Reprinted from
PHILOSOPHICAL MAGAZINE, Vol. 24, No. 188, p. 451, August 1971

The Mechanical Behaviour of Polymers under High Pressure

By A. W. CHRISTIANSEN†, E. BAER† and S. V. RADCLIFFE‡
Case Western Reserve University, Cleveland, Ohio 44106

[Received 17 March 1971]

ABSTRACT

The effect of pressure on the tensile deformation of amorphous polycarbonate and poly(ethylene terephthalate) and semi-crystalline polychlorotrifluoroethylene and polytetrafluoroethylene was investigated up to 8 kb. Tensile deformations of polycarbonate at atmospheric pressure at temperatures down to 116°K were also performed. The former three polymers showed increases of yield stress, yield strain and elastic modulus, and decreases of fracture strain. Polytetrafluoroethylene behaved in an analogous manner up to 4 kb, beyond which both the ' yield ' stress and elastic modulus deviated systematically from the lower-pressure behaviour. This was found to correlate with changes of bulk modulus at a solid–solid phase transition near 5 kb.

The pressure dependence of yield stress was fitted by modified von Mises and Mohr–Coulomb yield criteria. A material parameter describing this pressure dependence was obtained for these and other polymers and was found to correlate qualitatively with the strength-limiting temperature, T_g or T_m, polytetrafluoroethylene being an exception. It was found that the pressure dependence of yield strain in polycarbonate could be accounted for by free volume considerations.

Correlation of high-pressure behaviour with low-temperature behaviour led to two conclusions: firstly, from a knowledge of bulk physical properties and a pseudothermodynamic equation, developed here, changes in low-temperature yielding phenomena can be used to predict similar changes with high pressure, and, secondly, the ductile–brittle transition of a normally ductile amorphous polymer may be closely related to a specific dynamic mechanical relaxation, the temperature of observation changing with pressure.

§ 1. INTRODUCTION

HYDROSTATIC pressure has been shown to have a significant effect on the mechanical properties of polymers. Holliday, Mann, Pogany, Pugh and Gunn (1964) have shown that polystyrene, which normally fractures in a brittle manner in tension, can be made to undergo yielding at considerably greater stresses if tested under hydrostatic pressures of 7 kb. Ainbinder, Laka and Maiors (1964) demonstrated that the yield maximum of a ductile polymer in nominal uniaxial compression was increased 150% by application of 2 kb hydrostatic pressure. The elastic modulus of a number of elastomers has been found to increase over a range of pressures

---

† Division of Macromolecular Science.
‡ Division of Metallurgy and Materials Science.

from values characteristic of the rubbery state to those characteristic of the glassy state, and Paterson (1964) proposed that this was evidence for a pressure-shifted glass transition, the atmospheric-pressure glass transitions occurring at temperatures tens of degrees below the room temperature testing conditions.

Semi-crystalline polymers were studied by Ainbinder, Laka and Maiors (1965) and Laka and Dzenis (1967), though only to 2 kb. There were significant increases of strength under pressure for these also, and stress-whitening was eliminated in several cases. Sardar, Radcliffe and Baer (1968), utilizing an apparatus which enabled observation of the semi-crystalline polyoxymethylene at pressures to 8 kb, showed that not only did the strength increase markedly, but also the mode and rate of fracture changed. The trends of several properties with pressure changed between 5 and 8 kb, and after comparisons with property changes at low temperatures it was proposed that in this pressure range the normally low-temperature β-relaxation ($-75°$c) had been shifted to room temperature. Changes in the large-strain deformation behaviour of two other semi-crystalline polymers (Mears, Pae and Sauer 1969) may also involve the shifting of low-temperature relaxations, particularly when related to ductile–brittle transitions.

More extensive experiments have been published on normally brittle polystyrene (Holliday and Mann 1968, Biglione, Baer and Radcliffe 1969) including optical observations of its deformation behaviour. These showed a brittle to ductile transition between 2 and 3 kb, attributed to changes in the critical crack size for Griffith flaws (Biglione *et al.* 1969). In the latter study a rubber-modified polystyrene was no longer ductile at 1 kb, supposedly due to suppression of crazing between rubber particles, and thereafter behaved as a ' diluted ' polystyrene.

The purpose of the present study was to extend high-pressure studies with optical observations to the ductile amorphous class of solid polymers. This is a class which has been the most extensively treated by mechanistic theories of yielding because of ductility below their glass transitions, the onset of ductility being associated with low-temperature mechanical relaxations which may be amenable to pressure-shifting.

§ 2. EXPERIMENTAL

2.1. *Specimens*

Four types of polymers were investigated, two ductile amorphous materials, additive-free molded $\frac{1}{2}$ in. square bars of poly (bisphenol A carbonate)† with $M_w = 35\,000$ to $36\,000$ and 93 mil sheets of poly (ethylene terephthalate)‡, and two semi-crystalline polymers, commercial

---

† Merlon ® polycarbonate from the Mobay Chemical Company.

‡ From E. I. du Pont de Nemours & Co., Inc.