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Calculation of impact transition temperature of low density polyethylene from shift factor via a free volume approach

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A relationship between the impact transition temperature T_i and the stress concentration factor K_s is derived. The relationship involves the temperature shift factor a_T; in turn, a_T depends on the free volume. In earlier work in this problem Zewi and Corneliussen [6] utilized the W–L–F equation. Here a more direct relationship between a_T and the free volume is applied. Satisfactory values of K_s corresponding to given T_i are obtained for a wide temperature range; the range also includes temperatures below the glass transition point T_g. The opinion that a free volume exists between 0 K and T_g is upheld.

1. Introduction

Users of polymeric materials of all kinds have at least one common problem: the possibility of fracture. As a consequence, numerous papers and whole volumes (see for instance Kausch [1]) have been written on polymer fracture. In a somewhat different context, Jedlinski [2] stresses the connection between the usability of polymeric materials and the effects of temperature upon the properties of these materials.

Methods of strengthening are more or less common to all basic classes of engineering materials: metals, ceramics and polymers; see for instance Section 12.5 of Brostow [3]. For some time the ductile–brittle transition temperature has been used as an important parameter characterizing the mechanical behaviour of metals. At this temperature both brittle and ductile behaviour is possible in samples of identical geometry. For polymers, however, a similar transition has attracted less attention. Bueche [4] has discussed the so-called "brittle temperature", but he noted that the value of this temperature depends on the experimental procedure used. Andrews [5] has provided a fairly detailed, but only qualitative, discussion of the brittle–ductile transition. On the basis of experimental data Andrews has concluded that there are transition ranges (intervals of about 10 K) rather than points. Only in 1979 did Zewi and Corneliussen [6] attempt to relate the relaxation of polymeric chains to what they called the impact transition temperature.

The impact transition temperature T_i is defined as the temperature at which the response of a material changes from brittle to ductile. This resembles the usual ductile–brittle transition. The measurement, however, made under *high-impact* load conditions enables quite precise location of the temperature. That is, a single point and not a temperature interval is defined. It is believed on the basis of experimental results [7, 8] that the transition so measured represents a basic material property.

The present work represents a continuation and an improvement of [6]. The problem has been re-examined essentially upholding the basic assumptions of Zewi and Corneliussen [6], but modifiying some elements in the reasoning. Since the resulting equations are different, values calculated therefrom are also presented for the same low-density polyethylene which was treated in [6].

2. The Charpy impact test

A convenient procedure for the determination of the impact transition temperature consists of performing the Charpy test. A specimen of definite size with a notch of known size is impacted at high velocity. The geometry of the test represents three-point bending: a rectangular bar resting

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against two posts is struck midway between the supports. Details of the experimental procedure have been discussed by Zewi *et al.* [8]. Stress concentration takes place at the notch; at the same time, the notch tip constitutes a constraint to plastic deformation. Let us denote the energy furnished in the test to the specimen by U_0. The problem consists of analysing how this energy is expended.

Before proceeding further, let us note that our parameter U_0 is not related to a parameter represented by the same symbol and used in the kinetic Korsukov [9] and used by Slutsker and collaborators [10] and by others. The Zhurkov–Korsukov parameter is a molecular property; as noted by Zaitsev and Razumovskaya [11] it is approximately equal to one half of the dissociation energy.

A part of the energy U_0 "invested" by the hammer of the Charpy machine into the specimen certainty goes into breaking bonds in polymer molecules. Let us denote the energy so utilized by U_b, and the corresponding rate constant by c_b. At the same time, a part of the input energy goes into relaxation of macromolecular chains; denote this energy term by U_r, and respective rate constant by c_r. Take both bond rupture and molecular relaxation to be first-order processes. At any time, τ, denote the unutilized energy by U, that is, this part of the input energy which did not go as yet into either of the two competitive processes. Thus

$$U = U_0 - U_b - U_r. \tag{1}$$

All parameters featured in Equation 1, except for U_0, are in general functions of time, τ. Clearly

$$U(0) = U_0. \tag{2}$$

Consider now the derivative $\mathrm{d}U/\mathrm{d}\tau$. Given the two first-order processes which bring about a decrease in U, then

$$\frac{\mathrm{d}U}{\mathrm{d}\tau} = -(c_b + c_r)U. \tag{3}$$

Integrating Equation 3 and remembering Equation 2, then

$$U = U_0\,\mathrm{e}^{-(c_b+c_r)\tau}. \tag{4}$$

Substituting Equation 4 into Equation 3 gives

$$\frac{\mathrm{d}U}{\mathrm{d}\tau} = -\frac{\mathrm{d}U_b}{\mathrm{d}\tau} - \frac{\mathrm{d}U_r}{\mathrm{d}\tau} \tag{5}$$

where

$$\frac{\mathrm{d}U_b}{\mathrm{d}\tau} = c_b U_0\,\mathrm{e}^{-(c_b+c_r)\tau} \tag{6a}$$

and

$$\frac{\mathrm{d}U_r}{\mathrm{d}\tau} = c_r U_0\,\mathrm{e}^{-(c_b+c_r)\tau}. \tag{6b}$$

Integrating Equation 6a and again remembering Equation 2, then

$$U_b = \frac{c_b U_0}{c_b + c_r}[1 - \mathrm{e}^{-(c_b+c_r)\tau}]. \tag{7a}$$

Analogously

$$U_r = \frac{c_r U_0}{c_b + c_r}[1 - \mathrm{e}^{-(c_b+c_r)\tau}]. \tag{7b}$$

Thus, for $U(\infty) = 0$, separation of the original U_0 into U_b and U_r components depends on the fraction $c_b/(c_b + c_r)$. Various consistency checks of the present set of equations can be easily made: for instance, direct differentiation of Equation 1 produces Equation 5; summation of Equations 7a and b reproduces Equation 1.

3. Stress concentration factor and shift factor

From Equations 7a and b we have immediately, for any temperature

$$\frac{U_b}{U_r} = \frac{c_b}{c_r}. \tag{8}$$

Since molecular relaxation rate depends on the temperature, in general the parameters in Equation 8 depend on the material and also on the temperature. The c_b constant, however, is an exception: it can be reasonably assumed to be temperature-independent.

Experiments on polyethylene reported by Zewi *et al.* [8] were made with singly-notched rectangular bars. The tensile strength of such a specimen is generally characterized in terms of the stress concentration factor K_s. According to Griffith [12, 13]

$$K_s = l + 2\left(\frac{h}{l}\right)^{1/2}, \tag{9}$$

where h is the depth of the notch (the length of the major axis in an elliptical crack) and l is the radius of curvature at the end of the major axis. To relate K_s to the parameters featured in Equation 8, the simplest possible assumption is made, namely,

$$c_b = c_b' K_s\ , \tag{10}$$

where c_b' is a material parameter independent of the temperature.

Consider now the parameter c_r. According to Equation 8, an increase in c_r means that a larger share of the input energy U_0 goes into U_r. When the temperature T increases, the relaxation is faster, that is, the c_r parameter increases. Now introduce the shift factor, a_T, defined by Ferry [14]

$$a_T = \frac{\eta T_{ref}\rho_{ref}}{\eta_{ref} T\rho}, \qquad (11)$$

where η denotes viscosity, ρ denotes density, and the index ref represents a reference point. When T increases, a_T *decreases*. Consequently,

$$c_r = \frac{c_r'}{a_T} \qquad (12)$$

can be written where c_r' is another material constant and is independent of the temperature; it might be equal to unity, but its exact value is immaterial for the following considerations.

From Equations 10, 8 and 12, we now have

$$K_s = \frac{c}{a_T}\cdot\frac{U_b}{U_r}, \qquad (13)$$

where

$$c = \frac{c_r'}{c_b'}. \qquad (14)$$

In view of the definitions made at the beginning, it is only reasonable to assume that the ratio U_b/U_r at the impact transition temperature T_i is also a material constant. According to Equation 9, the value of K_s depends on what has been done to the specimen, in terms of the parameters h and l. However, for every notch, as characterized by its K_s value, there exists a single impact transition temperature. In other words, there exists a one-to-one correspondence between $K_i \equiv K_s(T_i)$ and T_i. Thus

$$K_i = \frac{f}{a_{T_i}} \qquad (15)$$

can be written, where f is also a constant, namely,

$$f = c\frac{U_b(T_i)}{U_r(T_i)}. \qquad (16)$$

The problem of predicting the polymer fracture now becomes that of calculation of the impact transition temperature T_i for a given value of K_s. Equation 15 tells us that for this we need to know the shift factor. Therefore, in the next section the problem of the temperature dependence of a_T will be considered.

4. Shift factor and free volume

The most-often used formula which leads to an $a_T(T)$ dependence is the viscosity equation of Doolittle [15]

$$\ln\eta = \ln A' + B\frac{(v - v_f)}{v_f}. \qquad (17)$$

A' and B are constants for a given material, v is the volume per molecule for nonpolymeric liquids while it is the volume per segment for polymers, v_f is the free volume, again per molecule or per polymeric segment. A problem which arises immediately is that of the definition of v_f. One such definition follows from the partition function of Flory [16, 17]. It is widely used in various applications of the Flory theory of the liquid state [16–19]. As discussed elsewhere [20], however, there is a variety of other definitions [20–25]. Another problem, sometimes closely connected with the preceding one, is that of the dependence of v and/or v_f on the temperature; here once more we have a variety of relationships, including the volume–entropy–energy equation proposed again by Doolittle [26–29]. In any case, Equation 17 substituted into Equation 11 relates the shift factor to free volume. The result can be written in terms of v_f, or else in terms of alternative and related quantities

$$v^* = v - v_f \qquad (18)$$

or

$$\tilde{v} = \frac{v}{v^*}. \qquad (19)$$

v^* is called the hard-core volume, and $\tilde{v}$ is the reduced volume. By using Equation 19, from Equations 11 and 17

$$\ln a_T = -\frac{B}{\tilde{v}_{ref} - 1} + \ln\left(\frac{T_{ref} v}{T v_{ref}}\right) + \left(\frac{B}{\tilde{v} - 1}\right) \qquad (20)$$

is obtained. The first right-hand-side term in Equation 20 is, by definition, a constant, which we will call B'. The second term varies only slowly with temperature, and a reasonable approximation consists of neglecting its temperature dependence. Thus,

$$A = B' + \ln\left(\frac{T_{ref} v}{T v_{ref}}\right) \qquad (21)$$

and it can be assumed that

$$\frac{dA}{dT} = 0. \tag{22}$$

Approximate validity of Equation 22 will be checked by numerical calculations in the following section. Now

$$\ln a_{\mathrm{T}} = A + \frac{B}{\tilde{v}-1}. \tag{23}$$

Equation 23 represents the key $a_{\mathrm{T}}(T)$ relation. The most widely used explicit $a_{\mathrm{T}}(T)$ formula has been obtained by Williams, Landel and Ferry [30] by assuming

$$\tilde{v} = \left[\frac{1}{\tilde{v}_{\mathrm{ref}}} - \alpha_{\mathrm{f}}(T - T_{\mathrm{ref}})\right]^{-1}, \tag{24}$$

where α_{f} is a constant. Substitution of Equation 24 into Equation 23 gives the Williams–Landel–Ferry (W–L–F) equation

$$a_{\mathrm{T}} = \frac{-\alpha_{\mathrm{f}}(T - T_{\mathrm{ref}})}{\left(1 - \frac{1}{\tilde{v}_{\mathrm{ref}}}\right)\left[1 - \frac{1}{\tilde{v}_{\mathrm{ref}}} + \alpha_{\mathrm{f}}(T - T_{\mathrm{ref}})\right]^{-1}}. \tag{25}$$

Equation 25 gives reasonable results above the glass transition temperature, T_{g}, up to $(T_{\mathrm{g}} + 100)$K. The best results are obtained at about $(T_{\mathrm{g}} + 50)$K. It should be observed that Equation 25 blows up when $(1 - \tilde{v}_{\mathrm{ref}}^{-1})/\alpha_{\mathrm{f}} = (T_{\mathrm{ref}} - T)$. More importantly, there exists no basis for Equation 24. Ferry [14] notes himself that Equation 24 certainly does not hold below T_{g}.

Under the circumstances, it would be more satisfactory to have, instead of Equation 25, an $a_{\mathrm{T}}(T)$ formula operative below as well as above T_{g}. Therefore, we return now to Equation 23. Remember that Equation 23 is an approximation; it results from Equations 17 and 22. But the reliability of Equation 23 has now been proven by many calculations. The relative success of the W–L–F formula, Equation 25, cannot be traced to Equation 24, so it clearly relies on Equation 23. Thus, the problem reduces to finding a suitable $\tilde{v}(T)$ formula to be used in Equation 23.

As noted above, there is a variety of v_{f} definitions and of $\tilde{v}(T)$ relationships. Zoller [31] has compared two $\tilde{v}(T)$ equations for polymer melts, namely that of Simha and Somcynsky [21] and of Sanchez and Lacombe [32, 33]. He has concluded that the former is better. Since a modification of the Simha–Somcynsky formula is applicable to solid polymers too, we have decided to use it. In the reduced form it reads

$$\frac{\tilde{P}\tilde{v}}{\tilde{T}} = [1 - 2^{-1/6}y(y\tilde{v})^{-1/3}]^{-1} + \frac{2y}{\tilde{T}(y\tilde{v})^2} \times \left[\frac{1.011}{(y\tilde{v})^2} - 1.2045\right] \tag{26}$$

where $(1 - y)$ is the fraction of holes; the reduced pressure $\tilde{P}$ and temperature $\tilde{T}$ are defined by analogues of Equation 19. The hard-core or scaling parameters are

$$T^* = \frac{s(z-2)}{c} \cdot \frac{\epsilon}{k} \tag{27a}$$

and

$$P^* = s(z-2) \cdot \frac{\epsilon}{sv^*}. \tag{27b}$$

s is the number of segments per chain, $3c$ represents the number of volume-dependent external degrees of freedom, the ratio c/s is known as the flexibility ratio, z is the co-ordination number, ϵ is the potential energy at the minimum and k is the Boltzmann constant.

Equation 26 is not very convenient for practical calculations. There exists, however, an interpolation formula [34]

$$\tilde{v} = 0.9299 + 0.4478\tilde{T} + 37.33\tilde{T}^2 - 327.3\tilde{T}^3 \tag{28}$$

which represents Equation 26 well, and is applicable in particular to polyethylene in the temperature range for which the experiments have been reported in [6]. Equation 28 has been devised for crystals and includes corrections for anharmonicity (in the temperature range of interest such corrections are not significant in any case). There exists a $v(T)$ relationship for the melt which has been extrapolated to the amorphous solid range; Fig. 1 in [34] shows, however, that the extrapolation produces considerable errors. Thus, the use of Equation 28 for the solid, even though it is not completely crystalline, represents a much better approach. In the following section the calculated results obtained by the substitution of Equation 28 into Equation 23 is presented.

5. Calculations for polyethylene

To test the validity of equations developed in the present paper, one can either calculate the stress concentration factors K_{i} for a given set of impact transition temperatures T_{i}, or else calculate the temperatures T_{i} for a number of K_{i} values. Since K_{i} is a directly determinable quantity for any

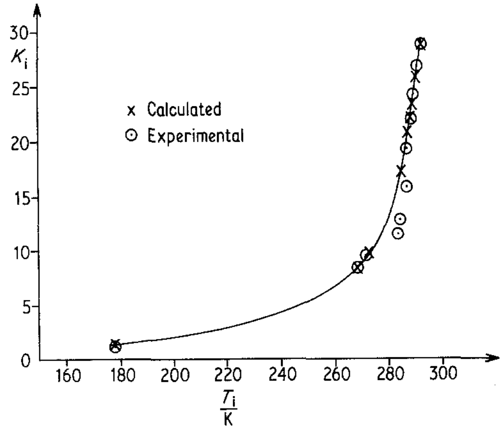

Figure 1 Experimental [6] and calculated values of the stress concentration factors K_i corresponding to impact transition temperatures T_i.

specimen, rather than average over a number of specimens, it was decided to follow the first route.

For each impact transition temperature of low-density polyethylene reported by Zewi and Corneliussen [6] the corresponding $\tilde{v}$ value from Equation 28 has been calculated. The hard-core temperature $T^* = 7956\,\text{K}$ was taken from [34]. The necessary relationship between K_i and $\tilde{v}$ is obtained by substituting Equation 23 into Equation 15; the result can be written as

$$K_i = F\,e^{-[B/(\tilde{v}-1)]}\,, \tag{29}$$

where the new constant F is

$$F = \frac{f}{e^A}. \tag{30}$$

Since Equation 29 involves two constants, we have simply solved a pair of such equations, taking the experimental values of K_i for $T_i = 269$ and 293 K. The results are $F = 0.1239$ and $B = 0.1053$. A slightly better agreement with the experiment could conceivably have been obtained by extracting F and B from all measured values. This, however, would have detracted from the fact that data for a pair of temperatures are sufficient to make predictions for an arbitrary temperature. Values of K_i calculated from Equation 29 are listed in Table I together with the experimental values for all T_i parameters reported in [6]. The reduced volumes, $\tilde{v}$, used in the calculations are tabulated too, as well as the factor $(\tilde{v}-1)^{-1}$ in Equation 23. For two temperatures, 285 and 288 K, there are two different experimental K_i values; this enables assessment of the scatter of the experimental points. Given this scatter, possibly a better perspicuity for the judgement of the theory can be provided by a graphical representation. Therefore, experimental as well as calculated K_i values are shown as a function of the impact transition temperature in Fig. 1. Clearly, the theory agrees with the experiment within the limits of experimental accuracy.

Already the key conclusion has been reached, but on the way to it we have promised to check certain things. One of them was the validity of the assumption of Equation 22. To do this, take the hard-core parameters as the reference ones; as noted by Ferry [14], there are no limitations on the choice of the reference state. Then Equation 21 can be rewitten as

$$A = B' + \ln\frac{\tilde{v}}{\tilde{T}}. \tag{31}$$

With the same T^* as before, and with $\tilde{v}$ values listed in the second column of Table I, the second term on the right-hand-side of Equation 31 is equal to 3.748 at 749 K and to 3.282 to 293 K.

TABLE I Impact transiton temperatures, T_i, and corresponding stress concentration factors, K_i, of low-density polyethylene

T_i(K)	$\tilde{v}$ (Equation 28)	$\frac{1}{\tilde{v}-1}$	K_i		R	
			Experimental	Calculated	Present work	W–L–F
179	0.9552	−22.32	1.0	1.3	2.6	–
269	0.9751	−40.16	8.5	8.5	16.7	1
273	0.9760	−41.67	9.4	10.0	19.6	2.9
285	0.9787	−46.95	12.6	17.4	34.1	24.0
285	–	–	11.9	–	–	–
288	0.9795	−48.78	19.4	21.1	41.3	36.0
288	–	–	16.0	–	–	–
289	0.9797	−49.26	22.2	22.2	43.5	41.0
290	0.9799	−49.75	24.5	23.4	45.9	46.0
291	0.9803	−50.76	27.0	26.0	51.0	51.0
293	0.9807	−51.81	29.0	29.0	56.8	63.0

This can be contrasted with considerable variations of $(\tilde{v}-1)$ in the same temperature interval, as seen in the third column of Table I. Given the present accuracy of the experiments, as seen in Fig. 1, the validity of the assumption of Equation 22 is thus upheld. Of course, any time the experimental accuracy improves, Equation 22 can be abandoned and $\ln(\tilde{v}/\tilde{T})$ easily calculated.

We have also promised to make a comparison with the calculations described in [6]. The latter were not made in terms of K_i, but of a function R, dependent on T_i and defined so that the ratio K_i/R is a constant. Denoting this constant by c'

$$K_i = c'R \tag{32}$$

and, using Equation 15,

$$R = \frac{f}{c'}\cdot\frac{1}{a_{T_i}}. \tag{33}$$

Disregarding for the moment (but see below) aberrations at the two lowest temperatures for which K_i/R ratios are reported in Table I of [6] the average value of c' is 0.51. Thus, from Equation 32, $R = 1.96K_i$, and these values of R are listed in the penultimate column of Table I. In the last column of the table the R values from [6] are reported, obtained from Equation 25, the W–L–F equation. There is reasonable agreement at the highest temperatures between the two sets of R values, but the agreement disappears rapidly with a temperature decrease. As noted by Zewi and Corneliussen [6], the constancy of their K_i/R ratio is dramatically lost at $T_i = 273$ K. The lowest experimental temperature of 179 K is far below the glass transition point, and any procedure which employs the W–L–F equation is useless. By contrast, our procedure is still applicable.

6. Discussion

It is recommended that the shift factor be calculated from Equation 23 and not from the W–L–F equation, Equation 25. The use of Equation 23 involves a relationship between reduced volume, v, and the temperature, T, or else between free volume, v_f, and T. A fairly satisfactory $\tilde{v}(T)$ formula is Equation 26 resulting from the hole theory of Simha and Somcynsky [21]; a convenient consequence of Equation 26 is the interpolation Equation 28. The main drawback of the W–L–F equation is the implication that molecular relaxations are entirely frozen below a certain temperature. Arguments against the complete freeze-in below the glass transition temperature have been discussed by Simha [35]. The fact that our procedure for calculating K_i is operative below T_g is thus significant. Substantial molecular mobility at T_g itself was found by Seigman and Geil [36] for crystals of polycarbonate and by Lam and Geil [37] for linear polyethylene. Discussing a qualitative model of the freezing-in process, Morèse-Séguéla and her colleagues [38] stress that the temperature range of the process depends on the cooling rate. The same Montreal group [38] also reports the existence of two glass transition temperatures, for the soft and hard phases, in styrene–isoprene di-block co-polymers.

Satisfactory relationships between the stress concentration factor and the impact transition temperature of solid polymers have been developed here. Each of these parameters can be calculated from the other. Two constants are needed if the shift factor, a_T, as a function of temperature is unknown. Only one material constant is necessary if the $a_T(T)$ relationship is provided. Further implications of the present results for the problem of polymer fracture are being explored. Among other things, we would like also to obtain more experimental data, for materials other than polyethylene in particular.

In a way, the present work explores the tip of an iceberg. Several further problems are involved: free volume changes not only with temperature but also with pressure. Fillers and Tschoegl [39] have obtained an important generalization of the W–L–F equation, Equation 25, to pressure changes. That is, they have a formula for the *general shift factor*, $a_{T,P}$, which depends on both external parameters. The Fillers–Tschoegl formula can be reduced to the usual W–L–F equation, Equation 25, or else to its pressure analogue proposed by Ferry and Stratton [40]. In practical calculations, Tshoegl and his school [39, 41] use the relationship between volume and pressure suggested by Murnaghan [42]. Also often used is the empirical relationship between volume and pressure proposed by Tait [43]. The Murnaghan and the Tait equations give results fairly close to each other; possibly a better relationship between volume and pressure than either of these two can be found, and then used in calculations of the generalized shift factor, $a_{T,P}$, introduced by Fillers and Tschoegl. We have a reliable relation between the isothermal compressibility of liquids (including polymeric ones) and the temperature [44]. A generalization of this relationship to describe compression of solid polymers should be possible.

Incidentally, there seems to be a common belief, voiced for instance by Ferry [14], that the B constant in the Doolittle equation, Equation 17, is close to unity. Fillers and Tschoegl [39] stress that this is not the case. For four materials studied by them the values of B vary between 0.175 for Viton B (a co-polymer of vinylidene fluoride and hexafluoropropylene, lightly filled with carbon black) and 0.608 for PVC. Their conclusion is confirmed by the value of $B = 0.1053$ reported here for polyethylene.

The shift factor can be related to even more parameters. Kenner and Knauss [45, 46] have studied the creep compliance of polyvinyl acetate in shear as a function of temperature and also of absorbed moisture. They have found that water concentration affects the time scale of creep in a similar manner to temperature. That is, a *concentration*-dependent shift factor exists too, and can be evaluated.

To conclude, let us return to the problem of molecular relaxations, as discussed in the beginning of the present section; below the glass transition temperature T_g in particular. We are not saying that molecular motions below T_g are strong ones: see the dramatic fall of the parameter R in the penultimate column of Table I between 269 and 179 K. It is simply stressed that a certain amount of free volume still exists, except of course at $T = 0$ K.

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