Ninel Komova and Gennady Zaikov

THE ANALYSIS OF CHANGES OF RELAXATION PARAMETERS OF POLYETHYLENE DURING THEIR MEASUREMENT

N. M. Emanuel Institute of Biochemical Physics, Russian Academy of Sciences
4 Kosygin str., 119334Moscow, Russia; komova_@mail.ru

Abstract. Low density polyethylene (LDPE) has been studied by dynamic mechanical analysis (DMA) under monoaxial compression. Particular attention was paid to the loss tangent and to dissipation of mechanical energy by internal friction. In this connection it is necessary to take into account the temperature-time conditions of the experiment or introduce appropriate amendments to the results obtained.

1. Introduction

Any measurement of characteristics of a physical system is made by means of some instruments. In the classical theory of measurements representation according to which the measurements do not change the state of the measured system is used. During the measurements the influence of the measuring system is insignificant and the situation is not changing. However, according to the quantum nature of all physical systems, measuring of the system characteristics changes its status. The greater the change, the more information it gives. In the theory of measuring increase of information corresponds to decrease in entropy [1]:

$$S = -\sum_{i}^{n} p_i \ln p_i$$

where p_i – aprioristic probabilities of various conditions of a system, n – quantity of conditions.

Thus, increased measurement accuracy necessarily increases the influence of measuring on the characteristics of the system.

John Neumann established and mathematically formulated the "reduction postulate" for a quantum system. According to this postulate at measurement of some observable size the system condition changes in such a manner that in a new condition the measured observable has already another certain value, and it has turned out as a result of measurement. Occurrence of this condition is called a condition reduction of a system.

In the theory of measurements two types of measuring systems are considered: passive and active [2]. In a passive measuring system there is a comparison of the defined size with the standard without any active influence on the system. The feature of active measuring system is influence on the characterized system, and the response of the system to this influence gives the information for calculation of the needed parameters.

As the active measuring system assumes a certain influence on characterized object in the course of this influence the object can undergo changes. That is why the operation of agreement between the measurement system and measured object is carried out for obtaining a more accurate value of estimated parameters and for decreasing the influence of the input action on the measured object.

For measurements related to complex systems or facilities, the measured quantity depends upon different conditions. Usually the nature and quantitative characteristics of these dependences are unknown. The ccircumstances affecting the measurement result do not remain constant during the measurements and, as a result, it is impossible to correct the measurement error. This means that the measurements are not unique, but also reflect the influences on these measurements. These principles are important for the values that use complex physical and mathematical models in the measurement and which require adjustments in accordance with conditions.

In the mechanic of polymers such values are the parameters that characterize the relaxation properties of the material. These values and their corresponding dependence allow to judge about the structure of polymers and to determine the structural transition temperature and operating temperature of materials [3, 4].

One of widely used methods in research of elastic and relaxation properties of polymers in the block at periodic sinusoidal loadings is the method of Aleksandrov-Lazurkin [6] or dynamic mechanical analysis (DMA). This method is used for the elastic-plastic deformation of polymers in the frequency range located much lower than the natural frequency of the sample, *i.e.* outside the resonance region. In this case, the phase relationships, such as the lag phase of strain from the strain, are defined only by the relaxation time (the spectrum of relaxation times) and the elasticity of the material. Investigations of the phase relationships do not depend on the shape, size and density of the sample. This allows to comparatively easy determine the relaxation time of the material.

The method is based on the conception of elastic-plastic deformation as a reflection of the deformation of tightly packed flexible molecules. The appearance of the elastic force during deformation and shape recovery after unloading is the result of thermal motion units of macromolecules. All relationships underlying the method refer to the equilibrium state of the sample under load. Studying the dependence of elastic-plastic deformation upon the time under the conditions of constant stress or deformation and under the conditions of periodic deformations confirmed the important role of relaxation phenomena for the behavior of polymeric materials under mechanical stress, and in the process of verification of polymers [5, 7].

Depending on the regime of impact the properties of the polymer change. Thus, at a constant temperature of the experiment with increasing speed or increasing the frequency of exposure the polymers "solidification" effect has been achieved [8].

Total deformation of the polymer consists of elastic, rubbery and viscous fluid components. Considering the polymer in the elastic-plastic state, it is assumed that the macroscopic viscosity of the material is high and flow of the material is absent. To obtain the dependence of rubbery and elastic component of deformation on the applied mechanical stress the simplest model for these conditions is used [9]. In this paper a three-element Kelvin model (parallel connected spring and damper) connected in series with a spring is used. The equation describing the relationship between stress and strain of this model is as follows:

$$\frac{ds}{dt} + \frac{E_0 + E_1}{h} s = E_0 \frac{de}{dt} + \frac{E_0 E_1}{h} e \qquad (1)$$

where σ – stress acting on the system being studied; ε – deformation occurring in the system under the applied stress, E_0 – the module of elasticity; E_1 – high elasticity module; η – microviscosity.

Deformation of the polymer consists of elastic ($\varepsilon_0 = \sigma/E_0$) and rubbery (ε_1) parts. Expressing the rate of change in strain and allocating highly elastic component ε_1 in the Eq. (1), we obtain:

$$\frac{de_1}{dt} + \frac{E_1}{h} e_1 = \frac{s}{h} \qquad (2)$$

If the stress varies with time harmonically with frequency ω according to the equation:

$$s = s_0 \cos(wt) \qquad (3)$$

Then the total deformation is described by the equation:

$$e = Ce^{-\frac{t}{t}} + s_0 \left\{ \left(\frac{1}{E_0} + \frac{1}{E_1} \frac{1}{1+w^2 t^2} \right) \cos wt + \right. $$
$$\left. + \frac{1}{E_0} \frac{wt}{1+w^2 t^2} \sin wt \right\} \qquad (4)$$

where the parameter $\tau = \eta / E_1$ is called the *relaxation time*.

In some papers [10, 11] this parameter is called the delay time and the relaxation time is presented as a parameter described by the equation:

$$t_1 = t \frac{E_1}{E_1 + E_0} \qquad (5)$$

The first member of the Eq. (4) contains a constant *C*. This constant depends on initial conditions, characterizes transient and decays with time part of the deformation.

After sufficiently long time since the beginning of the measurements the transitional process is over and a stationary regime is established. In this case, $C = 0$ and in the Eq. (4) only the expression in figured brackets should be considered. This part of the Eq. (4) describes the steady-stationary oscillations, which are studied in the experiment. They consist of oscillations, which are in phase with the mechanical stress, representing the elastic component, and the oscillations are lagging behind the stress in phase $\pi/2$ and determined by the rubbery component. Since the two harmonic oscillations are directed along one axis and the vectors of their velocities are collinear, the amplitude of deformation is described by the equation:

$$e_0 = s_0 \sqrt{ \left(\frac{1}{E_0} + \frac{1}{E_1} \frac{1}{1+w^2 t^2} \right)^2 + \frac{1}{E_1^2} \frac{w^2 t^2}{\left(1+w^2 t^2\right)^2} } \qquad (6)$$

Using the condition $E_0 >> E_1$ as highly elastic modulus E_1 for polymeric materials is several orders smaller than the elastic modulus E_0, the dependence of deformation on the mechanical stress and frequency of its application (ω) is as follows:

$$e_0 = \frac{s_0}{E_1} \frac{1}{\sqrt{1+w^2 t^2}} \qquad (7)$$

The obtained expression can be transformed into the following form:

$$\frac{e_0}{s_0} = \frac{1}{E_1\sqrt{1+w^2t^2}}$$ (8)

Parameter ε_0/σ_0 is the dynamic compliance (I) and equal to the inverse dynamic modulus (E). Dynamic compliance is the meaning of the deformation in a single mechanical stress.

Using a complex representation of harmonically varying deformation $\varepsilon(t) = \varepsilon_0 e^{i\omega t}$, the rate of deformation can be expressed as $d\varepsilon(t)/dt = \omega\varepsilon_0 e^{i\,(\omega t + \pi/2)}$. Substituting this expression in the differential Eq. (1) and dividing by $e_0 e^{iwt}$, gives the relation:

$$(ihw + E)E^*(iw) = iEhw$$ (9)

where E^* is a complex dynamic modulus, which can be represented as:

$$E^*(iw) = \frac{h^2w^2E}{E^2+h^2w^2} + i\frac{hwE^2}{E^2+h^2w^2}$$ (10)

The first member of the Eq. (10) is a real, and the second is the imaginary part of the complex dynamic modulus ($E^* = E` + iE``$), which is proportional to $E$ and depends on the frequency. $E``(\omega)$ determines the losses at harmonic deformation and is the module of losses.

Analogous to the complex dynamic modulus $E^*(i\omega)$ we can represent a complex dynamic compliance I^* ($I^* = 1/E^*$) as the sum of the imaginary $I`$ and real $I`$ parts. Taking into account that $I^*(i\omega) \cdot E^*(i\omega) = 1$, we can provide the corresponding expression in the form:

$$I^*(i\omega) = I`(\omega) + iI`(\omega)$$

where $I' = \dfrac{1}{E_0} + \dfrac{1}{E_1}\dfrac{1}{1+w^2t^2} = I_0 + \dfrac{I_1}{1+w^2t^2}$,

$$I'' = \frac{1}{E_1}\frac{wt}{1+w^2t^2} = I_1\frac{wt}{1+w^2t^2}$$ (11)

and $I_0 = 1/E_0$, $I_1 = 1/E_1$.

Absolute measured deformation has the form:
$$I = \sqrt{I'^2 + I''^2}$$

From condition $I_1 \gg I_0$ (as $E_0 \gg E_1$):

$$I \approx \frac{I_1}{\sqrt{1+w^2t^2}}$$ (12)

The phase angle δ between I and $I`$, *i.e.* between strain and stress is defined as:

$$tg\,d = \frac{I''}{I'} = \frac{I_1wt}{I_1 + I_0(1+w^2t^2)}$$ (13)

Angle δ characterizes the mechanical loss, *i.e.* the part of mechanical energy which came into heat or a part of the energy dissipated per cycle of the deformation per unit of volume. A measure of this transformation may be an area corresponding to the hysteresis loop formed by the deformation dependence of mechanical stress during the cycle of periodic actions. This loop is formed by the curves of loading and unloading.

At low frequencies, when it is possible to investigate the hysteresis loop and measure the mechanical losses, using the coefficient of mechanical losses [3]:

$$\chi = \Delta W/W$$

where W – the total work of mechanical forces in a single cycle ща deformation, and ΔW– dissipated energy per cycle of deformation, which is proportional to the square hysteresis loop.

2. Experimental

In this paper the low-density polyethylene (LDPE) was selected as an object of study. Samples in the form of a cylinder with dimensions: diameter d of 8 mm with a ratio $h/d = 1.5$ were made by pressing at the temperature of 453 K and the pressure of 1500 N/cm². To obtain a homogeneous sample the polyethylene was kept under pressure and temperature of 453 K, using repressing to remove air located between the grains of the original polymer.

The samples were subjected to a periodic monaxial compression at room temperature for installation on the relaxometer [12, 13]. As a result of periodic influence of mechanical stress on the sample the stress-strain during loading and unloading in the form of a hysteresis loop was received. The study used three discrete frequencies of loading: 0.017, 0.17 and 1.7 Hz. In each series of tests not less than three samples were used. Every sample was subjected to periodic mechanical stress for 30 min, the results were taken every 5 min.

Measurements were taken every five minutes for 30 min. Parameter of the mechanical loss is defined as the ratio of the hysteresis loop to the area between the curve and the loading axis of strain: $\chi = \Delta W/W = S_l/S_{hole}$. The measurement results were averaged and subjected to further processing in accordance with calculations given in the Introduction.

3. Results and Discussion

Fig. 1 shows kinetic curves of variation of the mechanical loss by prolonged exposure of three frequencies: 0.017, 0.17 and 1.7 Hz. With increasing time of deformation coefficient of mechanical losses of the samples varies, but for the different load frequencies these changes have different character.

For low frequencies 0.017 Hz (curve 1) and 0.17Hz (curve 2) the initial value of this parameter is higher than the next. Evidently, this is due to the fact that during the decreasing "χ" the system goes into the steady state, *i.e.* where the constant C in Eq. (4) becomes equal to 0. For the frequency of 1.7 Hz (curve 3) the establishment of such state is much faster.
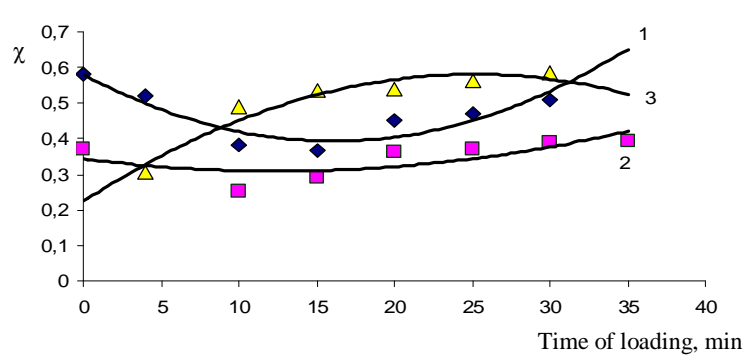
Fig. 1. Variation of the coefficient of the mechanical losses (χ) during periodic load.
Frequency of load, Hz: 0.017 (1); 0.17 (2) and 1.7 (3)

Between χ and tgδ there is dependence at all frequencies in terms of linear viscoelasticity. Thus, for asymmetric oscillations from 0 to $2\varepsilon_0$ according to work [14)] such dependence is found:

$$c = \frac{2ptgd}{4\sqrt{1+tg^2d}+ptgd} \qquad (14)$$

The solution of this equation concerning parameter tg δ gives the dependence:

$$tgd = \frac{4c}{\sqrt{4p^2(1-c)-6c^2}} \qquad (15)$$

This expression can be represented as: tg$\delta = \psi$

In expression (13) provided $E_0 >> E$ and $I_1 >> I_0$ at low frequencies to a first approximation we can obtain:

$$tg\delta = \omega\tau \qquad (16)$$

Equating the last two expressions leads to the relation: $\psi = \omega\tau$, where $\tau = \psi / \omega$.

According to the second postulate of the Boltzmann adopted in his theory of the elastic aftereffect, and the underlying Boltzmann-Volterra model that describes the relaxation phenomena [15]: effect on the stress at any given time of several deformations, that occurred in the past, does not depend on each other and therefore are added algebraically. This position was also the name of the Boltzmann superposition principle. It should be noted that for polymers the superposition principle holds in the upper-bounded range of deformation, stress and rate of their change.

According to this principle, considering the dissipative processes occurring during long-term effects of periodic stress on the material in the elastic-plastic state, we can conclude that there is an accumulation of mechanical energy dissipation in each cycle. Then, if the part of energy, transformed into thermal energy during one cycle, is determined by parameter χ_1, then under the condition of low thermal conductivity with the environment during N cycles, the part of dissipated energy during the time t is equal to:

$$\chi_{com} = \chi_1 \cdot t \cdot v, \quad \text{where } t \cdot v = N$$

Stored energy in the sample is converted into heat, which should lead to an increase in temperature. The principle of temperature-time superposition [16] establishes equivalence between the effect of temperature and duration of mechanical influence on the relaxation properties of polymers. Based on this principle, we can assume that the increase of impact load on the material is proportional to the action of temperature. Empirical dependence of temperature change ΔT on exposure time and frequency of deformation v in the first approximation can be expressed as follows: $T = bT\ v$, where "b" is a parameter characterizing features of converting mechanical energy into heat for the material under study.

Relaxation time of the supplied periodic stress decreases with increasing temperature and obeys the Arrhenius equation :

$$\tau = \tau_0 e^{U/RT} \qquad (17)$$

For elastic-plastic material similar dependence follows from Aleksandrov-Gurevich equation [17, 18] and has the form:

$$\tau = \tau_0 \exp[(U_0 - a\sigma)/RT] \qquad (18)$$

where U_0 – activation energy of relaxation process, the constant of the material.

This equation takes into account the dependence of the relaxation time on the load. If we assume that $U_0 - a\sigma \approx U$ and determine the relative relaxation time as τ_t/τ_1 (the ratio of the current value of the relaxation time to its initial value) then on the basis of equation (18) we can represented this value as an expression:

$$\frac{t_t}{t_1} = \exp\left(\frac{U}{R(T_1+\Delta T)} - \frac{U}{RT_1}\right) \qquad (19)$$

where the temperature T_1 corresponds to the beginning of load application, when the system is characterized by a relaxation time τ_1, and the increment of the ΔT is the change of temperature in the impact of load.

After simple algebraic manipulations (19) takes the form:

$$\frac{1}{\ln\dfrac{t_1}{t_t}} = \frac{RT_1}{U} + \frac{RT_1^2}{U}\Delta T^{-1} \qquad (20)$$

If instead of the increment of temperature ΔT we use time of impact of load (t) and frequency of the applied load (v) then the expression (20) becomes:

$$\left(\ln\frac{t_1}{t_t}\right)^{-1} = \frac{RT_1}{U} + \frac{RT_1^2}{U}(bnt)^{-1} \qquad (21)$$

Using this expression it is possible using the experimental data to find the estimated values of activation energy of relaxation process and to determine the extent to which the process is stationary (steady state). These evaluations will determine the degree of linearity of the relaxation processes and the range of conditions and the regime of correct determination of relaxation parameters for a periodic load.
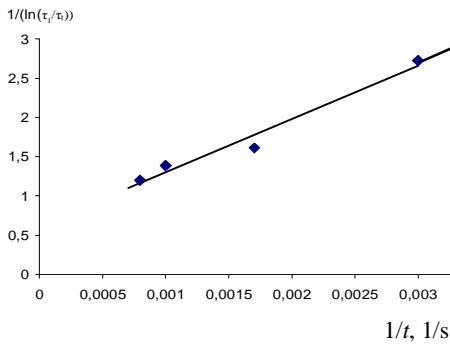

Fig. 2. The dependence of the relative relaxation time (τ_t/τ_0) on the time exposure of load (t). Frequency of load is 0.017 Hz

Fig. 2 shows the inverse logarithmic dependence of the relative relaxation time (which corresponds to the left side of the Eq. (21)) upon the inverse of the time exposure of load on the sample with a frequency of 0.017 Hz. The proposed coordinates of dependence of the relative relaxation time is directly proportional to the time of load effects. We can determine the activation energy of the current process by the value of this line intersection with the ordinate axis. Under these conditions (Fig. 2) it is equal to 4.9 kJ/mol. The slope in Fig. 2 allows to estimate the value of the parameter "b" in formula (21). The calculation shows that for the frequency of 0.017 Hz parameter "b" is 11.88. Since the dependence is linear in a rather wide time interval, this allows to conclude that the activation energy of relaxation process with periodic loading of LDPE under these conditions does not change.

A similar calculation allows to determine the appropriate parameters for the frequency of 0.17 Hz (Fig. 3). The calculated activation energy is 4.9 kJ/mol and $b = 0.414$.

In Fig. 4 this dependence is presented for the frequency of 1.7 Hz. The calculated value of activation energy is 2.4 J / mol. The value of $b = 0.04$.

With increasing frequency there is a reduction of the parameter b (Fig. 5). This indicates a difference in the relaxation processes at different frequencies. For

frequencies of 1.7 and 0.17 Hz sampling rate v on the parameter b is the same and equal to 0.07, while for the frequency of 0.017 Hz, this value is three times higher and amounts to 0.202. It should be noted the difference in the nature of the dependencies: Fig. 2 – for $v = 0.017$ Hz and Figs. 3 and 4 – for 0.17 and 1.7 Hz.
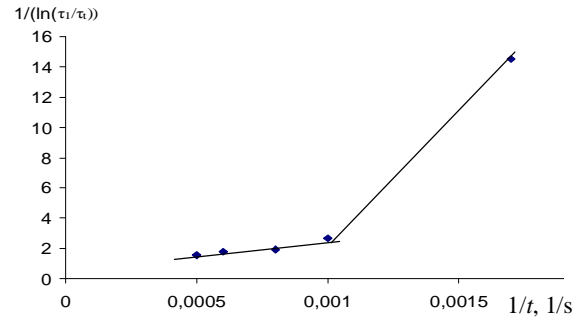

Fig. 3. The dependence of relative relaxation time (τ_t/τ_0) on the time exposure of load (t). Frequency of load is 0.17 Hz
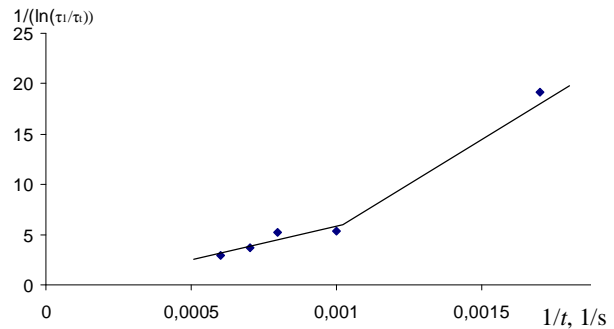

Fig. 4. The dependence of relative relaxation time (τ_t/τ_0) on the time exposure of load (t). Frequency of load is 1.7 Hz
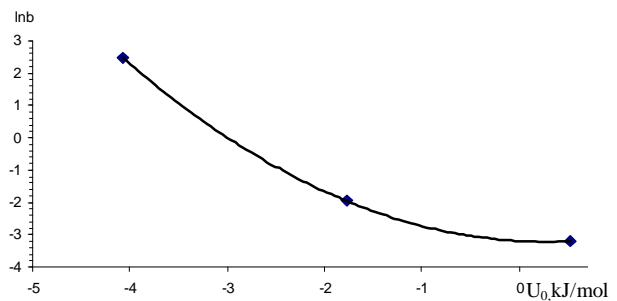

Fig. 5. The dependence of parameter "b" on the frequency of load (v)

The change of the angle of dependence of the relative relaxation time on the duration (Figs. 3 and 4) is most likely due to the establishment of dynamic equilibrium with the environment in the initial period of mechanical effects and change in the structure of the sample at times over 1000, which leads to a change in energy activation of the process. The activation energy of

changing the relative relaxation time is the smallest (2.4 kJ/mol) for the frequency of 1.7 Hz and for frequencies of 0.17 and 0.017 Hz, this energy is the same and equals to 4.9 kJ/mol.

If in the equation of Aleksandrov-Gurevich (18) instead of the stress (σ) we use the frequency v, instead of the coefficient "a" to use parameter "b", we can define a certain characteristic value U_0, similar to the initial activation energy of relaxation process: $U_0 = U + bv$.

Analysis of the dependence of the initial activation energy U_0 on the frequency (Fig. 6) shows that with increasing frequency v energy U_0 decreases linearly.
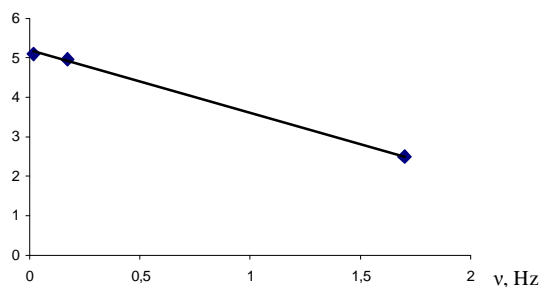

Fig. 6. The dependence of initial energy
of relaxation process on the frequency of load (v)

Using the principle of temperature-time superposition and kinetics coefficient of mechanical losses at different load intensities it is impossible to determine the time interval in which the measurements of relaxation parameters are correct. According to these approximations, we can preliminarily estimate the relaxation parameters and analyze the nature of relaxation processes by means of measurements without changing the initial temperature.

4. Conclusions

As a result of investigations we have shown that over time exposure periodic stress on the polymer sample a change in its relaxation time occurs. This process can be explained by a partial change in the structure of the polymer. For low frequency stress impacts (0.017 Hz) a change in the relaxation time of the sample occurs at a constant speed and activation energy for this process does not change.

For frequencies of 0.17 and 1.7 Hz, the rate of change of the relaxation time is high at the initial time and decreases by several times after 5–7 min of exposure. The activation energy of changes of relaxation time, calculated in accordance with the principle of temperature-time superposition, linearly decreases with the increase of frequency of deformation. The coefficient "b", which characterizes the structural changes in the polymer also decreases with increasing frequency. Thus, using the above approximation, we can give a preliminary

assessment of the relaxation parameters and analyze the nature of relaxation processes of measurement without changing the initial temperature.

Taking into account the principle of temperature-time superposition and features of the kinetics changes in mechanical losses at different load intensities it is possible to determine the time interval in which the measurements of relaxation parameters will be correct.

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АНАЛІЗ ЗМІН РЕЛАКСАЦІЙНИХ ПАРАМЕТРІВ ПОЛІЕТИЛЕНУ В ПРОЦЕСІ ЇХ ВИМІРЮВАННЯ

Анотація. Встановлено, що при дослідженні таких релаксаційних характеристик як тангенс кута механічних втрат і дисипація механічної енергії як наслідок внутрішнього тертя в процесі періодичної дії одноосної напруги стискування на зразок полімеру в пружно-пластичному стані відбуваються зміни цих характеристик. Необхідно враховувати температурно-часові умови проведення експерименту або вводити відповідні поправки в отримані результати. На основі принципу температурно-часової суперпозиції запропоновані оціночні залежності зміни часу релаксації поліетилену від тривалості дії періодичного навантаження, які задовільно узгоджуються з експериментальними даними.

Ключові слова: релаксаційний процес, дисипація механічної енергії, тангенс кута механічних втрат, принцип температурно-часової суперпозиції.