

The Mechanical Behaviour of Polymers under High Pressure

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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

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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.