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r, University of Massachusetts,

does not imply that they are Agriculture over other firms

Copolymers," Wiley, New

ymer Sci., <u>4</u>, 111 (1965). em., <u>32</u>, 556 (1967). n., <u>37</u>, 1018 (1965). em. Soc., <u>71</u>, 2790 (1949). Pat. 2,813,093 (1957) and

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RHEOLOGY OF POLYETHYLENE AT HIGH PRESSURES

Introduction

Recently interest has been expressed in the effect of mean stress on mechanical properties of polymers (1-5). For a great many materials, particularly the metals, yielding can be described quite accurately solely as a function of the shear stresses, e.g., the critical resolved shear, Tresca, and Von Mises criteria (6,7). Yielding in such materials does not depend on the hydrostatic component of the stress. Conversely, failure in some materials is known to be highly dependent on the mean component of stress. Information relating the dependence of mechanical properties on the hydrostatic component of applied stress should be useful in developing and understanding the mechanisms of plastic deformation and in the development of failure criteria.

Mechanical properties of most materials also shows some dependence on effects such as time and rate of loading and/or strain. These effects are perhaps most pronounced in polymers such as plastics and elastomers. These materials are generally classed as viscoelastic although most do not obey the formal mathematics of linear viscoelasticity (9). In studying the effect of pressure on the flow porperties of polymers, it appears, therefore, that it would also be helpful to investigate time effects.

A few years ago (1964-1965) the authors were interested in finding a material for use in seals suitable for long-term usage under high hydrostatic pressure. To obtain this information a study was undertaken of the flow properties of polymers at high pressure. From this information it was expected to be able to predict the useful life of seals. The material studied most thoroughly (and eventually used most extensively for seals) was polyethylene. With the recent upsurge in interest in pressure effects in polymers, it occurred to us that these results might be of more basic and general interest. Therefore, this letter was prepared.

Experimental Equipment and Techniques

The high-pressure equipment used is similar in all respects to that described elsewhere (10). It consisted of a thick-walled high pressure cylinder providing a working space 1 in. in diameter and approximately 5 to 6 in. in length depending on pressure. The pressure was developed and maintained by a press acting on a piston. The pressure media was technical grade kerosene.

Both relaxation and creep tests were conducted on the polyethylene. To measure the load, small cantilever load cells were constructed from tool steel and resistance strain gages. Output of the load cell was corrected for pressure effects that had previously been determined to be small (11,12). Displace-

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ment was measured with a LVDT that had likewise been calibrated under pressure. We would estimate the error of both load and displacement measurements to be less than 5 per cent.

The tensile load, superimposed on the hydrostatic pressure loading, was applied to the sample by springs or lead weights. Since the pressure has only a very slight effect on the elastic modulus of steel ($\sim 1\%$ at 10 kbar), the spring constant varies only slightly with pressure. As a result, it was possible in the creep tests to maintain constant load to within a few per cent as determined by the load cell.

The load was held from the sample while assembly in the pressure vessel and during the period preceding the actual testing by small fuse wires. After assembly and the desired pressure had been obtained, the load was applied by "fusing" this wire with a surge of electric current. In this way the "constant" load was applied for the creep tests or the samples elongated to mechanical stops for the fixed displacement or relaxation tests in a small fraction of a second. Load and displacement were recorded versus time on a Leeds and Northrup dual-channel speedomax recorder.

Two types of samples were used:

 Bulk samples in the form of beams with three-point loading constructed from bulk low density polyethylene

2) Tensile specimens fabricated from polyethylene film (0.002 in. thick). Both were commercial grade material purchased locally. The stress distribution for beams is more complex, of course, making the viscoelastic analysis more difficult. This incidentally would not present much of a problem for a linear viscoelastic material. However, since polyethylene does not fall in this class, we will report here only the results on the tensile tests. Qualitatively, at least, the phenomena were similar in the two types of tests.

Experimental Results

Consider first the creep tests of polyethylene film. Samples were cut and the apparent compliance computed by the equation

$$1/C(t) = \frac{W/dT}{\Delta \ell(t)/\ell}$$
(1)

where W is the applied constant load, d is the sample width, T is the sample thickness, & is the sample length, and $\triangle\&(t)$ is the sample extension. The results of six creep samples tested at several hydrostatic pressures is shown in Figure 1. Referring to Figure 1, it can be observed that as the mean stress is increased, the compliance was significantly decreased. This observation applies to both the initial and final values of compliance. Furthermore, creep rates were generally reduced at higher values of mean stress.

Stress relaxation tests produced similar but slightly different results. As with the creep tests the apparent modulus was determined from sample geo-

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where $\triangle R$ is the very rapidly applied sample extension (held constant for the test duration) and W(t) is the measured sample force. The results of five stress relaxation tests at several hydrostatic pressures are shown in Figure 2.

Referring to Figure 2, it will be noted that the apparent relaxation modulus change with pressure is smaller than the analogous results from Figure 1, i.e., the reciprocal of the compliance. The general trends in the creep and relaxation tests are the same, i.e., the hydrostatic pressure does increase the general stiffness and viscosity of the material. It might be hypothesized that part of the difference in the two tests results from the method of loading. In the creep tests, of course, a constant load is suddenly applied while in relaxation tests a sudden displacement was applied to the sample. This later displacement was applied in a very small fraction of a second and, consequently, at these pressures the sample could have behaved like a "glass." If this were the case, instantaneously, very high stresses could have resulted and as a consequence some structural damage and morphological changes could have occurred. Unfortunately, the recorder used to measure the stress had a response time of greater than one second and so was incapable of monitoring such response.

In conclusion, the mean stress does drastically effect the rheology of the polyethylene. As far as the original purpose of the study goes, pressure does indeed enhance the "strength" of polyethylene for use as a high-pressure seal. Subsequent experience with polyethylene seals (both of unsupported and wedge type) substantiated this effect. In fact, sealing at low pressures proved to be more of a problem than excessive seal flow at pressures to 10 kbar.

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References

(1) S. V. Radcliffe and E. Baer, paper to be presented at the Winter Meeting of the Society of Rheology, 1971.

(2) J. A. Sauers and K. D. Pal, paper to be presented at the Winter Meeting of the Society of Rheology, 1971.

(3) G. Biglione, E. Baer, and S. Radcliffe, "Fracture-1969," P. L. Pratt, Ed., Chapman & Hall, London, 1969, p. 503.

(4) L. A. Davis and C. A. Pampillo, "Deformation of polyethylene at High Pressure," Bull. Amer. Phys. Soc., <u>16</u>, 429 (1971).

(5) C. A. Pampillo and L. A. Davis, "On the volume change before yielding and pressure dependence of the yield stress," Bull. Amer. Phys. Soc., <u>16</u>, 429 (1971).

(6) P. W. Bridgman, "Studies in Large Plastic Flow and Fracture," McGraw-Hill, New York, 1952.

(7) A. Mendelson, "Plasticity Theory and Applications," Macmillan, New York, 1968.

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1re-1969," P. L. Pratt,

of polyethylene at High

e change before yielding ner. Phys. Soc., <u>16</u>, 429

v and Fracture," McGraw-

ions," Macmillan, New

POLYMER LETTERS

(8) P. M. Naghdi, F. Essenberg, and W. Kolff, J. Appl. Mechanics. 25, 201 (1958).

(9) J. D. Ferry, "Viscoelastic Properties of Polymers," Wiley, New York, 1970.

(10) K. L. DeVries, G. S. Baker, and Gibbs P., J. Appl. Phy., <u>34</u>, 2254 (1963).

(11) K. L. DeVries, G. S. Baker, and P. Gibbs, J. Appl. Phys., <u>34</u>, 3119 (1963).

(12) D. K. Backman, Master's Thesis, University of Utah, Salt Lake City, 1965.

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