Memory behaviour of an elastomeric glass by pressure- and temperature-perturbation methods

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The memory behaviour of structural relaxation of a polyurethane elastomeric glass (Solithane 113), by pressure and temperature perturbations from an original state of pressure (2.5 kbar) and temperature (15.0°C), is reported. The Young's modulus, obtained from the compressive stress–strain curves of the glassy samples, is used as a parameter to study its ageing behaviour. The glass samples were subjected to different hydrostatic pressure levels above 2.5 kbar, viz. 3.0, 4.0 and 4.5 kbar, at 15.0°C and held at those pressure levels for 10 h. The pressure was released to 2.5 kbar and the samples were then tested in compression after different ageing times. For temperature-perturbation experiments, the samples were initially pressurized to 2.5 kbar at 15.0°C. Without waiting at that state, they were each cooled down immediately to a lower temperature, viz. 10.0, 5.0 and 0°C, aged for a different time, returned to the initial stage and then tested in compression for the elastic response. The perturbed glass shows higher initial Young's modulus than that of the unperturbed glass, followed by a gradual decrease with ageing time. All relaxation curves eventually trace back to the unperturbed with longer ageing time. The experimental observation is attributed to the fluctuation of excess free volume with ageing time after perturbations by pressure or temperature, as the case may be.

(Keywords: memory behaviour; pressure perturbation; temperature perturbation; elastomeric glass; ageing; Young's modulus)

INTRODUCTION

Because of the heterogeneity of glass structure, the rate of structural change in glass with ageing time fluctuates from point to point, leading to a wide distribution of relaxation times. Asymmetrical and nonlinear relaxation behaviour after perturbation by heating or cooling have also been observed. Moreover, a glass has been shown to exhibit complex memory behaviour if it is subjected to multiple perturbations by cooling to a lower temperature and then heating to the experimental state, which is normally close to T_g (ref. 1). The structural relaxation of glassy polymers has been described in different ways, such as by phenomenological models[2-7], by statistical models[8-10] and by molecular dynamics by diffusion and stochastic models[11-13].

Complex relaxation behaviour would be revealed from a glass if any perturbation of temperature and/or pressure is given. By annealing polystyrene (PS) glass for a specified time at high pressure and then releasing the pressure, it was shown to expand in volume and decrease in density with time at atmospheric pressure[14]. Attention was focused on the relaxation behaviour of the PS glass that was formed from the pressure-densified melt (liquid) by application of additional pressure (pressure-vitrified glass) and the glass that was formed by cooling the pressure-densified melt (temperature-vitrified glass)[15,16]. But it should be noted that those glasses were studied at atmospheric pressure after depressurizing and in fact they were relaxing with memory, reflecting the nature of multiple perturbations of pressure. We report, for the first time, the memory behaviour of structural relaxation of a glass of Solithane 113, a polyurethane elastomer, by pressure perturbations and also by temperature perturbations at a state of pressure and temperature (P,T) of 2.5 kbar and 15.0°C.

EXPERIMENTAL

Solithane 113 is a commercially available polyurethane elastomer (Thiokol Chemical Co.), made by using castor oil and tolylene diisocyanate. It is formed from the reaction of a resin and a catalyst. The resin is a prepolymer formed by extending castor oil with tolylene diisocyanate. The catalyst consists essentially of castor oil. By varying the amounts of catalyst and resin the properties of the resulting elastomer can be greatly varied. In the present study only the equal-volume (50/50) composition was examined. For this composition, the specific volume at atmospheric pressure and room temperature was 0.97 $cm^3 g^{-1}$. On the basis of swelling measurements, the average molecular weight between crosslinks was determined to be about 2000 $g mol^{-1}$ (refs. 17 and 18). By high-pressure X-ray measurements, the material was found to be fully amorphous at various states of pressure and temperature and the T_g was found to be -20°C at atmospheric pressure[19].

We have used Young's modulus, obtained from the compressive stress–strain curves of the glassy samples, as a property to study its ageing behaviour. Young's modulus has been reported earlier as a parameter to monitor ageing behaviour of poly(ethylene terephthalate) (PET), polycarbonate (PC) and some linear epoxies[20]. The mechanical tests, used to monitor the ageing behaviour, were carried out in equipment capable of

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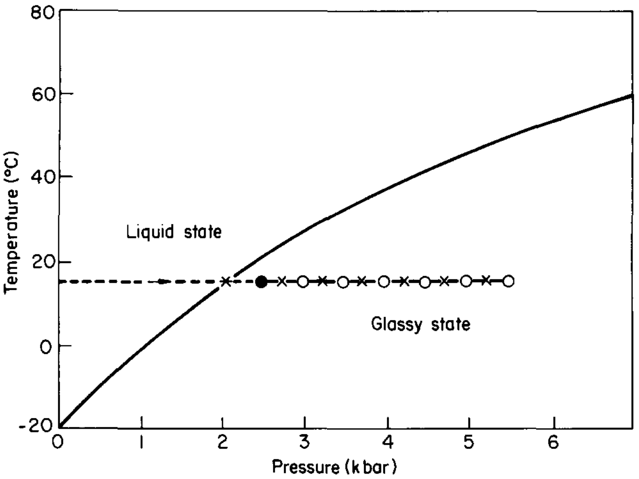

Figure 1 Scheme of pressure-perturbation experiments of different magnitudes. The star represents P_g at 15°C and the filled circle the control state

maintaining the sample at any combined state of pressure and temperature, ranging respectively from 1.0 bar to 7.0 kbar and from −100 to 100°C. The details of the equipment have been reported elsewhere[21]. Dow Corning 200 (5 cS viscosity) silicone oil was used as the pressure medium. The silicone oil was found to be inert with Solithane under our experimental conditions of pressure and temperature. By systematic step changes of pressure and temperature, Solithane could be brought to different states of pressure and temperature in the glass state. In all experiments, temperature was increased at a rate of 0.5°C min^{-1} and decreased at 1.0°C min^{-1}. Pressure was increased at a rate of 0.25 kbar min^{-1} and decreased at 0.5 kbar min^{-1}.

A rubbery (liquid) sample was first brought to the state of 2.5 kbar and 15.0°C (control state) by first cooling from room temperature and then increasing the pressure. The full curve in *Figure 1* represents variation of the glass transition temperature (T_g) with pressure for Solithane[22]. The liquid sample was transformed to a glass (or specific ζ_2 glass)[22,23] at a fixed point of 2.0 kbar and 15.0°C. As soon as the glass reached 2.5 kbar and 15.0°C (control state), ageing occurred with characteristics of that state (P,T). This unperturbed glass (control sample) was tested in compression to obtain the stress–strain curve after 1 h ageing time. The compressive strain was applied momentarily at a rate of $\dot{\varepsilon} = 0.02\,\mathrm{min}^{-1}$ on the relaxing glassy sample, so that the loading time was insignificant compared with ageing time. The test was stopped when the loading was close to the yield stress of the sample and the Young's modulus was obtained by drawing a tangent to the stress–strain curve through the origin. The test was repeated for three more samples and the average Young's modulus (E) was determined to be 0.38×10^{10} dyn cm^{-2}. In all of our experiments discussed above and hereafter, the scatter of the experimental values from the average value is within 2.0%.

In the next series of tests, a liquid sample was formed into glass by bringing it to the control state. It was immediately brought to 3.0 kbar at 15.0°C, annealed for 1 h, given a pressure perturbation by decreasing to 2.5 kbar, and then aged for 1 h. The glassy samples were tested in compression. The average E for four separate samples was found to be 0.52×10^{10} dyn cm^{-2}. This is 37% above that of the control sample. A series of samples were brought, respectively, to 3.5, 4.0, 4.5, 5.0 and 5.5 kbar at 15.0°C, annealed for 1 h at the respective pressure and given pressure perturbation, ΔP, of 1.0, 1.5, 2.0, 2.5 and 3.0 kbar to the control state. The perturbed glasses were aged for 1 h and then tested in compression.

Figure 2 shows the scheme of pressure- and temperature-perturbation experiments. First, a glass was formed at 2.0 kbar and 15.0°C and tested for the mechanical response after different ageing times at 2.5 kbar and 15.0°C (control state). All experiments began with a liquid sample at room temperature and atmospheric pressure, so that uniformity of the chronology of glass history for all samples was preserved. Once again, in all sets of experiments, the compressive strain was applied momentarily ($\dot{\varepsilon} = 0.02\,\mathrm{min}^{-1}$) on the glassy samples, so that the loading time was negligible compared with ageing time.

As shown in the scheme of *Figure 2*, pressure-perturbation experiments were carried out as follows. Test samples were subjected to different hydrostatic pressure levels above 2.5 kbar, viz. 3.0, 4.0 and 4.5 kbar, at 15.0°C and held at those pressure levels for 10 h. Then the pressure was released to 2.5 kbar, the samples still being in the glassy state. The samples were aged for 1 h and then tested in compression. The above procedure was repeated for different ageing times. The temperature-perturbation experiments were carried out in a similar way. The liquid samples were all initially pressurized to the control state (2.5 kbar at 15.0°C) and, without waiting at that state, they were cooled down immediately to lower temperatures under 2.5 kbar, held at those temperatures for 10 h, heated to 15.0°C, aged for a specific time, and then tested for the elastic response. It is emphasized here that, in all the experiments, only one kind of glass was formed at the state of 2.0 kbar and 15.0°C from the liquid state. The relaxation behaviour of that unperturbed glass at 2.5 kbar and 15.0°C is compared with that of the glass that is perturbed by different magnitudes of pressure or temperature beyond that control state.

RESULTS AND DISCUSSION

Figure 3 shows the variation of average Young's modulus, obtained for 1 h ageing at 2.5 kbar after

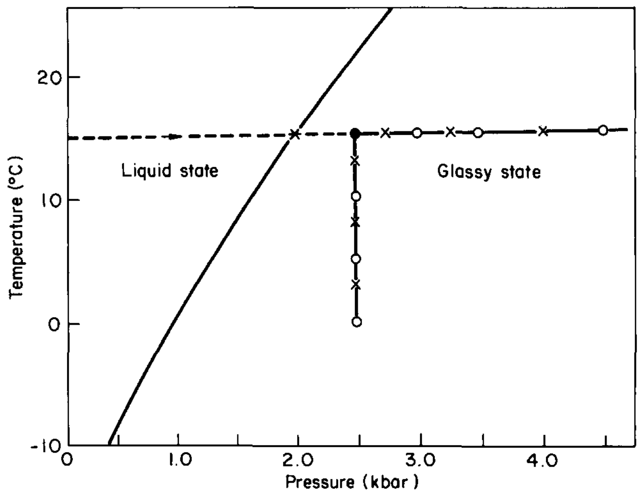

Figure 2 Scheme of pressure- and temperature-perturbation experiments

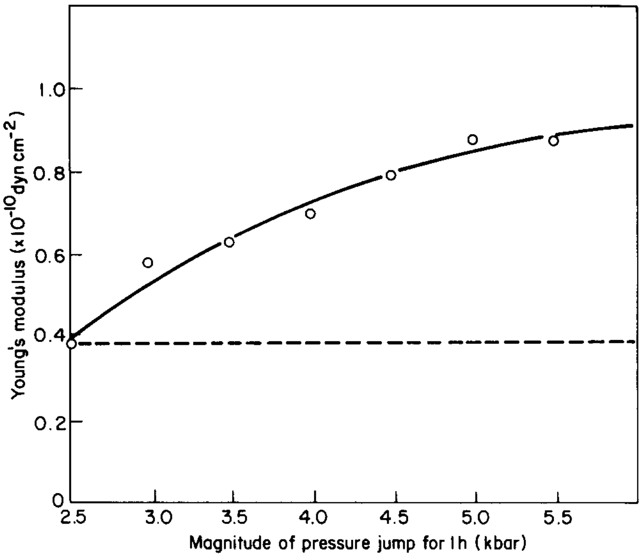

Figure 3 Deviation of Young's modulus obtained at 2.5 kbar and 15.0°C after different magnitudes of jumps of pressure were given. The samples were annealed for 1 h at 3.0, 3.5, 4.0, 4.5, 5.0 and 5.5 kbar

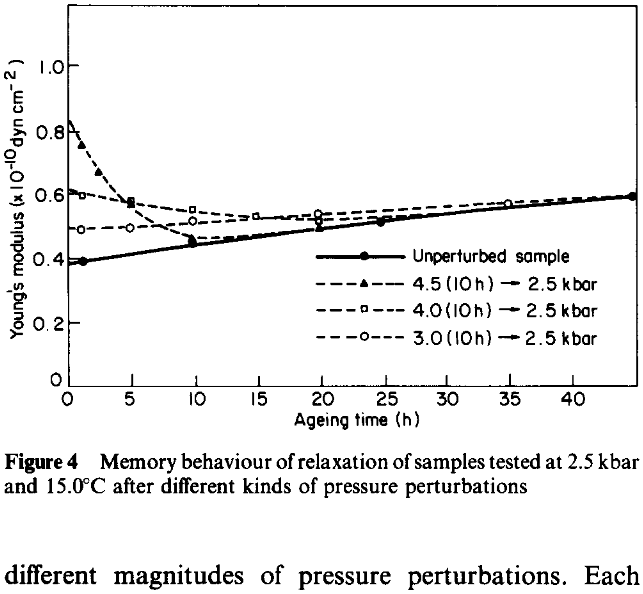

Figure 4 Memory behaviour of relaxation of samples tested at 2.5 kbar and 15.0°C after different kinds of pressure perturbations

different magnitudes of pressure perturbations. Each point in *Figure 3* represents an average of at least four samples. For any pressure perturbation given above 2.5 kbar, the modulus of the sample is higher than that of the unperturbed sample in proportion to the amount of pressure perturbation.

Figure 4 shows the memory behaviour of relaxation of the glass due to pressure perturbations as described above. The full curve (i.e. variation of E_{unp}) represents the ageing characteristic of unperturbed glass at 2.5 kbar and 15.0°C. The three broken curves, respectively, represent the relaxation behaviour at 2.5 kbar and 15.0°C of the glasses (i.e. variation of E_p) given pressure perturbations ΔP of 0.5, 1.5 and 2 kbar, each with annealing time of 1 h. Several observations are noted:

(1) The higher ΔP, the greater is the initial $\Delta E = E_p - E_{unp}$.

(2) The higher ΔP, the steeper is the slope of the initial modulus drop.

(3) All curves coincide eventually with the unperturbed one.

(4) The higher ΔP, the shorter time it takes to coincide with the unperturbed curve.

(5) All curves remain above the unperturbed one.

As shown in *Figure 5*, we observe very much the same kind of memory behaviour for temperature perturbation as for the pressure perturbation, which is described below:

(1) The larger ΔT, the greater is the initial $\Delta E = E_p - E_{unp}$.

(2) The larger ΔT, the steeper is the slope of the initial modulus drop.

(3) All curves coincide eventually with the unperturbed one.

(4) The larger ΔT, the shorter time it takes to coincide with the unperturbed curve.

(5) All curves remain above the unperturbed one.

The difference between the relaxation of both temperature- and pressure-perturbed glasses is that the former takes relatively less time to retrace the relaxation path of unperturbed glass than the latter.

At a particular instant, the experimentally observed physical quantity, such as the Young's modulus (E) in our case, reflects the statistical average of Young's moduli due to all relaxing molecular units at that instant. The 10 h ageing at pressure above 2.5 kbar or temperature below 15.0°C is enough for the molecules to undergo to a certain extent the relaxation processes characteristic of that state. When the state is perturbed to 2.5 kbar and 15.0°C, the molecules are forced to recover from their relaxation processes which were already set at the previous state ($P + \Delta P$, 15.0°C) or (2.5 kbar, $T + \Delta T$). Since there is a distribution of relaxation times of all relaxing units for any given state, we observe that the net experimental Young's modulus (E) has a higher value followed initially by a drop and then eventually coincides with the unperturbed value characteristic of 2.5 kbar and 15.0°C.

The relaxation due to a particular mode of molecular motion may be associated with a specific amount of free volume in excess of the equilibrium free volume[24]. There may be various modes of motion of different, but nearly the same, magnitudes of relaxation time which are possible for the same size of excess free volume. But considering the fact that a glassy polymer may have a very wide range of excess free volumes of various sizes, it would be possible to attribute each relaxation time (τ_i) arising from an excess free volume of a particular size. Shorter relaxation times are characterized by excess free volumes of smaller size and longer relaxation times by those of

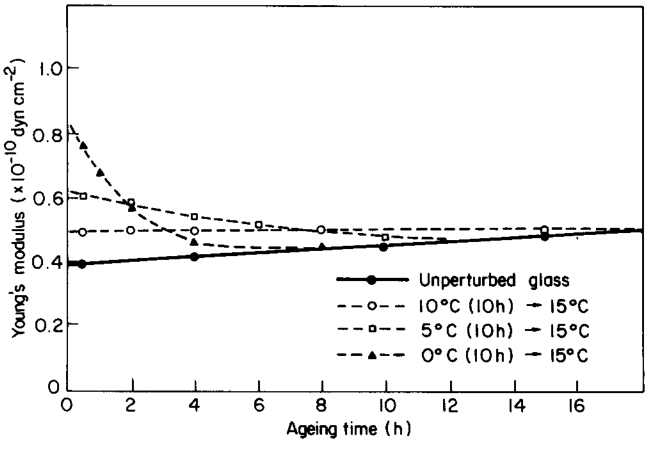

Figure 5 Memory behaviour of relaxation of samples tested at 2.5 kbar and 25.0°C after different kinds of temperature perturbation

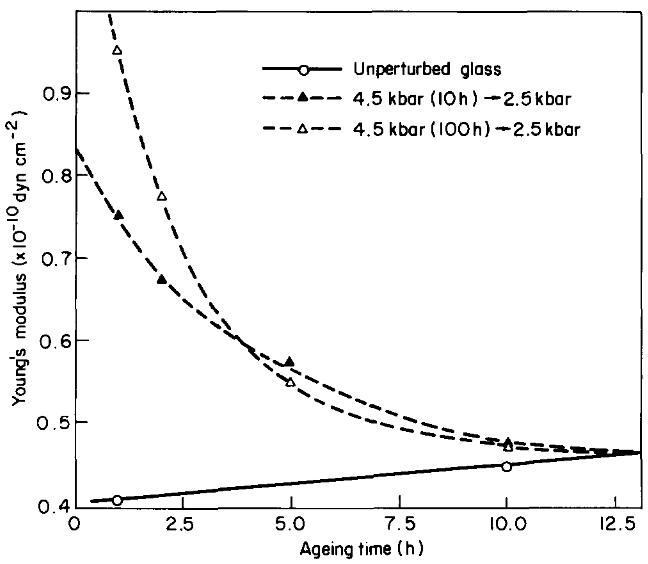

Figure 6 Memory behaviour of relaxation of samples tested at 2.5 kbar and 15.0°C after pressure pertubation from 4.5 kbar at which samples were annealed for 10 and 100 h

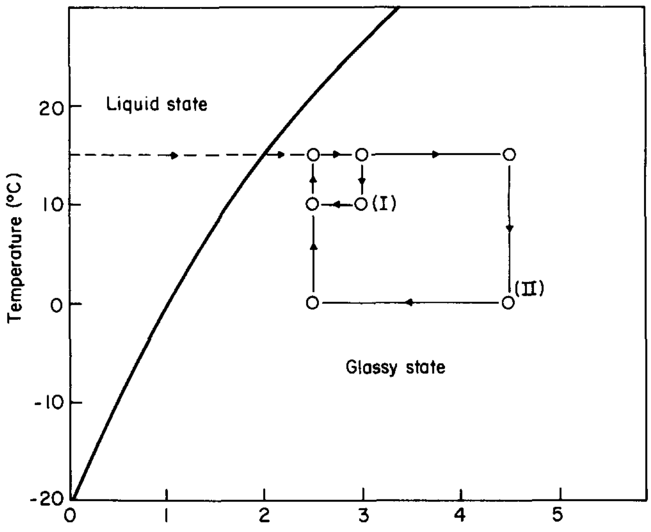

Figure 7 Scheme of multiple-perturbation experiments

larger size[24]. Hence, when a glass is brought to a state of 2.5 kbar and 15°C, after perturbations by either pressure or temperature, there may be different levels of perturbation on the excess free volume of different sizes. So the overall relaxation of a glass is history-dependent and may be observed as a fluctuating property with ageing time, such as volume, density or Young's modulus[1,14,25,26]. It is clearly evident from *Figures 4* and *5* that a glass with different history of pressure or temperature perturbation exhibits different relaxation behaviour.

The excess free volume diminishes with ageing time during the course of relaxation at a given experimental state. The progressive increase of Young's modulus with ageing time at 2.5 kbar and 15.0°C (i.e. unperturbed relaxation curve) reflects this phenomenon. On the other hand, the decay of excess free volume with ageing time occurs with a fluctuation that results in a distinct memory behaviour if the glass is already annealed at another state and then perturbed to the control state. Further, if the glass is annealed for a longer time at that state and then perturbed to the control state, it will result in a sharp memory behaviour. As shown in *Figure 6*, when the glass was annealed for different durations of 10 h and 100 h at the same state of 4.5 kbar and 15.0°C and then perturbed to the control state of 2.5 kbar and 15.0°C, the relaxation follows different schemes. Annealing for 100 h at 4.5 kbar causes more collapse of excess free volume than that for 10 h at that state. So, when we perturb these glasses to the control state, the former shows higher modulus and steeper modulus drop, initially, than the latter.

The collapse of various excess free-volume levels occurs at different rates after perturbations by pressure or temperature. This is further confirmed by experiments involving multiple perturbations and explained as follows. As shown in *Figure 7*, in one set of experiments the glass is formed at 15.0°C by pressurizing and then brought to 3.0 kbar and annealed for 3.0 h. The glass is cooled immediately to 10.0°C under 3.0 kbar and annealed for 4.0 h. Then the pressure is brought down to 2.5 kbar at the same temperature and aged for 3.0 h. Then the sample is brought to the control state, aged for 30 min and then tested for the mechanical response. The same procedure is repeated for samples of different ageing time. This kind of experimental scheme by multiple perturbations is designated as (I). In another scheme of experiments, designated (II), as shown in *Figure 7*, larger perturbations of pressure (4.5 kbar) and temperature (0°C) are used.

Figure 8 shows the memory behaviour due to multiple perturbations. The observations are summarized as follows:

(1) The higher the combinations of ΔP and ΔT involved, the greater is the initial $\Delta E = E_p - E_{unp}$.

(2) The higher the combinations of ΔP and ΔT involved, the steeper is the slope of the initial modulus drop.

(3) All curves remain above the unperturbed one and coincide eventually with the unperturbed curve.

(4) The higher the combinations of ΔP and ΔT involved, the less time it takes to trace back to the unperturbed state.

(5) It may be noted from the previous figures that the sample takes about 25 h to coincide with the relaxation of the control sample, if only a pressure perturbation of

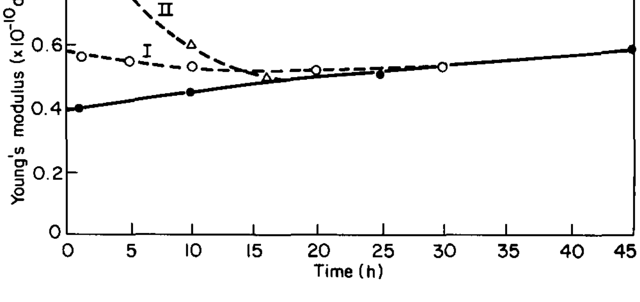

Figure 8 Memory behaviour of samples tested at 2.5 kbar and 15.0°C after multiple perturbation (I) and multiple perturbation (II), as indicated in *Figure 7*. ———, Unperturbed glass

4.5 kbar is used; and it takes about 8 h, if only a temperature perturbation is used.

On the other hand, as shown in *Figure 8*, the sample takes an intermediate time of about 17 h to coincide with the relaxation of the control state, if it is subjected to multiple perturbations by pressure up to 4.5 kbar and temperature up to 0°C.

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