THE NONISOTHERMAL OLIGOMER HARDENING REGIME

A. Ya. Malkin and A. E. Teishev

UDC 536.42

We have established general quantitative relationships linking the magnitude of the induction period in isothermal and nonisothermal regimes of oligomer hardening for the case in which the nonisothermicity is determined by the kinetics of heat generation in the chemical reaction.

The hardening of oligomers and oligomer-based compositions is a basic technological operation in the manufacture of items out of hardened plastics. In this case, an important technological characteristic of the material, governing its behavior during the treatment process, is its "viability," or the induction period, i.e., the time during which the material retains its fluidity, or in other words, the period of time until it reaches the gel point. Various conditional or objective methods exist for the determination of t*, but these, however, yield uniquely defined results only in the isothermal regime. We are also aware of standardized methods for estimating the time during which fluidity is maintained (the length of time in the viscous-fluid state) which are applicable to the nonisothermal hardening regimes; however, these estimates are strongly dependent on the specific condition of process behavior and the relationship of these estimates to t*, found in the isothermal regime, remains indeterminate.

It is the purpose of this paper to establish the general quantitative relationships which link the values of t*, measured in the isothermal regime, to the magnitudes of the induction period derived in the nonisothermal hardening regime. This task applies, in general, to oligomers, but pertains in equal measure to the nonisothermal vulcanization regimes for elastomers. In this connection, in this paper we study in considerable detail the release of heat governed by the kinetics of the chemical hardening reaction as the basic source of nonisothermicity.

The initial relationships for the solution of the stated problem, i.e., first of all, the relationship between the induction period and temperature t*(T), which we will write in the usual manner by means of the Arrhenius equation

$$t^*(T) = B\exp(U/RT), \tag{1}$$

and, second, the criterion of nonisothermal hardening. This criterion was presented in [1] in the form of a rule for the summation of the reactions occurring at various temperatures. In analogy with the familiar Bailey criterion for destruction under variable loads, it is written in the following manner:

$$\int_0^{t_n^*} \frac{dt}{\exp[U/RT(t)]} = 1. \tag{2}$$

We can eliminate the constant B by combining Eqs. (1) and (2) and assuming that at some "initial" temperature T_0, $t^* = t_0^*$. Then

$$\int_0^{t_n^*} \frac{dt}{\exp[U/RT(t)]} = \frac{t_0^*}{\exp(U/RT_0)}, \tag{3}$$

or

$$\int_0^{\tilde{t}^*} \exp(\tilde{U}\,\tilde{T})\, d\tilde{t} = 1, \tag{4}$$

Scientific Industrial Enterprise "Plastmassy," Moscow. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 56, No. 4, pp. 591-595, April, 1989. Original article submitted November 10, 1987.

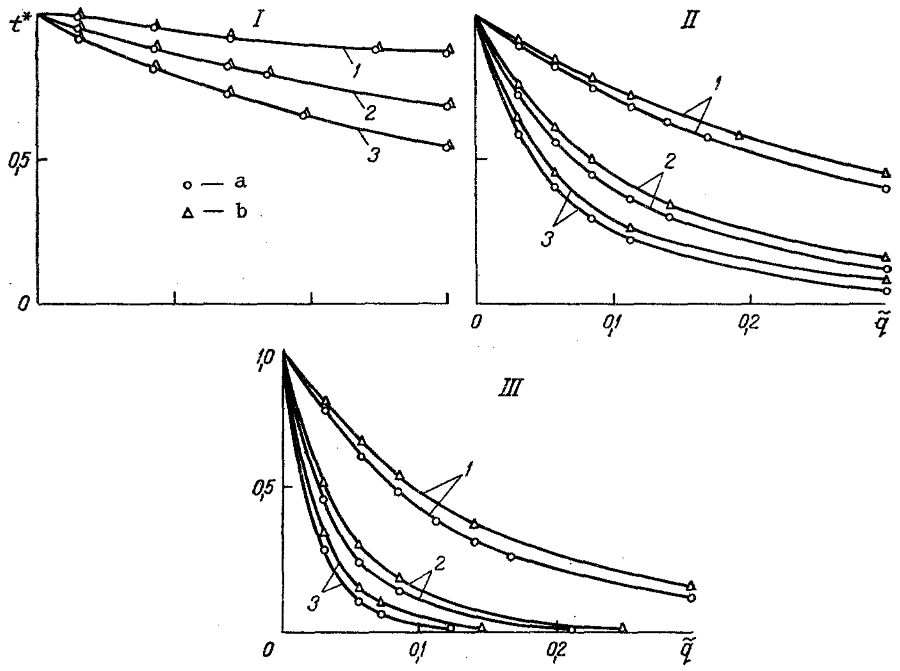

Fig. 1. Induction period as a function of certain parameters: initial reaction rate [I) $\tilde{k}_0 = 0.1$; II) 1; III) 10], activation energy [1, $\tilde{U} = 10$; 2) 30; 3) 50] and the thermal effect of the reaction; the results are presented for kinetic equations of the first (a) and second (b) order.

where $\tilde{t}^* = t_n^*/t_0^*$, shows the extent to which t^* diminishes in the nonisothermal hardening regime relative to t_0^*; the dimensionless time is also normalized to t_0^*: $\tilde{t} = t/t_0^*$; the dimensionless temperature $\tilde{T} = (T - T_0)/T_0$ depends on $\tilde{t}$; $\tilde{U} = U/RT_0$. The transition from (3) to (4) is valid if $\tilde{T} \ll 1$. The variations in $\tilde{t}$ range from 0 to 1.

Subsequently it becomes necessary to establish the law governing the change in $\tilde{T}(\tilde{t})$, and for this we have to ascertain the physical sources of the nonisothermicity, and in this connection we will then examine the adiabatic case.

The most obvious source is external heating. In this event, we can specify the law governing the change in temperature. In this simplest case (but not necessarily) this involves a linear rise in temperature over time:

$$T = T_0 + \alpha t, \quad \text{or} \quad \tilde{T} = (\alpha t_0^*/T_0)\tilde{t}. \tag{5}$$

In this case, combined consideration of expressions (4) and (5) leads to the following equation [2]:

$$\tilde{t}^* = \frac{1}{x}\ln(1 + x), \tag{6}$$

where $x = \tilde{U}(\alpha t_0^*/T_0) = U\alpha t_0^*/RT_0^2$ is a dimensionless parameter which determines the relative role of nonisothermicity in the reduction of the induction period. As is demonstrated by direct numerical estimates, the nonisothermal effects become significant when $x > 0.1$ or $\alpha > 0.1RT_0^2/Ut_0^*$.

The source of the second type of nonisothermicity is dissipative heating, caused by the release of heat at high strain rates in the hardening oligomer. The role of this factor has been analyzed in [3, 4]. Under certain simplifying assumptions, the nonisothermicity in this case leads to a change in $\tilde{t}^*$ in accordance with the same law as in (6), since the intensity of heat generation is constant, and in the absence of any removal of heat the temperature is the same as in relationship (5) and increases linearly. The coefficient α in this case exhibits the following physical sense: it is determined not by the external source, but by the intensity of deformation and is therefore expressed as $\alpha = \tau\dot{\gamma}/c\rho$ ($\tau\dot{\gamma}$ is the intensity of heat generation). Consequently, in this case

$$x = U\tau\dot{\gamma}t_0^*/c\rho RT_0^2. \tag{7}$$

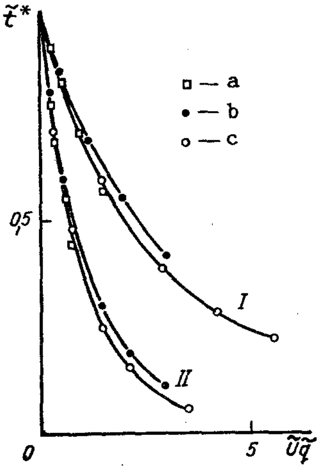

Fig. 2. Comparison of calculated relationships derived by linearization of the kinetic equation (8) (a), and the exact solution (b) ($\tilde{U}$ = 10), and (c) ($\tilde{U}$ = 50) for various initial reaction rates [I) $\tilde{k}_0$ = 1; II) 10].

The experiment confirmed the validity of this approach to the determination of the physical cause for the reduction in the induction period at high strain rates and its quantitative description by means of Eq. (6) [4]. Based on consideration of the relationship between temperature and the viscosity of the hardened oligomer, a number of refinements in the nature of the function $\tilde{t}^*(x)$ were examined in [5].

Let us now turn to the third source of heat generation, which is responsible for nonisothermicity in the hardening of the oligomer, but previously not considered quantitatively in the literature, although it applies in general to the entire problem. We are dealing here with the heat of the chemical reaction. It may be quite significant, and we cannot neglect this factor, even in the absence of an external source or dissipation of the work due to the deformation. Within the framework of the stated problem, the basic task here is to determine $\tilde{T}(\tilde{t})$.

In order to calculate $\tilde{T}(\tilde{t})$ we have to turn to the kinetics of the reaction. In order to make clear the process of our considerations, let us turn to two simple kinetic reaction equations, i.e., of first and second order. In this case, it is significant that nonisothermicity leads not only to a reduction in $\tilde{t}^*$, as follows directly from formula (2), but to an acceleration of the reaction itself. The initial first-order kinetic equation is written in the form

$$\dot{\beta} = k(1-\beta)\exp(-U/RT). \tag{8}$$

In the general case, the quantities U in formulas (1) and (8) may prove to be different, but this refinement is hardly of any significance for our subsequent evaluation and conclusions. Usually, we are dealing with identical or similar quantities.

Let us write formula (8) in dimensionless variables:

$$\frac{d\beta}{d\tilde{t}} = \tilde{k}_0(1-\beta)\exp[\tilde{U}\tilde{q}\beta/(1+\tilde{q}\beta)], \tag{9}$$

where $k_0 = k\exp(-U/RT_0)$; $\tilde{k}_0 = k_0t_0{}^*$; $\tilde{q} = Q/c\rho T_0$. The relationship between β and $\tilde{T}$ is rather obvious:

$$\tilde{T} = \frac{T-T_0}{T_0} = \frac{Q}{c\rho T_0}\beta = \tilde{q}\beta. \tag{10}$$

The simultaneous examination of Eqs. (4), (9), and (10) gives a solution for the stated problem, which is expressed in the form of a relationship between $\tilde{t}^*$ and the dimensionless parameters $\tilde{U}$, $\tilde{q}$, and $\tilde{k}_0$, i.e., it indicates the sensitivity of the reaction rate to the change in temperature ($\tilde{U}$), the quantities of evolved heat ($\tilde{q}$), and the initial reaction rate ($\tilde{k}_0$). Although a direct relationship exists betwen β and $\tilde{t}^*$ (see Eq. (4)), it is expressed in rather complex fashion, so that our interest lies not in the determination of β at the instant of gel, formation, but rather of the viability time, which is an important technological characteristic. The solution of the problem cannot be presented in quadratures, but it can be determined experimentally. We present the results of the calculations in the following.

A fully analogous approach is possible if the real kinetics are described by another, more complex, equation, different from Eq. (8). As an example, let us examine the frequently encountered case of the kinetic second-order equation, i.e., instead of formula (8) we write:

$$\dot{\beta} = k(1-\beta)^2 \exp(-U/RT). \tag{11}$$

The subsequent transformations are equivalent to the ones above.

Figure 1 shows the theoretical relationships $\tilde{t}^*(\tilde{q})$ for various values of $\tilde{U}$ and $\tilde{k}_0$ for kinetic equations (8) and (11). We can see from the figure that the larger the magnitude of the activation energy, the more rapid the reduction in the induction period as the thermal effect increases, which is quite obvious from the physical standpoint.

It should be noted that for both types of kinetic equations the curves $\tilde{t}^*(\tilde{q})$ are quite close, although the divergence between these curves increases as the initial rate of reaction increases (thus, when $\tilde{k}_0 = 0.1$ the curves being compared are virtually coincident, while in the case of $\tilde{k}_0 = 1$ and $\tilde{k}_0 = 10$ they remain significantly different). On the whole, it may apparently be assumed that the type of kinetic equation plays no decisive role. The derived results diverge most clearly if we compare the series of curves I, II, III (Fig. 1): the higher the initial reaction rate, the more pronounced the effect of induction period (or viability) reduction of the material.

When we use the numerical methods, there is no need of linearizing the exponential relationship between $\dot{\beta}$ in formulas (8) and (11) and the temperature. However, we are interested in the extent to which such a procedure is valid. Let us present formula (8) in the following approximate terms:

$$\dot{\beta} = k_0(1-\beta)(1+\gamma\beta), \tag{12}$$

where the dimensionless parameter $\gamma = UQ/c\rho RT_0^2$ in structure is quite analogous to the expression for x, given by formula (7), if we assume that $Q = \tau\dot{\gamma}t_0^*$. The transition from Eq. (8) to formula (12) is valid for $\tilde{q} \ll 1$ and $\gamma < 1$ (let us note that the second inequality is the stronger condition, since in actuality $\tilde{U} > 1$). Equation (12) clearly shows that even if the kinetics of the reaction is described by a first-order equation, the release of heat results in the nonisothermal self-acceleration effect that is represented by the cofactor $(1 + \gamma\beta)$.

The integral in Eq. (12) has the form

$$\beta = \frac{\exp[(1+\gamma)k_0 t] - 1}{\exp[(1+\gamma)k_0 t] + \gamma}.$$

Changing to dimensionless variables, for the function $\tilde{T}(\tilde{t})$ we obtain an analytical expression of the form

$$\tilde{T} = \tilde{q}\,\frac{\exp[(1+\tilde{U}\tilde{q})\tilde{k}_0\tilde{t}] - 1}{\exp[(1+\tilde{U}\tilde{q})\tilde{k}_0\tilde{t}] + \tilde{U}\tilde{q}}. \tag{13}$$

Having substituted expression (13) for $\tilde{T}$ into Eq. (4), we can solve the stated problem. It should be noted that, in this case, $\tilde{t}^*$ for each fixed $\tilde{k}_0$ always depends on the product $\tilde{U}\tilde{q}$, rather than on each of these parameters individually. In this connection, comparison of these solutions derived in the linearized case and in the exact formulation of the problem is clearly carried out in the coordinates $\tilde{t}^* - \tilde{U}\tilde{q}$.

Figure 2 shows that the application of linearization yields virtually exact results when $\tilde{U}\tilde{q} \leq 0.7$ for $\tilde{k}_0 = 10$ and with $\tilde{U}\tilde{q} \leq 1$ for $\tilde{k}_0 = 1$. For larger values of $\tilde{U}\tilde{q}$, the divergence of the curves $\tilde{t}^*(\tilde{U}\tilde{q})$ becomes noticeable, i.e., the curve obtained for the linearized case deviates from the numerically calculated curves. Nevertheless, in actual practice the divergence of the curves for various values of $\tilde{U}$ is not overly large, since the magnitude of $\tilde{q}\beta$ is generally smaller than 1 [see formula (9)], so that the linearization of the temperature relationship to the reaction rate is almost always correct.

NOTATION

t^*, the induction period, or the time required to reach the gel point; t_n^* is the induction period in the case of some arbitrary law governing the change in temperature; U, the activation energy of the hardening process; t, time; T_0, the temperature at the onset of hardening; $t_0{}^*$, the induction period in the isothermal process; $\tilde{t}^*$, the dimensionless induction period; $\tilde{t}$, dimensionless time; $\tilde{T}$, dimensionless temperature; $\tilde{U}$, dimensionless activation energy; α, the rate of temperature rise; τ, the shearing stress; $\dot{\gamma}$, the shear rate; c, heat capacity; ρ, density; K, reaction rate; β, rate of conversion; k_0, initial reaction rate at the temperature $\tilde{T}_0$; $\tilde{k}_0$, the dimensionless initial reaction rate at the temperature T_0; $\tilde{q}$, dimensionless characteristic of the thermal effect; Q, the thermal effect of the reaction.

LITERATURE CITED

1. A. I. Leonov and A. I. Shvarts, Vysokomolek. Soed. A, 14, No. 3, 695-700 (1972).
2. A. Ya. Malkin and S. G. Kulichikhin, Rheology in Processes of Formation and Conversion of Polymers [in Russian], Moscow (1985).
3. A. Ya. Malkin, Plasticheskiye massy, No. 4, 47-48 (1982).
4. A. Ya. Malkin and G. I. Snuvalova, Vysokomolek. Soed. B, 27, No. 11, 865-869 (1985).
5. A. Ya. Malkin and V. P. Begishev, Rheol. Acta, 21, No. 4/5, 629-631 (1982).

THE MACROKINETICS OF DIFFUSION CONVERSIONS IN METALS WITH A DISPERSION PHASE

Yu. A. Buevich and S. L. Komarinskii

UDC 539.2:548.5

The evolution of solid dispersions under isothermal conditions has been investigated for the situation in which the exchange of the mass of discrete inclusions with the matrix in which they are embedded is limited by the diffusion into that matrix. Expressions have been derived for the quantities which describe the kinetics of conversion and a comparison with experimental data is carried out.

When heterogeneous metals and certain other types of solid materials are subjected to processes of chemical or heat treatment, their thermodynamic stability is disrupted. If the resulting level of metastability is sufficiently small, the consequent transition of the solid dispersion into a new stable state is not associated with the fluctuating formation of the nuclei of a new phase, but comes about as a result of the growth or dissolution of the initial inclusions. The speed with which this conversion takes place is determined not only by the kinetics of the interphase exchange, but also by the rates of impurity diffusion transport within the heterogeneous system being examined. Therefore, the evolution of the inclusions and the "transit" mass transfer to solid dispersion whose properties vary with the change in the dimensions and diffusion displacement of the inclusions must be taken into consideration simultaneously with consideration of the diffusion interaction of the inclusions and the effect exerted by proximity on the transport of the impurity through the spaces between the inclusions.

A system of nonlinear equations has been formulated in [1] to describe the isothermal processes of diffusion conversion in solid local-monodisperse systems characterized by a uniform numerical concentration of spherical inclusions. This system determines the average concentration of the diffusing impurity in each of the phases, as well as the volumetric concentration of the inclusions in the dispersion, and it also contains a number of quantities which characterize the kinetics of the conversion and which, in rather complex fashion, depend on the physicochemical parameters of the dispersion. This relationship is examined in considerable detail in the following for the case in which the exchange of impurities between the surfaces of the inclusions and the solid solution within the matrix is limited by the diffusion within the matrix, which is most important from the standpoint of application [2, 3].

Gor'kii Ural State University, Sverdlovsk. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 56, No. 4, pp. 596-604, April, 1989. Original article submitted December 8, 1987.