polymer reports

The validity of the compensation rule

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Values of ΔH and τ_∞ for the mechanical relaxation times centred at ~700 s were obtained for isotactic polypropylene at three temperatures in the α-region by double T-jump. The values of ΔH and τ_∞ varied systematically in accordance with the compensation rule. The compensation temperature was observed to be $T_c \sim 240°C$. It is shown that the compensation rule is in good agreement with the predictions of theories of Wert and Zener and of Eby.

Keywords Mechanical behaviour; polypropylene; compensation rule; relaxation

We are concerned in this note with the dominant hypothesis of linear thermoviscoelasticity: this is the assumption that all components of the distribution of relaxation times have the same value of activation enthalpy, ΔH[1]. This hypothesis has been so widely used and for such a time that it is frequently taken as an axiom. It has never, however, been subject to a quantitative test using the classical procedures for determining ΔH: the time–temperature superposition of creep curves is insensitive, since unknown vertical shifts have to be applied to correct for the temperature dependance of the limiting compliances[1]: the more precise damping peak method measures ΔH for one relaxation time only, that at the centre of the distribution[2]. Nevertheless, the well known but sparsely recorded experimental fact that damping peaks become sharper the higher the temperature of observation, has always cast an unquantified doubt on the constant ΔH hypothesis.

Nowick and Berry[3] have reviewed alternative mechanisms for the existence of a distribution. These are that the distribution of relaxation times is caused by (i) a distribution in ΔH; (ii) a distribution in the pre-exponential term; (iii) an intermediate case in which there is a distribution both in ΔH and also in the pre-exponential term (see also Macdonald[4] and Zielinski, Swiderski and Kryszewski[5]). For the latter possibility, we consider the distribution of relaxation times to consist of many infinitesimal components, *Figure 1(a)*. The ith component has activation energy ΔH^i. As a special case of alternative (iii), the temperature dependence of all elements of the distribution is (following Lacabanne *et al.*[6])

$$\tau^i = \tau_c \exp\frac{\Delta H^i}{R}\left[\frac{1}{T} - \frac{1}{T_c}\right]; \qquad (1)$$

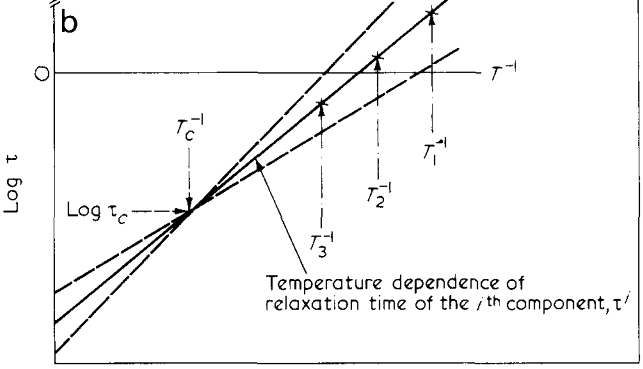

Figure 1 Illustration of the compensation rule. (a) The distribution of relaxation times at three temperatures, $T_1 < T_2 < T_3$. The distribution sharpens as T increases. The ith process is shown shaded: the temperature dependence of its relaxation time, τ^i, conforms to the Arrhenius equation (b) with constant activation energy, ΔH^i. The temperature dependence of all elements of the distribution (of which (b) shows three) conform to equation (1)

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when $T = T_c$ all relaxation times take the same value τ_c. Equation (1) is illustrated in *Figure 1(b)*: it is referred to normally as the compensation rule, a term drawn from chemical kinetics where the phenomenon is well known. It is also observed in the Zener relaxation in metallic alloys[7].

The compensation rule has been studied in polymers in both dielectric and mechanical relaxation[6,8] using the techniques of thermal sampling and is reported to be supported by data analysis based on the Bucci equation[9]. The validity of this important result we examine elsewhere[10]. Our purpose here is to point out that not only is equation (1) the most likely *a priori* hypothesis, but that it is also in agreement with our recent precision determination of ΔH at the α-relaxation in polypropylene using a thermal stimulation technique not based on the empirical Bucci equation.

Using Zener's formulation of the rate theory we have,

$$\tau^i = \tau_\infty \exp\left(\frac{\Delta H^i}{RT}\right) \tag{2}$$

$$\tau_\infty = \nu^{-1} \exp - \left(\frac{\Delta S^i}{R}\right) \tag{3}$$

in which ΔS^i is the entropy of activation of the ith component of the distribution and ν the natural frequency of the relaxing segment. In the theory of Wert and Zener[11],

$$\frac{\Delta S^i}{\Delta H^i} = \frac{\beta}{T_m} \tag{4}$$

in which T_m is the melting point and β a constant of order unity for metal crystals. The theory of Eby[12] yields,

$$\frac{\Delta S^i}{\Delta H^i} = 4\alpha \tag{5}$$

in which α is the isobaric coefficient of thermal volume expansion. From equations (2–4),

$$\tau^i = \nu^{-1} \exp \frac{\Delta H^i}{R}\left[\frac{1}{T} - \frac{1}{T_c}\right] \tag{6}$$

in which,

$$T_c = \frac{T_m}{\beta}. \tag{7}$$

Equations (2). (3) and (5) yield equation (6) with,

$$T_c = \frac{1}{4\alpha} \tag{8}$$

It follows therefore that a precise determination of ΔH for different components of the relaxation spectrum will yield, if the compensation rule holds, a value of T_c to be compared with equations (7) and (8).

The technique of double T-jump is particularly suited to the determination of ΔH when there is the possibility that ΔH varies with relaxation time. The reason is that the packet of elements yielding the observed $\dot{\gamma}$ (rate of change of shear strain in creep) is narrow: the packet width is governed by the imposed experimental conditions including the length of the temperature pulse. The assumption in the double T-jump theory[13,14] of a constant ΔH is restricted to the constancy of ΔH for the dominant packet, of order 1 decade wide.

Precision measurements of ΔH were obtained in the α-region[1] of isotactic polypropylene at 35.0°, 51.6° and 70.1°C using the double T-jump technique[13,14]. The specimen and procedure were identical to that of Chen, McCrum and Pizzoli[14]. Detailed model analysis shows that the value of ΔH, observed under the experimental conditions, was that of a packet of relaxation times centred in the region of $\tau = 700\text{s}$[15]. The values of ΔH obtained are given in *Table 1.*

An Arrhenius plot of the data is given in *Figure 2*: from the experimental data (ΔH at T for $\tau = 700\text{s}$) the lines are plotted as indicated. The values of τ_∞ so obtained are given in the Table.

It will be seen that the compensation rule is fully supported for this relaxation. The compensation temperature is $T_c = 513$ K and $\nu^{-1} = 1.2 \times 10^{-7}$ s. Use of equation (7) yields,

$$\beta = (T_m/T_c) = 0.9,$$

in fair agreement with values obtained for metal crystals

Table 1 Values of ΔH and τ_∞ for relaxation times at $\tau \sim 700\text{s}$ observed by double T-jump at three temperatures for polypropylene (α-process)

T (°C)	ΔH (kcal mol^{-1})	τ_∞ (s)
35.0	34.8 ± 0.3	1.5×10^{-22}
51.6	40.1 ± 0.4	7.2×10^{-25}
70.1	46.7 ± 1.5	1.3×10^{-27}

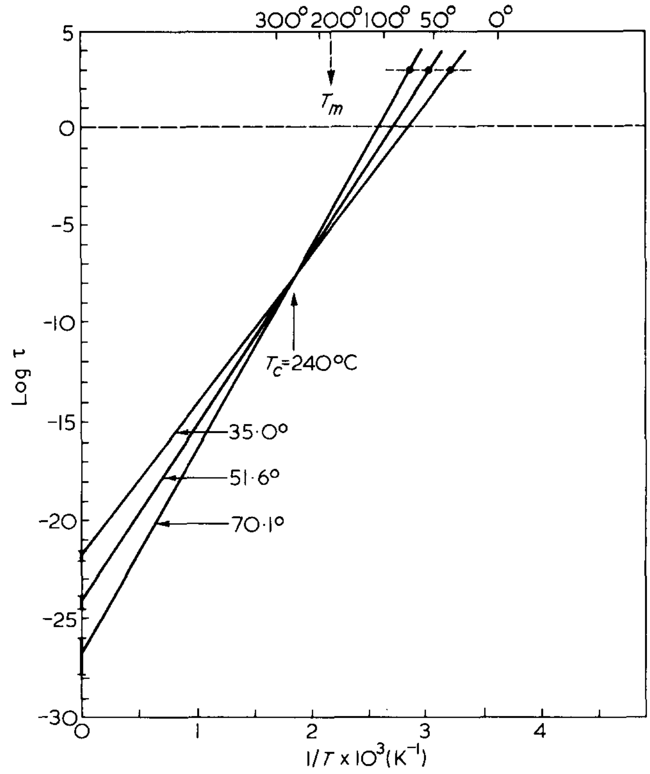

Figure 2 The dependence of log τ on T^{-1} for the α-relaxation in polypropylene. Values of ΔH were determined for the packet of relaxation times centred at $\tau = 700\text{s}$ by double T-jump at 35.0, 51.6 and 70.1°C. The values of ΔH so obtained (*Table 1*) yielded the slopes of the lines plotted and the values of τ_∞ (see *Table 1*)

which average at 0.35^{16}. Use of equation (8) yields,

$$4\alpha = T_c^{-1} = 20 \times 10^{-4}\ \mathrm{K}^{-1}.$$

This also is in reasonable agreement with the anticipated value[12] of

$$4\alpha = 25 \times 10^{-4}\ \mathrm{K}^{-1}.$$

A full account of this work, including a reformulation of the theory of the double T-jump experiment taking into account the variation of ΔH with relaxation time, will be presented elsewhere.

REFERENCES

1 McCrum, N. G., Read, B. E. and Williams, G. 'Anelastic and Dielectric Effects in Polymeric Solids', Wiley, London, 1967

2 Solunov, Ch. and Ponevsky, Ch. *J. Polym. Sci., Polym. Phys. Edn.* 1976, **14**, 1801

3 Nowick, A. S. and Berry, B. S. 'Anelastic Relaxation in Crystalline Solids', Academic Press, New York, 1972

4 Macdonald, J. R. *J. Chem. Phys.* 1962, **36**, 345

5 Zielinski, M., Swiderski, T. and Kryszewski, M. *Polymer* 1978, **19**, 883

6 Lacabanne, C., Chatain, D. G., Monpagens, J. C., Hiltner, A. and Baer, E. *Solid State Commun.* 1978, **27**, 1055

7 Berry, B. S. and Orehotsky, J. L. *Acta Met.* 1968, **16**, 683

8 Lacabanne, C., Chatain, D. G. and Monpagens, J. C. *J. Macromol. Sci. Phys.* 1977, **B13**(4), 537

9 Bucci, C., Fieschi, R. and Guidi, G. *Phys. Rev.* 1966, **148**, 816

10 McCrum, N. G. to be published

11 Wert, C. and Zener, C. *Phys. Rev.* 1949, **76**, 1169

12 Eby, R. K. *J. Chem. Phys.* 1962, **37**, 2785

13 McCrum, N. G. and Pizzoli, M. *J. Mater. Sci.* 1977, **12**, 1920

14 Chen, F. C., McCrum, N. G. and Pizzoli, M. *Polymer* 1979, **20**, 488

15 Chai, C. K. *Thesis*, Oxford (1980) to be published

16 Shewmon, P. G. 'Diffusion in Solids', McGraw-Hill, New York, 1963

Temperature dependence of X-ray diffractograms of amorphous lignins and polystyrenes

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Temperature dependencies of X-ray diffractograms of lignins and polystyrene derivatives were investigated. Bulky side groups, such as methoxyl functionalities were found to expand intermolecular distance, while hydroxyl groups reduce its mean value. Intermolecular distance expands discontinuously at the temperature corresponding to the glass transition temperature.

Keywords Diffraction; measurement; X-ray diffractogram; lignins; polystyrene derivatives; hydroxyl group; temperature; glass transition

The amorphous nature of lignins has been studied by various techniques: broad-line nuclear magnetic resonance[1], differential scanning calorimetry (d.s.c.)[1,2] and viscoelasticity[3].

X-ray diffractometry is a direct method of investigating polymer structure, but its usefulness is restricted to studying amorphous polymers such as lignins. However, the inter- or intramolecular regularity of randomly-packed molecular chains can be interpreted from X-ray analysis of amorphous polymers[4,5].

EXPERIMENTAL

Lignins, polystyrene and polystyrene derivatives used in this experiment are listed in *Table 1*. A sample of polystyrene (PST) with molecular weight distribution (M_w/M_n) of 1.01 were procured from the Pressure Chemical Co. Another sample of polystyrene with M_w/M_n of 3.0 was obtained from the Asahi Dow Chemical Co. Polystyrene derivatives, poly(4-hydroxystyrene) (PHS), poly(4-hydroxy-3-methoxystyrene) (PHMS) and their acetates (PAS, PAMS) and poly(4-methoxystyrene) (PMS) were synthesized as reported previously[6,7]. Isolated lignin, dioxane lignin (DL), methylated DL (MDL) and milled wood lignin (MWL) were prepared according to the procedure reported previously[8].

Table 1 Estimated temperature at which the intermolecular distance expands discontinuously (T) and glass transition temperature (T_g)[7]

Sample	M_n	M_w/M_n	T (°C)	T_g (°C)
PST	1.0×10^5	1.01	80	83
PST	1.0×10^5	3.0	90	93
PHS	6.6×10^4	2.9	110	100
PHMS	3.2×10^3	2.8	–	75
PMS	2.3×10^3	2.9	70	60
MWL	*	*	130	135
DL	*	*	130	127
MDL	*	*	120	118

* Not estimated, not found

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