pressure in the precombustion chamber of the tunnel; a, on the nozzle edge in the open working part of the nozzle.

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MATHEMATICAL MODEL OF THE PROCESS OF THERMAL DESTRUCTION OF POLYMER MATERIALS UNDER INTENSE THERMAL EFFECTS

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It is proposed to describe heat- and mass-transfer processes in decomposing materials by taking into account both the chemical and physical transformations and the phase transition temperatures.

The one-dimensional process of heat and mass transfer in polymer-based materials with thermal decomposition taken into account is described by the differential equation

$$c\rho \frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left(\lambda \frac{\partial T}{\partial x}\right) - c_g G_g \frac{\partial T}{\partial x} \pm \sum_i Q_i \frac{dC_i}{dt} \pm \sum_i Q_{\text{p}i} \frac{dx_i}{dt}, \qquad (1)$$

where dC_i/dt, dx_i/dt are the chemical reaction and physical transformation rates with the thermal effects Q_i and $Q_{\text{p}i}$.

Taken into account in (1) are physical processes such as evaporation, boiling, desorption of the initial products and decomposition products, etc. The transformation rates are associated in individual stages with the rate constants k_i and $k_{\text{p}i}$:

$$dC_i/dt = -k_i C_i^{\bar{n}}, \quad dx_i/dt = -k_{\text{p}i} x_i. \qquad (2)$$

We obtain as a result of integrating (2) for nonisothermal heating conditions and a reaction order $\bar{n} = 1$

$$C_i = C_{0i} \exp\left(-\int_0^t k_i dt\right), \quad x_i = x_{0i} \exp\left(-\int_0^t k_{\text{p}\,i} dt\right).$$

Substituting values of the variables C_i and x_i into (2) and then into the initial equation (1), we obtain

$$c\rho \frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left(\lambda \frac{\partial T}{\partial x}\right) - c_g G_g \frac{\partial T}{\partial x} \pm \sum_i Q_i k_i \exp\left(-\int_0^t k_i dt\right) \pm \sum_i Q_{\text{p}i} k_{\text{p}i} \exp\left(-\int_0^t k_{\Phi i} dt\right). \qquad (3)$$

Analysis of (2) and (3) permits making the following deduction. Under moderate thermal effects the temperature of a decomposing material is not high and is close to the equilibrium temperature of the beginning of decomposition $T_\infty = \Delta H/\Delta S$, where ΔH, ΔS are the changes in enthalpy and entropy of the chemical transformation, depolymerization, say [1].

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The time t to achieve a given temperature is shortened as the heating intensity increases. Under sufficiently powerful thermal effects the heating time t can become less than the characteristic time of progress of the most rapid chemical reaction τ_x with the appropriate reaction rate k_{max}: $\tau_x = 1/k_{max}$. For sufficiently small t ($t \ll \tau_x$) the chemical reaction in the material is not completed, $\int_0^t k_i dt \to 0$, and yields no contribution to a decrease in mass. In such a situation the contribution to the decrease in mass of substance governed by the physical transformation whose rates substantially exceed the chemical transformation rates will start to predominate.

As a thermodynamic analysis showed [2], the ultimate (highest) temperature for the existence of linear polymer macromolecules in the associated state is comparatively low and determined by the condition

$$RT_{\text{lim}} \simeq D_m \qquad (4)$$

Hence, there follows $T_{\text{lim}} \cong D_m/R$, $D_m \cong \Delta H_p - RT$. Equation (4) has a simple physical meaning: if the thermal energy becomes equal to the potential energy of intramolecular (physical) interaction, the macromolecules will go over into the isolated state, the so-called "polymer gas" with heat absorption ΔH_p. In conformity with thermodynamics [2], the "polymer gas" possessing an excess of free energy is unstable and furthermore decomposes to finite low-molecular volatile products [3].

A condition analogous to condition (4) in composites holds for the adhesion interaction of components with energy D_a, namely $RT \approx D_a$. For $T \geq D_a/R$ a composite is transformed into a simple mechanical mixture with uncoupled binder and filler particles. At such a temperature a material without a rigid skeleton can be destroyed even under the action of insignificant mechanical loads while the heat conductivity (effective) of a composite, dependent on the material continuity, diminishes substantially. Reticulated polymers in which additional cross-links occur during heating behave differently.

The limit temperatures can be determined by experimental methods [1] and by a computation in the intramolecular interaction energy. For linear polymers with a certain exaggeration the limit temperatures can be computed from the condition of internal stability of the liquid phase $(\partial T/\partial v)_p = 0$ by means of the spinodal equation which has the following form for a van der Waals medium [4]

$$pv^3 - av + 2ab = 0, \qquad (5)$$

where a and b are constants of the equation of state.

Having determined the magnitude of the volume v_{sp} on the spinodal line from (5), the value of the temperature at the spinodal point can easily be found from the equation of state from

$$T_{sp} = (p + a/v_{sp}^2)(v_{sp} - b)/R. \qquad (6)$$

Evidently $T_{\text{lim}} < T_{sp}$. As an example we present the characteristics of certain linear polymers. To do this, we determine the constants a and b by the dependences v(T) and v(p) from experimental data. For such polymer materials as polystyrene, shock-resistant polystyrene, polyethylene the values of the constants lie within the limits $a = (2.19\text{-}2.7)$ $(\text{Pa}\cdot\text{m}^6)/\text{mole}^2$, $b = (0.88\text{-}0.2)\cdot 10^{-4}$ m^3/mole. We find their corresponding volume $v_{sp} = 1.5\text{-}1.76$ m^3/mole from (5) and then the temperatures at the spinodal point from (6): $T_{sp} = 750\text{-}820°\text{K}$. For a possible spread in the experimental data and insufficient accuracy in the equation of state taken a satisfactory correspondence can nevertheless be noted between the results of computations and the test values of the temperatures of achievable heatings of the polymers considered: $T_{\text{lim(exp)}} = 773\text{-}813°\text{K}$ [1].

The limit temperatures can be calculated directly from (4) if the quantity D_m is known. The dipole–dipole interaction energy in polymers $D_m = 1620$ cal/mole corresponds according to the data [6] with the limit temperature $T_{\text{lim}} = D_m/R = 1620/2 = 810°\text{K} = 530°\text{C}$. This value correlates well with test data [2].

Crystal hydrates have comparatively low limit temperatures of thermal decomposition during dehydration. In particular, this temperature in the mineral colemanite, an inorganic substance with polymer configuration, is close to the critical temperature of water [7]. It is shown in the paper mentioned that explosive decomposition of the mineral at T_{lim} is not related to decrepitation.

Mechanical effects exert influence on the rate of thermal decomposition of polymers. The thermal energy stored in a material added to the elastic strain potential energy A of the interlinkage bonds cannot exceed the energy D_m

$$RT + A \leqslant D_m = RT_{lim}\,. \tag{7}$$

Under the action of a compressive pressure p and tangential stresses τ the magnitude of the elastic potential energy is $A = \zeta p^2 v/2K + \xi\tau^2 v/2G$, where K and G are the bulk elasticity and shear moduli, and v is the volume per mole of substance. The coefficients ζ and ξ take account of the distribution of all the potential energy in the deformation of the valence and interlinkage (intramolecular) bonds $\zeta < 1$, $\xi < 1$. In conformity with (6) the temperature causing the spinodal transition rises because of the mechanical loading. But for sufficiently high compression stresses of the polymer substance and subsequent pressure drop, its spinodal thermal destruction can even occur at normal temperature $T_1 = 300°K$. Equation (7) permits determination of the preliminary compression pressure, whereupon we obtain for $\tau = 0$ and $\zeta = 1$

$$\frac{p^2 v}{2K} = D_m - RT_1, \quad \text{or} \quad p = \sqrt{2(D_m - RT_1)K/v}. \tag{8}$$

If the pressure turns out to be sufficiently high, the dependence of the bulk elasticity modulus on it should be taken into account. It follows from the Tait equation of state [5] that $K = -v(\partial p/\partial v)_T = K_0(1 + p/B)$, where B is a constant equal to B = 310-350 MPa for the linear polymers (PMMA, PS, PE) and $K_0 = 5\cdot 10^3$ MPa [5]. Taking the dependence K(p) into account, (8) takes the following form

$$p^2 - 2K_0 D(T)\, p/B - 2K_0 \rho D(T) = 0, \tag{9}$$

where $D(T) = D_m - RT$ and $\rho = 1/v$.

Only the positive (+) sign has meaning in the solution of the quadratic equation (9)

$$p = K_0 D(T)/B \pm \sqrt{K_0 D(T)\rho/B^2 - 2K_0 \rho D(T)} \tag{10}$$

Substituting the value $T = T_1 = 300°K$ in this latter formula, we obtain p = 1.2 GPa for the linear polymers. Such a value is confirmed satisfactorily by experimental data [8] on the efflux of a jet of polymer substance from a filler. A so-called "rheological explosion" with the formation of decomposition products is observed for compressions to 1-2 GPa (depending on the filler diameter) and normal temperature. In contrast to a thermal explosion, the spinodal dissociation of the polymer is of entropy nature and proceeds with heat absorption and liberation of the mechanical energy accumulated during compression.

The temperatures T_∞ and T_{lim} determine the temperature range of the thermal destruction of polymer materials and are important characteristics of their thermal stability. A substantial change in all the physicomechanical and thermophysical properties of the materials, the viscosity, elastic moduli, density, heat conductivity, etc., occurs in this range. The change in the physical characteristics is determined by the change in the physical composition of the polymer, by its transition first into liquid, and then gaseous decomposition products. The numerical values of the characteristics can be calculated in a first approximation from data in the literature on the initial and final products in a first approximation according to the additivity law, and more exactly by statistical physics methods [9]. The pressure and mechanical stresses cause a change in the temperatures T_∞ and T_{lim}, $|p| \leq p_{sp}$ (at the spinodal point).

Furthermore, let us examine the kinetic relationships governing the change in time of the above-mentioned properties in which we include the chemical and physical transformations. To do this we take account of the difference in the destruction rate constants of the associated k_a and disassociated (isolated) k_i monomer linkages. If the macromolecule chains are arranged uniformly in the bulk, then the kinetics of polymer decomposition can be described by the following equation

$$\frac{dC}{dt} = -k_a N_a - k_i N_i, \tag{11}$$

where C is the concentration of the monomer linkages being formed under the assumption of no evaporation and reaction progress over the tip groups, where N_a and N_i are the associated and disassociated tip groups.

The material balance equation is

$$N_a + N_i = zN. \tag{12}$$

Here z is the quantity of reactable groups of the chain that is later inserted into the value of the constant. For reactions over two chain tips z = 2, for branched N macromolecules z > 2.

Since the equilibrium build-up rate of the physical (intermolecular) interaction is higher than the rates of the chemical processes, it can be written that

$$N_i = K_e N_a, \tag{13}$$

where K_e is the equilibrium constant whose dependence on the temperature is governed by the van't Hoff equation $K_e = K_{e0} \exp(-\Delta H/RT)$, where ΔH is the enthalpy increment. For elementary reactions the dependences of the rate constants on the temperature are ordinarily given in the form of the Arrhenius equation

$$k_a = k_{a0} \exp(-E_a/RT) \text{ and } k_i = k_{i0} \exp(-E_i/RT),$$

where E_a and E_i are the appropriate activation energies and k_{a0}, k_{i0} are the preexponentials.

Dividing (11) by the initial polymer concentration, we obtain after manipulation

$$-\frac{d\omega}{dt} = \frac{dC}{N_0 n_0 dt} = k_i p_i + k_a(1 - p_i), \tag{14}$$

where

$$p_i = \frac{N_i}{N} = \frac{K_e}{1+K_e};\quad 1 - p_i = \frac{N_a}{N} = \frac{1}{1+K_e};\quad \omega = C/N_0 n_0.$$

The solution of (14) has the following form

$$1 - \omega = \frac{k_i K_e + k_a}{1+K_e} t.$$

At low temperatures $K_e \ll 1$ and $p_i \to 0$ and mainly associate monomer linkages exist, $k_i K_e \ll k_a$. Consequently, $\ln(1/t) = -\ln(1-\omega) + \ln k_{a0} - E_a/RT$. The linear nature of this dependence on the reciprocal temperature is confirmed by numerous experimental data [1]. On the other hand, at high temperatures $K_e \gg 1$, $k_i K_e \gg k_a$ and mainly dissociated monomer linkages exist. In this case the activation energy of the process corresponds to E_i. Therefore, the model under consideration describes an increase in the effective activation energy of polymer thermal decomposition established experimentally [2] and relates this increase to the intramolecular physical interaction of macromolecules.

An increase in the number of isolated monomer linkages makes possible the formation and dissociation of blocks of dissociated linkages with the probability $p_i^n(1 - p_i)^2$, where n is the number of these linkages. We also take into account in the kinetic equation the increase in the number of reactive molecule tips for a discontinuity according to the law of the case (zN):

$$-\frac{d\omega}{dt} = k_a(1 - p_i)zN + k_i p_i zN + K \sum_{m}^{n_0-2} n p_i^n (1 - p_i)^2 N. \tag{15}$$

Ruptures of the bonds in macromolecules proceed with equal probability in all sections of the chain, hence at least two molecules are formed from one, which should be taken into account in the mathematical simulation by an appropriate kinetic equation

$$\frac{dN}{N} = KN(1 - p_i)^2 \sum_{m}^{n_0-2} p_i^n,$$

where m is the minimal quantity of dissociated linkages in the block for which an avalanche-like decomposition starts. The solution of the equation is

$$N = N_0 \exp\left[K(1 - p_i)^2 \sum_{m}^{n_0-2} p_i^n\right],$$

where N_0 is the initial molecule concentration in the system.

Substituting this value of N into (15), we obtain the complete kinetic equation of polymer chain destruction which is valid in a broad temperature range and permits taking account of the chemical transformation rates in (1). At temperatures close to the limit, we obtain in conformity with (15)

$$\ln(1/t) \simeq \ln\frac{Kp_i^{n_0}+k_i}{1-\omega} \simeq \ln\frac{Kp_i^{n_0}}{1-\omega} \cong \ln\frac{K}{1-\omega},$$

where t is the time of reaching the degree of decomposition ω.

At temperatures close to T_{lim} the system becomes thermodynamically unstable, the isolated macromolecules are a labile "polymer gas" which decomposes at the time of formation at the rate k approximating the maximally possible values of the reaction rate constant (10^7-10^{10} 1/sec), and the gasification time is governed by the time of flight of the decomposition products of the substance.

Let us examine the last component in (1) that takes account of the evaporation process, in particular. In conformity with the Knudsen–Langmuir equation, the evaporation rate of a mixture of substances of the initial composition and that being formed during decomposition is determined by summation of the components over all possible molecule lengths $dx_i/dt = k_{eva\,0i}\exp(-\Delta H_i/RT)$ and

$$G = \sum_1^{n_0}\frac{dx_i}{dt} = \sum_1^{n_0} k_{eva\,0i}\exp(-\Delta H_i/RT), \tag{16}$$

where $\Delta H_i = \Delta H_m n$, ΔH_m is the heat of monomer evaporation, and $Q_{pi} = -\Delta H_i$.

Evaporation of the components of polymer condensed systems during thermal decomposition occurs not only on the outer surface but also from the surface of the inner cavities, cracks, and other defects and gas inclusions. Evaporation is accompanied by a mass decrease only if the gas inclusion communicates with the external medium, $G_g = G + \int_0^\infty \partial\omega/\partial t\, dx$.

According to (16), all molecules can be evaporated; however, the rate of evaporation of molecules of great length is negligibly small and their thermal destruction will occur before they are evaporated. In conformity with (2), the number of monomer linkages diminishes with the lapse of time, and the rate of mass decrease because of evaporation grows. In addition, the heat of evaporation ΔH_p diminishes as the temperature rises, which can be taken into account by the empirical Watson-Gambil equation [10]

$$\Delta H_p = \Delta H_p^0\left(\frac{1-T/T_{sp}}{1-T_0/T_{sp}}\right)^{0,38},$$

where ΔH_p^0 is the enthalpy increment for $T = T_0$ and $H_p = \Delta H_i$ for $n = n_0$.

It follows from the last formula that the heat of vapor formation vanishes when the temperature T_{lim} is reached, and the rate of evaporation reaches its maximal value governed by the rate of vapor removal to the environment (Stefan mass transport equation), where molecules of arbitrary length can be evaporated. A definite increase in the rate of mass decrease occurs because of the increase in the area of the evaporating surface $S = S_0 + S_{add}$, where S_0, S_{add} are the initial and additional areas of the reacting surface formed because of heterogeneous nucleation.

The mathematical model proposed contains several parameters for whose determination it is convenient to use the thermal analysis method proposed in [11] from results of isothermal tests. As an example we present values of the thermal destruction parameters for the polyamide PA-12: $E_a = 24{,}700$ cal/mole; $E_i = 71{,}000$ cal/mole, $k_{a0} = 3.9\cdot10^5$ 1/sec, $k_{i0} = 1.5\cdot10^9$ 1/sec, $K_{e0} = 24$, $D_m = 1620$ cal/mole. The results presented and the results of other tests of linear monomers indicate that in conformity with the solution of (14), a temperature rise results in the passage from the destruction of associated monomer linkages to the destruction of isolated linkages and is accompanied by a rise in the activation energy. The activation energy of the gross-process, measurable in tests (the so-called "apparent" activation energy) in the temperature domain at which both processes proceed simultaneously, rises correspondingly. Such a change was observed earlier by many researchers but did not receive a satisfactory explanation [6].

The thermal decomposition of reticulated polymers differs from the behavior of linear and branched high-molecular compounds because of the absence of free reactionable chain tips, and dissociation of the blocks between the junctures according to the law of the case precedes evaporation. Under fast heating conditions, whose time t is less than τ_x – the reaction time for the formation of additional junctures and a coke residue, the formation of the coke residue is difficult and the mass of the substance diminishes to a finite value governed by the density of junctures. In such a case the value of the residual mass should be inserted into the kinetic relationships and a term taking account of the thermal synthesis process should be added for non-intensive heating modes.

In addition to the physical processes examined, processes to destroy the intermolecular bonds of the binder and filler elements proceed in composite materials in conformity with the kinetic equation

$$\frac{dx_{\text{ad}}}{dt} = k_0 \exp(-E_{\text{ad}}/RT), \tag{17}$$

where E_{ad} and k_0 are the activation energy for adhesion interaction destruction and the pre-exponential factor.

If it is taken into account that the activation energy E_{ad} is small (on the order of ΔH_p), and rate of destruction of the adhesion bonds is significantly higher than the chemical reaction rate, then equilibrium is established in conformity with (13) in which N_i and N_a should be taken as the number of isolated (destroyed) and associated (induced) interaction forces of the surface–surface type of the composite material phases.

NOTATION

c, ρ, λ, effective thermophysical characteristics; C_i, component concentration; x_i, coordinates of the physical processes; n, order of the reaction; n_0, initial number of monomer linkages in macromolecules; Q_i, Q_{pi}, thermal effects of chemical and physical transformations; k_i, k_p, rate constants of these transformations; T_{lim}, temperature of achievable polymer heating in the metastable state; D_m, energy of intermolecular interaction (cohesion energy); T_{sp}, v_{sp}, temperature and specific volume at the spinodal point; K_0, bulk elasticity modulus; z, number of tip reactive groups; $\omega = M/M_0$, relative mass of residue; G_g, mass flux of gaseous destruction products; A, elastic strain potential energy; p_i, probability of observing an isolated monomer linkage; S, area of the reacting surface; S_0, initial area; S_{add}, additional area.

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