is made by heating the sample, a procedure that in any case has a de-ageing effect. Thus physical ageing will show up with an endothermic peak at T_g only if a 'structure' capable of resisting heat without dissolving builds up during the annealing.

Moreover, different degrees of annealing may result since the height of the endothermic peaks strongly increase with increasing heating rate or, in some cases, such peaks do not develop at all. Similar remarks can be made when the effect of ageing on yielding is considered. As soon as the linear range is exceeded and before the yield point is reached the material de-ages, thus losing part of its annealing history.

ACKNOWLEDGEMENT

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