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DESCRIPTION OF THE SHAPE MEMORY EFFECT OF RADIATION-MODIFIED POLYMERS UNDER THERMOMECHANICAL ACTION

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The "shape memory" effect of crystallizing polymer materials is simulated. The polymer is considered to be an inhomogeneous medium with a moving boundary (temperature-dependent phase composition). Using a model based on the "frozen strain" hypothesis, the temperature dependences of stresses under isometric heating and cooling have been obtained. On the basis of the known data on the influence of γ-irradiation on the thermomechanical characteristics the dependences of thermorelaxation and thermoshrinkage stresses on the absorbed dose for high-density polyethylene have been found.

The phenomenon of thermal shrinkage of certain polymer materials (also referred to as the "shape memory" effect (SME)) consists of complete or partial restoration of the configuration of a previously strained and cooled sample of a material followed by its heating to a certain temperature. Such materials can be classified with functional materials, which in turn are elements of adaptive composites [1]. Thermoshrinkable products are used to make compounds and locate parts in rather inaccessible spots [2, 3], for example, to make and locate biologically compatible prosthetic appliances and implants. However, up to now there has been no mathematical model of the "shape memory" effect of polymers capable of predicting and optimizing the thermoshrinkage parameters.

The thermoshrinkage process is usually realized in the following sequence:

I) isothermal deformation ("stretching");
II) isothermal cooling ("freezing");
III) isothermal load removal;
IV) heating;
V) cooling down to the ambient temperature.

The first three stages permit obtaining a product with an SME. The subsequent stages (realization of the thermoshrinkage) can be realized in a free state, where the initial dimensions are restored, or under conditions close to isothermal ones, which leads to the appearance of thermorelaxation stresses σ_{tr} [4]. Compressive stresses arising under isothermal cooling are also called shrinkage stresses σ_{ts}. Stresses σ_{tr} and σ_{ts} determine the product's qualities (e.g., the bearing capacity, reliability and service life of the friction joint in which the shrinkage of the polymer part provides tension), and their prediction is of great interest.

Modeling of Thermal Shrinkage of a Polymer with an SME. The "shape memory" effect is realized in amorphous and crystalline polymers (in particular, polyethylene and mixed materials based on it [2–4]) with a specific "cross-linked" structure resulting from the formation of transverse bonds of macromolecules. The latter is attained, for example, under a high-energy γ-irradiation of a polymer at a temperature much higher than room temperature. Because of a certain structural-functional analogy of such effects and the crystallization process of the polymer [5], in the present paper we propose an SME model based on the phenomenological "frozen strain" approach [6]. We assume that at the moment of its formation upon cooling the crystal phase is in the stress-free state. Thus, the stressed-strained state of the polymer material is considered with regard for the temperature dependence of its phase composition. The relation between the axial stress σ and the longitudinal strain ε in the case of the uniaxial stressed state can be given in the form

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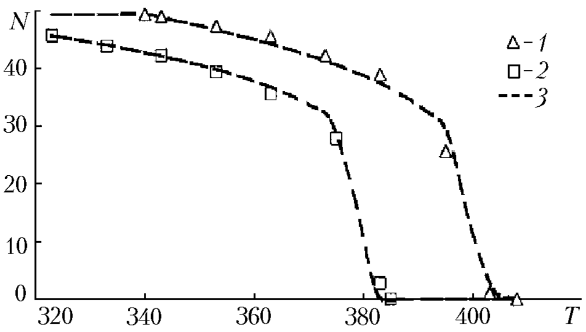


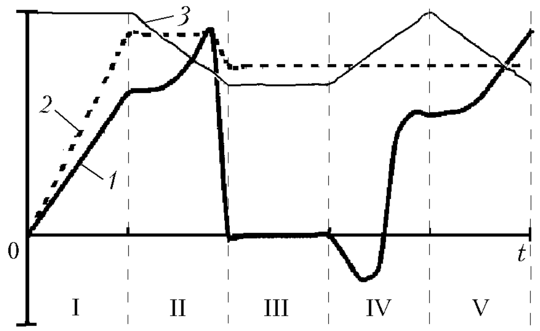


Fig. 1. Temperature dependence of the degree of crystallinity of polyethylene: 1) experimental data for the crystallization stage; 2) melting; 3) results of the approximation. N, %; T, K.

Fig. 2. Change in the stress (curve 1), strain (curve 2), and temperature (curve 3) of the specimen under thermoshrinkage (I–V, stages of thermoshrinkage).

$$\sigma(t) = E_1(T)\,\varepsilon(t) + [E_2(T) - E_1(T)] \int_0^t [\varepsilon(t) - \varepsilon^*(\tau)]\, dN(\tau) -$$

$$- [E_1(T) + N(t)(E_2(T) - E_1(T))]\,\varepsilon_T(t) + [E_2(T) - E_1(T)] \int_0^t \varepsilon_T(\tau)\, dN(\tau)\,. \tag{1}$$

The function $\varepsilon_T(T)$ is determined as follows:

$$\varepsilon_T(T) = \int_{T_0}^{T} [\alpha_1(x) + N(x)(\alpha_2(x) - \alpha_1(x))]\, dx\,. \tag{2}$$

The temperature dependence of the degree of crystallinity N is established experimentally by recalculating the curves obtained by the method of differential scanning calorimetry (DSC). Figure 1 shows the $N(T)$ dependences for high-density polyethylene given in [7]. These dependences have inflection points corresponding to the temperatures of the endopeak maximum of the DSC curve T_{melt} upon heating and the exopeak maximum T_{cr} upon cooling. To analytically describe the dependence $N(T)$ upon heating, it is necessary to experimentally determine the temperature of the beginning $T_{1\text{melt}}$ and completion $T_{2\text{melt}}$ of the melting process, the endopeak maximum temperature T_{melt}, and the degree of crystallinity $N_{1\text{melt}}$ at temperature $T_{1\text{melt}}$ (before the beginning of melting) and N_{melt} at temperature T_{melt}, respectively. It may be assumed that

$$N(T) = \begin{cases} N_{1\text{melt}}\,, & T < T_{1\text{melt}}\,; \\ A + C\,(T_{\text{melt}} - T)^{1/3}\,, & T_{1\text{melt}} < T < T_{\text{melt}}\,; \\ B + F\,(T_{2\text{melt}} - T)^3\,, & T_{\text{melt}} < T < T_{2\text{melt}}\,; \\ 0\,, & T > T_{2\text{melt}}\,. \end{cases} \tag{3}$$

The constants A, B, C, and F are determined from the continuity condition of the $N(T)$ function. A similar approximation can also be made for the temperature dependence of the degree of crystallinity upon cooling. To this end, the temperatures T_{cr}, $T_{1\text{cr}}$, and $T_{2\text{cr}}$ and the values of crystallinity N_{cr} and $N_{1\text{cr}}$ are determined experimentally. Analysis of the curves (see Fig. 1) permits concluding that, using approximation (3), one can fairly exactly describe the experimental dependences $N(T)$.

On the basis of relations (1)–(3) the dependences of $\sigma(t)$ and $\varepsilon(t)$ under thermal shrinkage of the polymer have been determined. The results obtained are schematically represented in Fig. 2. At the first stage (stretching), there is a

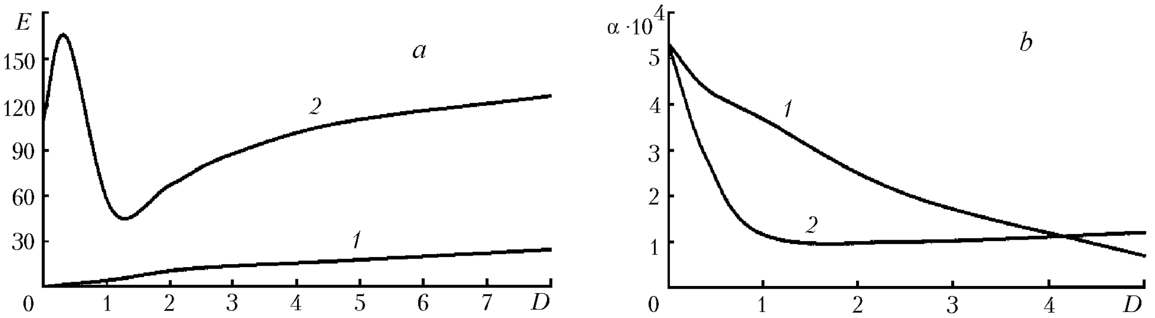


Fig. 3. Young modulus (a) and linear thermal expansion coefficient (b) versus the absorbed dose of γ-radiation for HDPE irradiated at a temperature of 423 K (curve 1) and 293 K (curve 2). E, MPa; $\alpha \cdot 10^4$, K^{-1}; D, MGy.

linear increase in the strain at a constant temperature. At the second stage (freezing), the temperature linearly decreases at a constant strain, i.e., under isothermal conditions. The increase in the stress here is due to the thermal expansion of the material. At the third stage, instantaneous removal of the load occurs. In so doing, the stress decreases down to a value of ε_{III} other than zero. At the fourth stage, the temperature linearly increases at a fixed strain $\varepsilon(t) = \varepsilon_{III}$. At the beginning of this stage the thermal expansion leads to a decrease in the stress. Then, in the melting process of the crystal phase the stress sharply increases. Upon reaching the temperature $T_{2\mathrm{melt}}$ ($N = 0$) the stress takes the value of σ_{tr} and remains practically unchanged with further increase in the temperature. At the last stage, the specimen is cooled down to the ambient temperature and the stress increases up to the value of σ_{ts}. To realize the memory effect, it is essential that the temperature at the third stage be below $T_{1\mathrm{cr}}$ and at the end of the fourth stage-above $T_{2\mathrm{melt}}$.

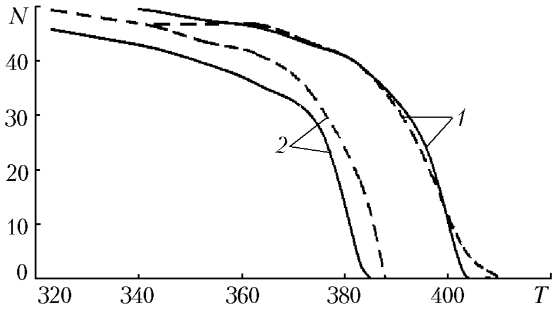
Thus, to describe the stressed-strained state of a polymer material in realizing the "memory" effect, it is necessary to know the thermomechanical characteristics of the amorphous ($E_1(T)$, $\alpha_1(T)$) and crystal ($E_2(T)$, $\alpha_2(T)$) phases of the material as well as the temperature dependence of crystallinity $N(T)$.

Influence of Ionizing Radiation on the Thermomechanical Characteristics of the Polymer Material. One method for modifying polymer materials that permits controlling their thermomechanical characteristics is radiation treatment [1–3]. Under the action of ionizing radiation in the polymer material two competing irreversible radiation-chemical processes are realized: destruction and cross-linkage. While in the destruction process the molecular mass of the polymer decreases, at cross-linkage, on the contrary, it increases. For many polymers (polyolefins, polyesters, etc.), the process of cross-linking, in which in the material an insoluble gel-fraction arises, dominates. It can be noted that the mechanical characteristics of the gel-fraction are fairly well described by the high-elasticity theory.

Cross-linkage is mainly realized in the amorphous phase. Therefore, under the action of ionizing radiation there is a marked increase in the Young modulus of the polymer material in the region of high temperatures ($T > T_{2\mathrm{melt}}$). This fact is illustrated in Fig. 3a. Figure 3a also gives the dependence of the Young modulus on the absorbed dose for high-density polyethylene (HDPE) irradiated at a low temperature ($T < T_{2\mathrm{cr}}$) [3]. The character of this dependence is determined by a complex of physicochemical processes: cross-linkage in the amorphous and crystal phases, destruction, interaction of the gel-function with crystallites, etc. An increase in the molecular mass as a result of the cross-linkage leads to a decrease in the thermal expansion coefficient (Fig. 3b).

At $T > T_{2\mathrm{melt}}$ the crystal phase is practically absent from the polymer. Consequently, curves 1 (see Fig. 3) give the thermomechanical characteristics of the amorphous phase E_1 and α_1 versus the absorbed dose. To simplify the calculations, we assume that in the temperature range near the fusion temperature (for HDPE $290 < T < 450$ K) the parameters E_1, α_1, E_2, and α_2 are not temperature dependent. This assumption is not a matter of principle and can be removed if sufficient information on the temperature dependence of the corresponding quantities is available. At a temperature $T < T_{2\mathrm{cr}}$ the material being investigated can be considered as an inhomogeneous one with a volume concentration of the crystal phase $N_{2\mathrm{cr}}$. In the first approximation the crystal-phase characteristics E_2 and α_2 can be determined by the mixture rule

$$E_2 = \frac{1}{N_{2\mathrm{cr}}} (E_{\mathrm{eff}} - E_1) + E_1 \,, \quad \alpha_2 = \frac{1}{N_{2\mathrm{cr}}} (\alpha_{\mathrm{eff}} - \alpha_1) + \alpha_1 \,. \tag{4}$$



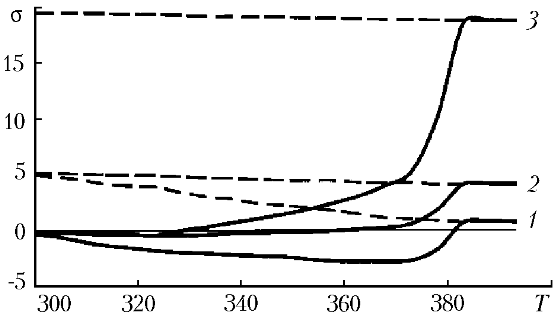


Fig. 4. Temperature dependence of the degree of crystallinity of HDPE: 1) melting; 2) crystallization. Solid lines correspond to D = 0.15 MGy, dashed lines — nonirradiated material. N, %; T, K.

Fig. 5. Temperature dependence of the stress under isothermal heating and cooling: 1) D = 0.15; 2) 1; 3) 8 MGy. σ, MPa; T, K.

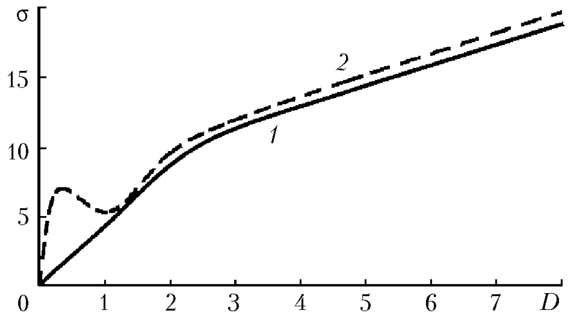


Fig. 6. Thermorelaxation σ_{tr} (curve 1) and thermoshrinkage σ_{ts} (curve 2) stresses versus the absorbed dose. σ_{tr}, σ_{ts}, MPa; D, MGy.

The dependence of the values of E_{eff} and α_{eff} on the absorbed dose D is given by curves 2 in Fig. 3. Thus, the analysis of the experimental data and the use of relation (4) permit determining the dependence of the material's thermomechanical characteristics needed to describe the "memory" effect of polymers on the absorbed dose upon radiation modification. The curves in Fig. 3 are based on the experimental data of [3].

Along with the above results, it is necessary to investigate the influence of the radiation irradiation on the function $N(T)$. Figure 4 shows the temperature dependences of the crystallinity fraction for the initial and radiation-modified HDPE presented in [7]. It can be noted that upon subsequent cooling the presence of the gel-fraction restrains the crystallization process and leads to a decrease in the temperatures T_{cr}, T_{1cr}, and T_{2cr} and in the values of N_{cr} and N_{1cr}. The relation between these parameters of the crystallization process and the absorbed dose is still not clearly understood. Therefore, we will use in the calculations the dependence $N(T)$ corresponding to a definite dose, namely, D = 0.15 MGy.

Computing Experiment and Analysis of the Results. As an example of using the proposed mathematical model, consider the process of realization of the SME of a specimen of radiation-modified high-density polyethylene. To this end, we propose the following temperature conditions: the duration of each of the five stages (see Fig. 2) is the same and equals 1 min; the temperature at the first stage and on completion of the fourth one is 393 K; the temperature at the third stage and on completion of the fifth one is 293 K; the temperature in the second, fourth, and fifth portions changes at a constant rate of 100 K/min. Along with the function $T(t)$, the initial parameter of the process under investigation is the tensile strain ε_I attained on completion of the first stage.

Of greatest interest for optimizing the thermal shrinkage and providing functional reliability of the product obtained are the temperature dependence of the stress at the fourth stage and the value of the stress σ_{tr} arising upon termination of isothermal heating. Figure 5 shows the temperature dependences of the stress under isothermal conditions in the fourth portion for an HDPE specimen with various absorbed doses in the temperature regime under consideration and strain $\varepsilon_I = 100\%$. It can be noted that nonzero thermorelaxations σ_{tr} arise even at a dose $D = 0.15$ MGy. With increasing absorbed dose the thermorelaxation phenomenon leads to a stress compensation. The dashed lines in Fig. 5 show the temperature dependence of stresses in the specimen upon isothermal cooling (the fifth stage). As the dose D increases, there is also an increase in the stress σ_{tr} attained upon termination of isothermal heating (Fig. 6).

The dependence of the thermoshrinkage stress σ_{ts} corresponding to the moment of completion of the fifth stage of isometric cooling on the absorbed dose at $D < 2$ MGy is nonlinear and has a maximum in the region of $D = 0.4$ MGy. This phenomenon is likely to be due to the nonlinear character of the dependence of the Young modulus of the polymer crystal phase on the absorbed dose at small values of D. At large doses the growth of the stress in the fifth portion of the "memory" effect realization is insignificant and the stress σ_{ts} exceeds σ_{tr} by no more than 8%.

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NOTATION

A and B, constants in approximation (3), dimensionless; C, dimensional constant in approximation (3), $K^{-1/3}$; D, absorbed dose of γ-radiation, Gy; E_1 and E_2, elastic moduli of the polymer in the high-elasticity and crystalline states, respectively, Pa; E_{ef}, effective elastic modulus of the polymer material at $T < T_{cr}$, Pa; F, elastic constant in approximation (3), K^{-3}; N, degree of crystallinity, dimensionless; T, absolute temperature, K; T_{melt} and T_{cr}, temperatures of the DSC curve endopeak maximum upon heating and of the exopeak maximum upon cooling, respectively, K; T_{1cr} and T_{2cr}, temperatures of the beginning and completion of the crystallization process, K; t, time, sec; x, variable of integration in (2), K; α_1 and α_2, linear thermal expansion coefficients of the polymer in the high-elasticity and crystalline states, respectively, K^{-1}; α_{eff}, effective linear thermal expansion coefficient of the polymer material at $T < T_{cr}$, K^{-1}; ε, longitudinal strain of the specimen, dimensionless; ε^*, strain corresponding to the degree of crystallization N upon cooling of the material ("frozen" strain), dimensionless; ε_T, temperature strain, dimensionless; ε_I and ε_{III}, strain upon completion of the first and third stages of thermal shrinkage, respectively; σ, axial stress in the specimen, Pa; σ_{tr} and σ_{ts}, thermal relaxation and thermal shrinkage stresses, respectively, Pa; τ, integration variable in (1), sec. Subscripts: 0, initial value; 1, high-elasticity state of the polymer; 2, crystalline state; 1melt, onset of the melting process; 2melt, completion of the melting process; 1cr, onset of the crystallization process; 2cr, completion of the crystallization process; I and III, completion of the first and third stages of thermal shrinkage, respectively; T, temperature (under a strain); melt, maximum point of the DSC curve endopeak upon melting; cr, maximum point of the DSC curve exopeak upon crystallization; tr, thermal relaxation; ts, thermal shrinkage; eff, effective characteristics of the polymer; *, superscript at a "frozen" strain.

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