### 3.2.6. *Fracture strain and the ductile–brittle transition*

For PBAC and PCTFE, and likely for PET, the strain to fracture decreases with increasing pressure, the trend pointing toward an eventual fracture before a yield maximum is reached, the usual behaviour of a brittle polymer. This behaviour is in fact qualitatively similar to behaviour with decreasing temperature. Perhaps here more markedly, the relationship between relaxations and changes in large-strain deformation modes may be shown to be of importance, whether the temperature is lowered to reach the relaxation or the pressure is increased to force the transition temperature upward to the test temperature. In this regard the work of Williams (1966) is instructive. His work on the pressure, temperature,

Fig. 9
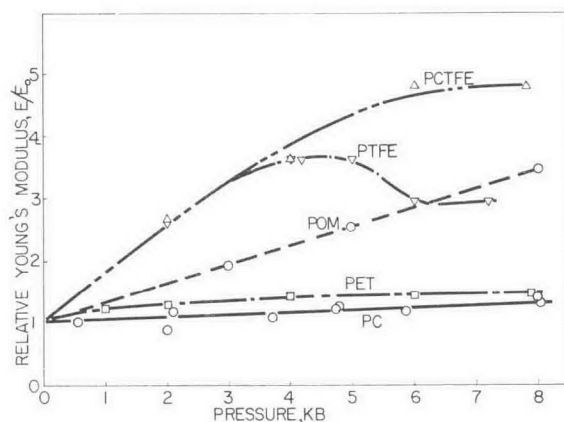
Relative Young's modulus as a function of pressure for five polymers.   Date for POM from Sardar *et al.* (1968).

and frequency dependence of the low-temperature dielection relaxation in PET (near 65°c), which has been associated (Armeniades, Kuriyama, Roe and Baer, 1967) with its ductile–brittle transition, provides the data for extrapolating this change of deformation mode to higher pressures. Extrapolating his data to 1 Hz, it can be replotted as pressure versus the temperature for observation of the frequency maximum, as in fig. 10. Extending the relationship to room temperature (27°c here), the transition in behaviour would be expected at pressures near 11 kb, which is above those attained in the present work but in a range that might be anticipated from the present fracture and yield strain results. Correlation of such large-strain mechanical tests with either dielectric or dynamic mechanical tests, all under pressure, would be most useful in pursuing this relationship.

Fig. 10
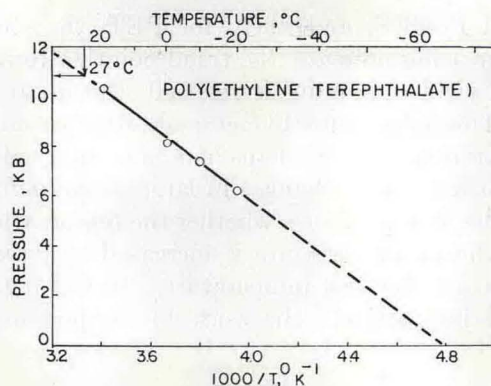
TEMPERATURE , °C

Pressure-temperature relationship for the γ-relaxation maximum of poly-(ethylene terephthalate) at 1 Hz.   Original data from Williams (1966).

§ 4. Conclusions

The pressure dependence of the yield stress was fitted using modifications of the common von Mises and Mohr–Coulomb criteria.   The parameter representing this pressure dependence showed no discrimination between classes of polymers, and was only found to correlate qualitatively with the strength-limiting temperature, T_g or T_m.

Three polymers, PBAC, PET, and PCTFE, exhibited an increase of yield strain with pressure, and for PABC a calculation based on a free volume concept predicts an increase of yield strain with pressure close to that determined experimentally.

An approximate method for superposing the effects on yield stress of temperature and pressure was developed as a pseudo-thermodynamic equation.   The decrease of fracture strains toward an implicit ductile–brittle transition with increasing pressure may be associated with a relaxation whose observation temperature shifts upward with pressure, but which normally is associated at low temperatures with a ductile–brittle transition.

For the materials considered, the relative Young's modulus increased with pressure, the semi-crystalline polymers showing larger changes than the amorphous materials.   However, it is felt this may be due to the proximity and magnitude of relaxations in these materials rather than to morphological factors.

Polytetrafluoroethylene behaved uniquely.   Although the arbitrarily defined yield stress showed a pressure-dependence similar to the other materials up to 4 kb, above that the yield stress, as well as Young's modulus, showed systematic deviations.   Using independent bulk modulus results, these deviations were correlated with a solid–solid phase transition in this pressure range.