RELAXATION OF HEAT TRANSFER PROCESSES IN POLYMERS

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It is shown that the appearance of relaxation properties, inherent to polymer materials, permits establishing a basis for applying the hyperbolic transfer equations and proposing a model permitting the description of heat transfer in polymers. The interrelation between the mechanical and thermal relaxation characteristics of a medium is indicated.

Many practical problems in the area of polymer material application, reworking, molding into items, etc., cannot be solved correctly without clarifying the nature of the progress of transfer processes in such materials and determining the appropriate phenomenological constants. Knowledge of the thermophysical characteristics which, for these materials, are strongly dependent on the temperature, method of fabrication, conditions of utilization, and a number of other factors [1-3], acquires special value. In particular, properties of the filler and the constitution of the composition, the mechanical loads, the polymerization mode, etc. [4, 5] exert a quite strong influence, where the presence of a quite definite anisotropy, indicating the sufficiently strong influence of internal orientation on the physicomechanical properties [6], is characteristic. A peculiarity of polymers is also the presence of a close correlation between the mechanical and thermophysical properties, which stresses the relaxation nature of the transfer processes in polymer materials and permits considering them as rheological media [7-12].

The interrelations established experimentally, between the temperature dependence of the diffusion coefficient and the temperature dependence of the shear viscosity [13, 14], the dependence of viscosity on the shear stress and velocity and heat conduction of these same parameters [10-12], etc., permitted the proposal of an invariant-temperature dependence of the transfer coefficient for polymers belonging to one homologous series using just two parameters: the vitrification temperature and the minimal (critical) molecular weight at which the polymer chains start to form a supermolecular structure [8, 15]. Therefore, the dependence of the physicomechanical properties on the strain rate and on the external energy supply rate affords a basis for asserting the presence of the same coupling with respect to both the thermal characteristics and the heat supply rate [16-19] and the widely used phenomenological transfer coefficients depend implicitly on the heat supply, i.e., the nature of the external action.

Test and computations show convincingly that the molecule structure and orientation in polymers vary substantially upon the imposition of external fields (of even low intensity), which causes a change in the nature of the thermal motion of the particles in turn, and in the long run, of the transfer properties. Any action causes a change in the isotropy of the medium; the material in which the transfer processes proceed becomes anisotropic.

This appears especially noticeably for polymers. The equal probability of micromolecule arrangement in the absence of external force fields is replaced upon their imposition by the orientation of prestrained macromolecules and supermolecular formations of some degree of complexity. It is hence necessary to take into account that the great complexity of the formations, and the low mobility, in thermal respects, indeed govern the high inertness of the medium in reaction to the external thermal effects than holds for the transfer of momentum.

Hence, the most general expression of the heat-transfer law for such relaxing media will be [12]

$$q + \tau_{r_2} \frac{\partial q}{\partial \tau} = -\lambda \left[\operatorname{grad} T + \tau_{r_1} \frac{\partial}{\partial \tau} (\operatorname{grad} T) \right]. \tag{1}$$

Considering the case of the joint progress of heat and momentum transfer (constraints resulting from the Curie principle are not considered because of anisotropy of the medium) with the relaxation of the processes themselves taken into account, the system of Onsager equations can be represented as

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$$J_i = \sum_{k=1}^{n} L_{ik} \int_0^{\tau} X_k K(\tau - \tau')\, d\tau', \tag{2}$$

where $K(\tau - \tau')$ is the relaxation kernel, which indicates the interrelation between themoelasticity problems for a finite rate of perturbation propagation.

Therefore, from the viewpoint of its transfer properties, the rate of propagation of excitation is an important characteristic of a medium. The rate of perturbation propagation (the rate of signal transmission) can be quite high in all real systems. However, it is always finite. The effect of reaction lag is a result. The relaxation nature of equilibrium build-up in a system subjected to external effects hence follows. The duration of the relaxation processes depends on the complexity of the system structure and if the relaxation time of the mechanical perturbations for gases is practically zero, it is counted in times on the order of 10^{-10} sec for simple fluids, and $\sim 10^{-5}$ sec in solutions of polymers and melts, then it is already hours and more [1, 12] in polymers in the vitrification state. The relaxation time in crystals is extraordinarily large; i.e., stress relaxation is not observed with the lapse of time in practice.

A similar picture can also be observed with respect to the transmission of a thermal signal. The rate of heat propagation in metals and crystals is quite large (practically infinite) and the build-up of equilibrium of a medium and the incoming signal occurs instantaneously (the relaxation time, the lag time equals 10^{-10} sec). It is on the order of 10^{-5} sec and more for amorphous bodies and polymers (depending on the complexity of the structure), and the slowest signal propagation holds in rarefied gases since $1/\tau \sim \sigma^* \bar{g} n$ [20].

Therefore, for a viscoelastic relaxing medium it is seen from the strain equation

$$\frac{d\varepsilon}{d\tau} = \frac{1}{E}\,\frac{d\sigma}{d\tau} + \frac{\sigma}{\mu} \tag{3}$$

and the corresponding solution

$$\sigma = \exp\left(-\frac{\tau}{\tau_p}\right)\left[\sigma_0 + E\int_0^{\tau} \frac{d\varepsilon}{d\tau} \exp\left(\frac{\tau}{\tau_p}\right) d\tau\right] \tag{4}$$

that for a given constant strain $\varepsilon = \varepsilon_0 = \text{const}$

$$\sigma = \sigma_0 \exp\left(-\frac{\tau}{\tau_p}\right), \tag{5}$$

i.e., stresses relax with the lapse of time. Upon giving $\sigma = \sigma_0 = \text{const}$ the instantaneous strain of the medium will equal $\varepsilon_0 = \sigma_0/E$ and a flow starts at a constant velocity. Upon removal of the stresses the strain rate vanishes but a certain residual strain remains.

As is seen, the magnitude of the stresses in such media is a function of the strain rate $d\varepsilon/d\tau$, i.e., the strain of the medium is related to the rate of energy coming in from outside, to the intensity of the external effect.

The use of the hyperbolic transfer equation of the form (1), which is written thus for the one-dimensional case

$$q = -\lambda \frac{dT}{dx} - \tau_r \frac{dq}{d\tau}, \tag{6}$$

has been given a theoretical foundation by A. V. Lykov, A. S. Predvoditelev, and a number of other scientists [12] for systems with a finite rate of signal transmission.

Let us introduce the notation $E_T = \lambda/c\tau_r$ and $\mu_T = \lambda/c$, to which the value of the elastic modulus of the thermal field in a given medium and the viscosity field can be ascribed by analogy exactly as in momentum transfer.

We therefore consider the process of thermal signal propagation in a certain viscoelastic medium of Maxwell type, where the characteristics of this medium depend on the structure of the real material in which the heat transfer proceeds.

Taking account of the notation used, the propagation velocity of the thermal perturbation is

$$W_r = \sqrt{\frac{a}{\tau_r}} = \sqrt{\frac{E_T}{\rho}}, \tag{7}$$

and (6) becomes

$$\frac{q}{\tau_T} = -E_T \frac{dU}{dx} - \frac{dq}{d\tau}$$

or

$$-\frac{dU}{dx} = \frac{1}{E_T}\frac{dq}{d\tau} + \frac{q}{\mu_T}. \tag{8}$$

According to [21], we can write

$$\frac{dU}{d\tau} = -W_T \frac{dU}{dx}, \tag{9}$$

where $W_T = dx/d\tau$ is the rate of displacement of an isothermal surface. It then follows from (8)

$$\frac{1}{W_T}\frac{dU}{d\tau} = \frac{1}{E_T}\frac{dq}{d\tau} + \frac{q}{\mu_T} \tag{10}$$

or introducing the notation $\varepsilon_T = U/W_T^2$, the relative strain of the thermal fields, and $\sigma_T = q/W_T$ the stress of the thermal field, we obtain the hyperbolic equation of heat propagation in a form analogous to (3) for the mechanical strains, i.e.,

$$\frac{d\varepsilon_T}{d\tau} = \frac{1}{E_T}\frac{d\sigma_T}{d\tau} + \frac{\sigma_T}{\mu_T}. \tag{11}$$

A solution of the equation obtained will be

$$\sigma_T = \exp\left(-\frac{\tau}{\tau_r}\right)\left[\sigma_{T_0} + E_T \int_0^\tau \frac{d\varepsilon_T}{d\tau} \exp\left(\frac{\tau}{\tau_r}\right) d\tau\right] \tag{12}$$

or

$$q = \exp\left(-\frac{\tau}{\tau_r}\right)\left[q_0 + \frac{E_T}{W_T} \int_0^\tau \frac{dU}{d\tau} \exp\left(\frac{\tau}{\tau_r}\right) d\tau\right]. \tag{13}$$

We hence obtain that for $q = \text{const}$ the temperature field receives an elastic strain equal to q/E_T in the initial instant and then starts to be propagated at a constant velocity. Upon removal of the thermal stress the strain rate of the thermal fields will drop exponentially, but the residual strain is conserved; i.e., the temperature of the medium is set at a new level (cases with negative sources, with the efflux of energy from the system are not considered). If the constant strain of a temperature field is given, then the thermal stresses, i.e., the flux, will relax with the lapse of time by decreasing exponentially.

The extreme limit cases we have considered are characteristic for real heat propagation processes in different systems and can be used to analyze the phenomena being observed.

The general regularity for perturbations propagation in relaxing systems is stressed still more if (3) is given the form

$$\frac{d\sigma}{d\tau} = -E\frac{dW}{dx} - \frac{\sigma}{\tau_p}, \tag{14}$$

analogous to

$$\frac{dq}{d\tau} = -E_T\frac{dU}{dx} - \frac{q}{\tau_r}, \tag{15}$$

by the evident substitution $d\varepsilon/d\tau = -(dW/dx)$.

Equations (14) and (15) are written in the form of dependences between the rate of energy supply and the shear-velocity gradient or the energy-distribution gradient, originating in the medium, and should be solved jointly in the general case or, as follows from the preceding examination, E (the elastic modulus of the medium) is a function of the temperature and E_T (the elastic modulus of the thermal field) is a function of the state of stress. Moreover, the relaxation time τ_p itself is a certain function of the temperature and the stress, i.e.,

$$\tau_p = \tau_{p_0} \exp\left(\frac{u_{0p} - \gamma_p \sigma}{RT}\right), \tag{16}$$

where τ_{p_0} and γ_p are certain constants dependent on the structure, and u_{0p} is the true activation energy of the relaxation process. An analogous dependence should exist also in respect to the time τ_r [21]. It is hence important to set up relationships between the stresses, strains, and the change in temperature in order to describe transfer processes in relaxing media quite exactly.

Turning to an examination of the system microstructure and keeping in mind that according to modern viewpoints heat is propagated because of the motion of phonons, it is easy to carry out an additional correlation between heat transfer and momentum transfer.

A phonon gas filling a volume of space occupied by a body is in constant thermal motion. Because of phonon collisions, energy is exchanged partially and is dissipated partially. The phenomenon of the so-called thermal resistance occurs. The more ordered the structure, the greater the mean free path of a phonon, the smaller the resistance of the medium to phonon motion, and therefore, the thermal conductivity of the medium grows, the relaxation time and the time of equilibrium build-up diminish, and the rate of signal transmission grows.

The rate of heat propagation should be infinite in a medium absolutely ordered structurally and the thermal relaxation time should tend to zero in the limit.

At the same time the coupling force between separate particles for such a system should be quite large because the particles are at the stable equilibrium position and the system energy is minimal.

The particle mobility is infinitesimal, which corresponds to an infinite value of the system viscosity, its elasticity is finite and determined by adhesion forces of the structural particles. In this case the activation energy should be infinite; i.e., an infinite force must be applied to extract the system from the equilibrium state.

Therefore, it follows from the condition of a finite propagation velocity for the perturbations (7) and the dependence (16) that the relaxation time of the mechanical stresses should be infinite for a perfect crystal.

The resistance to displacement of the phonon gas grows with the increase in disorder, the thermal resistance grows, and the thermal conductivity diminishes. The transmission velocity of a thermal perturbation is reduced and the relaxation time τ_r increases. The particle mobility simultaneously increases, the medium viscosity is reduced, and the stress relaxation time τ_p diminishes. In completely disordered media, among which are sufficiently rarefied gases, the thermal and dynamical viscosity are commensurate and there should be $\lambda/c\mu = \text{const}$ according to Maxwell [21]. In this case the relaxation times of the thermal and dynamical will be of the same order.

Thus, the thermal equilibrium build-up time τ_r grows from zero to a certain finite value in going from a completely ordered to a disordered structure, and the relaxation time of the elastic stresses is reduced from $\tau_p = \infty$ to a certain finite value also. The specific form of the dependences mentioned is determined by the nature of the medium in which the heat and momentum transfer processes occur.

A correlation can be established between the relaxation time of the thermal processes and the stress relaxation time. It is known on the basis of molecular-kinetic theory that the relaxation time is a function of the particle density in phase space n, the transition probability from the excited to the equilibrium state a_1^0, the energy of this state, and the temperature, i.e.,

$$\frac{1}{\tau(n,\ T)} = n a_1^0 \left[1 - \exp\left(-\frac{h\omega}{kT}\right)\right],$$

hence $h\omega[\exp(h\omega/kT) - 1]^{-1} = \varepsilon^0(T)$ is the equilibrium energy of a system of oscillators at a temperature T [20]. Going from the quantum over into the real space and using the model of a Maxwell gas with the potential $u = Kr^{-4}$, we obtain

$$\frac{1}{\tau_r} = 6\,\frac{A}{m}\left(\frac{8K}{m}\right)^{0.5} \rho \tag{17}$$

or in the notation already used

$$\tau_r \sim \frac{1}{n g \sigma^*}. \tag{18}$$

Therefore, it can be obtained from (17) or (18) that

$$\tau_r = CRT, \tag{19}$$

where C is some constant.

Substituting (19) into (16), we obtain a relationship between τ_p and τ_r in the form

$$\tau_p \sim A \exp\left(\frac{B}{\tau_r}\right). \tag{20}$$

The constants A and B depend on the structure of the real medium, have the dimensionality of time, and characterize the inertia of the medium with respect to the dynamical and thermal processes.

The relationship obtained again stresses the unity and mutual dependency of the progress of the transfer processes, their mutual influence on each other. Hence, not taking these peculiarities of real structures into account should inevitably result in an incorrect interpretation of the phenomena observed in general and in inaccuracies in the determination of the phenomenological coefficients in particular.

The mutual influence of the separate transfer processes on each other increases with the growth in the complexity of the construction of real structures and forces their joint examination in order to solve adjoint problems with interrelated transfer coefficients. The situation in the respects mentioned is especially acute for polymer materials: The complexity of the configuration at the molecular level, the formation of supermolecular structures and their relative flexibility, the tendency to rearrangement upon application of external fields, the relatively small stress relaxation time, and the comparatively high inertia to thermal processes, all together specify a more abrupt appearance of the relaxation properties inherent to this kind of materials and result in the need to get rid of traditional methods for estimating the transfer properties by using the phenomenological coefficients. In application to polymer materials, as in no other case, the ordinary transfer coefficients of the viscosity, thermal conductivity, or diffusion coefficient type, lose their clear meaning and it is impossible to use them to describe the true nature of the processes in progress. The correct determination of these coefficients under test conditions becomes difficult and their utilization in computations causes additional mathematical difficulties.

NOTATION

τ_{r_1}	is the relaxation time of the temperature gradient;
τ_{r_2}	is the relaxation time of the thermal fluxes;
J_i	is the flux;
L_{ik}	are the kinetic coefficients;
X_k	are the thermodynamic transfer forces;
$\bar{g}$	is the mean relative velocity of the ensemble of particles;
σ^*	is the effective collision cross section;
n	is the particle concentration;
ε	is the relative mechanical strain;
σ	is the stress;
τ_p	is the relaxation time of the mechanical stresses;
E	is the elastic modulus;
μ	is the coefficient of dynamic viscosity;
c	is the specific heat;
ρ	is the density;
$dU = d(cT)$	is the change in internal energy per unit volume;
m	is the particle mass;
h	is the Planck's constant;
R	is the universal gas constant.

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AN EXPERIMENTAL STUDY OF INFLUENCE OF DEGREE OF SWIRLING OF A PLASMA AIR JET AND INTRODUCTION OF NATURAL GAS INTO IT ON TEMPERATURE AND VELOCITY FIELDS

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The results of the measurement of temperature and velocity fields of swirled plasma jets are presented. An improved method is proposed for measuring the temperature of a plasma.

The swirling of gas streams finds application for the stabilization of arc burning in plasmotrons [1], for improvement of the process of mixing gas jets [2], and for increasing the coefficient of heat transfer to particles in the spraying of a number of materials [3]. In contrast to straight-flowing plasma jets, swirled jets possess a higher mixing intensity, a large expansion angle of the jet, and an increased ejecting capacity, which is particularly important in the creation of plasma-chemical reactors and of devices for plasma spraying.

The processes of particle heating in the plasma jet of an oblique-action plasmotron can be investigated only when the detailed pattern of the gas-flow dynamics and the three-dimensional pattern of the temperature field are known [4]. It has now been established that the variation in the velocity profiles in a plasma jet has a complex character depending on the degree of swirling, the distance to the nozzle cut of the plasmotron, and the gas flow rate [5, 6]. Unfortunately, the existing methods of calculating the propagation of swirled turbulent jets do not give satisfactory results for the main section of a plasma jet. Therefore, the dynamic structure of swirled plasma streams can now be established on the basis of experimental data obtained under one or another concrete conditions.

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