Prediction of Long-Term Service Performance of Polymeric Materials From Short-Term Tests: Creep and Prediction of the Stress Shift Factor of a Longitudinal Polymer Liquid Crystal

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The material studied is a longitudinal polymer liquid crystal (PLC). The creep behavior of the PLC is examined in the region of nonlinear viscoelasticity. The creep compliance D curves at nine different stress σ levels, from 10 to 50 J.cm^{-3} at a constant temperature are determined and shifted along the log time axis for σ_{ref} = 10 J · cm^{-3} to produce the D versus t/a_σ master curve. A fairly general formula for stress shift factor a_σ based on free volume v^f and the chain relaxation capability (CRC) derived by one of the authors is applied. The formula predicts values that agree with the experimental ones within the limits of the experimental accuracy. Thus, experiments at several stress levels can serve for prediction of long-term behavior from short-term tests. The same value of the Doolittle constant B is obtained separately from temperature shift and stress shift experiments for the PLC.

1. INTRODUCTION

Prediction of long-term behavior on the basis of short-term tests is possibly one of the most important areas of polymer science and technology. Viscoelasticity, that is, time and temperature dependence of mechanical properties of polymers, might be considered an inconvenience. In fact, viscoelasticity provides us with the capability of long-term service performance prediction.

Since polymer liquid crystals (PLCs) have excellent mechanical, thermal and electrical properties, there are investigations of their alignments under a mechanical field or a magnetic field (1–4), their unusual phase behaviors (5–7), their blends (8, 9) and also their surface tensions (10–12). Usually, either longitudinal or comb PLCs are investigated; for a classification of PLCs see Brostow (13, 14). In this paper we shall discuss an equation derived by one of the authors for the correspondence between time and stress (TSC), which shall be used to predict long-term behavior of a PLC. It is a longitudinal PLC, with the LC sequences in the main chain and oriented along the chain backbone (15). That PLC forms four coexisting phases in its service temperature range (7).

Before discussing the application of the TSC, we shall give a brief summary of long-term predictions from short-term tests on the basis of correspondence principles, starting with the time-temperature correspondence (TTC) principle. From mechanical measurements made at several temperatures one can create a master curve for a chosen temperature T_{ref} extending over several decades of time (16–18). Temperature shift factor a_T or log a_T is used to shift the individual curves, thus producing the master curve. Already half a century ago a connection between morphology and TTC principle applicability was studied (19). The first attempt to predict quantitative long-term properties of amorphous polymers came from Williams, Landel and Ferry (WLF) in 1955. They provided a formula for $a_T(T)$ (20). Unless an $a_T(T)$ equation is available, quite extensive experimentation at a number of temperatures is necessary. However, as discussed by Ferry himself (16), the WLF equation is limited in its use range, expected to work above the glass transition temperature T_g, but not below T_g nor for temperatures $T > T_g + 50$ K. Moreover, there are semicrystalline viscoelastic materials to which TTC does apply but the specific form of the $a_T(T)$ relationship produced by WLF does not. Starting from

the Doolittle equation (21), one of the authors has derived the following formula (22, 23):

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

Equation 1 is applicable below and above T_g. Here $\tilde{v}$ is the reduced volume, which will be defined below; A and B are material constants; B is Doolittle viscosity constant relating viscosity η to free volume v^f. A primitive and unfounded assumption reduces the general *Eq 1* to the WLF equation. Work on several kinds of polymers, including various polyethylenes (24, 25), a number of polyurethanes (26) as well as a PLC (27, 18) which contains four phases in its service temperature range (7), shows that *Eq 1* works well and TTC is applicable if only a reliable equation of state is available (see below).

Equation 1 involves two important assumptions. First, the response of the material to an external mechanical force is treated as a collective rather than individual reaction of polymer chain segments. This has been assumed by Kubat (28–30) to explain experimental stress relaxation curves and confirmed by molecular dynamics computer simulations (31, 32). The other assumption is the adoption of the concept of the chain relaxation capability (CRC) (21, 22). CRC can be defined as the amount of external energy dissipated by relaxation in a unit of time per unit weight of polymer. *Equation 1* has to be used in conjunction with an equation of state. The next section covers the connection of v^f to CRC, an equation of state used with *Eq 1* as well as the present theory, and also the effect of the stress level on CRC.

2. THEORY USED

2.1. Free Volume and Its Role

Let us list important processes that occur in a polymeric material when a mechanical force is applied to it: transmission of energy across a chain and to its neighbors where 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. All these processes inside the polymeric material require v^f. The larger v^f creates a larger maneuvering ability of the chains and thus higher CRC (15, 22). The v^f can be then defined (33) as

$$v^f = v - v^* \quad (2)$$

where v is the total specific volume (for instance in cm^3g^{-1}) and v^* is the characteristic (incompressible or hard-core) volume corresponding to a very high pressure and zero thermodynamic temperature. The reduced volume $\tilde{v}$ and the other reduced parameters are defined as follows:

$$\tilde{v} = v/v^*; \quad \tilde{T} = T/T^*; \quad \tilde{P} = P/P^* \quad (3)$$

where T and P are the thermodynamic temperature and pressure; T^* and P^* are the characteristic (hard-core) parameters for a given material. The former is related to the strength of interactions in the material. P^* is a complicated function of the intermolecular interactions and of the material structure represented by the binary radial distribution function g(R) (34).

2.2. The Equation of State

Equations 1–3 can be used only in conjunction with a specific equation of state. Good results have been obtained repetitively (26, 24, 27, 35, 18, 25) by using the Hartmann equation (36, 37), which is valid for both polymer melts and solids:

$$\tilde{P}\,\tilde{v}^5 = \tilde{T}^{3/2} - \ln \tilde{v} \quad (4)$$

2.3. The Correspondence of Stress and Time

We know that the stress level σ affects free volume and thus CRC. As early as 1948, O'Shaughnessy reported that compliance values of rayon from creep experiments for different stress levels can coalesce into a single master curve when plotted against time or a function of time (38). Later, more studies were performed, as discussed in Goldman's book (17). However, a reliable formula for the stress shift factor $a\sigma$ as a function of stress σ to predict long-term behavior of polymers was not available. Now, one of the authors has derived such a formula using the CRC concept; details of the derivation are provided elsewhere (15). The resulting equation is

$$\ln a_\sigma = \ln\left[v(\sigma)/v_{ref}\right] + B[(\tilde{v} - 1)^{-1} - (\tilde{v}_{ref} - 1)^{-1}] + C(\sigma - \sigma_{ref}) \quad (5)$$

where $v_{ref} = v(\sigma_{ref}, T_{ref})$, B is the Doolittle constant as before, while C is a constant representing the effects of varying stress on the chain conformations and structure of the material. Positive C corresponds to a viscosity increase under stress. Thus, experiments at several stress levels can serve for prediction of long-term behavior in a similar way as experiments at several temperatures are used.

The objective of the present paper is to test the validity of *Eq 5*. As already noted, PLCs form multiphase systems. Our test is based on results for a longitudinal PLC. If this would provide satisfactory results, one or two phase systems should then obey *Eq 5* even more easily.

3. EXPERIMENTAL

The stress dependence of the creep compliance of PET/0.6PHB has been investigated at the room temperature 20 ± 1°C. Here PET = poly(ethylene terephthalate), PHB = p-hydroxybenzoic acid (LC); 0.6 = the mole fraction of PHB. The PLC used in the study has already been well characterized in previous papers (7, 39). Experimental creep curves were measured for 2 h at nine stress levels in the range from 10 to 50 $J \cdot cm^{-3}$ with 5 $J \cdot cm^{-3}$ intervals by using an MTS universal testing machine (1 $J \cdot cm^{-3}$ = 1 MPa). The elongation was determined with the strain gauge, MTS Model 632.11 c-20, as reported by Brostow *et al.* (18).

4. EXPERIMENTAL RESULTS

The time dependence of creep compliance D as a function of logarithmic time at room temperature has been investigated at several stress values. *Figure 1* shows D versus log time curves at different stress levels in the range from 10 to 50 J · cm^{-3}. As reported previously (27), isochronous stress-strain curves at t = 0 (the strain at the loading time) are linear up to 30 J · cm^{-3}. Then a deviation from linearity is observed, first only slight, but the effect increases with increasing stress level. Moreover, significant nonlinear viscoelasticity was observed at t = 120 min (total strain before unloading). As an approximation to nonlinear creep, a multiple integral representation using several kernels between the stress levels 30–50 J · cm^{-3} has been applied (27). While an accurate representation can be achieved with a large number of parameters, clearly this is not a predictive approach.

5. APPLICATION OF THE TSC PRINCIPLE AND OF EQUATION 5

We now apply the TSC to the results shown in *Fig. 1*. We choose as the reference stress level σ_{ref} = 10 J · cm^{-3} for which a_σ = 1 by definition. Then, we shift the results of all other stress levels building a single master curve. The results are shown in *Fig. 2*. The respective shifting distance is the stress shift factor a_σ. We conclude that the TSC principle is well applicable to the creep compliance of our multi-phase system.

We now investigate the validity of *Eq 5*. The characteristic parameters v* = 0.682 cm^{3}g^{-1}, T* = 1400 K and P* = 3850 J · cm^{-3} for our PLC have been determined from the experimental PVT data (35). These parameters and *Eq 4* have been used to compute $\tilde{v}$ and v values for the corresponding stress levels. The results are then applied to *Eq 5*. B and C values computed by fitting to the experimental data are equal to 5.10 and –0.56, respectively.

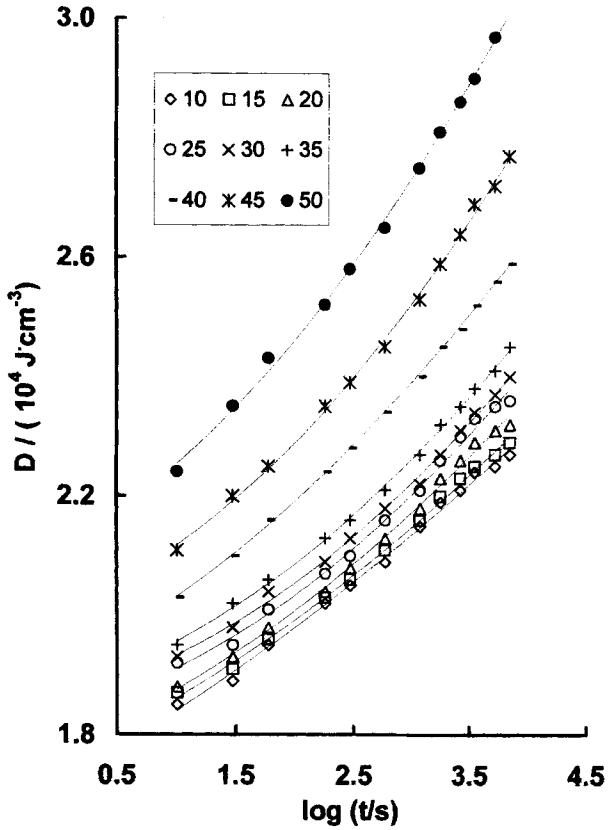

Fig. 1. Experimental creep compliance for PET/0.6PHB as a function of log time between 10 and 50 J · cm^{-3} stress levels with 5 J · cm^{-3} intervals at T = 20°C.

A good agreement between experimental and calculated a_σ is achieved—as represented in *Fig. 3*. The discontinuous line is fitted to the experimental a_σ values by using *Eq 5* in conjunction with *Eq 4*. A good conformity is then obtained between the experimental and

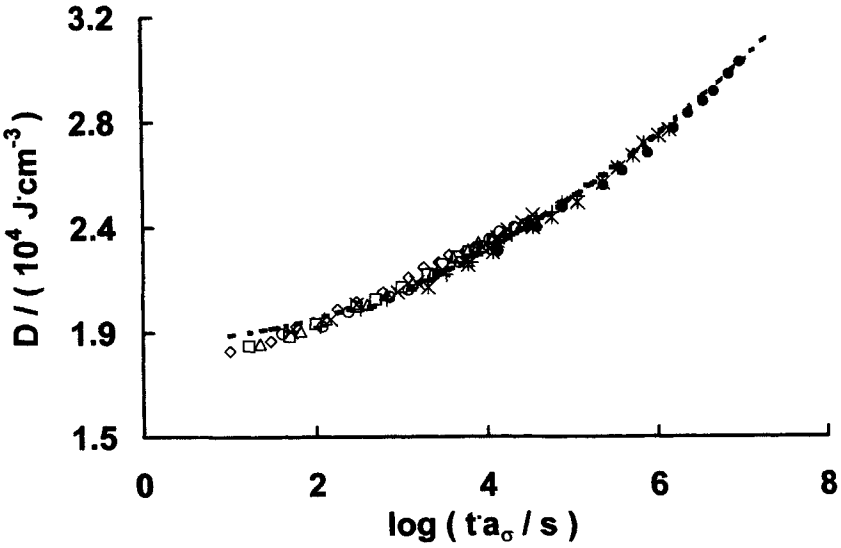

Fig. 2. The master curve for PET/0.6PHB of creep compliance D as a function of log t · a_σ for σ_{ref} = 10 J · cm^{-3}. Points are experimental values and symbols are the same as in Fig. 1. The broken curve is fitted by using Eq 5.

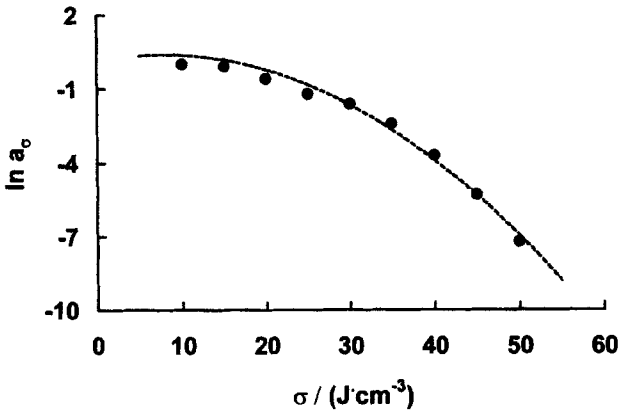

Fig. 3. The stress shift factor a_σ (σ) for the PET/0.6PHB for σ_{ref} = 10 J · cm^{-3}. Circles are experimental values; the broken line is computed from Eq 5 in conjunction with Eq 2.

the predicted master curve in *Fig. 2*. The dotted line in *Fig. 2* represents the values calculated from *Eq 5*. We see that prediction is within the limits of experimental accuracy.

The best fit to the experimental temperature shift factor a_T for the same PLC from creep measurements for T_{ref} = 20°C up to 120°C has already been achieved from *Eq 1* with B = 5.093 (18). This proves the assumption made in (15) that the Doolittle constant B in *Eqs 1* and *5* is indeed a material constant—regardless of its origin (such as from either a_T or a_σ experiments). Moreover, the negative value of C = – 0.56 computed from *Eq 5* is also in harmony with the logarithmic viscosity of binary molten blends of the same PLC as a function of logarithmic shear rate (8). The addition of the PLC to four compatible engineering polymers has resulted then in lowering of the viscosity. A particularly large effect was obtained when isotactic polypropylene was the second component. A further decrease in viscosity was observed with increasing shear rate. Hence, the inverse proportionality between viscosity and shear rate is well represented by the negative value of C, which reflects effects of stress on the chain conformations.

Therefore, we have reached our main purpose. Just as temperature, stress can serve equally well for the prediction of long-term behavior from short-term tests. We have tested with good results *Eq 5*, which thus provides the capability of using time-stress equivalence for reliable long-term quantitative predictions. The validity of the model is confirmed further by the same value of the Doolittle constant B obtained separately from temperature shift (18) and stress shift experiments for the same PLC material.

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REFERENCES

1. M. Zisenis, B. Prötzl, and J. Springer, *Polymer. Mater. Sci. & Eng.*, **71**, 41 (1994).
2. M. Zisenis and J. Springer, *Polymer*, **35**, 3156 (1994).
3. D. Ferri, D. Wolff, J. Springer, D. Francescangeli, M. Laus, A. S. Angeloni, G. Galli, and E. Chiellini, *J. Polymer Sci. Phys.*, **36**, 21 (1998).
4. W. Brostow, E. A. Faitelson, M. G. Kamensky, V. P. Korkhov, and Y. P. Rodin, *Polymer*, **40**, 1441 (1999).
5. F. T. Niesel and J. Springer, *Macromol. Rapid Commun.*, **15**, 7 (1994).
6. A. Schönhals, D. Wolff, and J. Springer, *Macromol.*, **28**, 6254 (1995).
7. W. Brostow, M. Hess, and B. L. Lopez, *Macromol.*, **27**, 2262 (1994).
8. W. Brostow, T. Sterzynski, and S. Triouleyre, *Polymer*, **37**, 1561 (1996).
9. W. Brostow, N. A. D'Souza, B. Gopalanarayanan, and E. G. Jacobs, *Polym. Eng. Sci.*, **40**, 490 (2000).
10. M. Selimovic, A. Bismarck, M. Pfaffernoschke, and J. Springer, *Acta Polym.*, **50**, 156 (1999).
11. A. Bismarck, M. Pfaffernoschke, B. Song, and J. Springer, *J. Appl. Polymer Sci.*, **71**, 1893 (1999).
12. A. Bismarck, M. E. Kumru, B. Song, J Springer, E. Moss, and J. Karger-Kocsis, *Composites*, **30**, 135 (1999).
13. W. Brostow, *Polymer*, **31**, 979 (1990).
14. W. Brostow, "Polymer Liquid Crystals," in *Physical Properties of Polymers Handbook*, Ch. 33, J. E. Mark, ed., American Institute of Physics Press, Woodbury, N.Y. (1996).
15. W. Brostow, *Mater. Res. Innovat.*, **3**, 347 (2000).
16. J. D. Ferry, *Viscoelastic Properties of Polymers*, 3rd Edition, Wiley, New York (1980).
17. A. Y. Goldman, *Prediction of the Deformation Properties of Polymeric and Composite Materials*, American Chemical Society, Washington, D.C. (1994).
18. W. Brostow, N. A. D'Souza, J. Kubat, and R. D. Maksimov, *J. Chem. Phys.*, **110**, 9706 (1999).
19. F. Schwarzl and A. J. Staverman, *J. Appl. Phys.*, **23**, 838 (1952).
20. M. L. Williams, R. F. Landel, and J. D. Ferry, *J. Am. Chem. Soc.*, **17**, 3701 (1955).
21. A. K. Doolittle, *J. Appl. Phys.*, **22**, 1741 (1951).
22. W. Brostow, *Mater. Chem. & Phys.*, **13**, 47 (1985).
23. W. Brostow, Ch. 10 in W. Brostow and R. D. Corneliussen, eds., *Failure of Plastics*, Hanser, Munich-Vienna-New York (1986).
24. Yu M. Boiko, W. Brostow, A. Ya. Goldman, and A. C. Ramamurthy, *Polymer*, **36**, 1383 (1995).
25. J. Mano, R. A. Sousa, R. L. Reis, A. M. Cunha, and M. J. Bevis, *Polymer*, **42**, 6187 (2001).
26. W. Brostow, J. V. Duffy, G. F. Lee, and K. Madejczyk, *Macromolecules*, **24**, 479 (1991).

27. J. Kubat and R. D. Maksimov, "Creep and Stress Relaxation", in *Mechanical and Thermophysical Properties of Polymer Liquid Crystals*, p. 407, W. Brostow, ed., Chapman & Hall, London (1998).
28. J. Kubat, *Phys. Status Solidi B*, **111**, 599 (1982).
29. J. Kubat and M. Rigdahl, Ch. 4 in Ref. 17.
30. M. J. Kubat, F. J. Jansson, M. Delin, J. Kubat, R. W. Rychwalski, and S. Uggla, *J. Appl. Phys.*, **72**, 5179 (1992).
31. W. Brostow and J. Kubat, *Phys. Rev. B*, **47**, 7659 (1993).
32. S. Blonski, W. Brostow, and J. Kubat, *Phys. Rev. B*, **49**, 6494 (1994).
33. P. J. Flory, *Faraday Soc. Disc.*, **49**, 7 (1970).
34. W. Brostow and W. Szymanski, *J. Rheology*, **30**, 877 (1986).
35. J. M. Berry, W. Brostow, M. Hess, and E. G. Jacobs, *Polymer*, **39**, 4081 (1998).
36. B. Hartmann and M. A. Haque, *J. Appl. Phys.*, **58**, 2831 (1985).
37. B. Hartmann and M. A. Haque, *J. Appl. Polymer Sci.*, **30**, 1553 (1985).
38. M. T. O'Shaughnessy, *Textile Res. J.*, **18**, 263 (1948).
39. W. Brostow, T. Dziemianowicz, W. Romanski, and W. Werber, *Polym. Eng. Sci.*, **28**, 785 (1988).