

AN EVALUATION OF A FREE VOLUME REPRESENTATION FOR VISCOELASTIC PROPERTIES

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Abstract—Creep data for two different polyethylenes which were not amenable to master curve formation have been adjusted using a simple free volume model to produce master curves characterizing creep at the limit of zero stress. The validity of these master curves has been checked against results from relaxation tests which are available for the same two materials.

INTRODUCTION

It has been recognized that “free volume” plays a fundamental role in viscoelastic response for polymeric materials (Ferry, 1980). A change in the free volume influences the mobility of the material and directly impacts upon its time-dependence. Volume change consequent to temperature change is the most frequently examined situation, but free volume effects associated with hydrostatic pressure (Fillers and Tschoegl, 1977), moisture absorption (Knauss and Kenner, 1980), and uniaxial stress relaxation (Knauss and Emri, 1981, 1987) have also been studied. The influence of free volume is usually accommodated through the introduction of a reduced time.

An informative illustration of the interplay between free volume and the classification of materials as linearly or nonlinearly viscoelastic is available for polyvinyl acetate. Torsion creep tests of this material (in which volume is conserved) show it to be linear (Kenner, 1978) and it is also found to be amenable to classical time-temperature superposition (Knaus and Kenner, 1980). However, tensile stress relaxation tests for the same polyvinyl acetate clearly demonstrate significantly nonlinear behavior; the material continues to be amenable to simple horizontal shifting to form master stress relaxation curves (Knauss and Emri, 1981, 1987). The nonlinearity observed in the stress relaxation behavior was found to be reconcilable if the influences of changes in the free volume on the reduced time was utilized.

If free volume is recognized as a factor in viscoelastic material characterization and classification, then obvious differences in characterizing tests must be considered. Thus, while uniaxial creep test and a relaxation test bear a reflective relationship to one another insofar as their origins in the theory of viscoelasticity, this relationship is lost if free volume changes are important. In a relaxation test after imposition of initial strain, the volume stays constant if time-dependent transverse deformation does not occur. In a creep test, the volume and, hence, the material's mobility are changing continuously if the material does not behave incompressibly. The varying mobility in a creep test complicates the interpretation of the results. For shear experiments in which volume is preserved regardless of material behavior (other than a requirement of isotropy), the reflective relationship between creep compliance and relaxation modulus would be expected to remain in force.

Both tensile creep and tensile relaxation data for polyethylene have been gathered in the authors' laboratory. In the case of relaxation data, bidirectional shifting was capable of generating a highly coherent master curve, but in the case of the creep data this was not

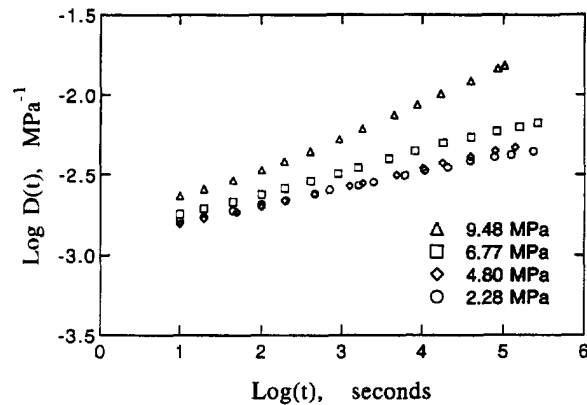


Fig. 1. Creep compliance data for PE2306 at several stress levels and 22°C.

possible. The objective of this study was to evaluate the ability of a simple model based on free volume to effect reconciliation of the two data sets.

Usually a single set of viscoelastic data, e.g. creep compliance or stress relaxation data, are examined and the question of consistency of the data beyond, say, generation of a coherent master curve (or curves) from the single data set is not open to examination. In this paper an elementary approach to free volume as it pertains to uniaxial isothermal creep data has been applied to data for two different polyethylenes, one of medium density and one of high density. This permits the generation of creep master curves for infinitesimal stress. For the medium density material, stress relaxation data were extrapolated to infinitesimal strain. Standard techniques of linear viscoelasticity were then employed to invert the creep data for zero stress and thereby permit a direct comparison to the relaxation data. In an additional test of data consistency, a bidirectional shifting procedure, which has been broadly applied to polyethylene data, is used to shift the several isothermal and infinitesimal master curves.

CREEP DATA

Figure 1 presents creep compliance curves for a medium density polyethylene (PE) at ambient temperature for four different stress levels. This material will be identified by its ASTM designation as PE2306. Figure 2 presents creep compliance data for PE2306 at a stress of 4.80 MPa and four different temperatures. The complete data set (not all presented in Fig. 1 and 2) corresponded to a nominal test matrix of four temperatures and four stress levels; however, at the highest temperature of 80°C it was possible to acquire data only at the lowest stress level. These data were obtained in a program to study slow crack growth in PE gas distribution pipe materials (Kanninen *et al.*, 1990).

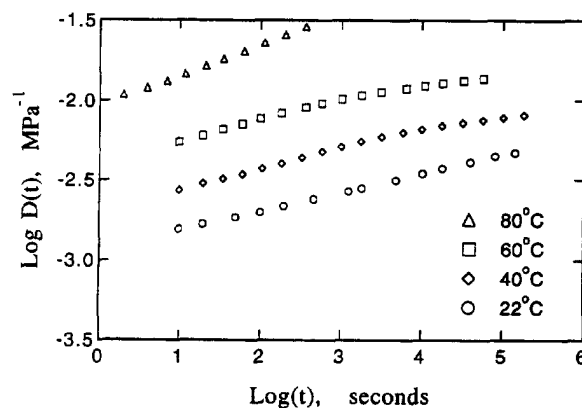


Fig. 2. Creep compliance data for PE2306 at several temperatures and 4.80 MPa.

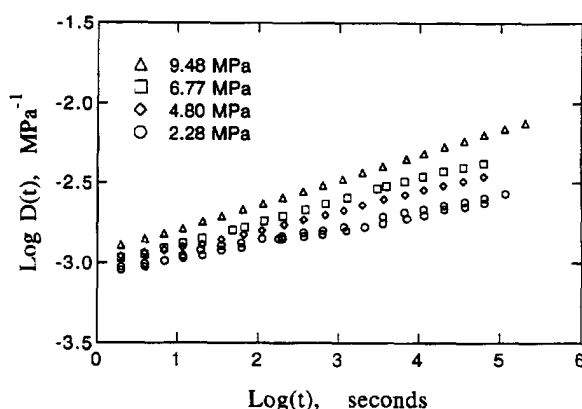


Fig. 3. Creep compliance data for PE3408 at several stress levels and 22°C.

It is clear from Fig. 1 that PE2306 is a nonlinearly viscoelastic material, i.e. the creep compliance is a function of the imposed stress. From Fig. 2 it is obvious that attempts to produce a coherent master creep compliance curve by horizontal shifting, vertical shifting or a combination of the two will not be fruitful.

Figures 3 and 4 present isothermal creep data for several stress levels and constant stress creep data for several temperatures, respectively, for a high density PE identified as PE3408. The matrix of test temperatures and stress levels used for PE2306 was also utilized here. For PE3408, it was only possible to gather 80°C data at the two lower stress levels. Figures 3 and 4 demonstrate that, as for PE2306, PE3408 is both nonlinearly viscoelastic and unamenable to master curve formation.

Replicate creep compliance curves are exhibited in Fig. 3 for PE3408 tested at 2.28 MPa. The difference between the two curves is less than 8%; this number also provides a conservative estimate of repeatability in the relaxation test data described below.

RELAXATION DATA

A series of relaxation tests on the same two polyethylenes has also been conducted (Popelar, 1989). It was found that coherent master curves could be formed using a combination of horizontal and vertical shifting, presumably because free volume remained fixed after initial loading. Master curves for imposed strain levels of 2.5, 5, 7.5 and 10% strain are presented in Fig. 5 for PE2306. As was illustrated by the creep data, the material is again seen to be nonlinearly viscoelastic. Similar master curves were generated for PE3408. The essential difference in the curves was that in the case of PE2306, distinct knees in all master curves (Fig. 5) aligned vertically, while for PE3408 this was not the case. This feature

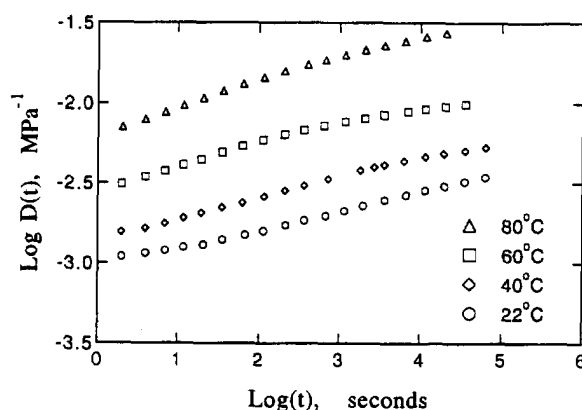


Fig. 4. Creep compliance data for PE3408 at several temperatures and 4.80 MPa.

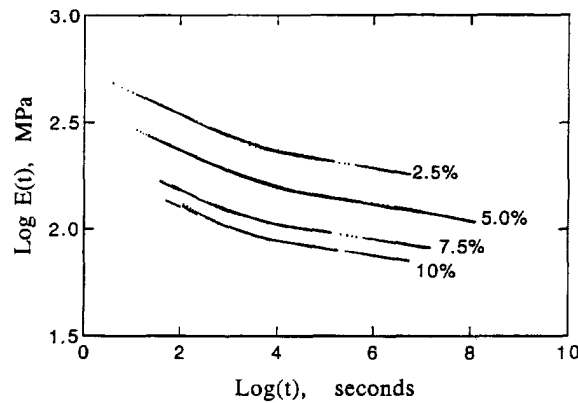


Fig. 5. Relaxation modulus master curves for PE2306 at several initial strain levels and 22°C.

of the PE2306 data permitted a simple representation of the strain dependence to be taken advantage of as discussed in the sequel.

FREE VOLUME CONTROLLED SHIFTING OF CREEP DATA

Ferry (1980) presents the Doolittle equation in the form

$$\log a = (B/2.303)(1/f - 1/f_0). \quad (1)$$

Here f is the free volume fraction and f_0 is this fraction at a reference state; B is a constant and a is the shift factor, i.e. the divisor by which time is scaled in shifting viscoelastic property data to reference conditions ($t \rightarrow t/a$). Following Knauss and Emri (1981) the free volume is written as

$$f = f_0 + \alpha \Delta T + \gamma \Delta c + \delta \varepsilon_{kk}. \quad (2)$$

The last three terms of eqn (2) represent the free volume contributions due to change in temperature T , absorbed solvent concentration c and dilatation ε_{kk} associated with stress. The coefficients α and γ are the coefficients of thermal and hygral (in the case where the solvent is water) expansion of free volume; the coefficient δ represents the fraction of dilatation ε_{kk} which is found as free volume. Writing eqn (2) in a discrete, as opposed to a differential form, requires that the coefficients α , γ and δ be independent of time.

Here interest is in isothermal and isohygral conditions. In the absence of more detailed information, it is assumed that the entirety of ε_{kk} occurs as free volume so that the coefficient δ is taken as unity. Clearly this represents an upper bound for δ . Within these conditions, the free volume is given by

$$f = f_0 + \varepsilon_{kk}. \quad (3)$$

For uniaxial creep, the dilatation ε_{kk} at any longitudinal strain ε_{11} will be given by

$$\varepsilon_{kk} = \varepsilon_{11}(1 - 2\nu). \quad (4)$$

Here ν is Poisson's ratio and ε_{11} is given by

$$\varepsilon_{11} = D(t, \sigma_0)\sigma_0 \quad (5)$$

where $D(t, \sigma_0)$ is the time- and stress-dependent creep compliance and σ_0 is the constant applied stress.

Equations (3)–(5) substituted into eqn (1) give

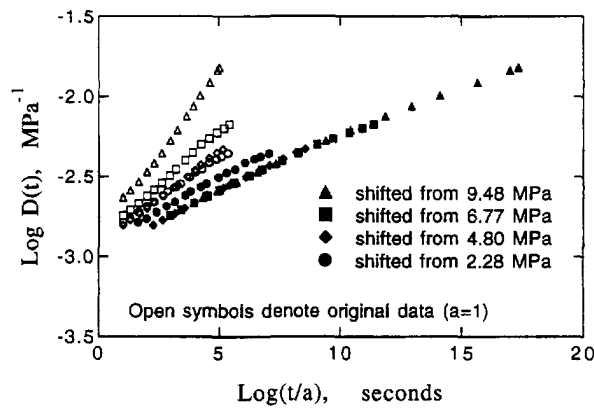


Fig. 6. Initial creep data and zero stress master curve for PE2306 at 22°C.

$$\log a = \frac{-B}{2.303 f_0} \left[\frac{1}{\frac{f_0}{\sigma_0(1-2\nu)D(t, \sigma_0)} + 1} \right] \quad (6)$$

Equation (6) shows that in a creep test, where deformation changes continually, the shift factor also changes steadily. This is in contrast to a relaxation test where (at least if ν can be taken constant) there is no time-dependent volume change subsequent to initial loading.

EVALUATION OF FREE VOLUME CONTROLLED SHIFTING FOR PE

Application of the time-dependent shift factor given by eqn (6) to the creep curves of Figs 1 and 3 *point by point* both reshapes and shifts these curves. The character of the reformation depends on the constant B and the reference free volume fraction f_0 (at the test temperature) as well as Poisson's ratio ν . In the present examination, an experimentally obtained value $\nu = 0.46$ (Popelar *et al.*, 1990) as well as the experimentally derived (engineering) creep compliance $D(t, \sigma_0)$ were used in eqn (6). B and f_0 were selected to generate best master curves, represented in Figs 6 and 7 for PE2306 and PE3408, respectively (solid symbols). The unshifted creep compliance curves (open symbols) are also shown in Figs 6 and 7 for comparison. The constant B was found to be 0.61 for both polyethylenes; similarly, f_0 was found for both materials to be equal to 0.011. Both of these values are consistent with reported estimates for these parameters (Ferry, 1980).

In Fig. 6 it is seen that three creep curves shifted quite satisfactorily while the curve representing the lowest stress did not. Examination of the initial data (Fig. 1) strongly suggests that the creep curve for 2.28 MPa is in error since it actually crosses over the 4.80

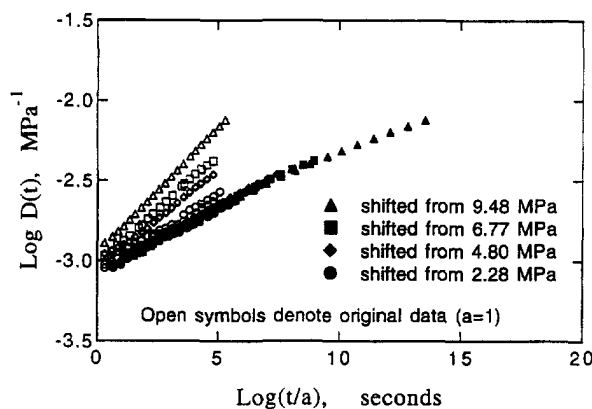


Fig. 7. Initial creep data and zero stress master curve for PE3408 at 22°C.

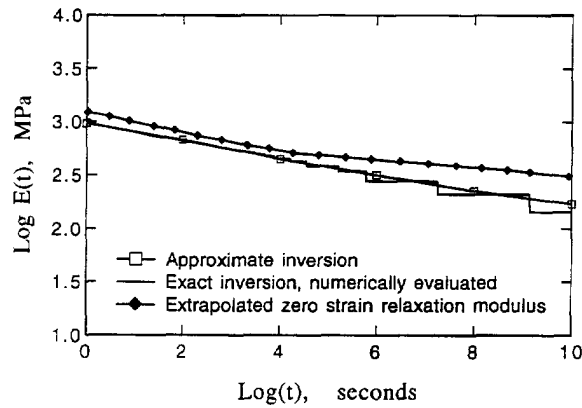


Fig. 8. Zero strain relaxation modulus.

MPa curve, which appears to be reasonably placed relative to the remaining curves in this set. For PE3408, all five curves (Fig. 3) shift to a single curve (Fig. 7) within the precision credited to the original experimental results.

The above process can be considered as a shifting of the antecedent creep curves to zero stress, i.e. the effect of stress-induced dilatation is removed from each curve point by point. Since this is the case, the master curves of Figs 6 and 7 are appropriate for infinitesimal linear viscoelasticity and thus may be inverted by classical means (Christensen, 1982) to produce relaxation curves at zero strain. The results of both the exact inversion (as carried out numerically) and an approximation given by Christensen (1982), are presented in Fig. 8.

The four isothermal master curves of Fig. 5 can be used to establish the nonlinear dependence of the relaxation modulus on the strain. This dependence can be extrapolated to a relaxation modulus at zero strain as detailed in Popelar *et al.* (1990) and this curve is also presented in Fig. 8. It is seen that good agreement is obtained between this curve (which originated with relaxation data) and the inverted zero stress curve (derived from creep data). In the case of the exact inversion, numerical limitations are responsible for the steps observed in the relaxation modulus curve at larger times.

The above manipulation of isothermal data at 22°C was also carried out for the elevated temperature data. It was found that the master curves generated from the 40°C, 60°C and 80°C data sets (i.e. master curves comparable to those presented in Figs 6 and 7) were increasingly less coherent. While space does not permit presentation of all these curves, Fig. 9 presents both the antecedent creep data and the master curve generated by the use of eqn (6) for PE3408 at 60°C. This plot is typical of other results for either of the two materials at the two higher test temperatures in that the coherence of the shifted curves at 2.28 and 4.80 MPa fails at the high-time ends of these curves.

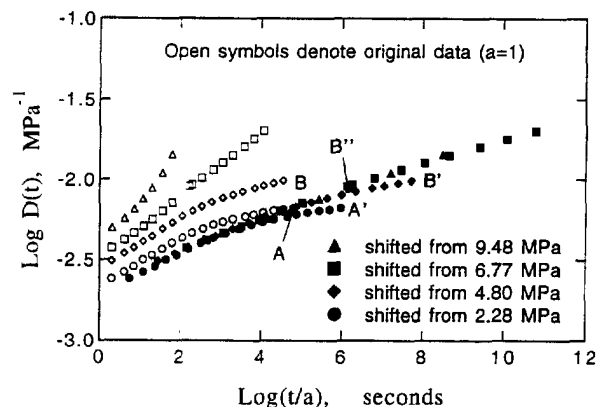


Fig. 9. Initial creep data and zero stress master curve for PE3408 at 60°C.

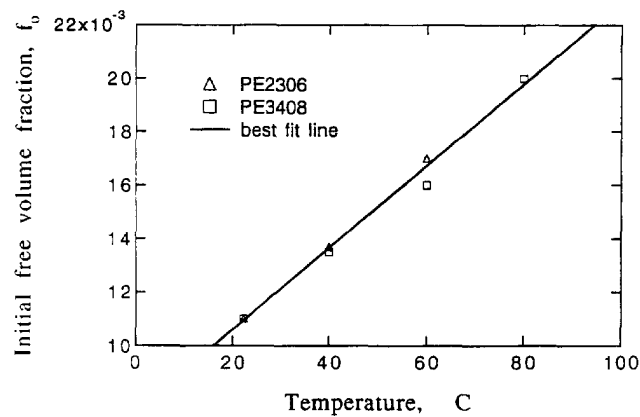


Fig. 10. Reference free volume fraction versus temperature.

In attempting to ascertain the source of this discrepancy, the following observations are made. First, the shifting was effected on the assumption that Poisson's ratio was constant. In fact, modest increases in Poisson's ratio were observed (Popelar et al., 1990); these were difficult to quantify because of limitations in the experimental precision for this measurement. In addition, softening of the PE at temperatures of 60°C and higher precluded this measurement altogether. Second, examination of Fig. 9 shows that the shifting is highly sensitive to the value of Poisson's ratio. This can be illustrated by considering the final data points for the unshifted 2.28 and 4.80 MPa data, labeled in Fig. 9 as points A and B, respectively. Were ν taken to be 0.5, these points would not shift at all, i.e. there would be no volume change during the creep test. In the case of point A, it happens that this would leave the point in concert with the other shifted data whereas the use of $\nu = 0.46$ moved the point of A'. In the case of point B, $\nu = 0.46$ produced point B'; calculation using eqn (6) shows that a value of $\nu = 0.477$ would move point B to point B'', i.e. into coincidence with the master curve. In view of the above two observations, it is concluded that discrepancies seen in the higher temperature master curves are associated with a temperature dependent increase of Poisson's ratio with time that is not accounted for by eqn (6).

A final observation supports this view. Since the best visual fit, empirically arrived at with the aid of the computer, determines the constant B as well as the quantity f_0 , consistency of these values must also be evaluated in assessing the validity of the master curves. Already noted for the room temperature data was the fact that B and f_0 in this case were consistent with previously reported values (Ferry, 1980). It proved to be the case that $B = 0.61$ (the previously obtained value) also provided the best fit of shifted elevated temperature data. The initial free volume fraction f_0 (empirically arrived at by selecting the "best" shift) for all data sets for both PE2306 and PE3408 is plotted as a function of temperature in Fig. 10. It is seen that this quantity is a linear function of temperature. This is consistent with a constant coefficient of thermal expansion, and the regularity exhibited by f_0 in Fig. 10 in concert with the constant value for B further supports the validity of the shifted curves. In fact, if the assumption is made that all volume change is free volume, the coefficient α in eqn (3) will be the cubical coefficient of thermal expansion. The slope of the linear fit in Fig. 10 then leads to a value for the linear coefficient of thermal expansion of $50 \times 10^{-6}/^\circ\text{C}$. This value compares favorably with a value of $67 \times 10^{-6}/^\circ\text{C}$ available from suppliers literature for PE3408. The fact that the value for the coefficient of thermal expansion as derived from Fig. 10 is less than the promulgated value is consistent with not all of the thermally induced volume increase being associated with free volume, as anticipated. Figures 11 and 12 present master curves arrived at as discussed above for PE2306 and PE3408, respectively, for all test temperatures.

In order to fully explore the efficacy of the above data manipulation, an additional consistency check can be made using the available data. This is to apply the bidirectional shifting functions developed for the relaxation tests to the creep curves of Figs 11 and 12. As noted by Tobolsky (1960), vertical shifting of PE data is necessary to account for the

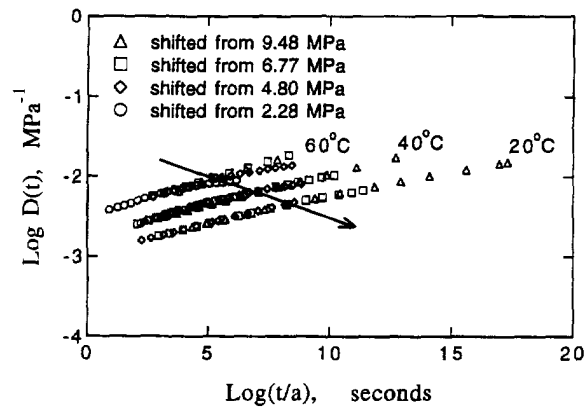


Fig. 11. Zero stress master creep curves for PE2306 at several temperatures.

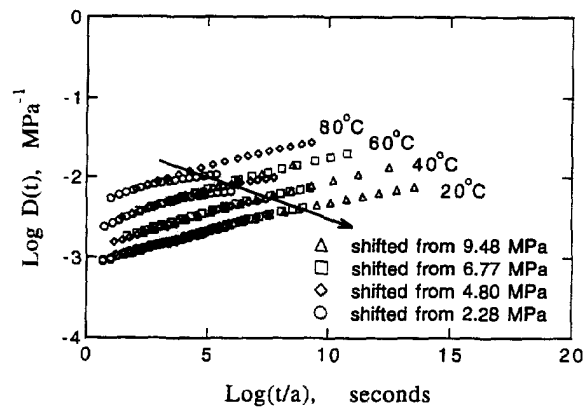


Fig. 12. Zero stress master creep curves for PE3408 at several temperatures.

influence of temperature changes on the degree of crystallinity that also influences its mechanical response. In earlier work (Popelar *et al.*, 1990) it was found that the horizontal and vertical shifting required to generate master curves from relaxation data were, to within experimental precision, identical for both the PE2306 and PE3408 materials. It was later demonstrated that, indeed, these shift functions appear to be applicable to all medium and high density polyethylenes (Popelar *et al.*, 1991). These horizontal and vertical shift functions are given by

$$a = \exp[-0.109(T - T_R)] \quad (7)$$

and

$$b = \exp[0.0116(T - T_R)], \quad (8)$$

respectively, where T is temperature (in °C) and T_R is an arbitrary reference temperature.

Bidirectional shifting of the master creep compliance curves of Figs 11 and 12 was effected by application of eqns (7) and (8). The results of this exercise are presented in Figs 13 and 14 for PE2306 and PE3408, respectively. The shifting does not coalesce the data set to a single coherent master curve. Nonetheless, the discrepancy, which amounts to approximately 0.2 decades vertically, is probably not excessive in view of the compound process employed to obtain it. It should also be noted that the direction of the shift [which is foreordained by eqns (7) and (8) and indicated by arrows in Figs 11 and 12], is consistent with that required to mesh the creep curves shown in these figures.

It is appropriate to remark that the shifting of isothermal data sets through use of eqn (6) was accomplished to meet the goal of achieving the best master curve at this level, i.e.

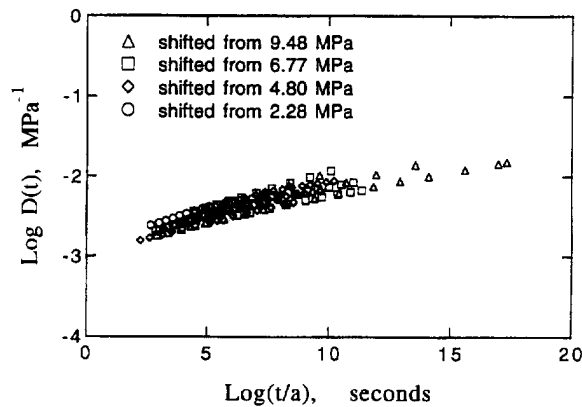


Fig. 13. Zero stress master creep curves for PE2306 shifted bidirectionally to a reference temperature of 22°C.

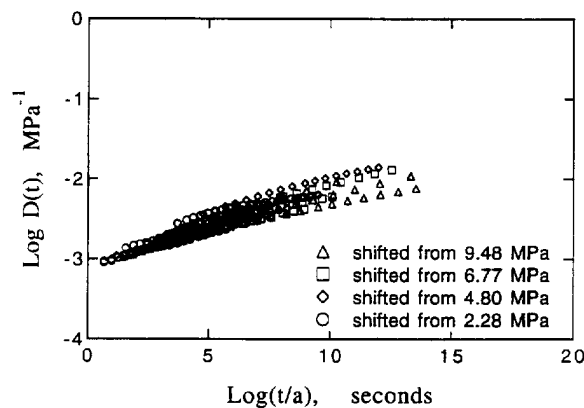


Fig. 14. Zero stress master creep curves for PE3408 shifted bidirectionally to a reference temperature of 22°C.

the smoothest curves as illustrated by Figs 6, 7 and 9. This process, as already discussed, determines the quantities B and f_0 . It seems likely, although as yet unexplored, that the process of shifting by eqn (6) could be modified to produce the best master curve at the level of Figs 13 and 14. While this would generate different values for B and f_0 as well as somewhat different fits at the level of Figs 6, 7 and 9, such refinement could be expected to improve the coherence of the master curves presented in Figs 13 and 14. It is felt that such secondary adjustments are probably not justified by the precision inherent in the experimental data.

CONCLUSIONS

Creep data have been adjusted to account for the change of free volume during time-dependent deformation at constant uniaxial stress. The adjustment was based on the assumption of a time-independent Poisson's ratio and its application to creep compliance data not initially amenable to master curve formation, produced generally coherent master curves for creep data at 22°C and 40°C. In the case of PE2306 at ambient temperature, the availability of a zero strain-stress relaxation curve permitted a check of the efficacy of the master creep curve obtained by free volume shifting. Good agreement was obtained.

For PE at 60°C and 80°C, examination of shifted creep data showed that in order for coherence to be attained, a sufficient condition is that Poisson's ratio not be constant, but rather increase during the creep test; such behavior would be in conformance with previous observations for the materials studied.

Another check of the free volume shifted creep compliance curves was mandated by the availability of bidirectional shift functions which have been found to be broadly

applicable for PE. Utilization of these shift functions was found to shift isothermal master curves in the direction required for optimal coherence; however, the amount of shifting proved to be somewhat short of that required for a coherent master curve.

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