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Volume Change during Deformation and Pressure Dependence of Yield Stress

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Polymers are distinguished from metals by the considerable pressure dependence of their yield stresses, and one might expect this to be associated with a plastic volume change during yielding. We have measured the macroscopic volume changes during uniaxial compression of PMMA and PC, using a mercury-filled dilatometer. For PMMA a plastic volume change cannot be defined unambiguously because the volume-stress curve is reversible upon unloading to the yield point. For PC the plastic volume change is negative. Hence, if the pressure dependence of yielding is associated with this volume change, one would predict a decrease of the yield stress with increasing pressure. Contrary to this, we find that pressure increases the yield stress of PC. Hence, the plastic volume change is not directly related to the pressure dependence of the yield stress.

INTRODUCTION

From the principles of thermodynamics, an increase in volume ΔV of a system under an applied pressure P requires work $\Delta W = P\Delta V$. If the system in question is a material deforming plastically, where the work is done by the applied stress, we may expect a pressure dependence of the flow stress τ , if ΔV is of sufficient magnitude. It is reasonable to suppose that the flow stresses of some polymers will be more sensitive to P than those of metals because their volume changes during deformation are relatively large. It remains important to understand the origin of the appropriate ΔV , and a number of such "volumes" have been proposed by various workers. In the accompanying paper¹ we have discussed the importance of one of these, the activation volume V^* . A second one is the free volume ΔV_f .² In this case yielding is imagined to occur when the volume increase occasioned by tensile elastic deformation supplies the "free volume" of a glassy polymer above its glass transition temperature. Other than the fact that it is only meant to apply to glassy polymers, this mechanism is also limited in that it cannot account for yielding in compression as indicated by Sardar *et al.*³ or in simple shear as indicated by Sternstein *et al.*⁴ This appears to be a critical failing, and it seems appropriate to exclude ΔV_f from further consideration at this time.

A third possibility is the residual volume change ΔV_r after deformation. In this case it is recog-

nized, as for crystalline materials, that a net volume expansion may result from plastic deformation in tension, compression, or torsion. In the case of polymers, however, Alksne *et al.*⁵ have shown that in some cases ΔV_r is negative after uniaxial compression. If ΔV_r were the important volume, a negative ΔV_r should cause a decrease in yield stress with pressure. This has not been observed in any polymer.

Finally, we may consider the *apparent* volume change during yielding which has been recently determined and discussed by Whitney and Andrews.⁶ This volume change at yielding is denoted by ΔV_p [or $(\Delta V/V_0)_p$]. As indicated by Fig. 1, it is given by the deviation (near the yield point) of a volume-stress curve from the linear extrapolation of the initial Poisson volume change. In the particular case shown, the Poisson change is negative (compression) and the deviation $(\Delta V/V_0)_p$ is an expansion. One could suppose, as suggested by Sardar *et al.*,³ that this "deviation expansion", i.e., positive $(\Delta V/V_0)_p$, is opposed by pressure. Therefore, a pressure dependence of the yield stress should result. In principle, the apparent $(\Delta V/V_0)_p$ could be positive in any mode of deformation—even when the net volume change ΔV_r is negative.

We note, however, that at the finite elastic deformations which are obtained prior to yielding in polymers, an elastic volume-stress curve is expected to be nonlinear (slightly concave to the stress axis). In principle, one could calculate this curve from nonlinear elasticity theory, but in prac-

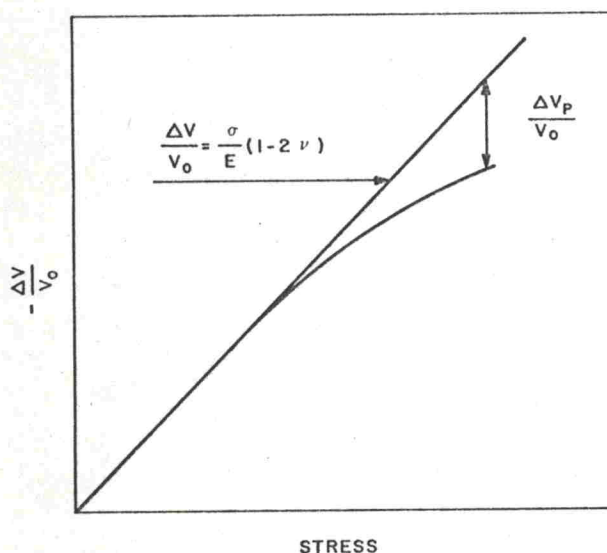


FIG. 1. Plastic volume ΔV_p , during deformation as defined in Ref. 5. The curvilinear path corresponds to the volume-stress behavior under conditions of increasing stress.

tice, one cannot easily determine the contribution of the elastic strain to the total strain on a σ - ϵ curve such as in Fig. 3. The straight-line variation of $\Delta V/V_0$ with stress is, thus, an approximation. On the other hand, in their experiments Whitney and Andrews apparently obtain reliable data for the change of volume only during an increase of the stress. But, if the curvilinear behavior of $(\Delta V/V_0)_p$ is reversible with decreasing stress, then an apparent volume deviation relative to any calculated "elastic" curve need not bear any relation to plasticity. Alternatively, if ΔV_p is really a macroscopic plastic volume, although the curve is reversible, one must conclude that it has a very small relaxation time. At any rate, if $(\Delta V/V_0)_p$ vs σ is reversible, one cannot unambiguously define ΔV_p as a "plastic" volume. For these reasons we have carefully examined the volume changes of poly-methyl methacrylate (PMMA) and Lexan polycarbonate (PC) during unloading as well as loading. Our results are presented below.

EXPERIMENTAL

The system used to measure volume changes is shown in Fig. 2. A cylindrical specimen 0.76 cm in diameter and 1.5 cm long is deformed inside a cylinder full of mercury by a piston driven by the crosshead of an Instron machine. The total volume of mercury displaced from the cylinder by the motion of the piston and the change in volume of the specimen are accurately monitored by the height of a mercury column in a capillary connect-

ed with the cylinder. By correcting for the displacement of mercury due to the motion of the piston when no specimen is in the cylinder, the volume change of the specimen during deformation can be determined. The motion of the piston is monitored by a linear variable differential transformer (LVDT) which gives the true displacement of the piston at all times; no correction is necessary for the deflection of the Instron machine. During an experiment, load-displacement curves are plotted on an x-y recorder and spikes corresponding to each 0.5 cm of capillary height are superimposed on the record by a brief manual interruption of the load signals; the height of the column is followed visually. The capillary system is quite sensitive: A 1-mm displacement of the mercury corresponds to a 3×10^{-4} relative volume change of the specimen. The deformation rate used is 10^{-3} sec^{-1} .

The unloading as well as the loading volume changes are of interest, so care is taken to minimize hysteresis effects. The piston that deforms the specimen is rigidly attached to the Instron crosshead so it cannot lag the crosshead when unloading begins. To minimize friction, a thin Halon (PTFE) sleeve is placed around the piston; friction then accounts for less than $\sim 1.5\%$ of the total load.

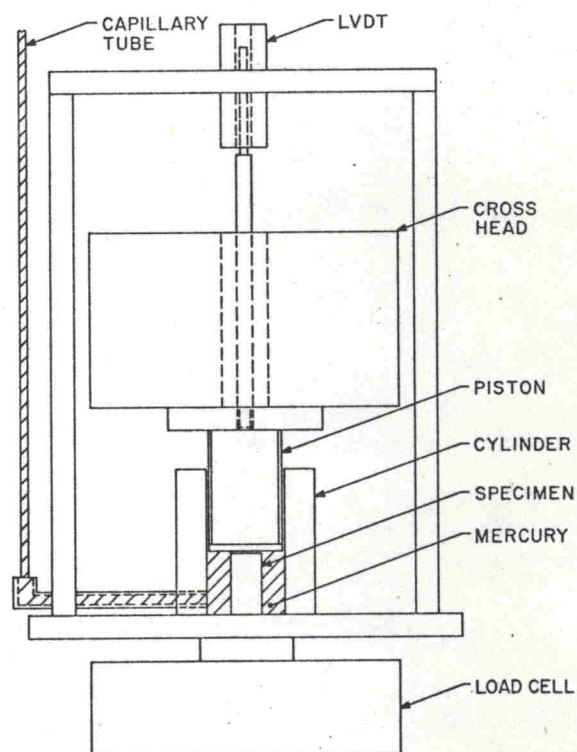


FIG. 2. System used to measure volume changes during deformation.

The loading surfaces of the specimens were coated with a very thin layer of PTFE applied by spraying. This was done to minimize friction against the platen; hence, no barreling is detected at the strains used in the present experiments. The PMMA specimens were machined from a 1.75-cm-thick plate supplied by Rohm and Haas. Lexan PC, of intrinsic viscosity 0.55 in the form of pellets, was molded into a 1.75-cm-thick plate from which specimens were machined. To determine whether annealing above and below the glass transition temperature ($T_g = 160^\circ\text{C}$) of PC would give different results as found for other properties,⁷ the PC specimens were subjected to two different annealing treatments. First, all specimens were annealed under vacuum at 165°C for 2 h and quenched in air to room temperature. A group of specimens were tested in this condition, and a second group was given an extra anneal in vacuum at 125°C for 16 h and slowly cooled to room temperature in the furnace. The results shown in Figs. 5 and 6 are those obtained after the 120°C treatment. For the specimens subjected to the 165°C anneal treatment alone, the results are slightly different and will be discussed later.

The birefringence of all PMMA and PC specimens was very small ($\sim 10^{-5}$). The Poisson ratios quoted in Figs. 4 and 6 are calculated by means of the

equation $\Delta V/V_0 = \sigma/E (1-2\nu)$ using Young's modulus E measured in Figs. 3 and 5 and the initial slopes of Figs. 4 and 6. The measurements shown in Figs. 3-6 are typical of five observations made under the same conditions.

EXPERIMENTAL RESULTS

In Fig. 3 the stress-strain curves for PMMA loaded and unloaded in uniaxial compression are shown, Fig. 4 shows the corresponding relative volume change $-\Delta V/V_0$ as a function of stress. We find, in agreement with Whitney and Andrews,⁶ that the volume-change-stress curve departs from linearity at about the same time the stress-strain curve does. However, while the stress-strain curve is observed to be irreversible, we find that the $\Delta V/V_0$ -stress curve is reversible, within experimental error. Therefore, we conclude that it is not possible to distinguish between a plastic volume change which recovers with a short relaxation time and a nonlinear elastic volume-stress relation.

For PC the results are quite different from those for PMMA. Figure 5 shows the uniaxial compression stress-strain curve for PC; a and b are the unloading paths after different amounts of deformation. Figure 6 shows the corresponding $-\Delta V/V_0$ -stress curves. This curve also departs from linearity, but unlike the results of Whitney and Andrews,⁶ the curve bends towards the volume axis. Upon unloading, the $\Delta V/V_0$ -stress curve is found to be irreversible. The results found for specimens subjected to the 165°C treatment alone only differ from these in that the maximum stress is about 10% lower. Also, upon unloading to zero stress through a curve such as a in Fig. 6, the volume of the specimen was smaller by ~ 0.2 - 0.3% than the volume of the specimen before deformation. Thus, for PC one could reasonably define a plastic volume in the manner of Whitney and Andrews (see Fig. 1), and in this case it is found to be negative, i.e., $\Delta V_p < 0$. In other words, plastic deformation in a uniaxial compressive stress field decreases the volume of PC at yield beyond the decrease due to Poisson's ratio. Moreover, for specimens subjected to the 165°C treatment alone, there is a negative residual volume change, i.e., $\Delta V_r < 0$.

DISCUSSION

The results of measuring the macroscopic volume change of PMMA and PC during deformation have demonstrated two cases: In PMMA there is no clear plastic volume change and in PC the volume change during deformation is negative. However, as stressed in the Introduction, it is desirable to

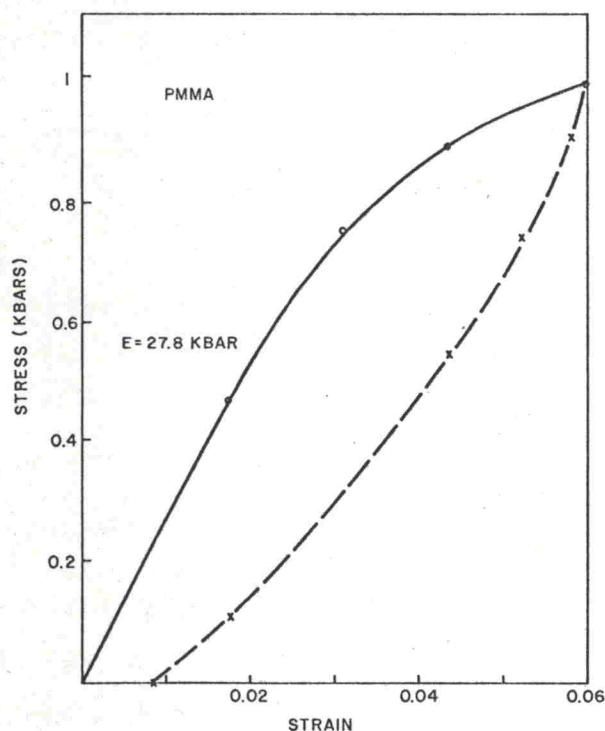


FIG. 3. Uniaxial compressive stress-strain curve for PMMA.

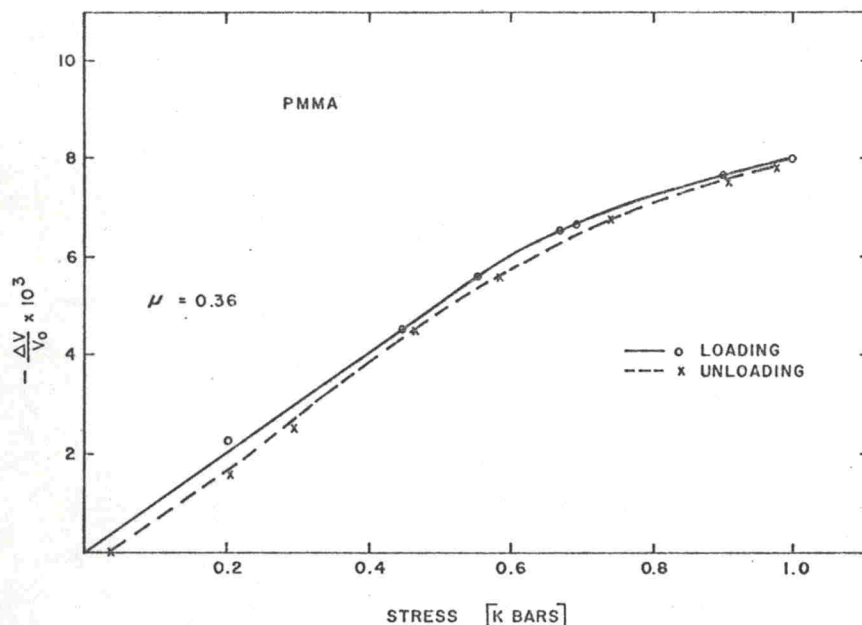


FIG. 4. Relative volume-change-stress curve for PMMA.

understand which volume change is the important one in relation to the pressure dependence of the yield stress.

In terms of the macroscopic volume change during yielding, ΔV_p , we expect no effect of a hydrostatic component of stress on the uniaxial compressive yield stress of PMMA. This is contrary to the results found in the literature⁸ which show that a hydrostatic pressure increases the yield stress of PMMA. The results for PC clearly predict, in

terms of ΔV_p , a decreasing yield stress with increasing hydrostatic pressure.

No results were found in the literature on the effect of hydrostatic pressure on the compressive yield stress of PC, so tests were performed here. The same PC was used, subjected to the 165 °C anneal treatment. This treatment provided the extreme condition to be tested, i. e., a negative plastic volume change at yield and also a negative residual

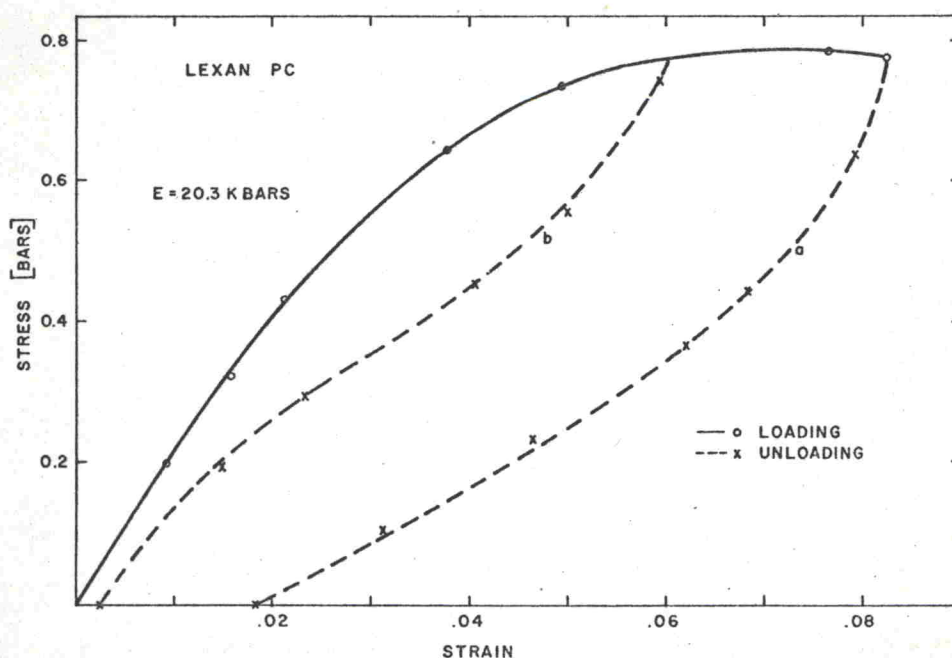


FIG. 5. Uniaxial compressive stress-strain curve for Lexan PC. a and b are the unloading paths after different amounts of deformation.

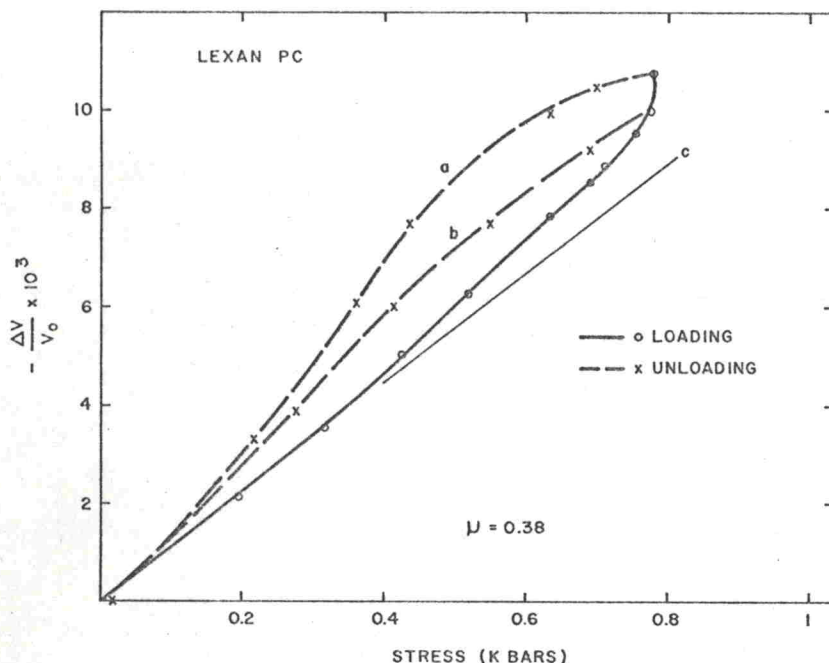


FIG. 6. Relative volume-change-stress curve for Lexan PC. Curves a and b are as in Fig. 5. Line c is the extrapolated linear Poisson's contraction.

volume change due to plastic deformation. The uniaxial compressive stress-strain curves shown in Fig. 7 were obtained with the system described in the accompanying paper,¹ using *n*-pentane as the pressurizing fluid. The stress-strain curves for specimens deformed at 1 atm and 4.3 kbar clearly show that the effect of pressure is to increase the yield stress. Also included is the stress-strain curve for a specimen deformed at 1 atm up to yielding, unloaded, reloaded, and deformed at 1.4 kbar, and afterwards again at 1 atm; it shows that the effect of pressure is not permanent. The difference in the flow stress at 1 atm before and

after deforming at 1.4 kbar is probably due in part to recovery, slight buckling of the specimen at large strains, and the normal load drop after yielding. These results clearly rule out either ΔV_p or ΔV_r as important volume changes in determining the effect of pressure on the yield stresses of polymers.

Yielding can be described in terms of the activated complex theory of deformation.⁹ The important volume change during deformation is then the activation volume which determines the pressure effect of yielding. Some effects of pressure on yielding due to ΔV_p are expected but at relatively very high pressures or very low strain rates. Details will be discussed in a future paper.

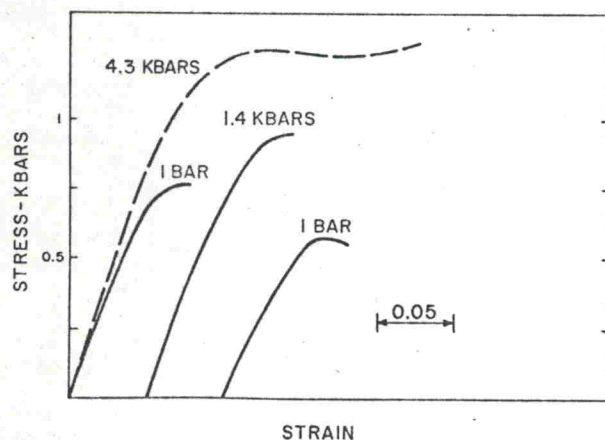


FIG. 7. Uniaxial compressive stress-strain curves under different hydrostatic pressures for Lexan PC.

CONCLUSIONS

The macroscopic volume changes during deformation of two typical amorphous polymers (PMMA and Lexan PC) were measured. The results show that it is incorrect to conclude, as is found in the literature, that these macroscopic volume changes during deformation are responsible for the pressure dependence of the yield stress of polymers. It is pointed out that the use of the rate theory of flow leads to the definition of the volume to be related to the pressure effect on yielding, i.e., the activation volume.

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