# Application of Time-Temperature Superposition to Energy Limit of Linear Viscoelastic Behavior

**O. Starkova, A. Aniskevich**

*Institute of Polymer Mechanics, University of Latvia, Riga LV1006, Latvia*

**ABSTRACT:** The energy approach for evaluation of the limits of linear viscoelastic (LVE) behavior is considered. The approach of Foux and Bruller based on the Reiner-Weissenberg dynamic theory of strength is developed for the temperature effect. Value of the stored energy at the limit of LVE is considered as the material characteristic independent on loading conditions and temperature. Time–temperature superposition principle is extended for the energy calculations. Curves of the stored energy calculated for different temperatures are shifted to each other in the logarithmic time axes similarly as creep compliance and relaxation modulus curves in creep and tension tests, respectively. Temperature is considered as a factor that accelerates transition form linear to non-LVE at the same stored energy threshold. This is proved by example of polyvinylchloride by comparing temperature dependences of the stress limits of LVE determined in two independent test series: tensile creep and constant strain rate tests. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 341–347, 2009

**Key words:** viscoelastic properties; stored energy; time–temperature superposition

## INTRODUCTION

Polymers and polymer-based composite materials exhibit time-dependent behavior. To predict the long-term behavior of those materials, it is necessary to know whether a linear or non-linear viscoelastic (LVE) theory should be used. There are two necessary and sufficient conditions required for applicability and validity of the theory of LVE: (i) stress-strain linearity at a given time and (ii) satisfiability of the linear superposition principles.[1] The most common conception about LVE limit is stress threshold above which actual behavior deviates from the behavior predicted on the basis of linearity assumption. It is usually determined in creep tests by construction creep isochrones and evaluation of their linearity up to a certain stress threshold. However, the stress limit is a time-dependent function strongly influenced by environmental action, particularly temperature.[2–4] This requires performing a great experimental work to get time and temperature dependences of the stress limits and to determine the region of LVE for a material. In the case of creep tests, this is time- and energy-consuming task. To overcome this problem, one can determine the limits of LVE in relatively easier constant strain rate (CSR) tests by constructing the reduced stress curves for different strain rates and temperatures.[5,6] However, because the stress limit of LVE is a time-dependent function, it depends on a test type, namely on a time range of given test. This makes the comparison of data obtained in different tests rather difficult. To exclude the time factor, the concept of an energy threshold as a criterion of LVE limit is used.[5–8] Initiating the nonlinear behavior (physical nonlinearity is considered, i.e., reversible deformations) is associated with only one physical function that combines the effects of both stress and strain. Analogously to the energy-based failure criteria,[9–13] the energy limit of LVE is assumed to be a material characteristic independent on time and action of external factors.

Time–temperature superposition principle (TTSP) is one of the most used accelerated method for predicting long-term behavior of polymers.[10,14] TTSP is based on the assumption that the time and temperature are interrelated and interequivalent. In the region of LVE, action of temperature leads to a parallel shift of the relaxation spectrum that is carried out by passing to the reduced time. However, growth in temperature accelerates not only the relaxation processes, but also promotes the development of nonlinear mechanisms of deformation in polymer materials. This fact is reflected by deviation from a master curve. Obviously, energy of deformation also changes due to increasing contribution of nonlinear effects. A plenty of papers were devoted to verification of TTSP for different kinds of materials under different loading conditions. At the same time,

*Correspondence to:* O. Starkova (olesja@pmi.lv).

application of this method to the energy calculations and investigation of the effect of temperature on the energy limit of LVE was not considered adequately in literature.

The aim of the present study was to extend TTSP to energy calculations and to evaluate the effect of temperature on the energy limit of LVE in independent mechanical tests with the example of polyvinylchloride (PVC).

## THEORETICAL BACKGROUND

### Stress–strain relationships

For characterization of the LVE behavior of a material, the constitutive equations are usually represented in the single integral form based on the Boltzmann superposition principle.[1] Strain response $\varepsilon(t)$ in uniaxial tension with a stress-history $\sigma(t)$ under isothermal conditions is given by

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

Representing creep function $J(t)$ as a sum of exponents in the simplest case of loading, creep at a constant stress $\sigma_0$ applied at time $t = 0$, after integration eq. (1) takes the form

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

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

In the case of relaxation-type tests with a strain history $\varepsilon(t)$, the stress response is given by

$$\frac{\sigma(t)}{E_0} = \int_0^t E(t-s)d\varepsilon(s) \qquad (3)$$

where $E_0$ is instantaneous elastic modulus and $E(t)$ is relaxation function usually expressed by a sum of exponents similarly as the creep function. The stress response in uniaxial tension at a CSR $\dot{\varepsilon}_0$ (i.e., strain history is $\varepsilon(t) = \dot{\varepsilon}_0 t$) can be written as

$$\sigma(t) = \dot{\varepsilon}_0 \left[E_0 t + \sum_{i=1}^{k} E_i \tau_i \left(1 - e^{-t/\tau_i}\right)\right] \qquad (4)$$

where $(E_i, \tau_i)$ is a discrete retardation spectrum. The relaxation modulus is defined by ratio $E_r(t) = \sigma(t)/E_0\varepsilon$.

In the LVE region, as seen from eqs. (2) and (4) creep compliances are the same for different $\sigma_0$,

whereas the relaxation moduli are the same for different $\dot{\varepsilon}_0$, respectively.[5]

### Energy of deformation

The total energy is converted into two parts: the isotropic energy connected with volume changes and the deviatoric one associated with shape changes. For viscoelastic material with time-dependent properties, each of the energy components is divided into two other parts: stored and dissipated parts.

Isotropic and deviatoric energy

In general case, work done by external forces during loading—energy of deformation $W$—is expressed by stress and strain as follows[9]

$$W = \frac{1}{2}\sigma_{ij}\varepsilon_{ij} \qquad (5)$$

where $i,j = 1, 2, 3$. Separating stress tensor $\sigma_{ij}$ and strain tensor $\varepsilon_{ij}$ on corresponding deviatoric $s_{ij}$, $e_{ij}$ and isotropic $\sigma$, $\varepsilon$ parts can be rewritten from eq. (5) in the following form:

$$W = \frac{1}{2}(s_{ij} + \delta_{ij}\sigma)(e_{ij} + \delta_{ij}\varepsilon) = \frac{1}{2}(s_{ij}e_{ij} + 3\sigma\varepsilon)$$
$$= W_{\text{dev}} + W_{\text{iso}} \qquad (6)$$

The last expression is obtained taking into account properties of Kronecker's delta $\delta_{ij}$ and $s_{ii} = e_{ii} = 0$. The first term in eq. (6) represents deviatoric part of the energy $W_{\text{dev}}$ associated with shape changes, whereas isotropic energy component $W_{\text{iso}}$ connected with volume changes is expressed by the second term.

Calculation of the total energy in general case of anisotropic material at complex loading conditions is quite complex. However, eq. (6) can be essentially simplified if one considers isotropic material under simple loading conditions. For example, in the case of isotropic material with a constant Poisson's ratio $\nu$ under uniaxial loading at $\sigma_{11}$, the deviatoric and isotropic components of the stress and strain tensors take the form

$$s_{11} = \frac{2}{3}\sigma_{11}; \quad s_{22} = s_{33} = -\frac{1}{3}\sigma_{11}; \quad \sigma = \frac{1}{3}\sigma_{11}$$

$$e_{11} = \frac{2}{3}\varepsilon_{11}(1+\nu); \quad e_{22} = e_{33} = -\frac{1}{3}\varepsilon_{11}(1+\nu);$$

$$\varepsilon = \frac{1}{3}\varepsilon_{11}(1-2\nu)$$

Then, the corresponding energy components can be written as follows:

$$W_{dev} = \frac{1}{3}\sigma_{11}\varepsilon_{11}(1+\nu) = \frac{2}{3}(1+\nu)W$$

$$W_{iso} = \frac{1}{6}\sigma_{11}\varepsilon_{11}(1-2\nu) = \frac{1}{3}(1-2\nu)W \quad (7)$$

The ratio of the isotropic and deviatoric energies depends only on the Poisson's ratio, which is usually assumed as a constant under relatively small deformations, when the effects of time and crazing are not essential. Besides, the deviatoric energy gives much higher contribution to the total energy than the isotropic one (in other words, volume changes are relatively small in comparison with shape changes). In this connection, in simple loading cases, the total energy is often considered instead of its deviatoric part.[12,13]

Stored and dissipated energy

We will consider isotropic LVE material under simple loading conditions. For simplification, all indexes in further discussion are hided.
*Uniaxial creep at a constant stress $\sigma_0$.* Energy of deformation is expressed by the rate of work $\dot{W}$ as follows[9]

$$W = \int \dot{W}\, dt$$

$$\dot{W} = \sigma\,\dot{\varepsilon} \quad (8)$$

where over-dot denotes derivative with respect to time. Let us rewrite eq. (2) in the form

$$\varepsilon(t) = \varepsilon_0 + \sum_{i=1}^{n}\varepsilon_i,$$

$$\varepsilon_i = \sigma_0 J_i\left(1 - e^{-t/\tau_i}\right) \quad (9)$$

By differentiating the last expression and performing some substitutions we can write[13]

$$\sigma_0 = \frac{1}{J_i}(\varepsilon_i + \tau_i\dot{\varepsilon}_i) \quad (10)$$

Then, taking into account eqs. (9) and (10), and $\dot{\varepsilon} = \sum_{i=1}^{n}\dot{\varepsilon}_i$ and carrying over the summation sign eq. (8) takes the form

$$\dot{W} = \sum_{i=1}^{n}\frac{1}{J_i}(\varepsilon_i\dot{\varepsilon}_i + \tau_i\dot{\varepsilon}_i^2) \quad (11)$$

The last term of eq. (11) represents the dissipative part of energy because it is independent on a loading direction (tension or compression), while the first

one is related with the stored energy. Then, by integrating each term separately one can obtain final relations for computation of the stored, dissipative, and total energies at uniaxial creep[8]

$$W_{st}(t) = \frac{\sigma_0^2}{2}\left[J_0 + \sum_{i=1}^{k}J_i\left(1 - e^{-t/\tau_i}\right)^2\right] \quad (12)$$

$$W_{dis}(t) = \frac{\sigma_0^2}{2}\sum_{i=1}^{k}J_i\left(1 - e^{-2t/\tau_i}\right) \quad (13)$$

$$W(t) = W_{st} + W_{dis} = \sigma_0^2\left[\frac{J_0}{2} + \sum_{i=1}^{k}J_i\left(1 - e^{-t/\tau_i}\right)\right] \quad (14)$$

The first term in eq. (12) corresponds to energy stored in a material elastically at the moment of load applying, while time effects are involved in the second term.
*Uniaxial tension at a CSR $\dot{\varepsilon}_0$.* Let us present eq. (4) in the form

$$\sigma(t) = \sigma_0 + \sum_{i=1}^{n}\sigma_i, \quad \sigma_i = \dot{\varepsilon}\tau_i E_i\left(1 - e^{-t/\tau_i}\right) \quad (15)$$

By differentiating the last expression and after some substitutions we obtain[7]

$$\dot{\varepsilon} = \frac{1}{\tau_i E_i}(\tau_i\dot{\sigma}_i + \sigma_i) \quad (16)$$

Then, taking into account eqs. (15) and (16), and $\sigma_i = \sum_{i=1}^{n}\sigma_i$ and carrying over the summation sign eq. (8) takes the form

$$\dot{W} = E_0\dot{\varepsilon}^2 t + \sum_{i=1}^{n}\frac{1}{E_i\tau_i}(\tau_i\sigma_i\dot{\sigma}_i + \sigma_i\sigma_i) \quad (17)$$

The last term of eq. (17) represents the dissipative part of energy because it keeps positive sign independent on a loading direction, while the first one is related with the stored energy. Then, after integration we obtain the final relations for the stored, dissipated, and total energies[8]

$$W_{st}(t) = \frac{\dot{\varepsilon}_0^2}{2}\left[E_0 t^2 + \sum_{i=1}^{k}E_i\tau_i^2\left(1 - e^{-t/\tau_i}\right)^2\right] \quad (18)$$

$$W_{dis}(t) = \sum_{i=1}^{k}\frac{\dot{\varepsilon}_0^2 E_i\tau_i^2}{2}\left[1 + \frac{2t}{\tau_i} - \left(2 - e^{-t/\tau_i}\right)^2\right] \quad (19)$$

$$W(t) = W_{st} + W_{dis}$$
$$= \dot{\varepsilon}_0^2\left[\frac{E_0 t^2}{2} + \sum_{i=1}^{k}E_i\tau_i^2\left(\frac{t}{\tau_i} - \left(1 - e^{-t/\tau_i}\right)\right)\right] \quad (20)$$

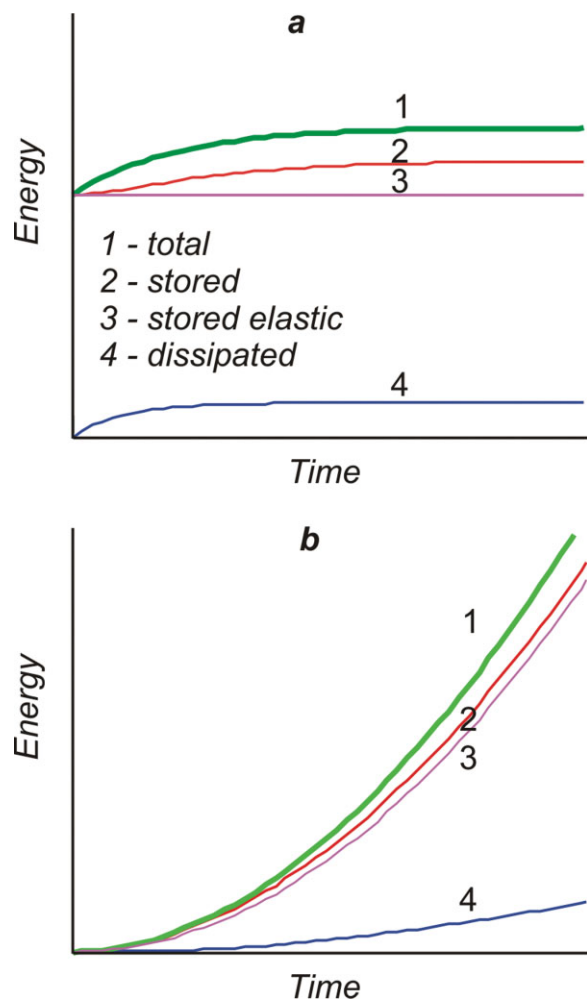Time dependences of the energy components are schematically shown in Figure 1 for both loading

**Figure 1** Time-dependences of energies in creep (A) and CSR tests (B). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

cases. The stored elastic energies were calculated by the first terms of eq. (7) or (9). It is seen that at short times the main contribution to the total energy brings the stored energy and mainly its elastic part. Shifting toward to long times contribution of both stored and dissipated energies gradually grows up. Kinetics of changes of energy curves is essentially different for two loading types. In the case of creep, the total energy and its components tend to an equilibrium, since time appears only under exponent [eqs. (12)–(14)]. The stored and total energy at CSR loading have square time relationships [eqs. (18) and (20)]. Because of these features of the energy time-dependences, a special attention should be made drawing an analogy for different test types. We will specify the differences in further discussion.

## Time-temperature superposition

Acceleration of relaxation processes in polymers due to action of external factors, such as temperature, is

taken into account by using superposition principles.[10,14] According to TTSP, temperature and time are interdependent and interequivalent. This makes valid passage to the reduced time $t > t'$:

$$t' = ta_T \qquad (21)$$

where $a_T$ is time-temperature reduction function.

If one writes relationships for the creep compliance or relaxation modulus [see eqs. (2) and (4)] for two different temperatures $T_1$ and $T_2$ using eq. (21), it can be noted that they will differ only by a time scale defined by functions $a_{T1}$ and $a_{T2}$. In other words, they can reach the same values at different time moments $t_1$ and $t_2$. Then, the following relations are valid:

$$t_1 a_{T1} = t_2 a_{T2}$$

$$\ln t_1 - \ln t_2 = \ln a_{T2} - \ln a_{T1} \qquad (22)$$

For simplification, the reference function $a_{T1}$ is usually taken as 1. Thus, creep compliance and relaxation modulus curves in logarithmic time axes are parallel and shifted to each other for the value $\ln a_T$.

By analogous discussion and by substituting eq. (21) into eqs. (12)–(14) and (18)–(20), it can be shown that TTSP is applicable also for the energies. We will
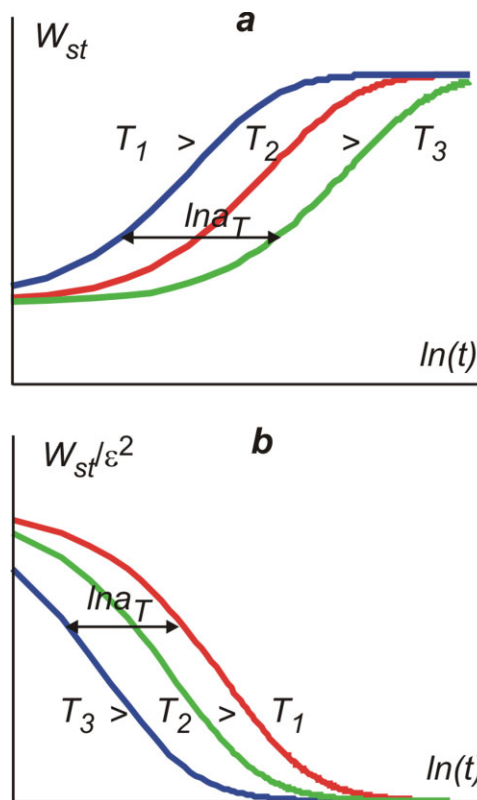


**Figure 2** Temperature dependence of the stored energy curves in creep (A) and CSR tests (B). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
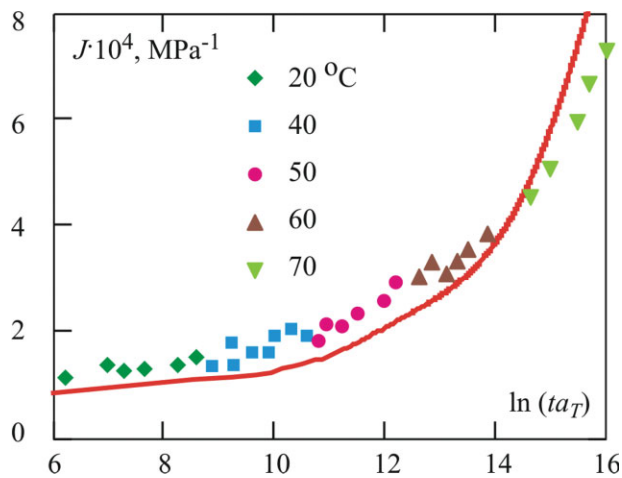
**Figure 3** Creep compliance master curve; $T_0 = 20°C$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

confine on consideration of the stored energy within the study. Parallel shift of the stored energy curves at creep for different temperatures is schematically shown in Figure 2(A). In the case of CSR tests, ratio $W_{st}/\varepsilon^2$ is considered to exclude the effect of strain rate, analogously to what is done by using the concept of relaxation modulus. It can be shown from eq. (18) that for two fixed strain rates $\dot{\varepsilon}_1 \neq \dot{\varepsilon}_2 = const$ at the same time $t$, difference in $W_{st1}/\varepsilon_1^2 - W_{st2}/\varepsilon_2^2 = 0$. In the region of LVE, time dependence of $W_{st}/\varepsilon^2$ is common dependence for every $\dot{\varepsilon}$. Following this discussion and passing to the reduced time by eq. (21), it is easy to show that curves $W_{st}/\varepsilon^2$ (and $W_{st}/\dot{\varepsilon}^2 a_T^2$) vs. ln $t$ for different $T_i$ are shifted to each other for value ln $a_{Ti}$ as it is demonstrated in Figure 2(B). Thus, the stored energy at one temperature can be identified with the stored energy at other temperature by changing time of the action. That is the basic statement of TTSP.

## ENERGY CRITERION AS A LIMIT OF LVE

The energy limit as a strength criteria has been widely developed since Hencky assumed that material property to store energy is limited.[9] It was stated that only shear strains (deviatoric energy) play role in failure, because hydrostatic pressure (isotropic energy) cannot bring plastic yield or infinite compression. According to Hencky's model, material can be represented as a vessel filled with a liquid or energy. Failure appears when the limit is reached, i.e., when the vessel is overflowed. Further energy supply has not influence since energy flows over the vessel.

The static strength theories could not explain time effects that appear at deformation with different strain rates. Then, Reiner and Weissenberg[9,10] developed dynamic theory of strength asserting that fail-

ure or plastic yield can bring only energy stored in a material while dissipated energy has no effect on it. In this case, Hencky's vessel should have so called "relaxation openings" and through them energy is dissipated. Energy can also be leaked through another opening placed on a higher level of the vessel representing energy limit for the plastic yielding. Obviously, at a very low liquid supply to the vessel it will flow through the openings in the bottom, i.e., energy is spend for relaxation. If energy supply is sufficiently high then part of the energy is stored in a material and creep occurs.

Foux and Bruller[7] extended the energy approach of Reiner and Weissenberg for determination of the limits of LVE. By similar discussion, it was stated that transition from linear to non-LVE behavior appears at time $t_{LVE}$ when stored deviatoric energy of the material reaches a certain value which is material property, i.e.

$$W_{st} = \int_o^{t_{LVE}} (\dot{W} - \dot{W}_{dis})dt = W_{st}^{LVE}, \tag{23}$$

where over-dot denotes derivative with respect to time. Value of the stored energy at the limit of LVE behavior $W_{st}^{LVE}$ is assumed to be a material constant called as "resilience." An assumption about the energy threshold for linearity of viscoelastic behavior was validated by various experiments under different loading conditions: creep and stress relaxation, CSR tension tests.[7,8]

Action of elevated temperature leads to both activation of relaxation processes and development of nonlinear mechanisms of deformation in polymers. As a result, transition from linear to non-LVE takes place in shorter time intervals than in room conditions. As it was schematically shown in Figure 2, character of the stored energy curves is similar for different temperatures and the difference appears only in a time scale. Combining the idea of time–temperature superposition and the concept of the energy limit of LVE behavior as a material

**TABLE I**
**Parmeters of Approximation of the Master Curves**

| | Creep tests[3] | | CSR tests | |
|---|---|---|---|---|
| $i$ | ln $\tau_i$, (s) | $J_i$ ($\times 10^4$ MPa$^{-1}$) | ln $\tau_i$, (s) | $E_i$ ($\times 10^{-3}$ MPa) |
| 1 | 4.7 | 1.04 | 6.2 | 0.1 |
| 2 | 11.6 | 1.04 | 6.9 | 0.2 |
| 3 | 15.7 | 9.52 | 9.2 | 0.6 |
| 4 | | | 11.5 | 1.15 |
| 5 | | | 15.2 | 1.7 |
| | | $E_0 = 3800$ MPa[a] | | |
| | ln $a_T = ca_T (T - T_0)$; $c = 0.143°C^{-1}$; $T_0 = 20°C$ | | | |

[a] The elastic modulus was determined in NDT resonance tests.

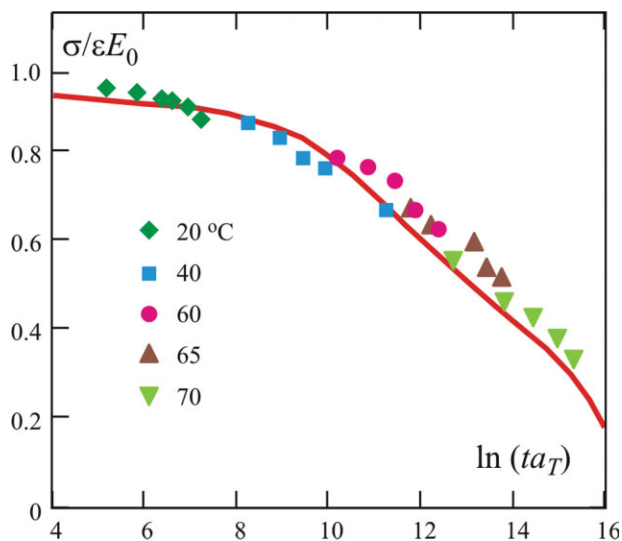**Figure 4** Relaxation modulus master curve; $T_0 = 20°C$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

characteristic, one can assume that growth in temperature leads to an acceleration of the transition to non-LVE at the same energy value.

Extending the analogy with the liquid vessel, one can assume that there exists a critical level when a level of liquid supplied into the vessel is higher than that, then changes in its storage occurs and linearity of viscoelastic behavior is violated. This level does not change with temperature, although time span required for filling the vessel is shortened.

### RESULTS AND DISCUSSION

Verification of the concept about the stored energy limit of LVE is made with PVC as an example. The experimental data of uniaxial tensile creep[3] and uniaxial CSR tension tests[15] in a wide temperature range from $T = 20$ to $70°C$ are considered.

The short-term 1-hr uniaxial tensile creep tests were carried out at various stress levels from 5 to 35 MPa (0.05–0.6 of the strength). Creep recovery control showed that the residual deformations are insignificant after 10 to 20 hr after the load removal. The considered temperature range corresponds to a glassy state of the material. Thus, one may assume that the main mechanism of deformation in the considered stress, temperature, and time range has viscoelastic nature. The creep compliance master curve constructed in the region of LVE applying TTSP is shown in Figure 3. The obtained master curve shifted to the basic curve for $T_0 = 20°C$ was approximated by eq. (2) taking into account eq. (21). Parameters of approximation and time–temperature reduction function are listed in Table I.

The CSR tests were performed at a strain rate $\dot{\varepsilon} = 1.1 \times 10^{-5}$ s$^{-1}$. The time–temperature reduction function was determined by shift of the relaxation modulus curves $\sigma/\varepsilon E_0$ for different temperatures to the basic curve for $T_0 = 20°C$ (Fig. 4). The obtained master curve was then approximated by eq. (4) with parameters shown in Table I. It was determined that the time–temperature reduction functions in both creep and CSR tests are in a good agreement and can be approximated by the same linear function.

The stress limits of LVE at creep were determined by construction of 1-hr isochrones for every test temperature and their further approximation by straight lines involving a statistical method for data treatment.[3] Obviously, that creep behavior of the material remains LVE as long as the loading pass is below the $\sigma_{LVE} - T$ curve shown in Figure 5. The stored energy for given $\sigma = \sigma_{LVE}$ and $t_{LVE} = 1$ hr was calculated by eq. (12). It was determined that with growing temperature $W_{st}$ changes are not regular and are within error range (Table II). The average value of the stored energy at creep $W_{st}^{LVE}$ ave $= 0.096$ N·mm/mm$^3$ was considered as the limit value of LVE behavior.

Let us now verify that the stored energy limit of LVE can be considered for the material characteristic independent on loading conditions. For that we will estimate the stress limits of LVE in CSR tests by using the stored energy limit determined in creep tests. Taking into account the above-mentioned discussion, the ratio $W_{st}^{LVE}/a_T^2$ is considered independent on $T$ and equal to 0.096 N·mm/mm$^3$. For this fixed value, by using eqs. (18) and (21) and parameters from Table I time instants $t_{LVE}$ were calculated for every $T$. The limit stress was determined from the experimental stress–strain diagrams for every $t_{LVE}$ and their values are listed in Table II. The obtained data are shown in Figure 5, temperature dependence of the limit stresses determined
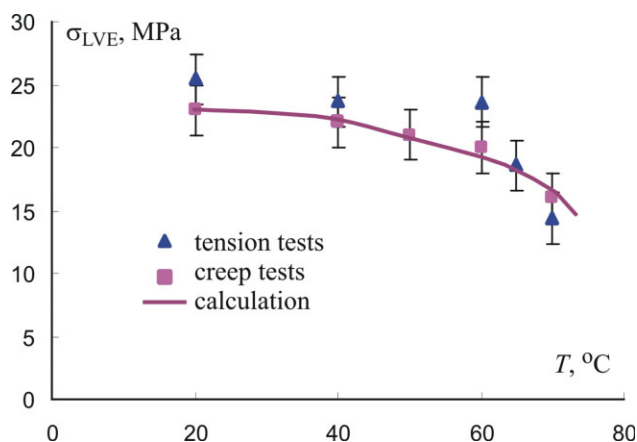


**Figure 5** Temperature dependences of the stress limit of LVE. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

**TABLE II**
**Stress and Energy Limits of LVE in Creep and CSR Tests**

| | | $T$ (°C) | | | | | |
|---|---|---|---|---|---|---|---|
| | | 20 | 40 | 50 | 60 | 65 | 70 |
| Creep tests | $t_{LVE}$ (s) | | | 3600 | | | |
| | $\sigma_{LVE}$ (MPa$^3$) | 23 | 22 | 21 | 20 | | 16 |
| | $W_{st}^{LVE}$ (N·mm/mm$^3$) | 0.097 | 0.094 | 0.100 | 0.099 | | 0.092 |
| | $W_{st}^{LVE}$ ave (N·mm/mm$^3$) | | | 0.096 (±0.003) | | | |
| CSR tests | $t_{LVE}$ (s) | 670 | 700 | | 770 | 810 | 880 |
| | $\sigma_{LVE}$ (MPa) | 25 | 24 | | 23 | 18 | 13 |
| | $W_{st}^{LVE}/a_T^2$ (N·mm/mm$^3$) | | | 0.096 | | | |

experimentally in creep tests is in a good agreement with that calculated from CSR data based on assumption about constancy of the stored energy.

In other words, the stored energy limit can be considered as the characteristic of given material independent on loading conditions and applied temperature. This fact can also be used for solving the opposite problem, mainly for calculation temperature dependence of the limit stresses. By using eq. (12) and (21) the following formula is obtained

$$\sigma_{LVE}(T) = \sqrt{\frac{2W_{st}^{LVE}}{J_0 + \sum_{i=1}^{k} A_i (1 - e^{-ta_T(T)/\tau_i})^2}} \quad (24)$$

The calculation by eq. (24) finely fit the data of creep and CSR tests as it is shown in Figure 5. Thus, one can determine the stored energy limit of LVE in CSR tests and to evaluate temperature dependence of $\sigma_{LVE}$ at creep. This can significantly reduce the number of the required tests and simplify characterization of LVE region of polymers. However, before generalization of the considered approach it should be carefully verified for other materials also.

## CONCLUSIONS

In the present study, energy approach for evaluation of the limits of LVE is considered by example of PVC. The data of two types of independent tests (uniaxial creep and CSR tests) were analyzed. TTSP was extended for the stored energy and analogy between the temperature effect on creep compliance and relaxation modulus curves was shown. Temperature is considered as a factor that accelerates transition from linear to non-LVE at the same limit of the stored energy. The value of the stored energy at the limit of LVE calculated by using parameters of approximation of creep compliance curves and stress limits determined from creep isochrones is almost constant for different temperatures. Stress limits calculated from CSR tests by using the same stored energy value are in a good agreement with those determined experimentally in creep tests. Thus, the energy limit of LVE is considered as the characteristic of given material independent on loading conditions and applied temperature.

## References

1. Ferry, J. Viscoelastic Properties of Polymers; Willey: New York, 1961.
2. Bertilsson, H.; Jansson, J.-F. J Appl Polym Sci 1975, 19, 1971.
3. Efimova, V.; Maksimov, R. Polym Mech 1977, 13, 196.
4. Papanicolaou, G. C.; Xepapadaki, A. G. J Appl Polym Sci 2008, 108, 640.
5. Starkova, O.; Aniskevich, A. Mech Time-Depend Mater 2007, 11, 111.
6. Starkova, O.; Zhang, Z.; Zhang, H.; Park,, H.-W. Mater Sci Eng A 2008, 498, 242.
7. Foux, A.; Bruller, S. Proceedings of the 1971 International Conference of Mechanical Behavior of Materials; Kyoto, 1972; 1, 237.
8. Bruller, O. S.; Smidt, H. H. Polym Eng Sci 1979, 19, 883.
9. Reiner, M. The Lectures on Theoretical Rheology; North-Holland: Amsterdam, 1960.
10. Brinson, H. F.; Brinson, L. C. Polymer Engineering Science and Viscoelasticity: An Introduction; Springer: New York, 2008.
11. Guedes, R. M. Mech Time-Depend Mater 2004, 8, 169.
12. Bruller, O. S. Polym Eng Sci 1981, 21, 145.
13. Bruller, O. S. Polym Eng Sci 1978, 18, 42.
14. Maksimov, R. D.; Urzhumtsev, Yu. S. Polym Mech 1977, 13, 531.
15. Efimova, V. N.; Maksimov, R. D. Polym Mech 1977, 13, 607.