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Pressure dependence of glass transition temperature in polymers*)

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With 1 table

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Abstract

The pressure dependence dT_g/dP of glass transition temperature T_g has received considerable interest due to its connection with solid state thermodynamic properties and theories of glass transition. Free volume considerations (1, 2) led to an estimate of the pressure effect on T_g, showing that dT_g/dP had to depend on thermal expansion and compressibility changes at T_g through the equation:

$$\frac{dT_g}{dP} = \frac{\Delta\beta}{\Delta\alpha} \qquad [1]$$

where $\Delta\beta = \beta_e - \beta_g$ and $\Delta\alpha = \alpha_e - \alpha_g$.

Later work (3, 4, 5, 6) has shown that eq. [1] is not verified by experimental facts, the ratio $\Delta\beta/\Delta\alpha$ being much larger than (dT_g/dP) exp.

Recent analysis of the properties of glasses obtained under different pressures have complicated the situation, showing that the experimental value of dT_g/dP depends, of course, on the polymer used *but also on the experimental procedure used in its determination.* Since it is obvious that in order to measure any ΔT_g-value we need to operate on at least *two glasses*, these should be identical in all properties which could influence T_g except pressure. Any difference in morphology, *which could lead to a change in T_g at constant pressure*, should therefore be avoided in order to get a sound value for the pure pressure effect dT_g/dP. To reveal this effect, we have performed (7) dT_g/dP determinations on two polymers, polyvinylacetate (PVAC) and polyvinylchloride (PVC), following three different procedures:

A. Measurement of the change ΔT_g induced by application of a pressure increment ΔP on the liquid polymer ($T > T_g$). This is the procedure normally used; the liquid is cooled down at a fixed rate of temperature change (~ 5 °C/day) and T_g is dilatometrically recorded at 1 atmosphere. Then the polymer is taken again to the liquid state, pressure ΔP is applied and, at the same rate, the system is cooled down isobarically; the new T_g is recorded and dT_g/dP calculated.

B. Measurement of the change ΔT_g induced by application of a pressure increment ΔP on the glassy polymer ($T < T_g$). Once determined T_g at 1 atmosphere, pressure ΔP is applied on the glass, time is given to the system to equilibrate; then the glass is heated isobarically. Intersection of the glassy line to the liquid line in a volume/temperature plot gives the new T_g and therefore allows the calculation of dT_g/dP.

C. Measurement of ΔT_g during the heating of a glass along an isochor (5, 8). Here the polymer glass is heated at constant volume, by application of an increasing pressure at increasing temperatures given by $(\partial P/\partial T)_v$. By repeating this procedure two times, starting from two different specific volumes of the glass, two values of T_g at different pressures can be recorded and dT_g/dP calculated.

Table 1 shows the result of this work

Polymer	dT_g/dP, °C/atm		
	A	B	C
PVAC	0.015	0.037	0.022
PVC	0.013	0.038	0.028

Comparison of values for different procedures shows quite convincingly how dT_g/dP, at a given heating or cooling rate, is a property not only of the polymer but also of the experiment. Any information which, like the pressure effect on T_g, is based on a comparison between two or more glasses, should be therefore carefully analysed in terms of other contributions, besides pressure, to the total change in T_g.

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