A Method for Determination of Time- and Temperature-Dependences of Stress Threshold of Linear–Nonlinear Viscoelastic Transition: Energy-Based Approach

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ABSTRACT: A methodology for determination of time- and temperature-dependences of stress threshold of linear–nonlinear viscoelastic transition is proposed and validated by example of uniaxial creep of epoxy resin. Energy approach is applied for characterization of the region of linear viscoelasticity (LVE) and the threshold of LVE is given in the stress–strain representation as the master curve independent of time and temperature. Time- and temperature-dependences of the stress threshold are calculated by extending LVE theory and time–temperature superposition principles (TTSP) to the energy relations. Reasonable agreement between experimental data and calculations is obtained. It is shown that number of tests required for characterization of LVE region in a wide range of test time and temperatures can be considerably reduced by applying the proposed methodology. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 2187–2192, 2011

Key words: creep; linear viscoelasticity; stress threshold; energy threshold; time-temperature superposition principle

INTRODUCTION

Most of polymers under certain service conditions exhibit nonlinear viscoelastic behavior. Then, use of the simplest and the most popular model of linear viscoelasticity (LVE) is limited and more complicated nonlinear models should be considered.[1–4] This significantly complicates the task of long-term prediction of deformability and reduces its reliability. To choose an appropriate model for characterizing long-term viscoelastic behavior of polymers, it is important to estimate when transition from linear to nonlinear region takes place.

Action of temperature accelerates relaxation processes in polymers and promotes development of nonlinear effects in them.[5–7] As a result, a region of applicability of LVE theory narrows. For reliable prediction of long-term viscoelastic behavior, there is a need to quantitatively estimate linear–nonlinear viscoelastic transition in a wide temperature range.

Traditionally, the limit of LVE is defined as a level of stress—stress threshold—above which actual behavior of a material deviates from that predicted on the basis of linearity assumptions. Time- and temperature-dependences of the stress threshold are commonly determined from isochronous creep curves.[6–8] For getting such dependences, a great number of creep tests performed under different stresses and temperatures is needed.[7] For example, to get five experimental points on the dependence stress threshold versus temperature, one needs to perform about 20 tests that is rather time- and energy-consuming task. Therefore, development of an alternative method for determination of the stress threshold in a wide range of temperatures and times is under great importance.

An energy-based approach for determination the threshold of linear–nonlinear viscoelastic transition was used in Refs. [5,8–10]. It has been shown that energy threshold is a material constant independent of time, temperature, and moisture content of materials. The energy threshold compared to the traditional stress or strain thresholds gives a great benefit in comprehensive characterization of LVE region under action of various external factors since it allows one to considerably reduce a number of the required tests. However, in some cases, for example, for characterization of long-term creep of polymers it is convenient to use a concept of the stress threshold. Then, by introducing the stress threshold into analytical prediction of nonlinearity parameters, the viscoelastic behavior of polymers can be reliably described in a wide range of applied stresses.[11] The aim of the study is to develop an alternative method for evaluation of the stress threshold of linear–nonlinear viscoelastic transition by using a concept of the energy threshold

of LVE to reduce the number of tests required for comprehensive characterization of LVE region of polymers.

In this work, the results discussed by the authors in previous studies[7–11] are combined and discussed comprehensively. The novelty of this study is related with an application of the energy approach for calculating time- and temperature-dependences of the stress threshold of linear–nonlinear viscoelastic transition. Before, the stress thresholds under different temperatures could be determined only experimentally from a great number of tests. The present results show that use of the energy relations allows us to calculate temperature-dependences of the stress threshold and to considerably reduce the number of required tests.

THEORETICAL BACKGROUND

Stress–strain relationships

For characterization of the linear viscoelastic behavior of a material the constitutive equations usually are represented in the single integral form based on the Boltzmann superposition principle.[12,13] Strain response $\varepsilon(t)$ in uniaxial tension with a stress-history $\sigma(t)$ under isothermal conditions is given by

$$\varepsilon(t) = \int_0^t J(t-s)\frac{d\sigma(s)}{ds}ds \tag{1}$$

Representing creep function $J(t)$ as a sum of exponents in the simplest case of loading, creep at a constant stress σ_0 applied at time $t = 0$, after integration eq. (1) takes the form

$$\varepsilon(t) = J_0\sigma_0 + \sigma_0 \sum_{i=1}^k J_i\left(1 - e^{-\frac{t}{\tau_i}}\right) \tag{2}$$

where J_0 is instantaneous creep compliance and (J_i, τ_i) is a discrete relaxation spectrum. The creep compliance is defined by ratio $J(t) = \varepsilon(t)/\sigma_0$.

Time–temperature superposition principles (TTSP) is used to take into account an influence of temperature on the viscoelastic response.[1,12] According to the superposition principles, temperature and time are interdependent and relatively equivalent. Then, it is valid a passage to the reduced time $t \rightarrow t'$:

$$t' = ta_T \tag{3}$$

where a_T is time–temperature reduction function.

By taking into account eqs. (2) and (3) the following relation is obtained for calculation of the creep compliance:

$$J(t) = J_0 + \sum_{i=1}^k J_i\left(1 - e^{-t \cdot a_T/\tau_i}\right) \tag{4}$$

Energy threshold

Energy of deformation is a physical function that combines both stress and strain effect and is given by relation[14]

$$W = \int \sigma d\varepsilon \tag{5}$$

or

$$W = \int \dot{W}dt \tag{6}$$

where $\dot{W} = \sigma\dot{\varepsilon}$ is rate of stress work. Total energy is divided into two parts: the isotropic W_{iso} energy connected with volume changes and the deviatoric W_{dev} one associated with shape changes. For viscoelastic material with time-dependent properties each of the energy components is divided into two other parts: stored W_{st} and dissipated W_{diss} parts.

Energy approach for evaluation of the limits of linear viscoelastic behavior was first developed by Foux and Bruller based on the thermodynamical theory of strength of Reiner and Weissenberg.[14,15] It was stated that transition from linear to nonlinear viscoelastic behavior appears at time t_{LVE} when stored deviatoric energy of the material reaches a certain value which is material property, i.e.,

$$W_{st} = \int_0^{t_{LVE}} \left(\dot{W} - \dot{W}_{diss}\right)dt = W_{LVE} \tag{7}$$

where $\dot{W}$ is rate of work done by external forces, $\dot{W}_{diss}$ is rate of energy dissipation, W_{LVE} is the value of the stored energy at the limit of linear viscoelastic behavior which assumed to be a material constant.

In general case, experimental evaluation of the stored deviatoric energy is a complex task. However, for an isotropic material in simple loading cases there are possible some simplifications. It was shown in Refs. 16 and 17 that contribution of the deviatoric energy to the total energy is much higher than that of the isotropic one. For most polymers with Poison's ratio in a range of 0.35–0.45 a ratio W_{dev}/W accounts for 90–97%. Thus, it is advisable to use the total stored energy as the energy limit instead of its deviatoric part. Furthermore, in the region of linear viscoelastic behavior an amount of the dissipated energy is low in comparison with the stored energy and can be neglected in most cases.[17] Finally, the total energy of deformation is supposed

to consider as the energy limit of LVE. While it is so the following relation should be valid

$$W_{LVE} = \frac{\sigma_{LVE}\varepsilon_{LVE}}{2} \qquad (8)$$

where σ_{LVE} and ε_{LVE} are limit stress and strain of linear viscoelasticity, respectively. Actually, eq. (8) is a quasi-elastic linear approximation of eq. (5) expressing the fact that the dissipated energy at the linear limit is negligible compared to the stored energy. However, this fact should not be generalized for all temperatures, especially in the region closed to the glass transition.

The total energy of linear viscoelastic material at uniaxial creep can be expressed in terms of relaxation spectra by using eqs. (2) and (6)[9,18]:

$$W(t) = W_{st} + W_{dis} = \sigma_0^2 \left(\frac{J_0}{2} + \sum_{i=1}^{k} J_i \left(1 - e^{-t/\tau_i} \right) \right) \quad (9)$$

It has been shown in Ref. 9 that basic statements of TTSP can be also extended to the energies. Then, analogously to the creep compliance, temperature action on the energy is taken into account by passing to the reduced time according to eq. (3).

By using eqs. (3), (8), and (9), the stress threshold of LVE is given by formula:

$$\sigma_{LVE}(t, T) = \left(\frac{W_{LVE}}{J_0/2 + \sum_{i=1}^{k} J_i (1 - e^{-ta_T(T)/\tau_i})} \right)^{1/2} \quad (10)$$

Temperature- and time-dependences of the stress threshold can be easily calculated by eq. (10) for any fixed t and T, respectively.

EXPERIMENTAL

The material under investigation is commercially available epoxy resin Araldite CY219 of CIBA-GEIGY (UK). The dumbbell-shaped samples of 170-mm length and 2-mm thick with operative part dimensions 80×12 mm^2 were applied. Creep tests were performed at four different temperatures: 25, 35, 40, and 45°C and at nine different stress levels: 10, 15, 20, 25, 30, 35, 40, 45, and 50% of the tensile strength. Duration of creep tests was 18 h for specimens conditioned at 25°C and 8 h for all the rest temperature levels. At least three duplicate samples were tested at each condition and the results presented in the study correspond to average values. Temperature dependence of the strength was determined in standard isothermal tensile tests at a cross-head speed of 2 mm min^{-1} in a temperature range of 25–50°C. Values of the strength at different tem-

TABLE I
Values of the Strength at Different Temperatures[7]

T (°C)	Strength σ_{max} (MPa)	20% σ_{max} (MPa)
25	46.5	9.3
35	33.2	6.6
40	28.2	5.6
45	18.1	3.6

peratures are given in Table I. Glass transition temperature T_g of the epoxy determined in DSC tests was about 58°C. The experimental details on tensile, creep and DSC test methods are comprehensively described in Ref. 7.

RESULTS AND DISCUSSION

The experimental data used in this study for validation of the energy approach to the calculation of linear–nonlinear transition are taken from Ref. 7. Therefore, only general dependences of creep behavior will be shown and discussed in the present study.

Typical creep compliance curves obtained at different temperatures at stress levels which corresponded to 20% of the strength at every given temperature (Table I) are shown in Figure 1 as an example.

Action of temperature essentially accelerates relaxation processes in the polymer that appears in a noticeable increase of creep with growing temperature. Amount of creep dramatically increases with approaching glass transition temperature. As seen from Figure 1, values of creep compliance achieved after 3-h creep at 25 and 35°C differ for 1.5 times, while temperature rise from 25°C up to 45°C leads to an increase of creep for about five times.

The isochronous stress–strain curves obtained in creep tests under various temperatures and calculated at the start of loading (conditionally at $t = 0$ s) and after 3-h creep are shown in Figures 2 and 3, respectively.

The isochrones are almost linear at short time of loading, while after 3-h creep noticeable nonlinearity of the isochrones is observed. An extent of the isochrones' nonlinearity increases with time and growing temperature. The stress threshold (σ_{LVE}) of linear-nonlinear transition is determined as the value of stress where deviation from the linear trend (thin solid lines on the figures), which corresponds to the case of linear viscoelastic behavior, do not exceeded 3–5%.[7,8] Correspondingly, the strain threshold (ε_{LVE}) is a value of strain at the given stress threshold on the creep isochrones.

The stress and strain thresholds were determined from the isochrones constructed for different time moments ($t = 0, 100, 1000, 10{,}020,$ and $28{,}000$ s) and temperatures. The corresponding values of σ_{LVE} and ε_{LVE}, are depicted in one graph in Figure 4. The
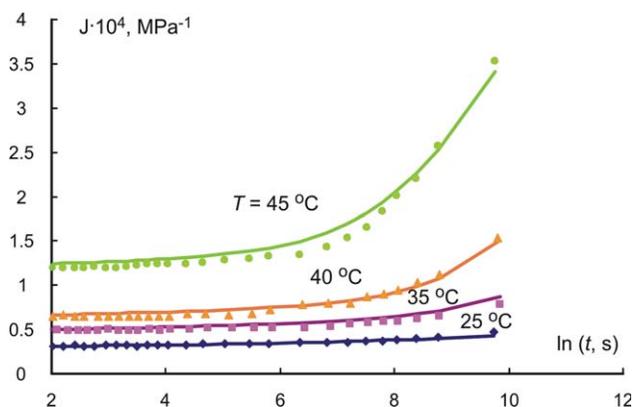
Figure 1 Creep compliance curves at different temperatures, $\sigma_0 = 20\%\sigma_{max}$. Lines are calculations by eq. (4). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 3 Creep isochrones for different temperatures at $t = 3$ h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

obtained data fit to a master curve—hyperbola—that is finely approximated by the energy relationship given by eq. (8) with $W_{LVE} = 0.052N$ mm mm^{-3}. This indicates to a fact that stress and strain are interrelated time-dependent functions and their contribution to the nonlinear behavior can be combined into one physical function—energy. Similar dependences for other materials were obtained by the authors in their previous works.[8,10]

As seen from Figure 4, the limit of linear viscoelasticity in the stress–strain representation is the master curve independent of time and temperature. Growth of temperature or creep time appears in a shift along the hyperbola to lower limit stresses and higher limit strains. Transition from linear to nonlinear viscoelasticity takes place once the master curve is crossed at given loading conditions. The benefit of data representation in this way is that transition from linear to nonlinear viscoelastic behavior is char-

acterized by only one parameter W_{LVE}, i.e., the energy threshold. It has been shown in Ref. 9 that W_{LVE} is independent of test type and its value can be determined, for example, in constant rate tests that are less time- and energy-consuming tests compared to creep tests.

Once W_{LVE} is determined, transition from linear to nonlinear viscoelastic behavior of a material is characterized comprehensively. In addition, if the relaxation spectra and time-temperature reduction function of a material are known, time- and temperature-dependences of the stress threshold can be obtained from eq. (10). Validation of the proposed method is discussed below in the text by example of creep of the epoxy resin.

The relaxation spectra (J_i, τ_i) and time-temperature reduction function of the epoxy resin were determined in the linear viscoelastic range. Based on linearity of the creep isochrones at $\sigma = 20\%\sigma_{max}$ shown in

Figure 2 Creep isochrones for different temperatures at $t = 0$ s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
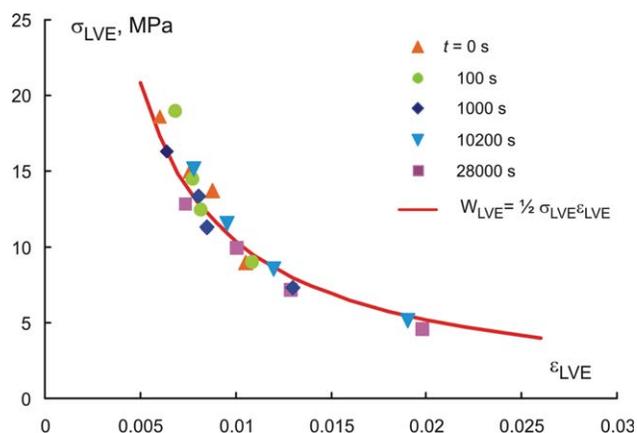
Figure 4 LVE transition threshold in stress–strain axis, i.e., energy threshold. Dots are experimental data; line is calculation by eq. (8). Each dot corresponds to the data obtained from one creep isochrone for a given temperature and time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
Relaxation Spectra of the Material Determined by Approximation of Creep Curves by eq. (4)

i	τ_i (s)	$J_i \cdot 10^4$, (MPa^{-1})
1	10	0.05
2	100	0.1
3	500	0.25
4	1500	0.2
5	15,000	0.5
6	10^5	0.5
7	10^6	7.5
8	10^7	35

Figures 2 and 3, the behavior of the material was considered as linear viscoelastic in the considered temperature- and time-ranges and the experimental data on creep at the given stress were chosen as a typical example of linear viscoelastic creep. The relaxation spectra (J_i, τ_i) was determined by approximation of creep compliance curves by eq. (4), while time–temperature reduction function a_T was obtained by horizontal shift of the creep compliance curves to the reference curve for $T_0 = 25°C$. As seen from Figure 2, the model finely fit the experimental data. The determined relaxation spectra (J_i, τ_i) is given in Table II. The temperature reduction function, as shown in Figure 5, follows polynomial dependence: ln $a_T = 0.0036(T - T_0)^2 + 0.2065(T - T_0)$, where $T_0 = 25°C$.

Now that parameters of the model eq. (4) and the energy threshold W_{LVE} of the epoxy resin are determined, temperature- and time-dependences of the stress threshold were calculated by eq. (10). The calculation results shown in Figures 6 and 7 are in a good agreement with the experimental data that indicates to appropriateness of the applied methodology for evaluation of the linear–nonlinear threshold. Every dot in Figures 6 and 7 is obtained from one creep isochrone at a given time and temperature, respectively.

Solving of such an "opposite" problem allows one to predict the limit stresses at any given temperature and time, i.e., time- and temperature-dependences of the stress threshold of linear–nonlinear transition
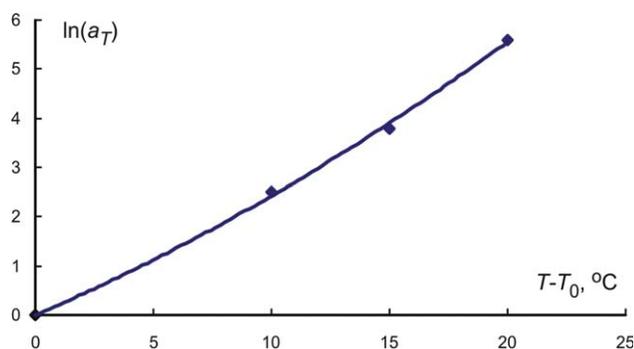
Figure 5 Time–temperature reduction function; $T_0 = 25°C$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
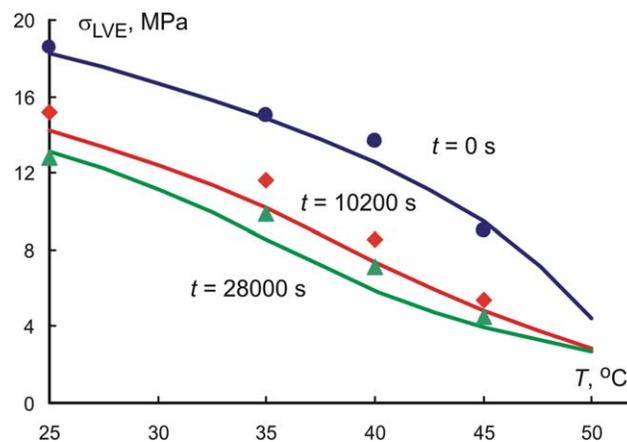
Figure 6 Temperature-dependences of stress threshold for various times. Dots are experimental data; lines are calculations by eq. (10). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

can be predicted without direct estimation of the stress threshold from variety of creep isochrones for different t and T. This can essentially reduce a number of tests required for comprehensive characterization of LVE transition region of polymers. For example, the energy threshold W_{LVE} can be determined in three to five creep tests performed under various stresses at room temperature or alternatively from the data of uniaxial tensile tests,[9] while three to five creep tests at a fixed stress under various temperatures are needed more for evaluation of the relaxation spectra (J_i, τ_i) and time-temperature reduction function a_T. Thus, for evaluating the stress threshold at any t and T by eq. (6) there are needed five to nine tests only that is several times less than by using the traditional procedure, i.e., by determining the stress threshold from the creep isochrones.

To conclude this study, some notes on applicability of the proposed methodology should be mentioned.
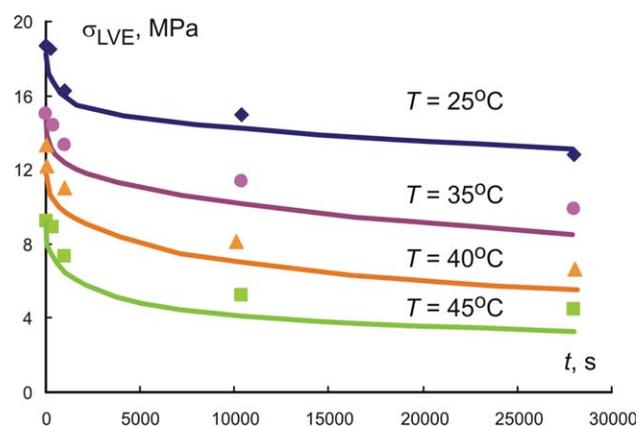
Figure 7 Time-dependences of stress threshold for various temperatures. Dots are experimental data; lines are calculations by eq. (10). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The proposed methodology is approved for only one material so far, i.e., thermosetting epoxy resin. The main problem in its generalization is a huge number of systematical tests that is required for extending the method to other materials. However, it has been shown in Refs. 8–10 that the energy approach is applicable for a wide range of polymers, both thermoplastics and thermosets. So we expect that the methodology can be applied for both thermoplastic and thermosetting polymers as well as composite materials. The main limitation is that time-dependent behavior of materials should be associated with their viscoelastic nature and not plasticity or damage of structure, i.e., "nonlinearity" should not be related with any irreversible changes of a material structure. The other point is that all parameters used in eq. (10) should be determined in the linear viscoelastic range.

CONCLUSIONS

In the present study, a methodology for determination of time- and temperature-dependences of the stress threshold of linear–nonlinear viscoelastic transition is proposed. Energy-based approach is successfully applied for characterization of LVE region of the epoxy resin and the threshold of LVE is given in the stress–strain representation as the master curve independent of time and temperature. The energy threshold value is $W_{\text{LVE}} = 0.052N$ mm mm^{-3}. By extending LVE theory and TTSP to the energy relations, time- and temperature-dependences of the stress threshold are calculated and reasonable agreement between experimental data and calculations is obtained. It is shown that number of tests required for characterization of LVE region in a wide range of test time and temperatures can be considerably reduced by applying the proposed methodology.

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