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VISCOPLASTIC BEHAVIOR OF A GLASS AT HIGH PRESSURES.(U)

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← approx. 200% at 1 Kbar and higher. In the glassy state, the samples exhibit yielding, yield drop, and cold drawing. The yield drop is not accompanied by necking. Rather the samples undergo uniform drawing throughout the entire gage length. A series of sequential loading, unloading, and reloading tests in the plastic range was also conducted in the glassy state. It was observed that the plastic strain recovers as a function of time, that the yield maximum reappeared and grew after a delay time, and that the Young's modulus in subsequent loadings was higher than the initial values and increased steadily with time. Various loading histories can be completely erased upon returning to a rubbery state by removal of applied pressure. The recovery of the plastic deformation, or the viscoplastic behavior, occurs at essentially the same rate at all pressures tested and thus the data were superimposable to form a master curve near P<sub>g</sub>. A molecular explanation for the various new phenomena observed is given.

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D. L. Questad, K. D. Pae, J. I. Scheinbeim, and B. A. Newman

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High Pressure Materials Research Laboratory  
Department of Mechanics and Materials Science  
College of Engineering  
Rutgers University  
P. O. Box 909  
Piscataway, New Jersey 08854

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D. L. Questad\*, K. D. Pae, J. I. Scheinbeim, and B. A. Newman  
High Pressure Materials Research Laboratory

and

Department of Mechanics and Materials Science  
Rutgers University  
P.O. Box 909  
Piscataway, N.J. 08854

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\*Present Address: Department of Engineering Science and Mechanics  
Pennsylvania State University  
University Park, PA 16802

## ABSTRACT

The glass transition pressure,  $P_g$ , for a polyurethane elastomer (Solithane 113, 50/50 resin-catalist ratio, manufactured by Thiokol Chemical Co.) is located at 2.5 Kbar at room temperature and the glass transition temperature,  $T_g$ , is at  $-20^\circ\text{C}$ . Mechanical behavior of the elastomer, namely the tensile and the compressive stress-strain behavior, in the glassy state as well as in the rubbery state has been determined. The Young's modulus increases from  $\sim 10^7$  dynes/cm<sup>2</sup> in the rubbery state to  $\sim 10^{10}$  dynes/cm<sup>2</sup> in the glassy state. The tensile fracture strain increases rapidly from 60% at atmospheric pressure to greater than  $\sim 200\%$  at 1 Kbar and higher. In the glassy state, the samples exhibit yielding, yield drop, and cold drawing. The yield drop is not accompanied by necking. Rather the samples undergo uniform drawing throughout the entire gage length. A series of sequential loading, unloading, and reloading tests in the plastic range was also conducted in the glassy state. It was observed that the plastic strain recovers as a function of time, that the yield maximum reappeared and grew after a delay time, and that the Young's modulus in subsequent loadings was higher than the initial values and increased steadily with time. Various loading histories can be completely erased upon returning to a rubbery state by removal of applied pressure. The recovery of the plastic deformation, or the viscoplastic behavior, occurs at essentially the same rate at all pressures tested and thus the data were superimposable to form a master curve near  $P_g$ . A molecular explanation for the various new phenomena observed is given.

## INTRODUCTION

Hydrostatic pressure has been shown to affect the mechanical behavior of polymer materials<sup>(1,2)</sup>. Depending on the type of polymer tested the properties may change dramatically. Generally, the modulus and yield or fracture stress increase with increasing pressure. These effects are similar to but not the same as those achieved by decreasing temperature. The strain to fracture may increase or decrease as the hydrostatic pressure increases. Fracture strain increases for polystyrene<sup>(3)</sup> whereas it decreases for polychlorotrifluoroethylene<sup>(4)</sup> as the pressure is increased.

The stress-strain response of elastomers has been well studied as a function of temperature<sup>(5,6,7)</sup>, but little work has been done as a function of pressure. Most of the pressure work has involved bulk measurements<sup>(8,9,10)</sup>. These latter studies have generally evaluated the bulk modulus or compressibility in the range of the glass transition.

As the temperature is lowered through the glass transition temperature,  $T_g$ , an elastomeric sample will be converted from a rubbery to a glassy state. The mechanical properties will undergo corresponding changes. The modulus will increase from values around  $10^7$  dynes/cm<sup>2</sup> in the rubbery state to around  $10^{10}$  dynes/cm<sup>2</sup> in the glassy state. At temperatures above  $T_g$  "rubber-like elasticity" will characterize the deformation. Below  $T_g$  the deformation will be elastic at low strains followed by a yield point and plastic deformation. The plastic deformation can be very large, similar to the deformation which occurs in the rubbery state.

The yield point in tension has, in fact, been interpreted as a strain-induced glass transition<sup>(11,12,13)</sup>. This interpretation is made within the

context of the free volume theory. During the elastic portion of the deformation the volume of the sample increases for all samples with Poisson's ratio less than 0.5. If the elastic volume increase results in a free volume increase, then the free volume may become large enough for a glass transition to occur. This glass transition will result in the yield point followed by flow or plastic deformation. The free volume interpretation encounters difficulty when shear and compression are considered. Only a slight volume increase results for shear, and the volume decreases in compression, yet in both cases yielding occurs.

Activated flow theories based on a model by Eyring are capable of describing yielding in tension, compression and shear<sup>(14,15,16)</sup>. According to these theories segments are capable of making configurational changes by jumping over rotational energy barriers. An applied stress results in a shear stress on the segments which places a bias on the energy barrier to rotation. Yielding occurs when enough of these segments are induced to jump in the preferred direction.

In creep experiments a sample below  $T_g$  will undergo essentially instantaneous elastic deformation followed by a period during which no deformation occurs. This is followed by a period of increasing deformation with time. This results in a bend in the creep strain versus log time curve. The beginning of this last section of the creep curve corresponds to the onset of flow or delayed yielding, and the time required for this point to be reached is called the delay time,  $t_d$ . Activated flow theories have been used to predict such delay times<sup>(16,17)</sup>.

Whitney and Andrews<sup>(18)</sup> have studied a number of amorphous polymers in compression in the post-yield region of the stress-strain curve. In these studies, samples were deformed through the yield point and into the flow region. At this point the deformation was stopped and the samples were allowed to relax at constant strain for a brief period of time. During this time the load relaxed to about two-thirds of the maximum load. Upon continuing the deformation the samples again went through an elastic region followed by a yield point. This time, however, the yield stress and modulus were higher than for the initial deformation of the sample. These results indicate that some molecular relaxations are occurring after the deformation is stopped in the post-yield region of the stress-strain curve.

The above experiments indicate a time-dependence of the mechanical properties beyond the yield point even though the polymer is below its  $T_g$ . This suggests that similar behavior is likely for a pressure formed glass. It is the purpose of this paper to examine some of the effects of hydrostatic pressure on the stress-strain behavior of polyurethane elastomer (Solithane 113). In addition, the effects of loading history will be examined for pressure formed glasses.

## EXPERIMENTAL

### Material

Solithane 113 is a polyurethane elastomer made from the reaction of a resin and a catalyst (Thiokol Chemical Co.). The resin is a prepolymer of tolylene diisocyanate and castor oil. The catalyst is essentially castor oil<sup>(19)</sup>. The ratio of resin to catalyst can be varied, resulting in different properties of the elastomer. The present experiments were performed on samples made from equal volumes of resin and catalyst. For this composition, at atmospheric pressure, the glass transition is  $-20^{\circ}\text{C}$ , and the specific volume is  $0.97 \text{ cm}^3/\text{g}$ <sup>(22)</sup>.

### Apparatus

The high pressure tension and compression apparatus has been described elsewhere<sup>(22)</sup>. Briefly, a sample is contained in a pressure vessel, and hydrostatic pressure transmitted through a pressure medium of 5 cs. silicone oil. A piston moves into the vessel to deform the sample at a rate of  $0.05 \text{ min}^{-1}$ . During the deformation the pressure is kept constant by a compensating system. A load cell within the piston measures load, and a linear variable differential transformer (LVDT) measures deformation. The deformation of the sample can be observed through sapphire windows in the pressure vessel. Fig. 1 shows a schematic diagram of the test apparatus.

## RESULTS AND DISCUSSION

Fig. 2 shows the tensile stress-stretch curves for Solithane 113 at various pressures. At atmospheric pressure and at room temperature Solithane is in the rubbery state in which a small stress produces a large strain. The strain to fracture at atmospheric pressure is quite low (~60%). With the application of 1 kilobar of pressure the sample still behaves like an elastomer, but now the strain to fracture increases to greater than 200%. Fig. 3 shows the fracture strain versus pressure for pressures less than 1 kilobar. This figure indicates again the rapid increase in fracture strain with applied hydrostatic pressure. This increase in fracture strain with pressure is analogous to the increase in fracture strain which occurs in elastomers as the temperature is lowered or the strain rate increased<sup>(19)</sup>. These latter two effects can be related by the WLF equation, and the pressure effects indicate that it may be possible to include pressure in the superposition principle as well.

As the pressure is increased further (Fig. 2) the Solithane sample eventually undergoes a pressure-induced glass transition. The modulus increases rapidly and at 4 kilobars and above the modulus attains a typical value of a glassy polymer. Also the pressure induced glass exhibits a yield maximum followed by a yield drop and cold drawing. At 5 kilobars the yield drop is very large, resembling the stress-strain curve of a semicrystalline polymer tested at high pressures<sup>(20)</sup>. The yield process at 5 kilobars was observed through the sapphire windows on the high pressure stress-strain apparatus. The sample yielded and underwent plastic deformation without necking. After yielding,

the sample elongates to very large strains typical of an elastomer in the rubbery state. In fact, the maximum strain at 4 and 5 kilobars is greater than the strain to fracture at atmospheric pressure. This phenomenon is similar to the "forced rubber-like elasticity" observed in stress-strain curves of elastomers at temperatures below  $T_g$  (6).

Fig. 4 shows stress-strain results for a sample deformed at 5 kilobars. Each curve corresponds to samples with different loading histories. First, the undeformed sample is pressurized to 5 kilobars and deformed through the yield point. The sample undergoes a certain amount of plastic deformation. From here the sample is unloaded and immediately reloaded. Some permanent deformation remains from the previous loading, and the sample begins to reload at a strain of about 20% (stretch = 1.2). The sample deforms elastically and then plastically without showing a yield maximum. It follows exactly the original stress-strain path. For the third loading history the sample is again unloaded. This time the pressure is removed and reapplied to 5 kilobars. The stress-strain curve is now identical to that observed for the initially deformed sample. The removal of the pressure took the sample back into the rubbery state, and the entire history of deformation was erased. This corresponds to the recovery which occurs upon heating plastically deformed samples above their glass transition temperatures.

Molecular motions are possible in the glassy state<sup>(21)</sup>, and this fact, coupled with the reversibility of the plastic deformation just noted, indicates that the recovery of the plastic strain should also be time dependent. This is demonstrated in Fig. 5. This figure shows the tensile stress-strain curve at 4 kilobars together with reloading curves obtained after waiting the lengths of time indicated in the figure. The initial curve and each reloading curve

were obtained by deforming to the same maximum strain,  $\epsilon_{\max}$ , prior to unloading. A reloading curve after 3 minutes was also produced. It is identical to the 8 minute curve. Three quantities are seen to change as the deformed sample is allowed to relax. First, the plastic strain,  $\epsilon_p$ , recovers. Second, the yield maximum,  $\sigma_y$ , which disappears after immediate reloading, reappears and grows with longer relaxation times. Third, the modulus,  $E$ , increases with increasing relaxation time. The quantity,  $\epsilon_p$ , appears to relax toward the value it had when the sample was undeformed. The yield stress,  $\sigma_y$ , appears to recover the original value that the sample exhibited on the initial loading. The modulus,  $E$ , on the other hand, is increasing above the value it had for the initial values of the sample.

Each of these quantities,  $\epsilon_p$ ,  $\sigma_y$ , and  $E$ , are plotted in Figures 6,7 and 8, respectively, as functions of log time. All of these curves indicate that a certain delay time is necessary before the recovery can begin. Fig. 6 has the appearance of an inverted creep curve. For a creep curve, an initial delay period is followed by a period of flow or delayed yielding. As shown in Fig. 6, the sample begins to recover the plastic strain after the delay period. The yield maximum requires the same delay time as the plastic strain before it reappears.

The recovery of the plastic strain and the yield maximum can be attributed to the diffusion of molecular segments from deformed configurations (i.e. stretched out) to undeformed configurations (i.e. random). The relaxation of the modulus must also be associated with this diffusion, but, because the modulus diverges from its initial value, there must be another process involved. This increase in modulus may be attributed to volumetric relaxations occurring

in the glassy state under 4 kilobar pressure.

These volumetric relaxations will occur because of the method in which the glass was formed. The sample was pressurized isothermally at room temperature to the test pressure of 4 kilobars. The glass transition pressure,  $P_g$ , occurred at about 2.5 kilobars<sup>(22)</sup>. So the glass tested at 4 kilobars was actually formed at 2.5 kilobars, and this glass will volumetrically relax to a structure it would have had had it been formed at 4 kilobars. This volumetric relaxation (densification) would then be responsible for the observed increase in modulus. In fact, one might expect the plastic strain and yield stress to relax to values which are not necessarily their initial values for the same reason.

The recovery of the plastic strain for compression tests is shown in Fig. 9 where each curve corresponds to a test run at a different pressure. The closer the pressure is to  $P_g$ , the more rapid is the recovery. Only the test at 3.5 kilobars has a delay period prior to recovery, whereas for the 2.5 and 3.0 kilobar tests the sample begins to recover before the first reloading. At short times the 3.5 kilobar curve shows that the plastic strain continues to increase even though the load has been removed. The cause of this contraction is not entirely clear, but it may be due to more than one effect. First, the temperature of the sample increased as the sample was compressively loaded. Upon removing the compressive load the sample will begin to cool, and this will result in a continued contraction. The contraction in Fig. 9 is too large, however, to be attributed only to cooling of the sample. Another possible explanation is that, after the deformation, motions of short segments of the chains

(with short relaxation times) allow for a volumetric relaxation of the sample. These short time volumetric relaxations would occur before the longer time relaxations of the chain segments would allow the plastic strain to be recovered. This would result in a continued contraction of the sample at short times followed by the recovery of the compressive deformation at longer times.

It can also be noted in Fig. 9 that the slopes of the curves in the recovery sections are essentially equal for all three pressures. This suggests a possibility of superimposing the data at various pressures into a master curve. Two such attempts are made in Fig. 10. Fig. 10a results from shifting the data in Fig. 9 horizontally only. The curves were shifted to superimpose in their recovery portions, but this results in poor superposition at the short time ends of the curves. Fig. 10b shows a master curve in which horizontal and vertical shifts are allowed. Although only three curves are used to construct the master curve, the superposition is quite good.

Fig. 11 shows the plastic strain versus log time for a single pressure: 3.5 kilobars. In this case the amount of strain applied prior to removing the load,  $\epsilon_{\max}$ , was varied. The behavior is somewhat more complex than in Fig. 10, and the curves are not superimposable. The delay time prior to recovery is essentially the same for all three strains indicating that it is the pressure only which governs the delay time.

The slopes of the curves in the recovery portion increase with increasing plastic strain magnitude. In fact, the total recovery time extrapolated in Fig. 11 (dashed line) is essentially the same in all three cases. The relaxation rate increases with increasing strain, and by plotting  $-d\epsilon_p/d(\log t)$  versus  $\epsilon_{\max}$ ,

Fig. 12 is obtained. Fig. 12 shows that there is a linear relationship between  $d\epsilon_p/d(\log t)$  and  $\epsilon_{max}$ .

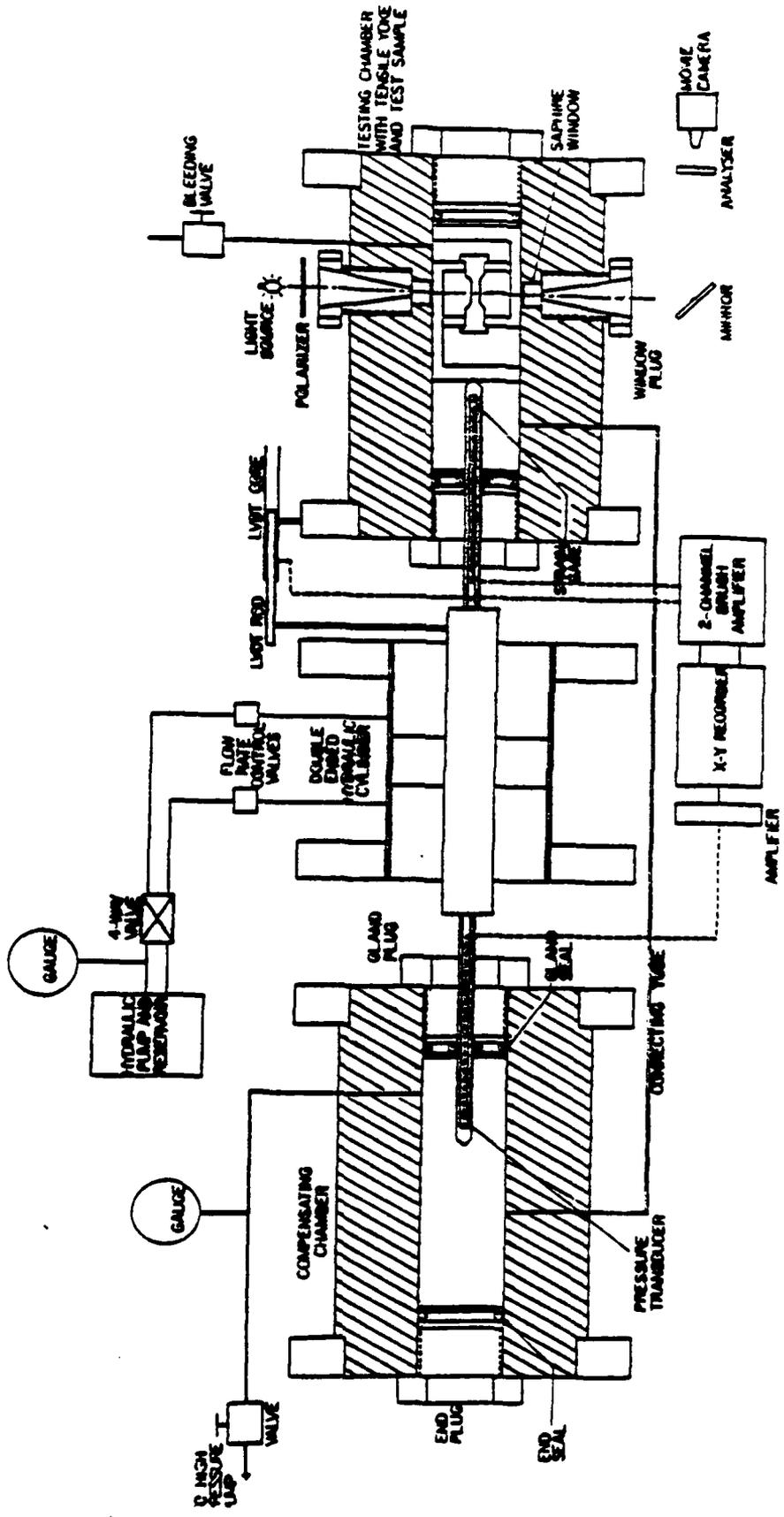
The results in Figures 9-12 indicate that the relaxation behavior of glasses in the plastic region is fairly complicated. The results also indicate, however, that even in this region of high strains, superposition procedures may be applicable to the data, and that it may be possible to incorporate pressure into a general time-temperature-pressure superposition principle in the plastic deformation region.

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### FIGURE CAPTIONS

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