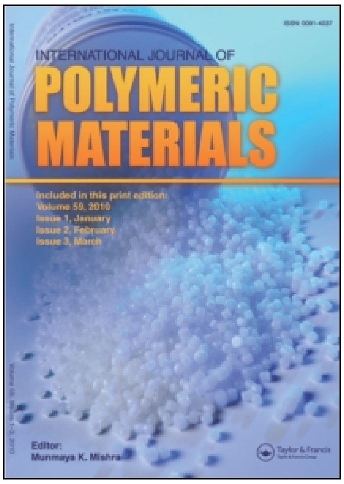

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Service Performance of Polymeric Materials: Prediction from Short-term Tests

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Service Performance of Polymeric Materials: Prediction from Short-term Tests

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Service performance seems to be the ultimate test of successful synthesis, processing, characterization and testing of polymeric materials. Viscoelasticity and the time dependence of mechanical properties can be considered as a nuisance, but in fact they provide us with the capability of prediction of long-term performance in service on the basis of short-term tests. The material characteristics and their influence on long-term life prediction are evaluated using two concepts, the cooperative response of the material and the chain relaxation capability (CRC). We show quantitative predictions using the time–temperature correspondence, time–strain correspondence, frequency-temperature correspondence, stress–time correspondence and the slow crack propagation on the basis of these concepts. The predictions include the use of a generalized temperature shift factor a_T formula. Our formula includes the W-L-F equation of 1955 as a special case and has a much larger range of applications. Our stress shift factor a_σ equation provides a prediction tool for a phenomenon demonstrated experimentally already in 1948.

Keywords: Polymer service performance; time dependence of mechanical properties; viscoelasticity; correspondence principles; shift factor

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1. INTRODUCTION

Service performance plays a special role in polymer science and engineering (PSE). The best synthesis, careful processing, detailed characterization, *etc.*, will not help if the resulting component will fail prematurely.

Metals and ceramics are in general much easier to deal with than polymers because of relative absence of dependence of their mechanical properties on time t in broad ranges of temperature T. The dependence of polymer properties on t can be considered a nuisance, or else it can be considered an opportunity. We shall adopt this latter point of view.

The approach used by the present team of authors makes extensive use of the notion of free volume v^f. That notion was already discussed by Kuhn in 1934 [1]. The importance of v^f for thermophysical properties of polymers (and not only) has been demonstrated quantitatively by Flory [2, 3]. The importance of the same concept for mechanical properties of viscoelastic materials has been demonstrated already in the 1950-ies by Ferry and his colleagues [4]. However, numerical predictions from the equations of Ferry and coworkers were satisfactory only in a limited number of cases. This prompted some researchers to abandon the quantitative aspect and use the free volume concept for qualitative (so as not to say hand-waving) arguments only. In fact, since the work of Ferry, equations with distinctly better prediction capabilities have been developed. The present paper describes some of these results.

Our approach involves two important assumptions. First, the response of the material to an external mechanical force is treated as a *collective* rather than individual reaction [5–9] of atoms, ions, polymer chain segments and possibly other entities at the same level. The other, also elaborated by one of us [10, 11], is based on the concept of the chain relaxation capability (CRC). In the following we shall see how these concepts – in conjuction with the seminal work of Flory and Ferry – are applied to solve specific problems. As already intimated, in the present context by problem solving we shall mostly mean providing equations with predictive powers.

2. CHAIN RELAXATION *vs.* DESTRUCTIVE PROCESSES

We can write a general equation [10, 11]

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

where U is the energy furnished from the outside (by a force) which at a given time has not yet been spent one way or the other; U_b (b for bond breaking) at the same time has been spent on destructive processes (such as crack formation or propagation); U_r at the given times has been dissipated, that is spent on non-destructive processes. Since dissipation in a viscoelastic material is largely related to relaxational processes, the subscript r stands for relaxation. The quantities in Eq. (1) may refer to the material as a whole, but it is usually more convenient to take them per unit weight of polymer such as 1 g.

Equation (1) provides us with the separation between destructive and non-destructive absorption and use of the external energy. Since at long times U_0 goes down to zero, only U_b and U_r remain. U_r is related to the chain relaxation capability (CRC). We define [10] CRC as the amount of external energy dissipated by relaxation in a unit of time per unit weight of polymer. In the following we shall use the abbrevation CRC for the concept and the symbol U_{CRC} for the respective amount of energy. Thus, at a given time t

$$U_r = \int_0^t U_{\text{CRC}}\, dt \tag{2}$$

The utility of the definition of CRC is not necessarily obvious. We note, therefore, that it takes approximately 1000 times more energy to break a primary chemical bond, what corresponds to U_b and to crack propagation, than to execute a conformational rearrangement. There is an important consequence of the above statements [10, 11]: relaxational processes have priority in the utilization of external energy. This is very convenient for us. It is only the excess energy – which cannot be dissipated by relaxational processes – which goes into destructive processes.

To have first a qualitative idea of the occurrence of relaxation, let us make a short list of typical processes which absorb energy by relaxing the polymeric chains. We should name at least: transmission of energy across the chain producing intensified vibrations of the segments; a somewhat similar transmission of energy from a given chain to its neighbors where "pure" segmental motions as well as entanglements play a role; conformational rearrangements in the chains; and elastic energy storage resulting from bond stretching and angle changes. None of the factors named can be neglected. For instance, Moe and Ediger [12] simulated local dynamics in polyisoprene in vacuum, solution and melt and concluded that substantial C—H vector relaxation results from coupled small amplitude motions of groups of adjacent torsions which do not involve conformational transitions.

3. FREE VOLUME AND ITS ROLE

To obtain relations usable for numerical calculations, first we have to quantify the free volume. We need it because a larger free volume creates a larger manoeuvering ability of the chains – and therefore a higher CRC. We shall use specific quantities (typically per 1 g). Then

$$v = v^* + v^f \tag{3}$$

where v is the total specific volume and v^* is the characteristic (incompressible, hard-core) volume. The last two names are based on the qualitative picture of applying an infinitely high pressure and zero thermodynamic temperature so that all free volume is "squeezed out" and only v^* remains. Some people like to work instead with the reduced volume defined as

$$\tilde{v} = v/v^* = 1 + v^f/v^* \tag{4}$$

We also need two more reduced parameters:

$$\tilde{P} = P/P^* \quad \text{and} \quad \tilde{T} = T/T^* \tag{5}$$

Here P denotes pressure and T (thermodynamic) temperature; P^* and T^* are, like v^*, characteristic (hard-core) parameters for a given material. T^* constitutes a measure of the strength of interactions in the material. P^* is a complicated function of the interactions and of the material structure represented by the binary radial distribution function $g(R)$ [13].

Equations (3)–(5) can only be used in conjunction with a specific equation of state of the general form $\tilde{P} = \tilde{P}(\tilde{v}, \tilde{T})$. Consistently, we have good results [14–17] by using the Hartmann equation of state [18–20].

$$\tilde{P}\tilde{v}^5 = \tilde{T}^{3/2} - \ln \tilde{v} \tag{6}$$

Since experiments are often conducted at the atmospheric pressure $P \approx 0.1\ \mathrm{J \cdot cm^{-3}}$, then the term containing P in Eq. (4) is negligible, and we have simply

$$\tilde{v} = \exp[\tilde{T}^{3/2}] \tag{7}$$

To connect free volume with the mechanical properties and with CRC, we now use [10, 11] the Doolittle equation

$$\ln \eta = \ln A' + Bv^*/v^f \tag{8}$$

where η is the viscosity. With the above set of equations we are now ready to deal with specific problems.

4. THE CORRESPONDENCE OF TIME AND TEMPERATURE

This principle has been extensively discussed by Ferry [4]. We discuss, therefore, its basis only briefly, but cover in more detail the recent capabilities of making accurate predictions using the principle.

To see how the principle works, consider a conformational change in the chain at the room temperature so fast that we cannot follow it experimentally. As stated above, processes inside polymeric materials require free volume v^f. By lowering the temperature, we decrease the amount of free volume; eventually the process under investigation will be slowed down to such an extent that we shall be able to measure it. More important for our predictive capabilities is often the opposite direction. Instead of performing experiments for a long time at room temperature, we can heat the specimen, thus produce higher v^f, and capture in, say, 10 hours a series of events which otherwise would take 50 years.

Given this situation, we can perform experiments isothermally at a number of temperatues. There is one temperature of particular interest, say 20°C. There is at least one parameter of particular interest, say the tensile compliance D. The compliance of viscoelastic materials depends on time, that is

$$D(t) = \varepsilon(t)/\sigma = E^{-1}(t) \tag{9}$$

where ε is the engineering strain, σ the engineering stress and E the tensile modulus. We create a large diagram of $D = D(t)$, or more often of $\log D = \log D(\log t)$. In the present case we start with the results at 20°C, and then put results at all other temperatures so that they would build a single curve; the result is called the master curve for 20°C. The respective shifting distance, known as the shift factor a_T, is different for each temperature; here $a_T(20°\mathrm{C}) = 1$ by definition. In other words

$$D(t, T; \sigma = \mathrm{const}) = D(t/a_T,\ T_{\mathrm{ref}};\ \sigma = \mathrm{const}) \tag{10}$$

where T_{ref} is the temperature to which the master curve pertains.

By using the correspondence principle one can predict the behavior over, say, 16 decades of time from experiments such that each was made over four decades only. However, unless an equation for calculation of the temperature shift factor as a function of temperature $a_T(T)$ is available, fairly extensive experimentation is necessary. The principle has been known for decades, and alaready in 1955 Williams, Landel and Ferry (WLF) [21] developed a pioneering $a_T(T)$ formula. Unfortunately, the WLF equation is usable only in a limited temperature range above the glass transition temperature T_g, namely up to $T_g + 50\,\mathrm{K}$ or so. Therefore, Van Krevelen [22] recommended for $T \leq T_g$ a different equation. However, calculations – including ours [10, 16] – show that the other equation is not reliable either. By using the Doolittle Eq. (8), one of us [10, 11] derived the following formula:

$$\ln a_T = A + B/(\tilde{v} - 1) \tag{11}$$

where A is related to A' in Eq. (8) while B is the same. Equation (11) is fairly general, applicable below and above T_g. We shall use it together with the Hartmann Eq. (6), or its simplified form Eq. (7).

To put the W-L-F equation into perspective, let us assume that $\tilde{v}^{-1} = \tilde{v}_{\mathrm{ref}}^{-1} - f(T - T_{\mathrm{ref}})$, where f is a constant. This assumption has no basis whatsoever. However, substituting it into Eq. (11) we obtain the W-L-F formula as a special case. It so happened that Williams, Landel and Ferry worked (using our terminology) with $\tilde{v}^{-1}$; apparently in default of information they have assumed a linear relationship. In small intervals of an independent variable almost any assumption wold work. Therefore, fitting f to experimental data, one can obtain reasonable results in small temperature ranges. It is clear from the above why the W-L-F equation works only in small temperature ranges.

5. THE CORRESPONDENCE OF TIME AND STRAIN

To improve mechanical properties of plastics for automobile and other applications, we have developed a procedure of solidification by hot drawing from a highly deformed melt (Sodem) [16]. To describe such a process, we need the draw ratio $\lambda = (\varepsilon + 1)$. To predict the properties of materials obtained using Sodem, we have generalized [16] Eq. (11) – so as to have the shift factor a_T as a function of both the draw ratio and temperature:

$$\ln a_T = 1/[a + c\lambda] + B/(\tilde{v} - 1) \tag{12}$$

Clearly the first parameter in Eq. (11) is now $A = 1/[a + c\lambda]$; a and c are constants for a given material independent of the degree of orientation and of temperature. The denominator of the first term in Eq. (12) reflects the fact that a deformed material with $\lambda > 1$ has a smaller number of conformational states available to its chains than the undeformed one. The effect of varying λ is taken into account also in the second term in Eq. (12), albeit implicitely. To calculate $\tilde{v}$, we use Eqs. (6) or (7) together with Eqs. (4) and (5). Since T^* depends on the strength of intersegmental interactions, which in turn vary with λ, we use

$$T^* = f_0 + f_1\lambda + f_2\lambda^2 \tag{13}$$

where the f_i parameters are constants for a given polymer [16]. We now provide in Figure 1 just one example of the application of Eq. (12),

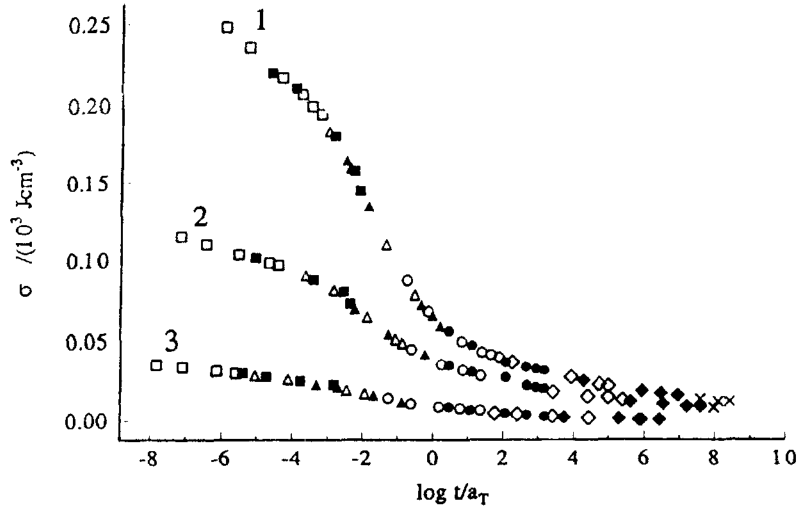

FIGURE 1 Master stress relaxation curves for HDPE of σ *vs.* t/a_T at the reference temperature $T = 313.2$ K (= 40°C), the constant tensile strain $\varepsilon = 0.025$ and at different values of the draw ratio: $\lambda = 12.2$ in the top (1) curve; $\lambda = 5.5$ in the middle (2) curve; and the material without predeformation ($\lambda = 1$) in the bottom (3) curve. The symbols pertaining to the experiment temperatures are the same in all three curves: □ for − 50°C; ■ for − 30°C; △ for − 10°C; ▲ for 0°C; ○ for + 20°C; ● for + 40°C; ◇ for + 60°C; ◆ for + 80°C; and × for + 100°C. The vertical coordinate is the tensile stress σ and the horizontal is log t/a_T; after [16].

for high density polyethylene (HDPE) subjected to the Sodem procedure. More examples of sucessful use of Eqs. (11) and (12) are provided in the papers already quoted.

6. THE CORRESPONDENCE OF FREQUENCY AND TEMPERATURE

Viscoelastic materials are also investigated by dynamic mechanical methods, usually applying an oscillating sinusoidal force. If the frequency ω of the oscillations is low, the chains have time to adjust better to the externally imposed field, just as they do at higher temperatures. Conversely, at high frequencies there is not enough time for rearrangements, a situation similar to having the free volume low and the temperature low also. We should also note that application of a high stress results in changes occurring faster than under a low stress. Increasing stress in creep produces a stronger reaction and thus causes an efffect comparable to increasing T. Thus, we can show the key "players in this game" as a series of approximate proportionalities:

$$\mathrm{CRC} \sim v^f \sim T \sim \sigma \sim \nu^{-1} \sim \rho^{-1} \tag{14}$$

where $\rho = v^{-1}$ is the mass density. Except for the appearance of stress σ, the other members of this series have been already displayed in [23]. The roles of stress will be discussed more in detail in the following Section.

We shall provide again just one example of the application of the temperature – frequency correspondence principle. In Figure 2 we show tan ∂ as a function of log a_T/ω for the same HDPE [16]. This time we are dealing with $\lambda = 12.2$ and with the atmospheric pressure, hence Eqs. (12), (13) and (7) are appropriate – and provide log a_T values in agreement with the experimental results within limits of the

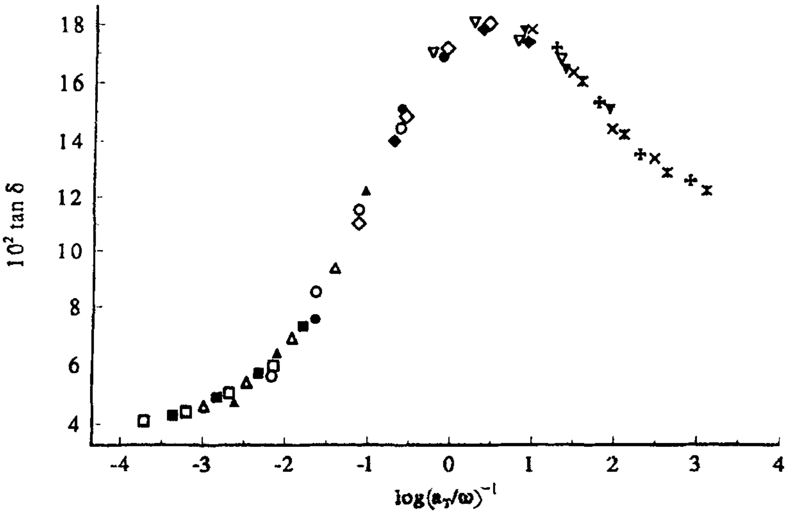

FIGURE 2 The master curve for HDPE of tan ∂ *vs.* log ω/a_T for 40°C and $\lambda = 12.2$ based on results at the following temperatures: 0°C (□); 10°C (■); 20°C (△); 30°C (▲); 40°C (○); 50°C (●); 60°C (◇); 70°C (◆); 80°C (▽); 90°C (▼); 100°C (×); 110°C (∗) 120°C (+); after [16].

experimental accuracy. We see that the existence of the maximum does not affect the applicability of the correspondence principle. Similar results have been obtained for other values of λ; for $\lambda = 1$ there is no maximum.

7. THE CORRESPONDENCE OF STRESS AND TIME

The proportionality (14) tells us that the stress level σ also affects CRC. We now consider creep when σ is kept constant while we are measuring strain ε as a function of time at $T = \text{const}$.

Already in 1948 O'Shaughnessy reported on work started he says in 1945: compliance values of rayon from creep experiments for different levels of stress σ "will fall on a single locus when plotted against time or a function of time" [24]. This was followed by more studies later on, including that by Urzhumtsev and one of us in 1968 [25].

Using the concepts described briefly in Sections 1–3, we have derived a quantitative relationship for the correspondence between stress and time. Details of the derivation will be provided elsewhere; the result is

$$\ln a_\sigma = \ln\,[v(\sigma)/v_{\text{ref}}] + B[(\tilde{v} - 1)^{-1} - (\tilde{v}_{\text{ref}} - 1)^{-1}] + F(\delta) \qquad (15)$$

where $v_{\text{ref}} = v(\sigma_{\text{ref}}, T_{\text{ref}})$, B is the Dolittle constant as before, while $F(\delta)$ is a function representing the effects of varying stress on the chain conformations and structure of the material.

For brevity we provide again just one example of application of our formula (15). The material is a polymer liquid crystal (PLC), namely PET/0.6PHB, where PET is poly(ethylene terephthalate), PHB is *p*-hydroxybenzoic acid while 0.6 is the mole fraction of the second component. The results are shown in Figure 3. It is clear that stress can serve equally well as temperature for the achievement of our title objective: prediction of long-term behavior from short-term tests.

The equivalence principles do not always work. However, their application range seems wider than generally believed. Some researchers who find that the W-L-F equation does not work conclude that the principles are not applicable. Historically W-L-F was the first

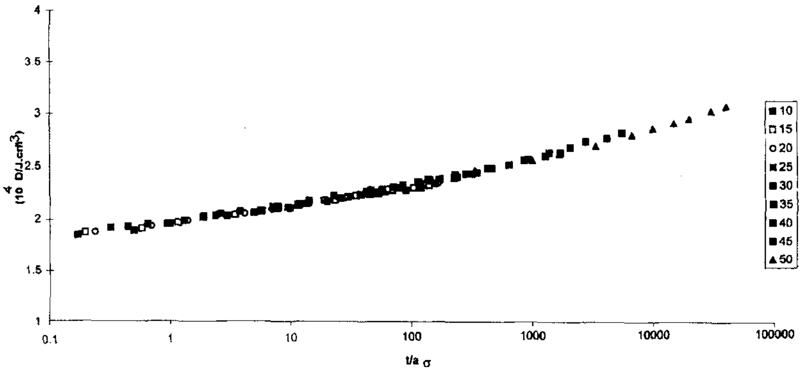

FIGURE 3 The master curve for PET/0.6PHB of compliance D *vs.* t/a_σ for the $\sigma_{\text{ref}} = 30\,\text{J}\cdot\text{cm}^{-3}$. Points are experimental values, with different symbols pertaining to different stress levesl (values in $\text{J}\cdot\text{cm}^{-3}$ for each symbol explained in the insert); the broken curve is calculated by using Eq. (15).

attempt to convert the time-temperature equivalence into a quantitative statement, but it is good that we now have equations with a much wider application range.

The principles discussed in this and in the preceding Sections can be connected pairwise, or perhaps all together. Moreover, they do not exhaust the possible list of equivalence principles. We are pursuing work along these directions as well.

8. SLOW CRACK PROPAGATION

We shall now discuss an example of applying the concepts defined in the beginning to fracture mechanics (FM). We shall deal with slow crack propagation (SCP), a "quiet" and insidious process. The crack propagation rate dh/dt, where h is the crack length, might be, say, only 1 mm per month. An observation for instance two weeks after installing a polymeric component might reveal nothing.

Experimentalists customarily present the dh/dt rates as a function of the logarithmic stress intensity factor $\log K_I$; K_I is defined as

$$K_I = \alpha^* \pi^{1/2} \sigma h^{1/2} \tag{16}$$

The factor characterizes the stress distribution field near the crack tip. The Roman one, 1, refers to the opening or tensile mode of crack extension; α^* is a geometric factor appropriate to a particular crack and component shape. For an infinite plate in plane stress, the geometric factor $\alpha^* = 1$. For other geometries there exist tabulations of α^* values [26]. Apart from K_I, there exists also the stress concentration factor K_t. Boths factors have similar symbols, similar names, and are expressed in terms of the same quantities; unfortunately, the terminology is so entrenched that we would not succeed trying to change their names and/or symbols.

The problem consisted in deriving an equation relating the crack propagation rate dh/dt to K_I. It was solved [23] by using the CRC approach in conjunction with the following FM equation due to Griffith:

$$\sigma_{cr} = (2\Gamma E/\pi h)^{1/2} \tag{17}$$

Here σ_{cr} is the stress level at and above which the crack will propagate; Γ is the surface energy per unit area; E is the elastic modulus; h has been defined before, strictly speaking it pertains to an internal crack of length $2h$ or a surface crack of depth h. Thus, if the actual stress imposed $\sigma < \sigma_{cr}$, the material will sustain that stress without the crack growing. The equation is identical for both constant load and constant displacement conditions, hence it should work also for any intermediate conditions.

Our problem is different than that of Griffith since we need to know whether the crack length h is below a certain critical value, call it h_{cr}, so that the crack will not propagate [23]. We therefore reformulate the Griffith Eq. (17) as

$$h_{cr} = 2\Gamma E/\pi\sigma^2 \tag{18}$$

Now we know that the crack will propagate only when $h > h_{cr}$. This not only is a consequence of the CRC concept, but also is supported by molecular dynamics (MD) computer simulations [27, 28] showing the existence of a crossover from the force field region dominated by chain relaxation to one in which crack propagation occurs.

By definition, notches with $h < h_{cr}$ do not cause crack propagation. Therefore, it was only natural to assume

$$dh/dt = \beta(h - h_{cr}) \qquad \text{for } h \geq h_{cr} \tag{19}$$

where β is a time-independent proportionality factor, characteristic for a material since it depends on CRC. Using Eqs. (18) and (19), the following equation [23] has been derived:

$$\log K_I = 1/2 \cdot \log(\alpha^{*2} 2\Gamma E) + (1/2) \cdot \log[1 + (1/\beta h_{cr}) \cdot dh/dt] \tag{20}$$

Equation (20) provides the connection between values od K_I and dh/dt which can be determined experimentally. In the derivation both the stress level σ and the initial crack length h_0 were used, but these quantities canceled out. – The result that the crack propagation rate is independent of both was not expected. However, the experimental results support Eq. (20). An example is shown in Figure 4 for polyethylenes manufactured by Hoechst and studied under uniaxial tension in water medium for 60°C. Each symbol pertains to a different stress

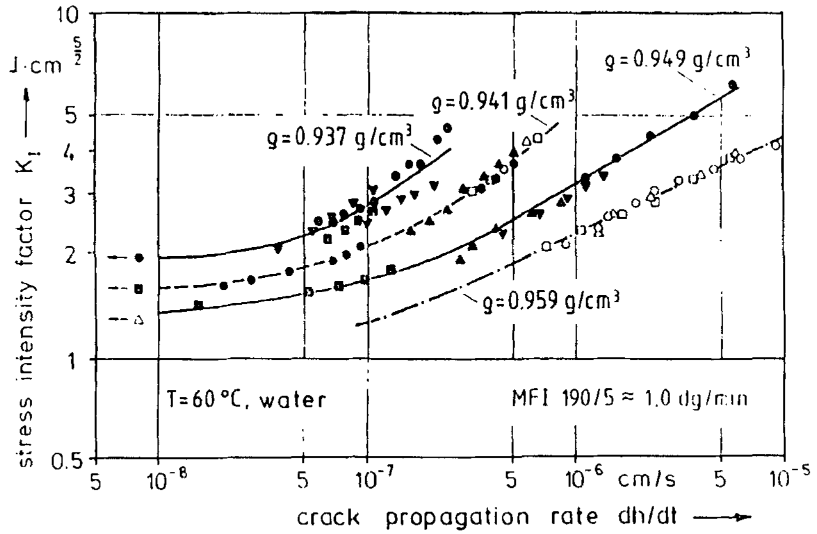

FIGURE 4 Stress intensity factor K_I as a function of crack propagation rate *dh/dt* for polyethylene specimens of varying density. Uniaxial tension in water at 60°C. Each symbol pertains to a different stress level and initial crack length. Full curves calculated from Eq. (20). After [23].

level and a different original notch length. It is clear that all polyethylenes with the same density form a common curve. Moreover, we see that a lower density, that is higher v^f, results in a lower crack propagation rate. This is a direct confirmation of the role of free volume discussed above in Section 3

In the beginning of this Section we have mentioned the crack propagation rate dh/dt = 1 mm/month. The lowest crack propagation rate measured and shown in Figure 4 is $dh/dt = 10^{-8}$ cm.s^{-1}; this is equal to 0.315 cm/year. The crack does grow – what give us an idea about the usefulness of Eq. (20).

9. PREDICTION OF OTHER SERVICE PERFORMANCE PARAMETERS

There are other parameters pertinent to the service performance which can be predicted from short-term tests. We shall briefly mention some of them and provide references in which details can be found.

Stress relaxation is typically measured in the uniaxial mode in a specimen or part kept at constant deformation. It is a thermally activated process, hence the relaxational processes (see the end of Section 2 for the constituents of CRC) require energy from somewhere. The relaxing stress usually settles on a level called the internal stress σ_i. The stress relaxation curves for metals, ceramics and polymers all have similar shapes. This applies not only to flexible polymers, but also to Nomex^{TM} (poly(*m*-phenylene isophthalamide), Kevlar^{TM} (poly (*p*-phenylene terephthalamide)) and polypropylene fibers [29], One of us [5–9] has assumed that the reason for this common behavior is the collective character of the relaxation process. Atoms (in metals) or polymer chain segments relax collectively as clusters rather than individually. A distribution of cluster sizes has been defined. The theory predicts the experimental stress relaxation curves. Computer modeling of cluster formation largely confirms the theoretical cluster size distribution [30]. Even more importantly, molecular dynamics computer simulation of stress relaxation for metals [31] and polymers [32] shows the collective character of stress relaxation and produces curves analogous to experimental ones. Thus, there is a convergence of experiments, theory and computer simulations.

In the preceding Section we have discussed slow crack propagation. There exists also rapid crack propagation (RCP) a vastly different phenomenon, with dh/dt values between 100 and 400 m/s (= between 300 and 1400 feet/s). It occurs usually in pressurized fuel plastic pipes and is accompanied by explosion of the fuel. A criterion based on the Charpy impact test has been developed using the CRC concept: RCP will not occur in materials with impact energy higher than a certain limiting value [33].

Finally, we shall note the ductile-brittle impact transition temperature T_l. A method of prediction of T_l from the stress concentration factor (a quantity similar to but distinct from the stress intensity factor defined by Eq. (16)) has been developed. The procedure involves the use of the temperature shift factor Eq. (11) and gives good results [11].

Acknowledgments

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