population of bonding electrons in the compound if models of Figs. 1a and b were correct, because In atoms entering Bi sites should, under the influence of the lattice, promote their three valence electrons into hybrid p^3d^3 orbitals, to satisfy the trigonal antiprismatic co-ordination. Consequently, In would form the same two-electron resonating covalent bonds with the six nearest neighbours $Te^{(1)}$ and $Te^{(2)}$ atoms, just as Bi atoms of the compound do. The model of Fig. 1c, on the other hand, is apparently unable to accommodate two-electron bonds thoughout the lattice, when a few In atoms are substituted for Bi atoms. Several one-electron bonds would necessarily form, instead, rendering the compound paramagnetic (Fig. 1d).

Adequate materials were prepared and measurements of magnetic susceptibilities were carried out using the Faraday method. Pure Bi_2Te_3 was found to be diamagnetic ($\chi = -0.5 \times 10^{-6}$ c.g.s. units per gram at room temperature), which is consistent with both proposed models, having all their electrons paired. This value is in very good agreement with previously reported measurements [1, 2, 4]. Partially substituted samples, however, corresponding to the compositions $Bi_{1.8}In_{0.2}Te_3$ and $Bi_{1.6}In_{0.4}Te_3$ were found to be less diamagnetic or markedly paramagnetic ($\chi = -0.2 \times 10^{-6}$ and $+5.2 \times 10^{-6}$ c.g.s. units per gram at room temperature, respectively). The observed gradual increase of paramagnetism with the substitution of In for Bi atoms, produces evidence that model of Fig. 1c provides a better description of the bonding in Bi_2Te_3, than the combination of models of Figs. 1a and b.

The above analysis is based on the assumption that the magnetic effects of the deletion of paired electrons, caused by the above-mentioned substitution, are negligible. It is also assumed that the contribution of free carriers to magnetic susceptibility is practically the same in all cases. In fact, electric resistivity and Hall coefficient measurements have shown that at temperatures between 77 and 300 K the material is in the exhaustion region with similar carrier concentrations, of the order of 2×10^{25} m^{-3}, in all samples [12].

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The prediction of creep at long times in polymeric solids

This note describes the principles and experimental test of a method for predicting long time creep in the linear viscoelastic region of polypropylene. It is based upon the recent precision determination of the activation energy for creep (ΔH) of the α-relaxation process using the temperature pulse technique [1, 2]. The shift factor a_T

$$\ln a_T = \frac{\Delta H}{R}\left[\frac{1}{T} - \frac{1}{T_0}\right] \qquad (1)$$

is therefore known precisely in the temperature region of interest (25 to 80° C).

For a linear viscoelastic solid the relationship between the shear compliance master curve at reference temperature T_0 and time (t/a_T) and the observed shear compliance at an arbitrary temperature T and time t, is [3, 4]

$$J^{T_0}(t/a_T) = \frac{J^T(t)}{b_T} + J_U^{T_0}\left(1 - \frac{c_T}{b_T}\right) \qquad (2)$$

in which

$$(J_R^T - J_U^T) = b_T(J_R^{T_0} - J_U^{T_0}) \qquad (3)$$

$$J_U^T = c_T J_U^{T_0} \qquad (4)$$

J_R and J_U are the relaxed and unrelaxed compliances at temperatures T and T_0 according to superscript. Consideration of Equation 2 shows that in order to superpose the measured values of $J^T(t)$ to form the master curve it is necessary to normalize the data in two ways: (i) a vertical shift of $J_U^{T_0}(1 - c_T/b_T)$, (ii) a second vertical shift and rotation produced by b_T^{-1}. The normalized creep data should then superpose onto the matter curve with a shift along the time axis of $\log a_T$.

The purpose of the experiment was to obtain a master curve by superposition at $T_0 = 25.0°$ C. from measurements taken at 80, 59, 40 and 25° C. in the range of time between 1 and 2×10^3 sec. The predicted creep curve was then to be tested by comparing it with data observed at 25° C at times between 2×10^3 and 10^5 sec.

The specimen studied was a thin walled tube of isotactic polypropylene of density 0.905 g ml^{-1} at 20° C. It was mounted in a torsional creep machine [3] and surrounded by a cavity through which deionized water was passed at the required temperature. The specimen was stress-relaxed at 85° C for 15 h and then cooled to 80.0° C and maintained at that temperature for 100 h. The creep compliance was then determined between 1 and 2000 sec. The specimen was then cooled to 59.0° C maintained at that temperature for 100 h and the compliance determined between 1 and 2000 sec. This procedure was repeated at 40.0° C. The specimen was finally cooled to 25.0° C, maintained at that temperature for 100 h, and the compliance determined between 1 and 10^5 sec.

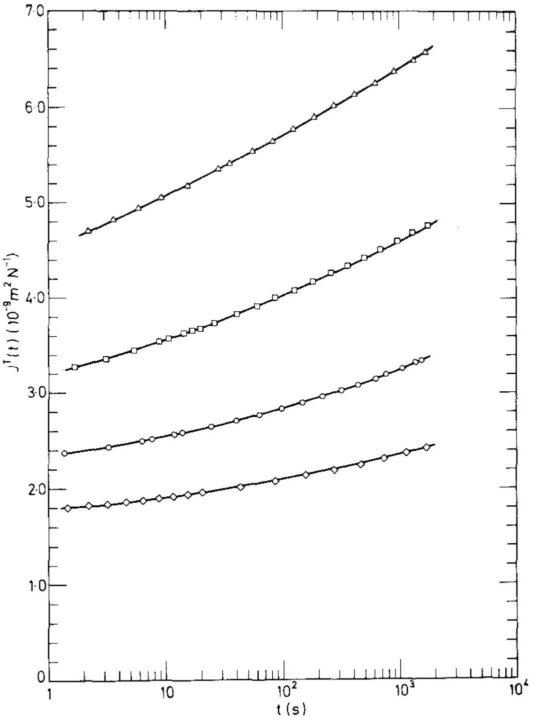

Figure 1 The dependance of creep compliance $J^T(t)$ on log t at four temperatures between 1 and 2×10^3 sec: △, 80.0° C: □, 59.0° C: ○, 40.0° C: ◇, 25° C.

Fig. 1 shows the compliance at the four temperatures between 1 and 2×10^3 sec. The analysis proceeds as follows. For a reference temperature of $T_0 = 25°$ C each $J(t)$ curve was shifted along the log time axis by $\log a_T$, calculated according to an activation energy $\Delta H = 34.5$ kcal mol^{-1} determined using the temperature pulse technique [1, 2]. The curves were then moved vertically to obtain the superposition shown in Fig. 2. It will be observed that the superposition so achieved is extremely good; this implies that for the present purposes the assumption $b_T = 1$ (no rotation) is valid. The data observed at 25° C between 2×10^3 and 10^5 sec is compared with the predicted curve in Fig. 2. It will be seen that to within the precision of the superposition the agreement out to 10^5 sec is perfect.

Apart from the detailed vindication achieved for the principle of time–temperature equivalence, the procedure offers a practicable method for predicting long term creep in the linear region. There are excellent grounds however for the hypothesis that at higher strains when the specimen

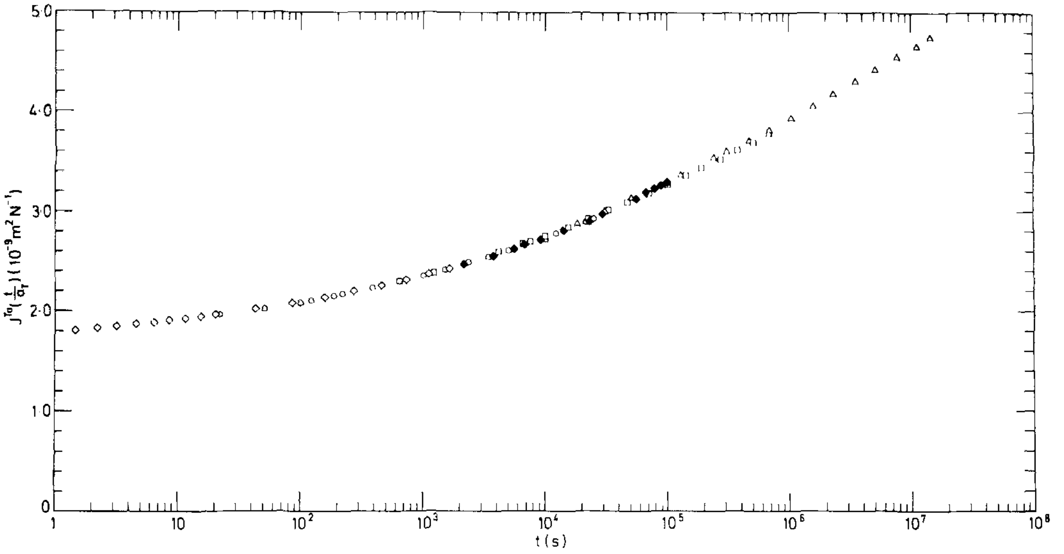

Figure 2 Open points: data of Fig. 1 superposed to form the predicted compliance curve at $T_0 = 25.0°$ C. Closed points: data taken at 25.0° C at times between 2×10^3 and 10^5 sec to test the prediction. Symbols as in Fig. 1.

becomes non-linear the same procedure wil also be successful. This follows from the determination by Morgan and Ward [5] of $\Delta H = 36\,\text{kcal mol}^{-1}$ for the non-linear creep of a polypropylene monofilament. This determination (by time–temperature shift without normalization) is based on the premise that at high strains (approximately 10 × those in the linear region) the effect of normalization is negligible. The close agreement between the value of $\Delta H = 36\,\text{kcal mol}^{-1}$ and our value [1, 2] of $\Delta H = 34.5\,\text{kcal mol}^{-1}$ supports this premise. Therefore according to the evidence, at low creep stresses superposition will be achieved with appreciable vertical shift, but as the stress is increased the vertical shifts will diminish. It will be noted that the fact which permits the same treatment of data in both linear and non-linear regions is the constancy of ΔH. The effect of elapsed time, t_e [6] (in these experiments constant at $t_e = 100$ h) is significant. This work is continuing and will be reported in detail elsewhere.

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