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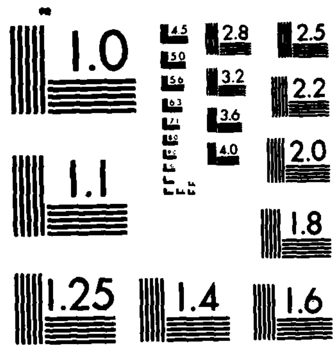


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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The memory behavior of structural relaxation of glass of Solithane 113, a polyurethane elastomer, by pressure perturbation and also by temperature perturbation from an original state of pressure and temperature (P,T) of 2.5 KBar and 15°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 aging behavior. The liquid samples were transformed to a glass at a fixed point 2.0 KBar and 15°C. They were subjected to

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered) different hydrostatic pressure levels above 2.5 KBar, viz., 3.0, 4.0 and 4.5 KBar at 15°C and held at those pressure levels for 10 hours. The pressure was released to 2.5 KBar and the samples were then tested in compression after different aging time. Temperature perturbation experiments were carried out similarly, i.e., the samples at 2.5 KBar were initially annealed for 10 hours at lower temperatures, viz., 10°C, 5°C and 0°C, heated back to 15°C and then tested after different aging time. In both cases, the perturbed glass shows higher initial Young's modulus than that of unperturbed glass, followed by gradual decrease with aging time. All relaxation curves trace eventually back to the unperturbed with longer aging time. The higher the perturbation, the shorter it takes to trace back to the unperturbed.

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TECHNICAL REPORT NO. 6

# MEMORY BEHAVIOR OF AN ELASTOMERIC GLASS BY PRESSURE- AND TEMPERATURE-PERTURBATION METHODS

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## Memory Behavior of An Elastomeric Glass by Pressure- and Temperature-Perturbation Methods

Because of the heterogeneity of glass structure, the rate of structural change in glass with aging time fluctuates from point to point leading to a wide distribution of relaxation times, asymmetrical and nonlinear relaxation behavior after heating or cooling. Moreover, a glass has been shown to exhibit the complex memory behavior if temperature history is given [1]. The structural relaxation of amorphous polymers has been dealt in different angles such as by phenomenological models [2-7], statistical models [8-10] and by molecular dynamics by diffusion and stochastic models [11-13]. Complex relaxation behaviors would be revealed if any perturbation of temperature and/or pressure were given. By annealing for a specified time at high pressures and releasing the pressure, the polystyrene glass was shown to expand in volume with time, an analogous memory behavior [14]. Attention was focused on the relaxation behavior of the PS glass that was formed from the pressure-densified melt by application of additional pressure (pressure-vitrified glass) and the glass that was formed by cooling the pressure-densified melt (temperature-densified glass) [15, 16]. In fact, those glasses were relaxing with memory at atmospheric pressure, reflecting the nature of perturbations previously applied.

We report, for the first time, the memory behavior of structural relaxation of glass of Solithane 113, a polyurethane elastomer, by pressure perturbations and also by temperature perturbations from an original state of pressure and temperature (P,T) of 2.5 KBar and 15$^{o}$C. We have used Young's modulus, obtained from the compressive stress-strain curves of the glassy samples, as a parameter to study its aging behavior. Young's modulus has been reported earlier as a parameter to monitor aging behavior of PET, PC, and some linear epoxies [17]. The mechanical tests, used to monitor the aging behavior, were carried out in an equipment capable of keeping the sample under different combined conditions of pressure and temperature, ranging respectively from 1.0 Bar to 7.0 KBar and from -100° to 100°C. 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 different conditions of pressure and temperature. By systematic steps of changes of pressure and temperature, Solithane could be brought to different glassy states of pressure and temperature. In all experiments, temperature increases were carried out at a rate of 0.5°C/min. and decreases at 1.0°C/min. All pressure perturbations were applied at a rate of 0.25 KBar/min. in increasing and 0.5 KBar/min in decreasing.

As shown in the scheme of Fig. 1, a rubbery (liquid) sample was first brought to the state of 2.5 KBar and 15°C, by first cooling from room temperature and then increasing the pressure. The solid line in Fig. 1 represents variation of the glass transition temperature ($T_g$) with pressure for Solithane [18]. The liquid sample was transformed to a glass (or specific $\zeta_2$ glass) [18, 19] at a fixed point 2.0 KBar and 15°C. As soon as the glass reached 2.5 KBar and 15°C, aging started with the characteristics of that state (P,T). This unperturbed glass (Control sample) was tested in compression to obtain the stress-strain curve after one hour aging time. The compressive stress was applied momentarily at a rate of $\dot{\varepsilon} = 0.02$/min. on the relaxing glassy sample, so that the loading time was insignificant compared with aging time. The test was repeated for three more samples and the average Young's modulus (E) was determined to be $0.38 \times 10^{10}$ dynes/cm$^2$. In the next series of tests, liquid samples, after formed into glass at the same condition as the Control sample, were brought to 3.0 KBar at 15°C, annealed for one hour, given a pressure perturbation by decreasing to 2.5 KBar, and then aged for one hour. The glassy samples were tested in compression. The average E for four samples was found to be $0.52 \times 10^{10}$ dynes/cm$^2$ which is 37% above that of Control sample. A series of samples were brought, respectively, to 3.5, 4.0, 4.5, 5.0, and 5.5 KBar at 15°C, annealed for one hour at the respective pressure and given pressure perturbation, $\Delta P$, of 1.0, 1.5, 2.0, 2.5 and 3.0 KBar to 2.5 KBar. The perturbed glasses were aged for one hour and then tested in compression. The Fig. 2 shows the variation of average Young's modulus, obtained for one hour aging at 2.5 KBar after different magnitudes of pressure perturbations. Each point in Fig. 2 represents an average of E from at least four samples. For any pressure perturbation given above 2.5 KBar, the modulus of the sample is higher than that of unperturbed sample in proportion to the amount of pressure perturbation.

The Fig. 3 shows the scheme of pressure- and temperature-perturbation experiments. First, a glass was formed at 2.0 KBar and 15°C and tested for mechanical response after different aging time at 2.5 KBar and 15°C (Control sample). 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 this series of tests, the compressive stress was applied momentarily ( $\dot{\varepsilon} = 0.02$/min) on the glassy samples, so that the loading time was negligible compared with aging time.

As shown in the scheme of Fig. 3, pressure perturbation experiments were carried out as follows. Compressive test samples were subjected to different hydrostatic pressure levels above 2.5 KBar, viz., 3.0, 4.0 and 4.5 KBar at 15°C and held at those pressure levels for ten hours. Then the pressure was released to 2.5 KBar, samples still being in the glassy state. The samples were aged for one hour and then tested in compression. The above procedure was repeated for different aging time. The temperature perturbation experiments were carried out in a similar way. The liquid samples were all initially pressurized to 2.5 KBar at 15°C and, without waiting at that state, they were cooled down immediately to lower temperatures, held at those temperatures for ten hours, heated to 15°C, aged for a specific time, and then tested for the elastic response. It is emphasized here that, in all cases of experiments, only one kind of a glass was formed at the state of 2.0 KBar and 15°C from liquid state. The relaxation behavior of that unperturbed glass at 2.5 KBar and 15°C is compared with that of the glass which is perturbed with different magnitudes of pressure or temperature beyond the point 2.5 KBar and 15°C.

The Fig. 4 shows the memory effect due to pressure perturbations whcih was described above. The solid line represents the aging characteristic of unperturbed glass at 2.5 KBar and 15°C. The three dashed lines, respectively, represent the relaxation behavior at 2.5 KBar and 15°C of the glasses which were given pressure perturbations $\Delta P$ of 0.5, 1.5 and 2 KBars, each with annealing time of ten hours. Several observations are noted:

1. The higher the $\Delta P$, the greater the initial $\Delta E = E_p - E_{unp}$ is.
2. The higher the $\Delta P$, the steeper the slope of the initial modulus drop is.
3. All curves trace back to the unperturbed.
4. The higher the $\Delta P$, the shorter it takes to trace back to the unperturbed.
5. All curves remain above that of unperturbed.

As shown in Fig. 5, we observe very much the same memory behavior for temperature perturbation as for the pressure perturbation, which is described below:

1. The larger the $\Delta T$, the greater the initial $\Delta E = E_p - E_{unp}$ is.
2. The larger the $\Delta T$, the steeper the slope of the initial modulus drop is.
3. All curves trace back to the unperturbed.
4. The larger the $\Delta T$, the shorter it takes to trace back to the unperturbed.
5. All curves remain above that of unperturbed.

The difference between the relaxation of both temperature- and pressure-perturbed glasses is that the former takes less time relatively to retrace the unperturbed relaxation path 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 ten-hour aging at the state of pressure above 2.5 KBar or temperature below 15°C is enough for the molecules to undergo certain extent of relaxation processes characteristic of that state (P,T). When the state is perturbed to 2.5 KBar and 15°C, the molecules are forced to recover from their relaxation processes which were already set at the previous state ($P + \Delta P$, 15°C) or (2.5 KBar, $T + \Delta T$). Since there is a distribution of relaxation times of all relaxing units, we observe that the net experimental Young's modulus (E) has a higher value followed by a drop initially and then eventually "remember" its characteristic state value.

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 [20]. There may be various modes of motions of different but nearly the same magnitudes of relaxation times 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 volume fractions of various sizes, it would be possible to attribute each relaxation time ($\tau_i$) arising from a particular size of excess free volume fraction. The shorter relaxation time is characterized by smaller size excess free volume and the longer relaxation time by larger size [20]. Hence, when a glass is perturbed to a state of 2.5 KBar and 15°C, either by pressure or temperature, there may be different levels of perturbation on the excess free volume of different sizes and so the overall relaxation of a glass is history dependent. This is clearly evident in Figs. 4 and 5. The glass with different history of pressure or temperature perturbation exhibits different relaxation behavior. In both cases, the glass relaxes with entirely different relaxation time.

The excess free volume diminishes with aging time during the course of relaxation. Such kind of time-dependent excess free volume decay results in a distinct memory relaxation behavior, if the glass has a different annealing history. As shown in Fig. 6, when the glass was annealed for different duration of 10 hours and 100 hours at the same state of 4.5 KBar and 15°C and then perturbed to second state of 2.5 KBar and 15°C, the relaxation follows different scheme. The annealing for 100 hours at 4.5 KBar causes more collapse of excess free volume than that for 10 hours at that state. And so, when we perturb these glasses to the test state, the former shows higher modulus and steeper modulus drop, initially than the latter.

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## LIST OF FIGURES

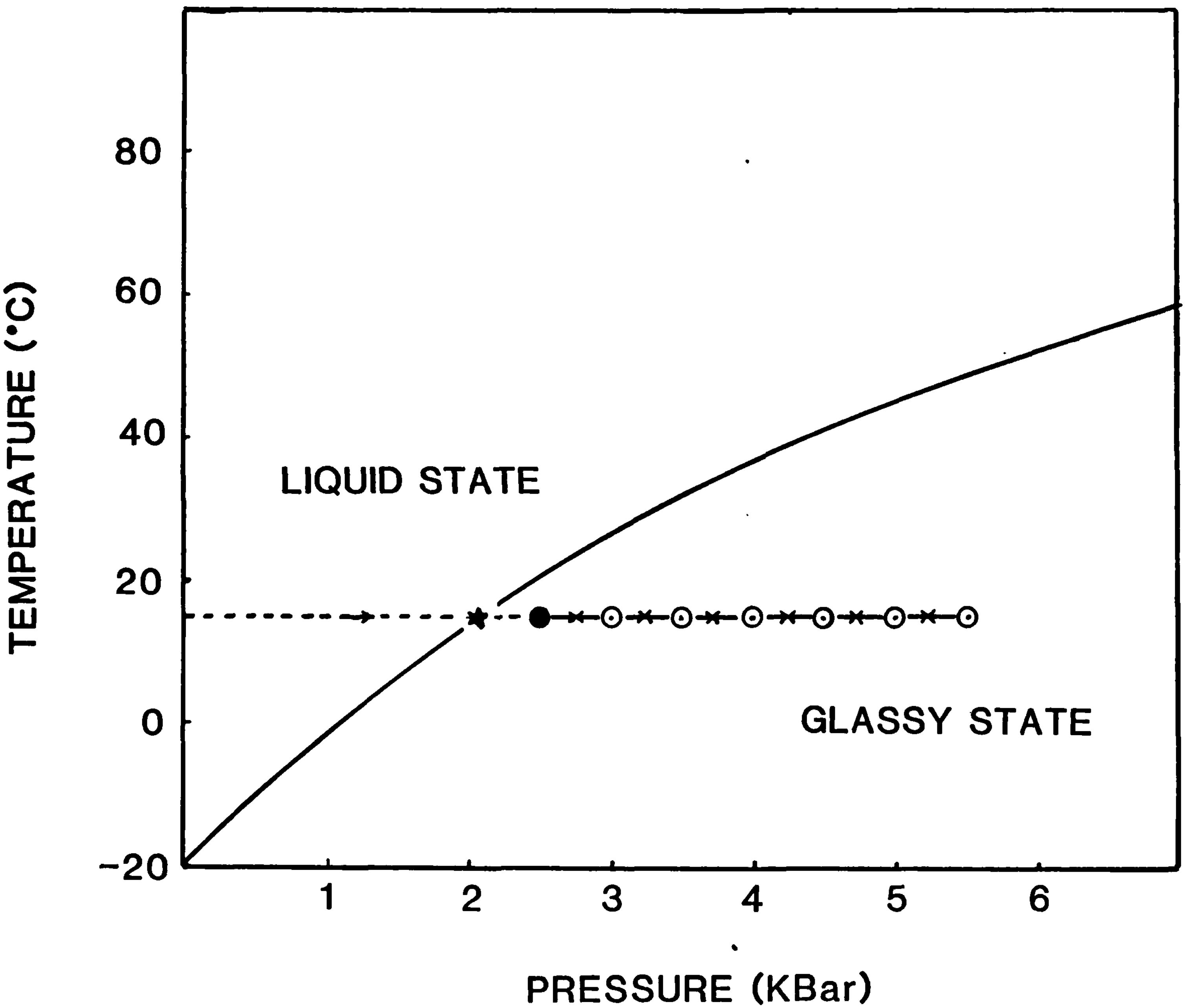

LIQUID STATE
GLASSY STATE
TEMPERATURE (°C)
80
60
40
20
0
-20
1
2
3
4
5
6
PRESSURE (KBar)

Fig 1

Fig 2

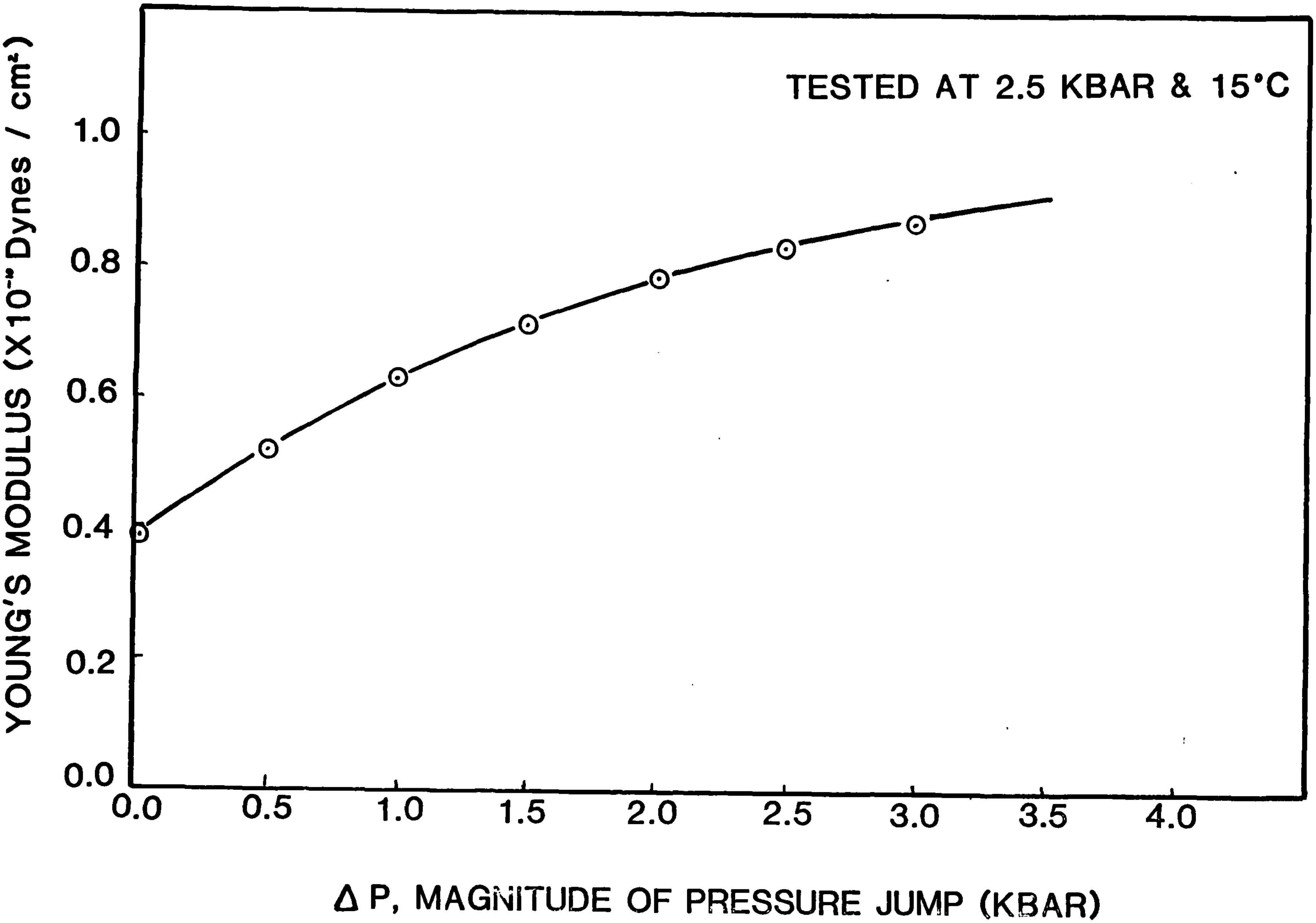
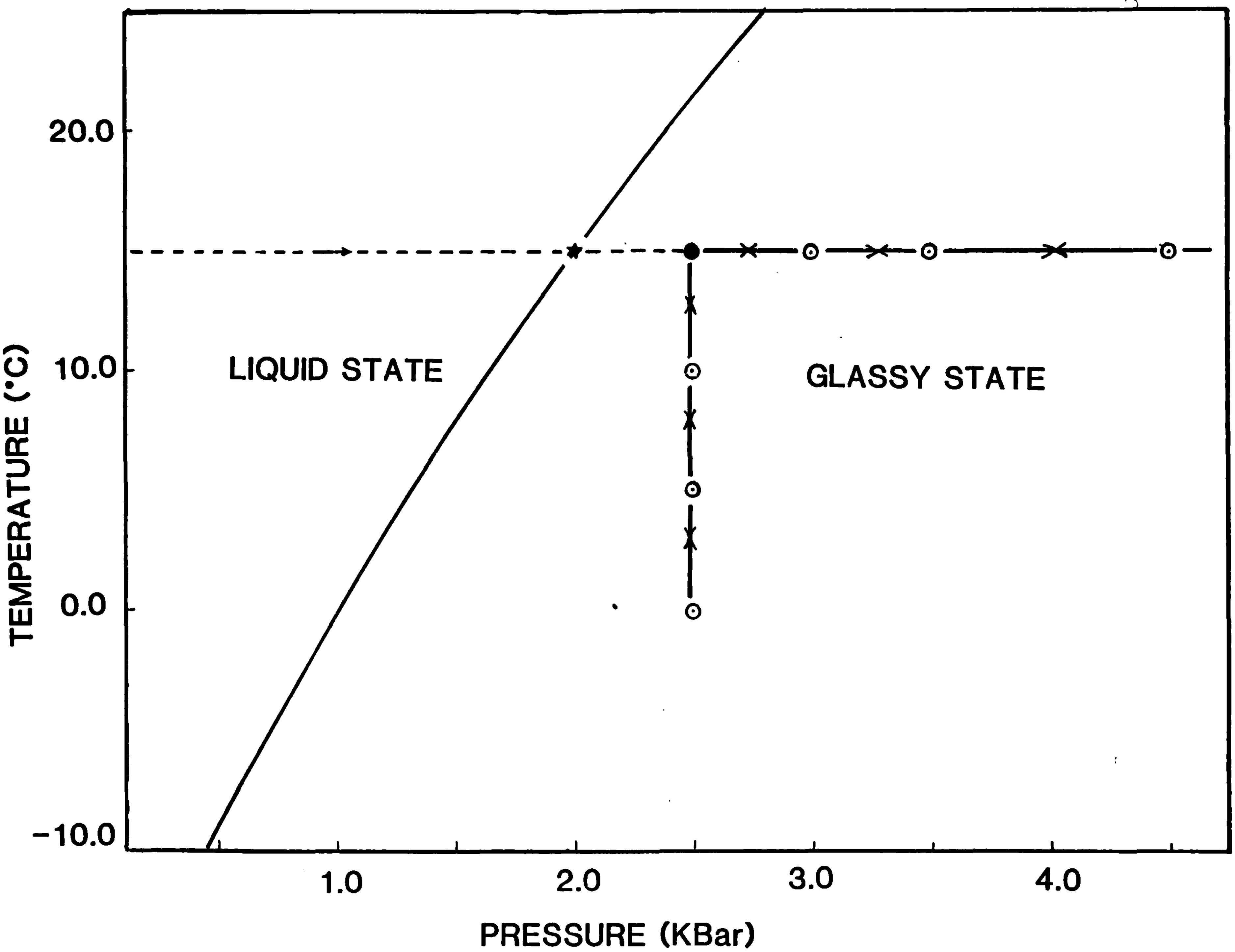
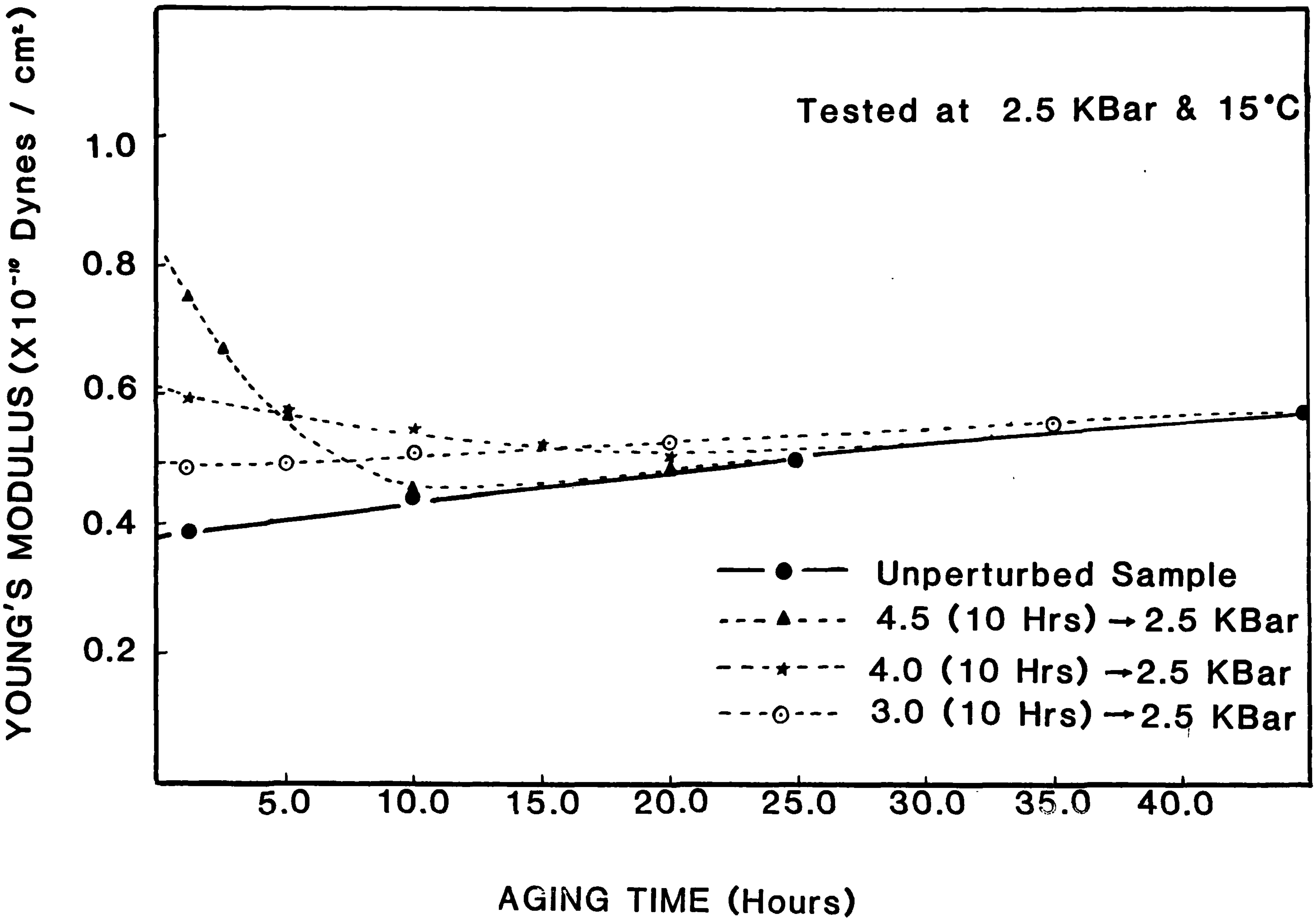

TESTED AT 2.5 KBAR & 15°C
YOUNG'S MODULUS (X10 Dynes / cm$^2$)
1.0
0.8
0.6
0.4
0.2
0.0
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
Δ P, MAGNITUDE OF PRESSURE JUMP (KBAR)

Fig 3



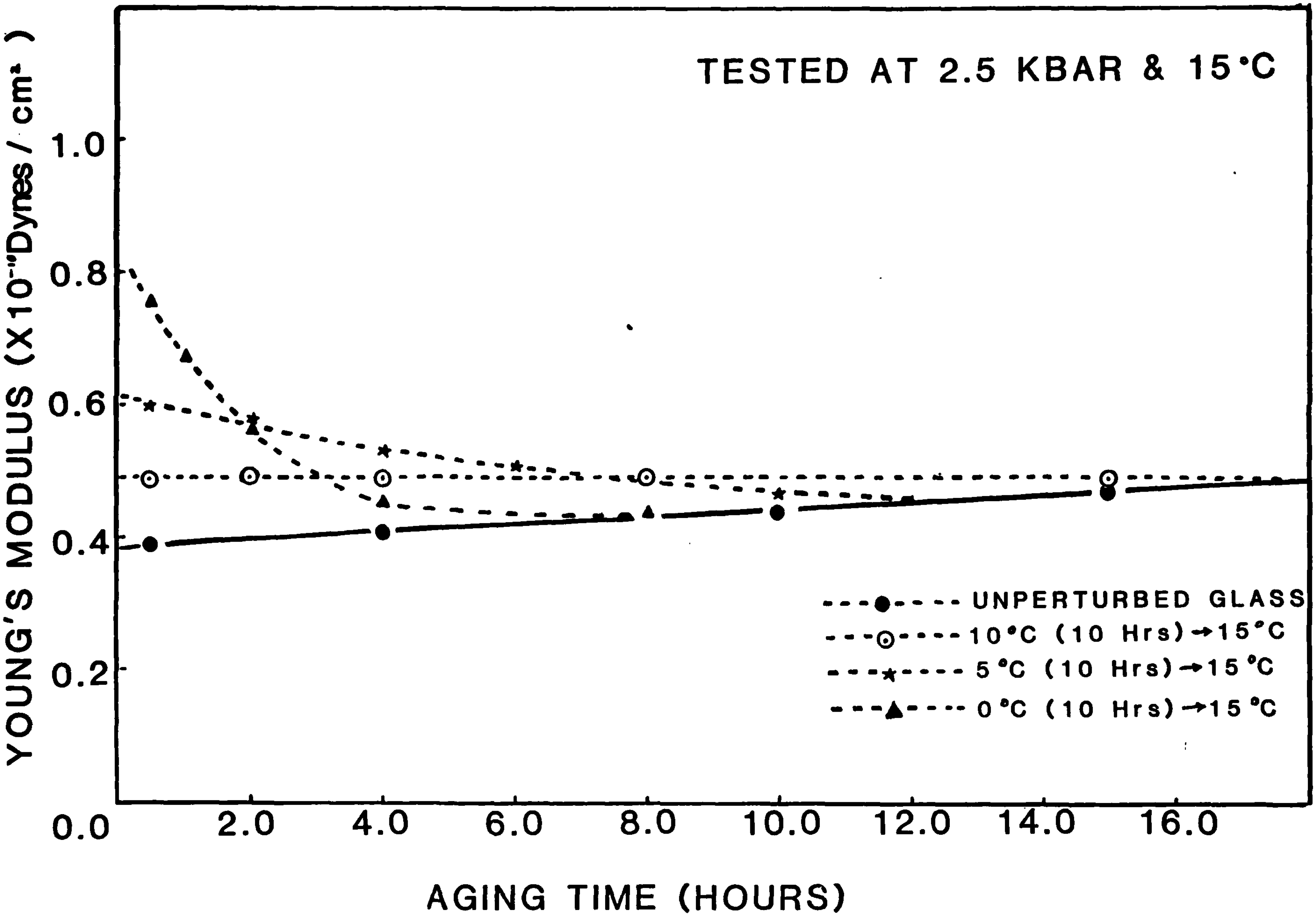
LIQUID STATE
GLASSY STATE
TEMPERATURE (°C)
20.0
10.0
0.0
−10.0
1.0
2.0
3.0
4.0
PRESSURE (KBar)

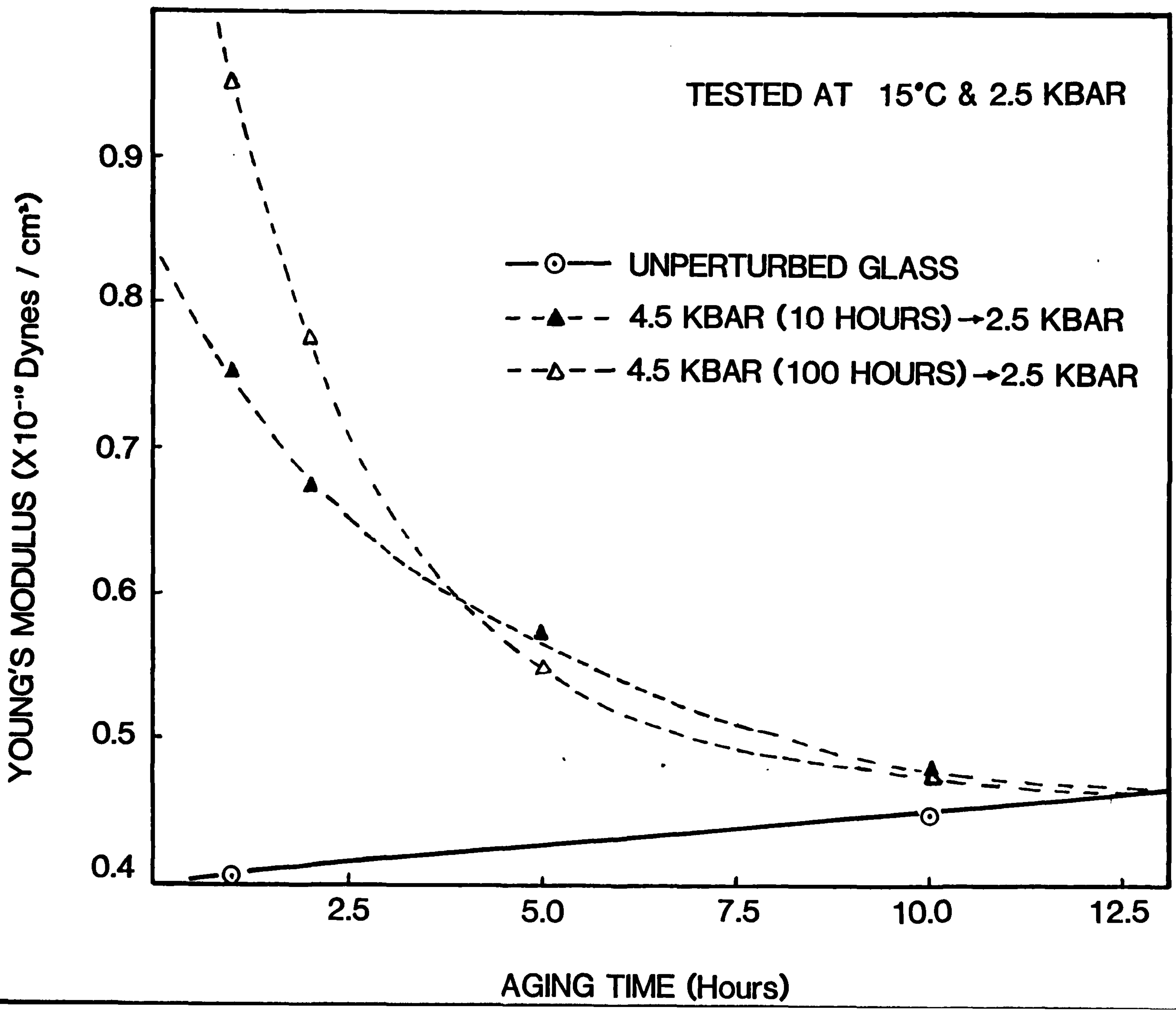
Fig 4



Tested at 2.5 KBar & 15°C
YOUNG'S MODULUS (X10⁻¹⁰ Dynes / cm²)
1.0
0.8
0.6
0.4
0.2
5.0
10.0
15.0
20.0
25.0
30.0
35.0
40.0
AGING TIME (Hours)
Unperturbed Sample
4.5 (10 Hrs) → 2.5 KBar
4.0 (10 Hrs) → 2.5 KBar
3.0 (10 Hrs) → 2.5 KBar

Fig 5


TESTED AT 2.5 KBAR & 15°C
YOUNG'S MODULUS (X10^-11 Dynes / cm²)
1.0
0.8
0.6
0.4
0.2
0.0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
AGING TIME (HOURS)
UNPERTURBED GLASS
10°C (10 Hrs)→15°C
5°C (10 Hrs)→15°C
0°C (10 Hrs)→15°C


TESTED AT 15°C & 2.5 KBAR
UNPERTURBED GLASS
4.5 KBAR (10 HOURS) → 2.5 KBAR
4.5 KBAR (100 HOURS) → 2.5 KBAR
YOUNG'S MODULUS (X10-10 Dynes / cm2)
0.9
0.8
0.7
0.6
0.5
0.4
2.5
5.0
7.5
10.0
12.5
AGING TIME (Hours)

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