# PREDICTING THE DEFORMATION CHARACTERISTICS OF POLYMER MATERIALS

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UDC 678:539.376

Theoretical methods of predicting the deformation characteristics of polymers are considered. The principles of reduced variables are examined. The relation between characteristics functions of polymers is analyzed. A prediction method is considered for polymers; the method is based upon the use of macroscopical mechanical models having a basis in terms of physics.

Changes in the macroscopical properties of polymers and materials based on polymers during changes in the parameters of external forces or simply in the course of time are characteristic indicators resulting from relaxation processes. In this connection, the determination of the rates at which relaxation processes occur and the changes of these processes in dependence on external conditions are of great importance for the prediction of macroscopical characteristics. Since experimental methods provide scarce information for a well-founded prediction of polymer properties, theoretical methods must be developed.

1. Methods based on the principles of reduced variables are among the widely used techniques of predicting the deformation characteristics of polymer materials. The principle of temperature–time superposition has been most frequently used. This method resides on the fact that when the temperature changes, the viscoelastic properties of polymers change so that their description by a proportionate change in the time scale is possible, i.e., the time scale is multiplied with a certain coefficient $a_T$ for each temperature. This coefficient is termed reduction coefficient and is equal to $\tau_T/\tau_{T_0}$, where $\tau_T$ denotes the relaxation time at some temperature T, and $\tau_{T_0}$ denotes the relaxation time at a particular temperature $T_0$. But the relaxation time depends not only upon the temperature but also upon the stress, the deformation, the moisture, and other external parameters. Changes in these parameters result in modifications of the deformation characteristics of polymers. The influence of these changes can be taken into account by a generalized reduction coefficient

$$a_x = \tau_x / \tau_{x_0} \tag{1.1}$$

where any of these parameters is denoted by x. The case $x = T$ corresponds to the principle of temperature–time superposition [1]; for $x = \sigma$, where $\sigma$ denotes the stress, we are concerned with stress–time superposition [2, 3]; and for $x = \chi$, where $\chi$ denotes moisture, we have the principle of moisture–time superposition [4], etc. When we use the methods of reduced variables, we can expand the time (frequency)-dependent range by several orders of magnitude and predict changes in the basic relaxation characteristics of polymers during variations of the parameters of an external interaction force. The principles of reduced variables can be applied in a limited variability range of the parameter x. The determination of this variability range is a problem per se.

The reduction method, which is based upon the principle of stress–time superposition, makes use of experimental results which were obtained under various, but not greatly different loads. When experimental data for a relatively small time interval are available at various loads and when the curves are shifted relative to a selected fixed curve along the logarithmic time axis until partial coincidence of the curves is obtained at a fixed stress value, it is possible to expand the time interval by several orders of magnitude

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Moscow. Translated from Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki, No. 2, pp. 147-152, March-April, 1973. Original article submitted June 5, 1972.

of variations of the corresponding characteristics. The extent of the shift on the time scale is equal to the logarithm of the coefficient of stress–time superposition ($a_\sigma = \tau_\sigma / \tau_{\sigma_0}$).

When the principle of stress–time superposition is used, it is not possible to employ equations which were obtained with the linear theory of viscoelasticity [5]. However, when a reduced time $\varphi$ is introduced so that the equations of viscoelasticity are invariant with respect to the reduced time, it is possible to express the formulas of viscoelasticity theory through a reduced time and to switch afterwards to the true time with the aid of the formula

$$\varphi = \int_0^t a[\sigma(t)]\,dt \tag{1.2}$$

where $a(\sigma)$ denotes some function of the stress. Let us show that this postulate can theoretically predict phenomena which are observed in practice in the case of vibration-induced creep. It was shown* that the function $a_\sigma$ can be assumed in a form which is an analog to the Williams–Landell–Ferry formula:

$$\ln a_\sigma = \frac{a_1(\sigma - \sigma_0)}{a_2 + \sigma - \sigma_0} \tag{1.3}$$

Since the quantity $\ln a_\sigma$ varies only insignificantly, we replace Eq. (1.3) by the approximation formula

$$a_\sigma = \frac{b_1\sigma - b_2}{a_2 + \sigma - \sigma_0} \tag{1.4}$$

where $b_1 = 1 + a_1$ and $b_2 = (1 + a_1)\sigma_0 - a_2$.

Vibration-induced creep can be observed when a constant stress $\sigma_1$ is applied to a sample and when, in addition, a periodically variable load with amplitude $\sigma_2$ is superimposed:

$$\sigma = \sigma_1 + \sigma_2 \sin \omega t \tag{1.5}$$

By substituting Eq. (1.4) into Eq. (1.2) and taking into consideration Eq. (1.5), we obtain

$$\varphi(t) = \int_0^t a[\sigma(t)]\,dt = \int_0^t \frac{b_1\sigma_1 + b_1\sigma_2 \sin\omega t - b_2}{a_2 + \sigma_1 + \sigma_2 \sin\omega t - \sigma_0}\,dt \tag{1.6}$$

and, after integration,

$$\varphi(t) = b_1 t + \frac{2(b_1\sigma_0 - b_2 - a_2 b_1)}{\omega\sqrt{(a_2 + \sigma_1 - \sigma_0)^2 - \sigma_2^2}}\left[\operatorname{arc\,tg}\frac{(a_2 + \sigma_1 - \sigma_0)\operatorname{tg}\omega t/2 - \sigma_2}{\sqrt{(a_2 + \sigma_1 - \sigma_0)^2 - \sigma_2^2}} + \operatorname{arc\,tg}\frac{-\sigma_2}{\sqrt{(a_2 + \sigma_1 - \sigma_0)^2 - \sigma_2^2}}\right] \tag{1.7}$$

When, during a single oscillation period, the true time t changes by $2\pi/\omega$, the reduced time changes by the amount

$$\frac{2\pi}{\omega}\left(b_1 + \frac{b_1\sigma_0 - b_2 - a_2 b_1}{\sqrt{(a_2 + \sigma_1 - \sigma_0)^2 - \sigma_2^2}}\right)$$

After dividing this formula by the increment of the reduced time at the stress amplitude $\sigma_2 = 0$, we obtain the coefficient of the average acceleration of the creep process:

$$K(\sigma) = \frac{a_2 + \sigma_1 - \sigma_0}{b_1\sigma_1 - b_2}\left(b_1 + \frac{b_1\sigma_0 - b_2 - a_2 b_1)}{\sqrt{(a_2 + \sigma_1 - \sigma_0)^2 - \sigma_2^2}}\right) \tag{1.8}$$

Thus, application of an additional small, sinusoidally-varying load results in a sharp acceleration of the creep process, i.e., we have the phenomenon of vibration-induced creep.

2. One of the prediction problems concerns the theoretical calculation of various deformation curves from a single, experimentally-obtained curve. This problem is usually solved by employing integral equations which describe the viscoelastic properties and include the distribution function of the relaxation times (or delay times). We emphasize that this method is not sufficiently accurate, because at the beginning, the formulas of successive approximations must be used to determine the distribution function of the relaxation times which is then further approximated after substituting the function obtained into the corresponding integral formulas; after the corresponding calculations, the unknown characteristics are obtained.

The problem can be solved in another way. When one of the characteristic functions is known, the Fourier transform can be used to determine a relation between the static and dynamic characteristics func-

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*Yu. S. Urzhumtsev, Author's Abstract of Dissertation, L. Ya. Karpov Physicochemical Scientific-Research Institute (1969).

tions of a polymer. For example, when the modulus of elasticity E(t) in static relaxation is known, the components of the complex dynamic modulus can be determined by the formulas

$$E'(\omega) = \omega \int_0^\infty E(t)\sin\omega t\,dt, \quad E''(\omega) = \omega \int_0^\infty E(t)\cos\omega t\,dt \qquad (2.1)$$

in the case of a linear polymer, or vice versa, if any of the components of the complex dynamic modulus of elasticity is known, the inverse Fourier transform can be used to determine the relaxation modulus from equations of the form

$$E(t) = \frac{2}{\pi}\int_0^\infty E'(\omega)\frac{\sin\omega t}{\omega}\,d\omega, \quad E(t) = \frac{2}{\pi}\int_0^\infty E''(\omega)\frac{\cos\omega t}{\omega}\,d\omega \qquad (2.2)$$

The formulas which several researchers [5, 6] obtained with the aid of the Fourier transform were not experimentally checked for the conversion of the static polymer characteristics to dynamic characteristics with Eq. (2.1). It is in this connection interesting to compare the experimental data with calculated values which were obtained with Eq. (2.1). The stress relaxation figures for polyisobutylene [7] (T = 300°K) were used to determine (Fig. 1) the frequency dependence of the modulus of elasticity (curve 1); this dependence was compared with the experimentally-determined dependence (curve 2). Calculations were made with a computer. It was assumed that $E(t) = 10^{10.6}$ dyn/cm² for $t \to 0$ and that $E(t) = 0$ for $t \to \infty$.

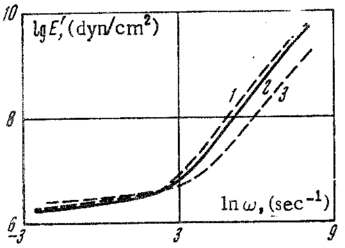

Fig. 1

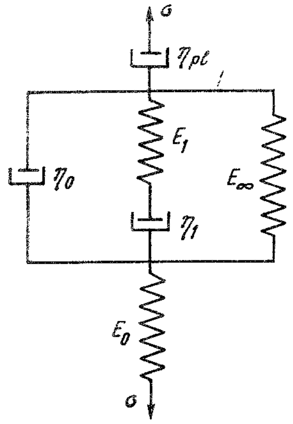

Fig. 2

Satisfactory agreement between the curves can be inferred from the figure. A certain spreading of the curves is related to the fact that it is impossible to obtain an accurate description of the relaxation modulus in the entire variability range of the time coordinate (from 0 to ∞). We note that this method, as well as the method based upon the relaxation-time spectra (or delay-time spectra), is characterized by the shortcoming that knowledge of a certain characteristic function of the polymer in an infinitely long time interval is required.

3. In practice, it is frequently necessary to predict, with a certain degree of accuracy, the basic deformation characteristics of a polymer from results of short tests, i.e., the basic deformation characteristics must be determined when only a finite number of points of measurements is available. This problem can be solved with a method which is based upon mechanical, macroscopical models with a sound basis in terms of physics. Considerations of the general laws of polymer deformation are used to construct a mechanical model, each element of which has a certain meaning in terms of physics. The basic relaxation processes which occur during deformations are brought into account.

Independent experimental results concerning any one of the characteristic functions of a polymer in a small frequency range and time interval (actually only a few discrete points are required) can be used to determine the numerical values of the elements of the model. All other characteristic functions are determined from the solution of the differential equation which corresponds to the model adopted. Rather simple models for which the differential equations can be derived and solved without problems for both the dynamic and static load application case are used in each of the three states in which a polymer material can exist. For example, a six-element model (Fig. 2) was successfully used for the description of the deformation characteristics of linear polymers which are in a highly elastic state.

The various elements of this model have the following meanings in terms of physics. The spring with modulus $E_0$ describes the elastic deformation which in the polymer results from deformations of valence angles and changes in the interatomic distances (this type of deformation is particularly visible in the case of rapid load application). The Kelvin element ($E_\infty - \eta_0$) describes the development of the delayed deformation and accounts for the molecular process which is related to both mobility and orientation of polymer segments.

Large side chains and polar groups in macromolecules imply the development of time-dependent bonds which reduce the mobility of segments. The Maxwell element ($E_1 - \eta_1$) is used to bring into account those segments whose rupture is of the type of a relaxation process. The viscoplastic deformation com-

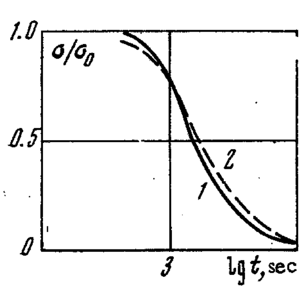

Fig. 3

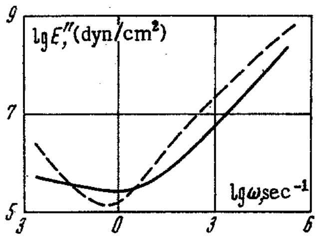

Fig. 4

ponent, which is always present in the deformation of linear polymers and which appears most clearly in long interaction times and at high temperatures, is brought into account by the element $\eta_{pl}$. A third-order differential equation of the form

$$\sum_{i=1}^{3} b_i \frac{d^i}{dt^i} \varepsilon = \sum_{i=0}^{3} a_i \frac{d^i}{dt^i} \sigma \tag{3.1}$$

corresponds to this model, where $b_i$ and $a_i$ depend upon $\eta_i$ and $E_i$.

In the case of a dynamic load application, a solution to Eq. (3.1) can be obtained in the form

$$E'(\omega) = \frac{\omega^6 a_3 b_3 - \omega^4 (a_2 b_2 - a_1 b_3 - a_3 b_1) + \omega^2 (a_1 b_1 - a_0 b_2)}{\omega^6 a_3^2 + \omega^4 (a_2^2 - 2a_1 a_3) + \omega^2 (a_1^2 - 2a_0 a_2) + a_0^2} \tag{3.2}$$

$$E''(\omega) = \frac{\omega^5 (a_2 b_3 - a_3 b_2) + \omega^3 (a_1 b_2 - a_0 b_3 - a_2 b_1) + \omega a_0 b_1}{\omega^6 a_3^2 + \omega^4 (a_2^2 - 2a_1 a_3) + \omega^2 (a_1^2 - 2a_0 a_2) + a_0^2}$$

The experimental static and dynamic characteristics of polyisobutylene were compared with the results obtained with the six-element model of Fig. 2 for the purpose of illustrating our method. The numerical values of the model parameters were determined from the experimental values of the real part of the complex modulus of elasticity of polyisobutylene [5, 7]. The stress relaxation data are depicted in Fig. 3. It follows from a comparison of calculated curve 1 and experimental curve 2 that the agreement between the curves is satisfactory. The frequency dependence of the imaginary part of the complex dynamic modulus is shown in Figs. 1 and 4. Satisfactory agreement between the calculated curves (dashed lines) and the experimental curves is observed.

The largest quantitative discrepancies are found between calculated and experimental curves for the loss modulus (though qualitative agreement between the curves is observed). When a more accurate quantitative description of these characteristic functions is desired, one must employ models of greater complexity, but the mathematical calculations are very complicated in this case. Furthermore, one must increase the number of the required experimental values of any of the polymer characteristics used to determine the model parameters.

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