

Creep and stress relaxation in a longitudinal polymer liquid crystal: Prediction of the temperature shift factor

Witold Brostow^{a)} and Nandika Anne D'Souza^{b)}

Department of Materials Science, University of North Texas, Denton, Texas 76203-5310

Josef Kubát^{c)}

Department of Polymeric Materials, Chalmers University of Technology, 412-96 Gothenburg, Sweden

Robert Maksimov^{d)}

Institute of Polymer Mechanics of the Latvian Academy of Sciences, 23 Aizkraukles iela, 1006 Riga, Latvia

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The polymer liquid crystal PLC is the PET/0.6PHB copolymer; PET=poly(ethylene terephthalate), PHB= ρ -hydroxybenzoic acid (LC); 0.6=the mole fraction of PHB. This is a multiphase system with PHB-rich islands in a PET-rich matrix. Tensile creep compliance was measured isothermally from 20 °C to 160 °C in 10 °C intervals. Master curves were determined using the time-temperature superposition for 20 °C and for the glass transition temperature of the PET-rich phase $T_{gPET} = 62$ °C. Experimental values of the temperature shift factor a_T as a function of temperature T agree in the entire T range with those from Eq. (7) relating a_T to the reduced volume \bar{v} and the Hartmann equation of state Eq. (10). Values of $a_T(T)$ calculated from the Williams-Landel-Ferry (WLF) formula give very large errors below T_g . A control 14 months creep experiment agrees with the theoretical predictions from Eq. (7). Stress relaxation experiments were performed under the constant strain of 0.5% from 20 °C to 120 °C, again master curves were determined for 20 °C and for T_{gPET} and $a_T(T)$ values calculated. The stress relaxation $a_T(T)$ results agree with those from creep and with those from Eq. (7). © 1999 American Institute of Physics. [S0021-9606(99)51218-X]

I. INTRODUCTION AND SCOPE

Prediction of long term behavior from short term tests is possibly the most important area of polymer engineering and science. Except for the phenomena of fatigue and thermal fatigue (see for instance, Ref. 1), properties of metals and ceramics can largely be assumed time-independent. While we have a different situation with polymers, and viscoelasticity is a challenge, we also have here an opportunity.

In this paper we analyze the foundations as well as consequences of the time-temperature correspondence principle. Since the principle has its limitations, we provide experimental creep and stress relaxation data for a polymer liquid crystal (PLC). The PLC in its service temperature range contains four phases,² hence conventional wisdom says that the equivalence principle does not apply. We intend to prove the contrary.

II. THEORY

A. Time-temperature superposition

In 1874 Boltzmann presented the fundamental equation of linear viscoelasticity.^{3,4} By considering an elastic “after-effect” under a strain $d\epsilon$ for a short time dt , Boltzmann

evaluated the aftereffect at a later time t , namely that an associated stress is proportional to the original strain and is a decreasing function of the time lapse. He then further postulated that the stress at time t due to a strain ϵ is not affected by other deformations that occurred in the intervening period. Thus, although the application of a driving force (be it stress, temperature, etc.) causes time-dependent deformation, it can still be assumed that each increment in the driving force makes its independent contribution. We can investigate these effects separately through changes of the reduced volume \bar{v} caused by temperature and stress; the temperature effects are considered in this paper.

Following the classical Boltzmann approach, the strain response to an applied load is given by

$$\epsilon(t) = \left[\frac{\sigma}{E_u} \right] + \int_{-\infty}^t D(t-\tau) \frac{d\sigma(\tau)}{d\tau} dt, \quad (1)$$

while the stress response to an applied strain is

$$\sigma(t) = [E_r \epsilon] + \int_{-\infty}^t E(t-\tau) \frac{d\epsilon(\tau)}{d\tau} dt. \quad (2)$$

Here $D(t)$ is the creep compliance, E_u is the unrelaxed storage modulus, E_r is the relaxed storage modulus, $d\sigma/dt$ and $d\epsilon/dt$ represents the incremental stress and strain corresponding to the time increment dt . The integral is a result of the stress being analyzed at times other than $t=0$, i.e., a history dependence called the hereditary integral.

^{a)}Electronic mail: brostow@unt.edu

^{b)}Electronic mail: ndsouza@jove.acs.unt.edu

^{c)}Electronic mail: josef@polymm.chalmers.se

^{d)}Electronic mail: maksimov@edi.lv

As discussed in some detail by Markovitz,⁵ a broad look at the Boltzmann results can lead us to the time t -temperature T 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.⁶⁻⁹ Shifting of individual curves to produce the master curve is performed using the temperature shift factor a_T , or $\log a_T$. To make as extensive use as possible of the principle, we now need to discuss it in relation to free volume, an aspect Markovitz did not cover.

Consider a conformational change in the chain at the room temperature, so fast that we cannot follow it experimentally. Processes inside polymeric materials require free volume v^f —a fact discussed repeatedly for thermo-physical properties by Flory,^{10,11} for mechanical by Ferry,⁶ and which also forms the basis of the chain relaxation capability (CRC) approach.^{12,13,8,9} 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. Often more important for our predictive capabilities is 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.

The applicability of the TTC to *amorphous* materials was proven in numerous experiments. However, there are *semicrystalline* viscoelastic materials to which TTC supposedly does not apply. Relation between morphology and TTC principle applicability was studied already decades ago by Schwarzl and Staverman.¹⁴ They postulated that two classes of material be defined: class A where a change of temperature is equivalent to a shift on the logarithmic time scale and class B where equivalence was seen not to exist. They called the class A materials thermorheologically simple, and class B, thermorheologically complex.

Ignoring the effects of temperature on the forces, according to Schwarzl and Staverman, in a thermorheologically simple material, the characteristic times are mutually proportional if all the viscosities show the same dependence on temperature. Thus for any molecular rate process i , the process will be accelerated to the same extent by a specified change of temperature:

$$\frac{\eta_i(T_1)}{\eta_i(T_2)} = f(T_1, T_2), \quad \text{independent of } i. \quad (3)$$

Here $\eta_i(T_j)$ is the viscosity at a temperature T_j . Thus, in thermorheologically simple materials the master curve reflects the fact that all retardation times $\tau_i(T)$ at a temperature T bear a constant ratio a_T to the corresponding retardation times $\tau_i(T_{\text{ref}})$ at the temperature T_{ref}

$$\tau_i(T)/\tau_i(T_{\text{ref}}) = a_T = \eta_\sigma T_{\text{ref}} \rho_{\text{ref}} / \eta_{\sigma \text{ref}} T \rho, \quad (4)$$

where $\rho = v^{-1}$ represents the mass density and v is the specific volume. In other words, using the elastic modulus E as

an example, and considering it as a function of time, the changing of temperature is seen to be equivalent to applying the shift factor a_T to the time scale

$$E(T_i, t) = E(T_{\text{ref}}, t/a_T). \quad (5)$$

The reasoning of Schwarzl and Staverman can be related to the well-known theory of reaction rates of Glasstone, Laidler, and Eyring which assumes that there is an energy barrier called the activation energy which needs to be overcome for a process to occur. The activation energy concept has to be taken with some caution; it is supposedly universal, so that it deals with physical processes such as chain relaxation in an analogous way as with chemical reactions. Applying this concept here, one finds that the apparent activation energy for all molecular rate processes must be identical. The microrheological condition for thermorheological simplicity of Schwarzl and Staverman (their class A) can be formulated as follows: in similar deformations at different temperatures always the same sequence of molecular events takes place. In materials of class B not only the velocity but also the sequence of molecular processes changes when the temperature of the experiment changes. This implies that a heat treatment of materials of class A cannot form a special structure which would not be obtained at a single temperature. This statement does not apply to class B. The approach of Schwarzl and Staverman leads to the conclusion that thermorheologically simple materials do not contain crystallites or pronounced polar groups. For the time being we note that this conclusion deserves further scrutiny.

Given a material to which TTC applies, we can perform experiments isothermally at a number of temperatures. There is one temperature of particular interest, say T_{ref} . There is at least one parameter of particular interest, say the tensile compliance $D(t) = \epsilon(t)/\sigma = E^{-1}(t)$, where ϵ is the engineering strain, σ the engineering stress, and E the tensile modulus already featured in Eq. (5). 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 the *master curve* for 20 °C. The respective shifting distance, that is the shift factor a_T , is different for each temperature while here $a_T(20\text{ °C}) = 1$ by definition. Thus

$$D(t, T; \sigma = \text{const}) = D(t/a_T, T_{\text{ref}}; \sigma = \text{const}). \quad (6)$$

Formulas of the type of (5) and (6) can also be written for other mechanical properties of viscoelastic materials. However, apart from the applicability range of such relations, another important issue is involved. Unless an $a_T(T)$ equation is available, quite extensive experimentation at a number of temperatures is necessary. Since TTC has been known for decades, already in 1955 Williams, Landel, and Ferry (WLF)¹⁵ 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 $T_g + 50\text{ K}$ or so; this warning comes from Ferry.⁶ Under these circumstances, van Krevelen¹⁶ recommended for $T \leq T_g$ an Arrhenius type equation, reminiscent also of the theory of rate processes. However, calculations,

including ours,^{12,17} show that the other equation is not reliable either. It appears that this situation resulted in the belief that TTC itself is not applicable. Bicerano,¹⁸ whose book provides a fairly detailed account of current methods of prediction of properties of polymeric materials, notes that TTC has a limited quantitative application range.

This situation suggests the following question: Is it the TTC principle itself which fails so often, or rather are various computational procedures based on TTC inaccurate? There is a way to provide an answer to this question; one of us^{12,13} has derived the following fairly general formula

$$\ln a_T = A + B/(\bar{v} - 1), \quad (7)$$

applicable *below and above* T_g . Here \bar{v} is the reduced free volume (see the next subsection), and A and B are materials constants; B is called the Doolittle constant since it comes from the Doolittle equation relating viscosity η to v^f . The WLF equation can be derived from Eq. (7) as a special case if one makes a simple (but unfounded) assumption.¹³ Eq. (7) has to be used in conjunction with an equation of state, a topic to be covered below. For predrawn materials there exists a further generalization of Eq. (7) which includes the draw ratio λ .¹⁷

B. The equation of state

The method of reduced variables has been known for more than a century, recommended by Johannes D. van der Waals. We write

$$\bar{v} = v/v^*; \quad \bar{T} = T/T^*; \quad \bar{P} = P/P^*, \quad (8)$$

where v^* , T^* , and P^* are the characteristic (“hard-core”) parameters for a given material. The free volume v^f can be then calculated as

$$v^f = v - v^*. \quad (9)$$

We now need an equation of state to be used in conjunction with Eq. (7). Good results have been obtained repetitively^{19,18} with the Hartmann equation^{20–22}

$$\bar{P}\bar{v}^5 = \bar{T}^{3/2} - \ln \bar{v}. \quad (10)$$

We shall apply Eq. (10) together with (7) to our experimental results reported below.

C. Cooperative theory of stress relaxation

Already in 1965 one of us²³ suggested a representation of the stress relaxation curves in the coordinates $(\sigma - \sigma_i)/(\sigma_0 - \sigma_i)$ versus t ; here σ is the effective stress, σ_i the so-called internal stress which corresponds to the time $t = \infty$, while σ_0 pertains to $t = 0$. A comparison was made for a variety of materials, including metals and polymers. It turned out²³ that the curves for so vastly different materials look similar, and all exhibit three regions: initial, nearly horizontal (a long central region, descending approximately linearly), and final (again approximately horizontal), which provides us with the value of σ_i . Curves for one material at several temperatures also look quite similar in these coordi-

nates. Also experiments show²³ that the maximum value of the slope of the central region obeys the formula

$$F = [d\sigma/d(\ln t)]_{\max} = C(\sigma_0 - \sigma_i), \quad (11)$$

where c is a proportionality factor approximately equal to 0.1 at ambient temperatures for metals, polymers, as well as for a number of other solids.

A number of theoretical models has been developed for the prediction and explanation of stress relaxation. Such models have been reviewed²⁴ and their various deficiencies pointed out. Briefly, models which can explain the behavior of metals serve poorly for polymers, and vice versa. In this situation a *cooperative* model which seems to possess sufficient generality was developed.^{25,24,26,27} The model assumes a two-level system, with unrelaxed flow units in the upper level. Thus, the number n of such units at any given time serves as the measure of stress σ , or more accurately of the difference $\sigma - \sigma_i$. The flow process consists of elementary events (transitions) of varying multiplicity; that is, each spontaneous event may produce a certain number (a cluster) of induced or secondary events. The theory provides a cluster size distribution and also leads to our Eq. (11). A somewhat more generalized model which allows transitions in both directions, that is, to lower as well as to higher energy states,²⁶ leads to essentially the same results.

Assumptions of the cooperative theory can be neither confirmed nor denied by experiments. Therefore, we have performed computer simulations of two kinds. We have simulated cluster relaxation recording cluster sizes.²⁸ It turns out that the competition for particles not yet relaxed increases somewhat the number of smaller clusters at the expense of clusters with six or more members, but the deviations from the predicted distribution are not large. More importantly, we have simulated stress relaxation as well as stress σ vs. strain ϵ curves using the method of molecular dynamics (MD) for metals as well as for polymers.^{29,30} The stress vs. strain curves for metals were quite different than those for polymers, and both kinds agree with the curves known from the experiments. By contrast, the stress relaxation curves for both classes of materials were quite similar. We have found consistently that stress relaxation is mainly caused by plastic deformations which occur in the vicinity of defects. There is a certain similarity here between crystal nucleation from a melt and “nucleation” of cracks. In the ideal lattice, relatively large forces were needed to create a crack but then the same forces were sufficient for quick brittle crack propagation. In lattices with defects such as holes, relatively small forces cause atomic size (atom, polymer chain segment) movements, but the movements are mainly of the ductile or flow type and take much longer time. Thus, the structural defects determine the time span of the relaxation in these two series of simulations. Since real materials invariably contain defects, experimental stress relaxation curves for different kinds of materials at comparable temperatures have comparable linear descending parts, which confirms Eq. (11). Details of each curve depend on the free volume v^f present in the system (as imposed by the temperature) and on the initial effective stress $\sigma_0^* = (\sigma_0$

$-\sigma$). Thus, MD simulations provide *a posteriori* the necessary justification^{29,30} for the assumptions of the cooperative theory.^{25,24,26,27}

III. CHOICE OF THE MATERIAL

Given the conventional wisdom quoted above that TTC does not apply to polymers with polar groups nor to those containing crystalline regions, we have decided to study a polymer liquid crystal (PLC) which does *not* fulfill either of these conditions.

Properties of PLCs are strongly dependent on their molecular structures; we have chosen a longitudinal PLC so that the LC sequences are in the main chain and oriented along the polymer backbone.^{31–33} Among this class, we have chosen the PET/0.6PHB copolymer; PET=poly(ethylene terephthalate), PHB= ρ -hydroxybenzoic acid, the LC component; 0.6=the mole fraction of PHB sequences in the copolymer. It has been studied before by us and others by a variety of techniques, including differential scanning calorimetry (DSC), thermomechanical analysis (TMA), thermally stimulated depolarization (TSD), internal friction (IF), scanning electron microscopy (SEM), diffractometry including wide-angle x-ray spectroscopy (WAXS), in tensile, flexural, and notched Izod impact testing (see Ref. 2 and references to Fig. 10 therein). Dielectric spectroscopy has been investigated over eight decades of frequencies.³⁴ Pressure–volume–temperature (PVT) relationships are available.³⁵ Rheology of melts of this PLC, pure as well as in blends with some flexible polymers (FPs), was studied as well.^{36–38}

PET/0.6 PHB is a multiphase system with PHB-rich islands in a PET-rich matrix. The relatively rigid LC sequences aggregate to form the islands with diameters between 1.0 and 1.4 μm , as determined by SEM.³⁹ In turn, the islands contain PHB crystallites with the diameters of about 12 nm determined by WAXS.⁴⁰ The semirigidity or semiflexibility has consequences also for mechanical properties; the linear viscoelastic region is limited to relatively small strains. Under these circumstances, we have studied linear viscoelastic creep and stress relaxation along a number of isotherms, covering a fairly large temperature range.

IV. EXPERIMENT

Since the PLC used in this study was the same as thoroughly characterized in earlier papers,^{39,40,2,34,35} we are not going to repeat the respective data here. To minimize moisture effects, the material was vacuum-dried at 120 °C for 6 h. Plates with the dimensions 140×16×2 mm were used for specimen preparation by casting. The polymer melt temperature was 260 °C while that of the casting mold, 160 °C. The specimens used had dimensions 70×7×2 mm.

Creep and stress relaxation measurements were conducted on an MTS universal testing machine; the elongations were determined with the Model 632.11 c-20 MTS strain gauge attached directly to the specimens. Tensile creep testing was carried out using a specially built apparatus provided with a thermal chamber. The loading time was approximately 1 s. Then the creep curves were obtained during 1 h at each temperature between 40 °C and 160 °C, in 10 K in-

tervals. Each time the load was removed, the inverse creep (creep recovery) curve was also determined. At a given temperature and stress level at least three but usually five identical specimens were studied; the results below constitute the averages calculated for a given testing condition.

Stress relaxation experiments were conducted under the constant strain of 0.5% in the temperature range from 20 °C to 120 °C. A first value of stress was measured 10 s after loading. To minimize scattering, here also at least three but usually five specimens were investigated.

V. CREEP RESULTS

Isothermal tensile creep compliance D results at 20 °C and then in the temperature range from 40 °C to 160 °C in 10 K intervals in the linear viscoelastic region are shown in Fig. 1. It was necessary to gradually reduce the stress level along with the temperature increase so as to stay inside that region. Thus, the stresses varied from 20.0 J·cm⁻³ (at the lowest temperature) to 0.2 J·cm⁻³ (at the highest temperature). In all cases, total strains at the moment of specimen unloading did not exceed 0.5%. Afterwards the samples were completely unloaded and creep recovery curves determined. It should be noted that 24 h after unloading, the residual strain were negligibly small; in other words, the materials exhibit reversible viscoelastic deformation or time-recoverable creep.

As could be expected, effects of temperature on the creep of the PLC are fairly large. At the same time, the material exhibits considerable creep even at room temperature. The compliance after one hour creep at 20 °C is larger than the initial D value at the loading time by a factor of 1.26.

Using the time–temperature correspondence principle, the master curve of the compliance for the glass transition temperature of the PET-rich phase $T_{g\text{PET}}=62$ °C has been created from the experimental results. That glass transition temperature has been determined by several methods.² The master curve is shown in Fig. 2 and covers approximately 16 decades of time. A similar master curve has been produced for 20 °C but it is not shown here for brevity.

The experimental logarithmic temperature shift factors $a_T(T)$ used to create Fig. 2 are plotted as a function of temperature in Fig. 3. The translation of the master curves using the variance of temperature only establishes the thermorheological simplicity.

We have then tested the WLF equation and also the generalized Eq. (7) in conjunction with the Hartmann equation of state (10). Calculations were made for the full T interval investigated, and also separately for $T \leq T_{g\text{PET}}$ and above $T_{g\text{PET}}$. The calculations for limited T intervals give good results for both equations and in both intervals. However, using two totally different sets of parameters in the WLF equation can hardly be justified; three out of four phases in our PLC are the same above and below $T_{g\text{PET}}$ (Ref. 2; see also the next section). Calculations for the entire T range with the WLF equation give good agreement with experiment above T_g , but large errors below T_g (the dotted line in Fig. 3). Other problems related to the WLF formula have been discussed.¹³ Using a different type of equation below

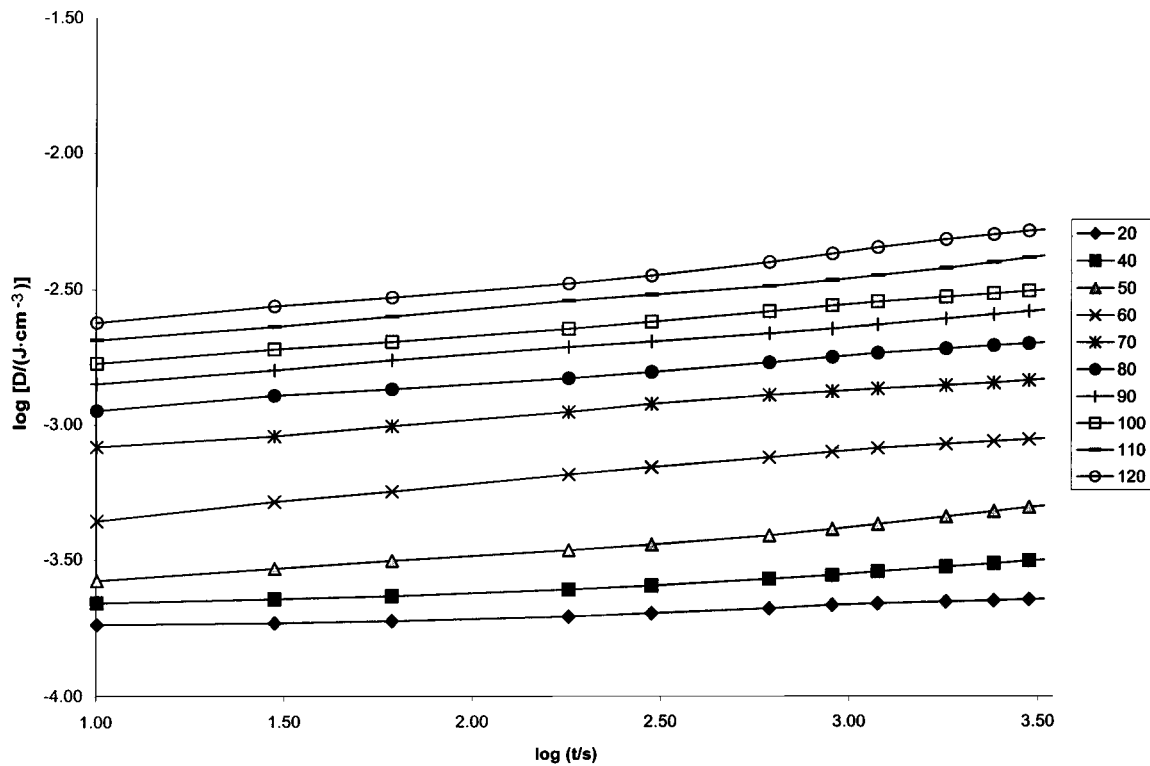


FIG. 1. Experimental tensile creep compliance for PET/0.6PHB in logarithmic coordinates at 20 °C (the bottom curve), 40 °C (the second curve from the bottom), and then in 10 K intervals up to 120 °C (the top curve).

T_g advocated by van Krevelen¹⁶ is unfounded for the same reason; we are not dealing with two distinct polymers. Fortunately, these different sets of parameters or different equations are not needed; as seen in Fig. 3, Eq. (7) in conjunction

with (10) gives satisfactory $a_T(T)$ values for all temperatures. We recall that the use of Eq. (7) when it was first derived¹² has already shown its applicability to a polymeric adhesive both below and above its glass transition. More-

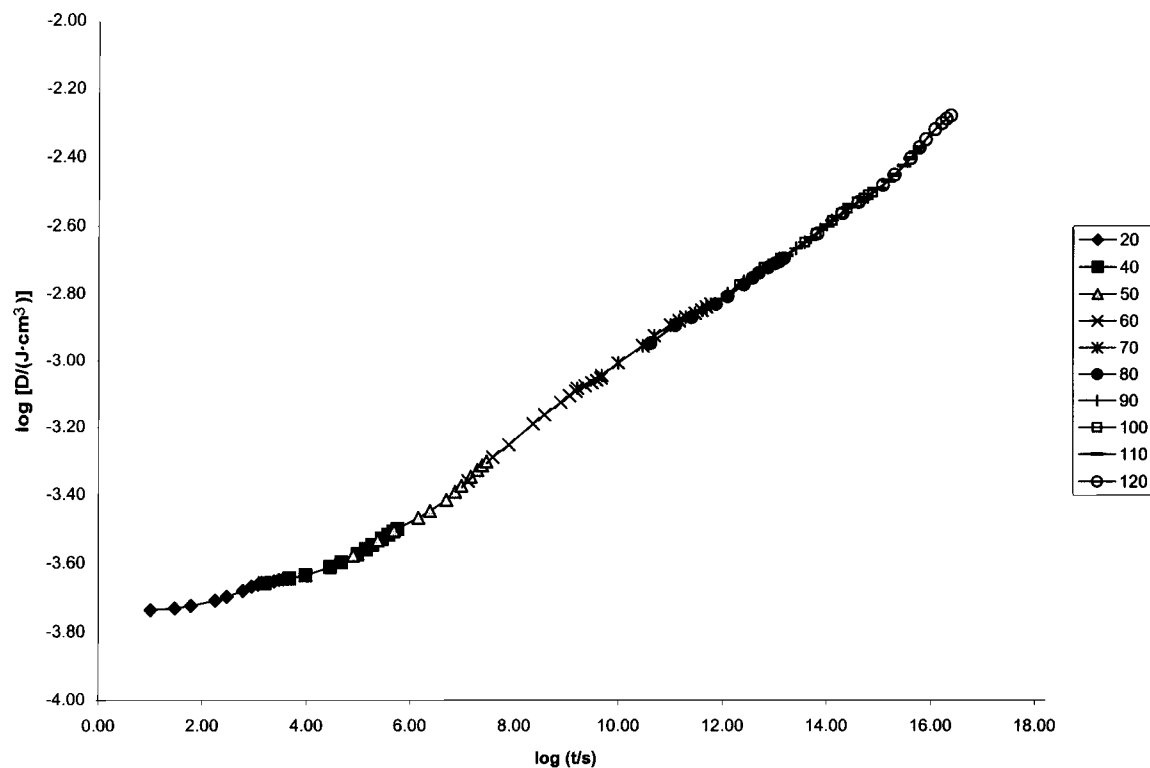


FIG. 2. Logarithmic tensile creep compliance for the PLC as the master curve for the $T_{ref} = T_{gPET} = 62$ °C.

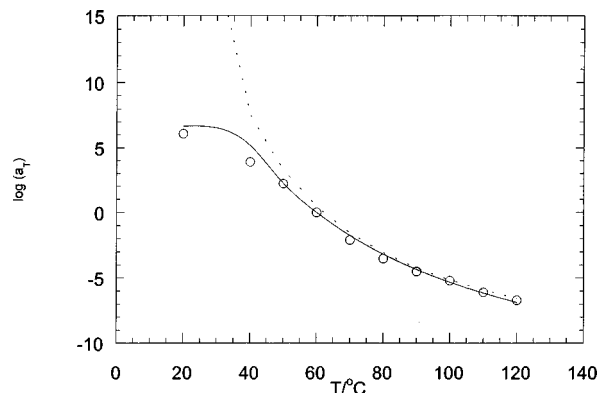


FIG. 3. The temperature shift factor $a_T(T)$ for the PLC for $T_{\text{ref}}=62^\circ\text{C}$: circles are experimental values from creep measurements (from Fig. 2), the dotted line represents values calculated from the WLF equation, the continuous line those calculated from Eq. (7) in conjunction with Eq. (10).

over, we have performed a control long-term (14 months, that is, three decades of time) creep experiment for our PLC. The results are in agreement with predictions from Eq. (7).

The characteristic parameters for Eq. (10) have been obtained from the experimental PVT data³⁵ and are: $v^*=0.682\text{ cm}^3\text{ g}^{-1}$; $T^*=1400\text{ K}$; and $P^*=3850\text{ J}\cdot\text{cm}^{-3}$ (recall that $1\text{ J}\cdot\text{cm}^{-3}=1\text{ MPa}$ exactly). The best fit to the experimental $\log a_T$ values has been obtained from Eq. (6) with $A=-53.18$ and $B=5.093$.

VI. STRESS RELAXATION RESULTS

Experimental isothermal stress relaxation curves under the constant strain of 0.5% in the temperature range from 20°C to 120°C are shown in Fig. 4. The corresponding master curve for 20°C derived from experimental results is shown in Fig. 5, plotted in the coordinates used first by one of us²³ and discussed above in Sec. II C. This brings out common features of our PLC with the materials studied before. We further note that PLCs are semiflexible (or semirigid), while highly rigid aramid fibers including KevlarTM were studied by Wortmann and Schulz⁴¹ and also similar curves have been obtained. The cooperative theory of stress relaxation as well as the MD simulations, both also discussed

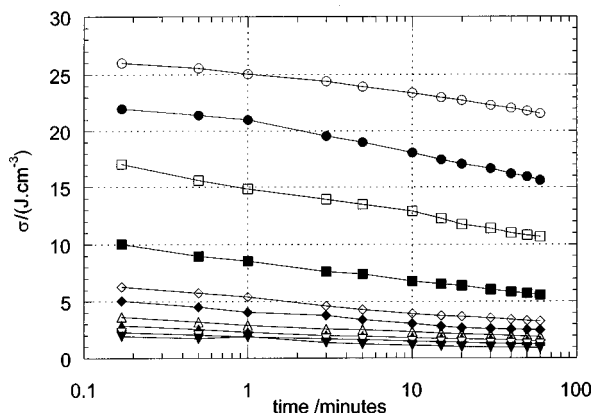


FIG. 4. Experimental stress relaxation results for the PLC under the constant strain of 0.5% at 20°C (top curve), 40°C (the second curve from the top), and then in 10 K intervals up to 120°C (the bottom curve).

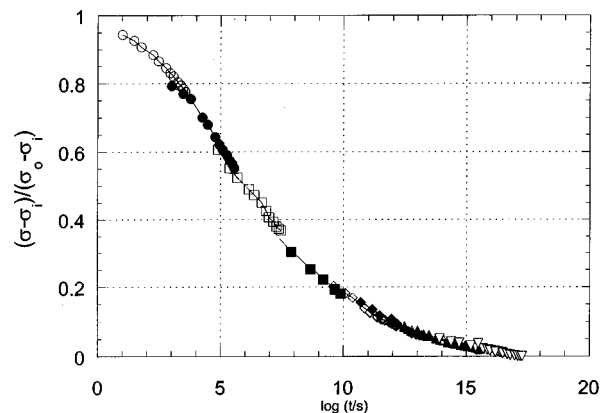


FIG. 5. Master curve of stress relaxation for the PLC in the coordinates defined in Ref. 23 and explained in Sec. II C; symbols the same as in Fig. 4.

above in Sec. II C, explain why this is so. Thus, our experimental results in conjunction with those of Wortmann and Schulz show that also in semirigid or virtually rigid polymeric materials, stress relaxation occurs via cooperative plastic deformations of clusters of chains segments. Further, we recall here the MD simulations of an isolated polyisoprene chain by Moe and Ediger.⁴² They have found that C–H vector relaxation results largely from coupled small amplitude motions of groups (apparently our clusters) of adjacent torsions rather than via conformational transitions. Thus, results of experiments on an even larger variety of materials, theory, and computer simulations all converge to a joint picture.

Given the results shown in Fig. 5 and also Fig. 2, we now consult the phase diagram of PET/*x*PHB copolymers.² Below $T_{g\text{PET}}=62^\circ\text{C}$ we are in region IV in the diagram, which contains PET crystals, PHB-rich islands, approximately isotropic PET-rich glass, and PHB-rich glass. Above $T_{g\text{PET}}$ we are in region VII, where because of crossing the glass transition we have the quasiliquid instead of the PET-rich glass, while the other three phases are the same. We find that in spite of the fact that our window of experiments covers two regions in the phase diagram, with each region containing four phases, the time–temperature correspondence is applicable.

In Fig. 3 we have shown $a_T(T)$ results for the $T_{\text{ref}}=T_{g\text{PET}}=62^\circ\text{C}$. We also have master curves for $T_{\text{ref}}=20^\circ\text{C}$, in the same coordinates as in Fig. 2 as well as in those shown in Fig. 5. Thus, we have $a_T(T)$ values for 20°C from stress relaxation experiments represented in the coordinates of Fig. 2. Now Fig. 6 shows the equivalence between the shift factors for $T_{\text{ref}}=20^\circ\text{C}$ from the creep compliance, from the stress relaxation, and those calculated from Eq. (7) in conjunction with the Hartmann equation of state (10). We see that Fig. 6 establishes the veracity of the TTC for our multiphase PLC. As stated by Markovitz⁵ already in 1975: “much less stringent conditions are needed in some cases to prove, without approximation, that temperature superposition for one of the functions implies the same for the other.”

VII. CONCLUDING REMARKS

Thermorheological simplicity and validity of the time–temperature superposition has been established for a longitu-

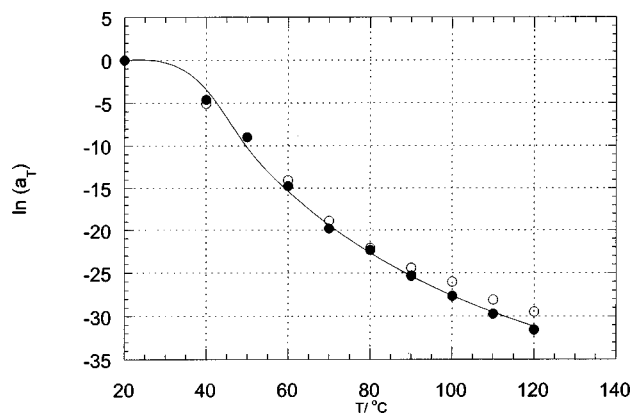


FIG. 6. Overlay of $a_T(T)$ shift factors for $T_{ref}=20^\circ\text{C}$ from creep (●) and stress relaxation (○) for the PLC showing equivalence. The continuous line is calculated from Eq. (7) in conjunction with Eq. (10) and the characteristic parameters listed at the end of Sec. V.

dinal polymer liquid crystal. In contrast to the limited temperature region over which the WLF relation is valid, we have successfully applied relation (7) between the temperature shift factor and reduced volume, this below, at, and above the glass transition region of the flexible constituent of the PLC. The equation is confirmed by creep data including a 14 month experiment and by stress relaxation results. The Hartmann equation of state (10) provides reliable results for PVT data *per se*³⁵ as well as in conjunction with Eq. (7). The last conclusion for our PLC reinforces similar conclusions reached before for a number of polyurethanes¹⁹ and for polyethylenes subjected to predrawing to a various degree.¹⁷

More pessimistic than us and Markovitz, Fesko and Tschoegl⁴³ said that “the nature of retardation processes in two-phase systems makes it unlikely that valid master curves should result from simple translation of the measured viscoelastic responses along the logarithmic time or frequency axis.” We have valid master curves for four-phase systems. However, Fesko and Tschoegl say also that “a two-phase system would fulfill this requirement over the entire time scale only if the responses of both phases would be identical.” There is an interesting issue here which we would like to address in our future papers.

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- ¹W. Brostow, *Science of Materials* (Wiley, New York, 1979), Chap. 12.
- ²W. Brostow, M. Hess, and B. L. López, *Macromolecules* **27**, 2262 (1994).
- ³L. Boltzmann, *Sitzungsber. Kaiserl. & Kgl. Akad. Wiss. Wien, Math.-Naturwiss. Classe* **70**, Abt. 2, 275 (1874).
- ⁴L. Boltzmann, *Pogg. Ann. Phys. & Chem. Ergänzungsband* **7**, 624 (1876).
- ⁵H. Markovitz, *J. Polym. Sci., Polym. Symp.* **50**, 431 (1975).
- ⁶J. D. Ferry, *Viscoelastic Properties of Polymers*, 3rd ed. (Wiley, New York, 1980).
- ⁷A. Ya. Goldman, *Prediction of the Deformation Properties of Polymeric and Composite Materials* (American Chemical Society, Washington, DC, 1994).
- ⁸W. Brostow, J. Kubát, and M. J. Kubát, in *Physical Properties of Polymers Handbook*, edited by J. E. Mark (American Institute of Physics, Woodbury, NY, 1996), Ch. 33.
- ⁹W. Brostow, N. A. D'Souza, J. Kubát, and R. D. Maksimov, *Internat. J. Polym. Mater.* (to be published).
- ¹⁰P. J. Flory, *J. Am. Chem. Soc.* **87**, 1833 (1965).
- ¹¹P. J. Flory, *Faraday Soc. Disc.* **49**, 7 (1970).
- ¹²W. Brostow, *Mater. Chem. Phys.* **13**, 47 (1985).
- ¹³W. Brostow, in *Failure of Plastics*, edited by W. Brostow and R. D. Corneliusen, (Hanser, Munich, 1986), Ch. 10; W. Brostow, *Makromol. Chem., Macromol. Symp.* **41**, 119 (1991).
- ¹⁴F. Schwarzl and A. J. Staverman, *J. Appl. Phys.* **23**, 838 (1952).
- ¹⁵M. L. Williams, R. F. Landel, and J. D. Ferry, *J. Am. Chem. Soc.* **77**, 3701 (1955).
- ¹⁶D. W. Van Krevelen, *Properties of Polymers*, 3rd ed. (Elsevier, Amsterdam, 1990), Ch. 13.
- ¹⁷M. Yu. Boiko, W. Brostow, A. Ya. Goldman, and A. C. Ramamurthy, *Polymer* **36**, 1383 (1995).
- ¹⁸J. Bicerano, *Prediction of Polymer Properties*, 2nd ed. (Marcel Dekker, New York, 1996).
- ¹⁹W. Brostow, J. V. Duffy, G. F. Lee, and K. Madejczyk, *Macromolecules* **24**, 479 (1991).
- ²⁰B. Hartmann, *Proc. Can. High Polymer Forum* **22**, 20 (1983).
- ²¹B. Hartmann and M. A. Haque, *J. Appl. Phys.* **58**, 2831 (1985).
- ²²B. Hartmann and M. A. Haque, *J. Appl. Polym. Sci.* **30**, 1553 (1985).
- ²³J. Kubát, *Nature (London)* **204**, 378 (1965).
- ²⁴J. Kubát and L. Rigdahl, in *Failure of Plastics*, edited by W. Brostow and R. D. Corneliusen (Hanser, Munich, 1986) Chap. 4.
- ²⁵J. Kubát, *Phys. Status Solidi B* **111**, 599 (1982).
- ²⁶C. Högfors, J. Kubát, and M. Rigdahl, *Rheol. Acta* **24**, 250 (1985).
- ²⁷J. M. Kubát, J.-F. Jansson, M. Delin, J. Kubát, R. W. Rychwalski, and S. Uggla, *J. Appl. Phys.* **72**, 5179 (1992).
- ²⁸W. Brostow, J. Kubát, and M. J. Kubát, *Mater. Res. Soc. Symp. Proc.* **321**, 99 (1994).
- ²⁹W. Brostow and J. Kubát, *Phys. Rev. B* **47**, 7659 (1993).
- ³⁰S. Blonski, W. Brostow, and J. Kubát, *Phys. Rev. B* **49**, 6494 (1994).
- ³¹W. Brostow, *Kunststoffe* **78**, 411 (1988).
- ³²W. Brostow, *Polymer* **31**, 979 (1990).
- ³³W. Brostow, in *Physical Properties of Polymers Handbook*, edited by J. E. Mark (American Institute of Physics, Woodbury, NY, 1996), Ch. 33.
- ³⁴H.-E. Carius, A. Schoenhals, D. Guigner, T. Sterzynski, and W. Brostow, *Macromolecules* **29**, 5017 (1996).
- ³⁵J. M. Berry, W. Brostow, M. Hess, and E. G. Jacobs, *Polymer* **39**, 4081 (1998).
- ³⁶M. Heino, *Acta Polytech. Scand.* **220**, 1 (1994).
- ³⁷M. T. Heino, P. T. Hietaoja, T. P. Vainio, and J. V. Seppälä, *J. Appl. Polym. Sci.* **51**, 259 (1994).
- ³⁸W. Brostow, T. Sterzynski, and S. Triouleyre, *Polymer* **37**, 1561 (1996).
- ³⁹W. Brostow, T. Dziemianowicz, W. Romanski, and W. Werber, *Polym. Eng. Sci.* **28**, 785 (1988).
- ⁴⁰W. Brostow and M. Hess, *Mater. Res. Soc. Symp. Proc.* **255**, 57 (1992).
- ⁴¹F.-J. Wortmann and K. Schulz, *Makromol. Chem., Macromol. Symp.* **50**, 55 (1991).
- ⁴²N. E. Moe and M. D. Ediger, *Macromolecules* **29**, 5484 (1996).
- ⁴³D. G. Fesko and N. W. Tschoegl, *J. Polym. Sci., Part C: Polym. Symp.* **35**, 51 (1971).