property is a constant regardless of the stress system, then the yield criteria are those of Tresca and von Mises, respectively. This is generally the case for ductile metals. When $\tau_{\max}$ is linearly dependent on the sum of the major and minor principal normal stresses $(\sigma_1 + \sigma_3)$ then this is referred to as the Mohr–Coulomb or Guest criterion.

In every relevant study to date, polymers have been found to exhibit significant increases of yield stress with pressure. Thus a yield criterion for polymers must include provision for the effect of pressure or mean normal stress, $\sigma_{\mathrm{m}} = (\sigma_1 + \sigma_2 + \sigma_3)/3$, on the magnitude of the critical shear stress. This would then result in either a slightly modified Mohr–Coulomb criterion, in the form

$$\tau_{\max} = \tau_0 - \mu' \sigma_{\mathrm{m}}$$

or a modified von Mises criterion in the form

$$\tau_{\mathrm{oct}} = \tau_{\mathrm{s}} - \mu \sigma_{\mathrm{m}},$$

where τ_0 and τ_{s} are the atmospheric pressure pure shear maximum and octahedral yield stresses, and μ' and μ are materials parameters describing the pressure dependency of the respective yield stresses. Whitney and Andrews (1967) and Bowden and Jukes (1968) have applied the former equation to uniaxial and biaxial stress experiments. The latter equation was proposed by Sternstein and Ongchin (1969) after fitting biaxial stress data on poly (methyl methacrylate). Graphical analysis of these criteria for biaxial stress states shows that the modified Mohr–Coulomb criterion is represented by a distorted hexagon and the modified von Mises criterion by a distorted ellipse, the distortion occurring along the $\sigma_1 = \sigma_2$ direction and tending to foreshorten in the biaxial tensile direction and elongate in the biaxial compression direction. A modified von Mises criterion ellipse could just as well have been selected to fit the original data of Whitney (1964).

In the present case, where only uniaxial tension experiments were performed, no discrimination between the two is possible, since they are then mathematically related as $\tau_{\mathrm{s}} = \tau_0(2\sqrt{2})/3$ and $\mu = \mu'(2\sqrt{2})/3$. For engineering use the differences between the two are insignificant, the modified von Mises criteria providing a slightly more conservative prediction.

For the application of yield criteria, true stress data should be used. When this was not possible, as with PET, estimates were made using engineering equations. Assuming a value for a Poisson's ratio (defined as the ratio of the transverse to axial nominal strains) independent of pressure, the true and nominal stresses are related as

$$\sigma = \frac{S}{(1 - \nu e_1)^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where σ is the true stress, S is the nominal stress, ν has the value of the assumed Poisson's ratio, and e_1 is the nominal axial strain.

Using experimentally determined values of true yield stress where possible, and estimates of the true stress at yield from eqn. (1), in other cases, it was possible to calculate the points for plots of τ_{oct} versus σ_m for the materials used in the present study, fig. 6, and for those investigated previously. The slopes, μ, and the intercepts at $\sigma_m = 0$, τ_s, describing the relationships for the materials which exhibited linear behaviour are collected in table 1. Attempts to relate μ to values of bulk modulus, or to the pressure-dependence of the bulk modulus, were fruitless. However, an ordering by magnitude of the strength-limiting temperature, in separate categories of crystalline and amorphous, agreed qualitatively to a corresponding ranking by magnitude of μ, PTFE providing an exception in this case. The parameter μ may vary with crystallinity and other factors which affect yielding, and thus μ would not be expected to correlate with either T_g or T_m directly.

Fig. 6
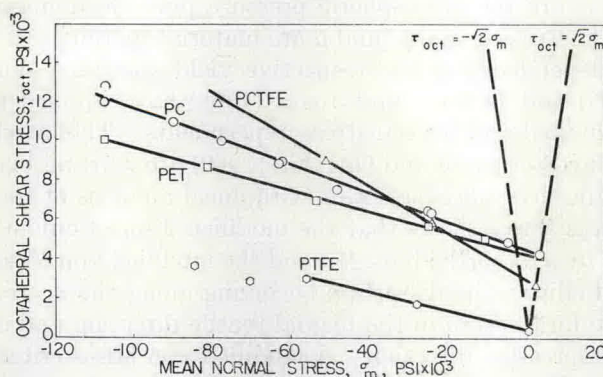
Yielding condition for four polymers plotted according to the Sternstein–Onchin (1969) shear yielding criterion.

3.2.2. *Pressure–temperature correlation of yield stresses*

Ainbinder (1969) formulated a relationship between changes of failure stress and changes of volume, such that for a specific volume change, caused by either a change of pressure or temperature, there will be a specific change of yield stress. That this is not generally true can be be shown with the high-pressure and low-temperature data obtained in this study plus dilatometric data from the literature, at high pressure (Warfield 1967) and low temperature (Hellwege, Hennig and Knappe 1962). As temperature is decreased from a reference condition there will be a change of volume and a simultaneous change of yield stress. This would likewise be true if the pressure were raised. If we plot the observed yield stresses against a common volume change abscissa (additional abscissa axes being incorporated to indicate the particular temperature or pressure) a graph such as fig. 7 results, from which it can be seen that there is not a unique