MATHEMATICAL DESCRIPTION OF COMBUSTION
OF INTUMESCENT POLYMER SYSTEMS

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A review of the literature on mathematical description of combustion of intumescent polymer systems is given. Basic approaches to the modeling of combustion of intumescent systems are considered.

INTRODUCTION

Polymers are widely used in industry and practice. Polymers are 5 to 6 times lighter than metals, and their manufacture and processing requires much less energy. Having special, frequently unique properties, polymers are irreplaceable in many engineering designs. Finally, articles made of plastics are beautiful and hygienic. However, an essential drawback of polymers is their high combustibility [1].

One of the traditional methods of decreasing the combustibility of materials is the introduction into them of special additives — fire retardants [2, 3]. The principles of action of fire-retardant systems are different. Thus, for example, the introduction of halogen-containing retardants, according to [4], leads to evolution of hydrogen halides during combustion, which "poison" the flame by decreasing the concentration of active radicals in the preflame zone. Boron-containing fire retardants (for example, a mixture of boric acid and antimony) act differently: they produce a continuous protective coating [5].

So-called intumescent fire-retardant systems [6–8] occupy a special position. Under the action of external heat flux, these systems are capable of forming a volumetric carbonized residue — a foamed char — which protects the surface of the polymer. Tram was the first who patented an intumescent fire-proofing coating as early as 1938 [9]. Since 1950, intumescent fire-proofing coatings have begun to be actively used in various industries. At present, protective coatings of this type are widely used where highly efficient fire protection along with a minimum mass of the coating itself are required (aircraft engineering, protection of oil storages, etc.). Recently, both scientific and practical interest in these systems has considerably increased.

Previously, it has been suggested [10] that, besides protecting the surface of a polymer from external heat flux, a foamed char layer prevents fuel transport to the combustion zone. However, it has been shown [11, 12] that a porous char layer cannot serve as a reliable obstacle to motion of destruction products. The primary role of a char cap in combustibility reduction was proved [11] by comparing the limiting oxygen indices (OI) of samples burnt by the conventional method and samples from which the char layer was continuously removed during burning. The OI values were much higher in the first case than in the second (Fig. 1).

It is known that formation of a carbonized layer on the surface of a polymer frequently decreases the combustibility and ignitability of the polymer and the velocity of flame propagation over its surface [13–15]. Van Krevelen [16], studying the carbonization mechanism of coals, established the following empirical relationship between the oxygen index and the char yield:
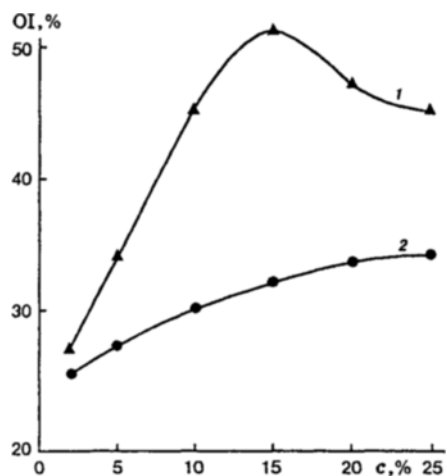
$$OI = 17.5 + 0.4 \cdot CR.$$

Fig. 1

Fig. 2

Fig. 1. OI values of samples burnt by the conventional method (1) and samples from which a char cap was removed during burning (2) [11]: (c is the concentration of phosphorus-containing oligomer).
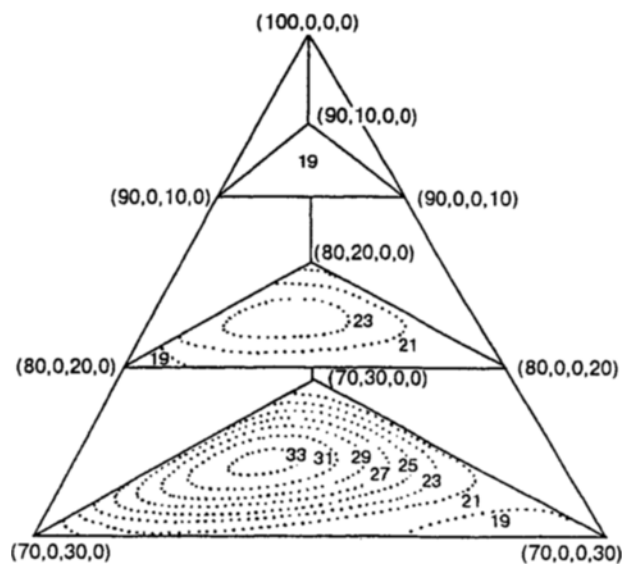
Fig. 2. Oxygen index (the figures near the curves) as a function of the proportion of components for a mixture of polypropylene–ammonium polyphosphate–pentaerythritol–melamine [23]: the figures in parentheses denote the component concentration (in percentage) in the indicated order.

Here CR is the portion of undecomposed char residue in pyrolysis in the absence of air at 850°C (expressed in percent) for 35 min.

For intumescent materials, the situation is much more complicated, because the carbonized layer has a porous structure. Various attempts have been undertaken to describe combustion of intumescent systems — from searches for empirical relations between the combustibility criterion (as a rule, OI) and a characteristic of the combustion process (for example, a char residue) to numerical modeling of the physical structure of a char cap and the foaming process. At present, considerable advances have been made in the area of mathematical description of combustion of intumescent polymer systems. However, up to now, there has been neither a unified "universal" approach nor models that describe satisfactorily all features of combustion of intumescent systems.

The issues of the chemistry of intumescent processes have been repeatedly systematized (see, for example, [6, 10]), whereas the authors are aware of only one attempt to review mathematical models for combustion [17]. In this paper, a narrow class of foaming models is considered; the remaining aspects of the combustion process are not touched on. The present paper seeks to analyze the existing mathematical models and approaches to the description of combustion of intumescent polymer systems. For convenience, the paper is divided into sections, each of which describes a particular direction of modeling.

EMPIRICAL APPROACHES

One of the widely used optimization methods for combined fire retardant systems, which, in particular, include intumescent systems, is the one proposed in [18]. It consists in searching for a regressive dependence of a certain parameter of the system (for example, the OI) on the content of components of the system using

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experimental data; usually, the dependence is chosen in polynomial form.

Using this method, Gnedin [19, 20] investigated the dependence of the efficiency of an intumescent system (a mixture of ammonium polyphosphate–pentaerythritol–melamine) on the component concentrations in a polymer matrix (polypropylene). He obtained a dependence of the form

$$OI = 124.4\alpha + 38.43\beta + 3048.07\gamma + 547.18\alpha\beta - 10{,}520\alpha\gamma - 47{,}830\beta\gamma + 233{,}400\alpha\beta\gamma - 2.35 \cdot 10^{-3}\alpha^2\beta$$

$$+132{,}700\beta^2\gamma - 43{,}740\gamma^2\alpha + 700{,}000\gamma^2\beta - 218{,}900\alpha^2\beta\gamma - 303{,}400\alpha\beta^2\gamma - 453{,}200\alpha\beta\gamma^2,$$

where α, β, and γ are the concentrations of ammonium polyphosphate, pentaerythritol, and melamine at a 30% concentration of a foaming agent in the polymer matrix. For the dependence of the OI on the foaming ratio n_k and the char yield m_k, he obtained a similar formula

$$OI = 1.6n_k + 406.3m_k + 23.49n_k m_k - 309m_k^2 n_k - 0.1n_k^2 + 0.58n_k^2 m_k - 974.49m_k^2.$$

The basic advantage of this approach is that it permits finding optimum proportions of the components of an intumescent system. This method was used in [21–24] (often, without representation of the resulting polynomial in explicit form). Calculation results are generally represented as a diagram (two- or three-dimensional, depending on the number of parameters), where values of varied parameters are plotted on the axes, and the examined criterion is given by lines of equal value. As an example of such a diagram, Fig. 2 shows the OI of a polypropylene-based system with the intumescent system of ammonium polyphosphate–pentaerythritol–melamine versus the component concentrations [23].

This approach, however, is very labor-consuming and requires a large body of experimental data. In addition, it is not always possible to set up a regressive dependence. This approach can be used, for example, to search for optimum proportions of components in studies of multicomponent intumescent retardant systems when other methods become practically inapplicable.

STEADY COMBUSTION

A basic parameter of steady combustion of polymers is the mass burning rate [1]. The expression for the mass burning rate U_m obtained from the thermal-balance equation under the assumption that the total heat absorbed by the polymer from the flame goes to heating, destruction, and gasification can be written as

$$U_m = \frac{Q_{fl}}{c_p(T_s - T_0) + Q_l},$$

where Q_{fl} is the density of the heat flux from the flame, c_p is the effective thermal capacity of the polymer at temperatures from the surface temperature T_s to the initial temperature T_0, and Q_l is the heat expended on gasification of the polymer.

In the case of carbonized polymers, the combustion process can be divided into several stages: heating to the decomposition temperature, pyrolysis, ignition, and formation of a char on the polymer surface. After formation of a char, the combustion rate decreases, and the polymer extinguishes or the combustion rate stabilizes. The latter occurs when the rate of char formation is equal to the rate of its heterogeneous combustion and/or ablation. In the latter case, the expression for the mass rate of steady combustion can be written as [25, 26]

$$U_m = \frac{\alpha(T_{flame} - T_{s1}) + \sigma\varepsilon T_{flame}^4 - \sigma\varepsilon_{s1}T_{s1}^4}{C[c_c(T_{s1} - T_{s2}) + q_{gas}] + c_{pol}(T_{s2} - T_0) + q_{trans} + G[c_g(T_{s1} - T_{s2})]},$$

where α is the heat-transfer coefficient, T_{flame} is the flame temperature, T_{s1} and T_{s2} are the surface temperatures of the char and the polymer, respectively, c_c, c_{pol}, and c_g are the average thermal capacities of the char, the polymer, and the gas, respectively, T_0 is the initial temperature, σ is the Stefan–Boltzmann constant, ε and ε_{s1} are the degrees of blackness of the flame and the char surface, respectively, C and G are the portion of the polymer that are converted into char and the portion of the gaseous combustion products (C + G = 1), and q_{gas} and q_{trans} are the heat releases due to the chemical reactions of char gasification and
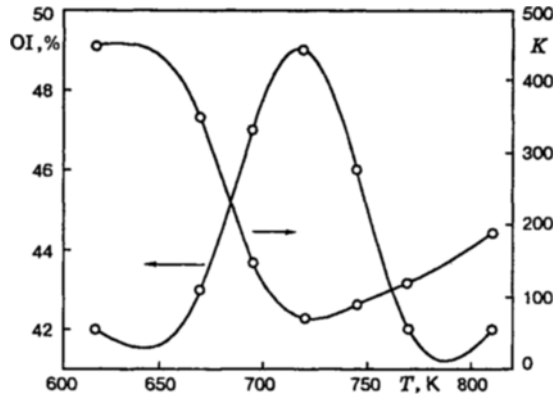
Fig. 3. Combustibility of epoxy samples covered with a 1-mm-thick char layer with different permeability [29]: the temperature corresponds to conditions of production of a char foam from intumescent composition.

polymer transformations. However, the practical value of the given formula is questionable because of the large number of parameters that can be obtained only experimentally and, moreover, can vary during combustion.

Note that, in the described steady combustion regime, the height of the char cap practically remains unchanged. Gibov [27], assuming that the destruction rate in this case is determined only by the rate of diffusion of the polymer destruction products through the porous char layer, obtained the following expression for the mass rate of pyrolysis:

$$U_m = \frac{\lambda}{(\delta - x)c_p} \ln \frac{T_{s2} - T_{s1}}{T - T_{s1}}.$$

Here λ is the effective thermal conductivity of the char, δ is the thickness of the char layer, x is the height of rise of the liquid products in the char, and T is the gasification temperature of the liquid destruction products.

In [12, 27–29], the influence of a porous carbonized layer on combustibility has been studied in greater detail both theoretically and experimentally. In particular, investigating motion of liquids (acetone, ethanol, and benzene) through a porous material (phenolformaldehyde resin and polyphenylene dimaleimide subjected to pyrolysis at 500°C for 10 min) 1–3 mm thick, Gibov et al. found [12] that the velocity of liquid flow due to capillary forces, described by the Darcy equations, is higher than the combustion rate of the free material, and, as a consequence, the combustion rate does not vary with variation in the height of the porous layer. For such materials, the combustion rate is determined by the combustion rate of the matrix. The Darcy formula for the velocity of liquid flow through a porous medium has the form [30]

$$V = \frac{KS}{\eta L} \frac{2\sigma}{R} - \rho g L \cos \Theta,$$

where V is the volumetric velocity of the liquid flow, K is the Darcy constant, L and S are the thickness and area of the material, respectively, η, ρ, and σ are the viscosity, density, and surface tension of the liquid, respectively, g is the free-fall acceleration, R is the radius of pores in the material, and Θ is the tilt of the sample.

For materials with high-viscosity melts, for which the determining stage is the filtration rate of the products, the expression for the pyrolysis rate is written in [29] as

$$U_m = U_c k + (1 - k)\frac{K}{L}\left(\frac{\rho_g}{\eta_g} \Delta p + \frac{\rho_l}{\eta_l} \frac{2\sigma}{R}\right),$$

where U_c is the mass rate of char gasification, Δp is the difference between the pressures above and below the char layer, and k is the portion of the polymer that is converted into char; the subscripts g and l correspond to gaseous and liquid destruction products, respectively. Studying combustion of epoxy compositions, Gibov

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et al. [29] showed that the oxygen index correlates with the permeability of the char [the Darcy constant K calculated from experimental data (Fig. 3) was used as the permeability criterion].

The above expressions can appear to be useful for analysis of particular problems and qualitative dependences, but they do not describe the foaming dynamics and do not contain parameters that describe a particular system. At the same time, these relations can be used to describe filtration of products of polymer destruction through a porous bed in developing mathematical models of combustion.

THERMOPHYSICAL MODELS

Combustion of intumescent systems has been described most extensively within the framework of the thermal approach. Thermophysical models (sometimes they are called thermodynamic) are developed on the basis of the nonstationary thermal-conductivity equation [31]

$$c_p(T)\rho(T)\frac{\partial T}{\partial t} = \frac{\partial}{\partial y}\lambda(T)\frac{\partial T}{\partial y},$$

where y is the foaming coordinate and λ is the thermal conductivity. The gasification and coking reactions are taken into account by introducing appropriate additional terms.

Clark, Cagliostro, and others [32, 33] were the first to employ this approach. They used the equation

$$\rho_s c_{ps}\frac{\partial T}{\partial t}\bigg|_y = \frac{\partial}{\partial y}\left(\frac{k}{E_f}\frac{\partial T}{\partial y}\right)_t - \bar{h}\frac{\partial\rho}{\partial t}\bigg|_y + \frac{\dot{m}}{A}\frac{\partial h_g}{\partial y}\bigg|_t + h_g\frac{\partial\rho}{\partial t}\bigg|_y,$$

where $\bar{h} = (\rho_p h_p - \rho_c h_c)/(\rho_p - \rho_c)$, ρ_p and ρ_c are the densities of the polymer and the char, respectively, h_p and h_c are the enthalpies of the polymer and the char, $\dot{m} = \int_y^{y_b} A\frac{\partial\rho}{\partial t}\bigg|_y dy$ is the decomposition rate, y is the foaming coordinate, y_b is the distance from the surface to the material that did not undergo destruction, ρ_s and c_{ps} are the density and specific heat of the solid phase, E_f is the foaming coefficient, A is the cross-sectional area, k and k/E_f are the thermal conductivities of the solid phase and the porous layer, respectively, and h_g is the thermal diffusivity of the products. The second, third, and fourth terms on the right side of the equation describe, respectively, the heat release due to the chemical reactions, the heat absorbed upon evolution of the gaseous destruction products, and the heat absorbed upon heating of these products. For the foaming coefficient E_f, the following empirical expression was used:

$$E_f(y,t) = E_{f,\max} - (E_{f,\max} - 1)\left[\frac{\rho_B(y,t) - \rho_{rB}}{\rho_{0B} - \rho_{rB}}\right]^n.$$

Here $E_{f,\max}$ is the maximum foaming ratio obtained experimentally, and ρ_{0B}, ρ_{rB}, and $\rho_B(y,t)$ are, respectively, the initial, final, and current densities of the foaming agent B. The model system was assumed to consist of components A, B, and C. The kinetic parameters were calculated from thermogravimetric data using the expression

$$\frac{\partial\rho_i}{\partial t}\bigg|_y = -B_i e^{-Ea_i/RT}\rho_{0i}\left(\frac{\rho_i - \rho_{ri}}{\rho_{0i}}\right), \qquad i = \text{A, B, C,}$$

where ρ_{0i} and ρ_{ri} are the initial and final densities of the ith component. The mass loss for the entire system was calculated as the sum of mass losses for the individual components.

Investigating the influence of foaming and material properties on the temperature of the rear side of the sample under unilateral heating using model parameters obtained experimentally, the authors showed that the theoretical data coincide with the experimental results with an accuracy of about 20%. This difference was attributed primarily to the impossibility of accurately determining the characteristics of the sample. For example, in successive measurements under the same conditions, the thermal conductivity of the char varied within ±100%. The correctness of the kinetic model for component B and the correctness of the approach to the description of foaming have also been discussed.

More recently, Anderson and Wauters [34, 35] analyzed some variations of the model proposed by Clark by taking into consideration the rate of each particular point. This rate is zero for the starting material, constant for points of the char, and a function of the foaming coefficient E_f and the rate of mass loss dm/dt for the pyrolysis zone:

$$v(x,t) = \frac{dy}{dt} = -\int_0^x \frac{n}{m_0 - m} [E_f(m) - 1] \frac{dm}{dt} dt.$$

Here x is the initial coordinate and m_0 is the initial mass. To take into account the heat loss by the char surface via radiation, the boundary conditions were written as

$$k \frac{\partial T}{\partial x}\Big|_{x=x_B} = H(T_f - T_s) + \varepsilon_s(\varepsilon_f \sigma T_f^4 - \sigma T_s^4),$$

where H is the convective heat-exchange coefficient and ε_f and ε_s are the degrees of blackness of the surface and the flame, respectively. The initial system of equations was supplemented with the continuity equation:

$$\frac{\partial \rho}{\partial t} + \rho \frac{\partial v}{\partial y} = -\dot{\Gamma}_g.$$

Here $\dot{\Gamma}_g$ is the gasification rate. In addition, the influence of the substrate was taken into account by introducing the following boundary conditions on the substrate: the total heat supply goes to heating. The surface temperature was evaluated from the expression for heating of a half-infinite space by a constant heat flux q:

$$T_{\text{surf}} = T_0 + \frac{2q\sqrt{\alpha t/\pi}}{k}.$$

Here T_0 is the initial temperature and α and k are the thermal diffusivity and thermal conductivity of the coating material. The mass-loss function for the system was written as the sum of cosines:

$$\frac{d(m/m_0)}{dT} = \frac{a_0}{2} + \sum_{n=1}^{30} a_n \cos\left(\frac{n\pi T}{T_{\text{max}}}\right).$$

Here T_{max} is the boundary of the temperature interval of interest, and the Fourier coefficients a_n were calculated from experimental data. The number of terms on the right side of the equation was chosen so as to obtain satisfactory agreement with experiment. For the model parameters (a $7.6 \times 7.6 \times 0.08$ cm sample is coated with an intumescent coating 0.097 cm thick) at a heat flux of 2.68 cal/cm^2, it is shown that the calculated and experimental temperatures of the substrate agree well with one other for $E_{f,\text{max}} = 4.5$ and $n < 1$.

Buckmaster et al. [36] significantly simplified the model using the experimental fact that foaming proceeds in a very narrow layer compared to the initial thickness of the coating. Assuming that the temperature of this layer is fixed, they reduced the problem to motion of the pyrolysis layer through the material. For the gasification rate $\dot{g}$, it was proposed to use the expression

$$\dot{g} = \rho D e^{-\Theta/T} (m - m_f)^\alpha, \qquad \alpha > 0,$$

where ρ is the density of the material and D is a coefficient. The condition that foaming proceeds in a narrow layer was written mathematically using the new coordinate ξ, which was introduced as $x = h + \delta\xi$, where the small quantity $\delta \to 0$ characterizes the thickness of the pyrolysis zone and $h = h(t)$ is its position. Then, the continuity and thermal-conductivity equations were rewritten in terms of the independent variables ξ and t. In particular, it was shown that the instantaneous rate of a point behind the foaming front is defined as

$$u_f(t) = \dot{h}\left[1 - \frac{\rho_i m_f}{\rho_f m_i}\right],$$

where the subscripts i and f refer to the initial and final (after foaming) states, respectively.

After introduction of dimensionless variables, the problem reduces to the Stefan problem. In this approximation, the system of equations is solved without difficulty by numerical methods. However the proposed model does not take into account chemical reactions that occur during foaming. Nevertheless, this

model correctly describes qualitative effects that occur during foaming, in particular, motion of the pyrolysis zone through the material. Comparison of the theoretical results obtained using the described simplifications with experimental results is performed by Anderson et al. [37].

Gibov et al. [27, 38-40] employed a similar approach. The boundary condition on the char surface was set as

$$\lambda \frac{\partial T}{\partial y}\Big|_{y=0} = \alpha(T_s - T_f) + \varepsilon\sigma T_s^4,$$

where λ is the thermal conductivity, T_f is the flame temperature, and T_s is the surface temperature. The thermal conductivity of the porous layer was given by the expression $\lambda = \lambda_1\psi + \lambda_0(1 - \psi)$, where ψ is the porosity, and the density was described by the fixed function $\rho = \rho(\xi, V)$, where ξ is the initial coordinate and V is a function of build-up of the coating. The equation was solved by a numerical method using a computer. Analysis of the results obtained showed that the efficiency of an intumescent coating depends greatly on the height of the char cap and its thermal conductivity.

Transforming from Lagrangian to Eulerian coordinates, which are related by

$$x(\xi,t) = \xi + \int\limits_0^t u(\xi,\Theta)\,d\Theta,$$

where x is the Eulerian coordinate, ξ is the Lagrangian coordinate, and u is the linear velocity of motion of a point of the material, Mamleev and Gibov [41-43] considered the following expression for the foaming coefficient $E(\xi,t)$:

$$E(\xi,t) = \frac{\partial x}{\partial \xi} = \exp\left(\int\limits_0^t \frac{\partial v(x(\xi,\Theta),\Theta)}{\partial x}\,d\Theta\right).$$

Here $v(x,t) = dx/dt$. The algorithm of calculation of $E(\xi,t)$ is based on the assumption that the gas evolved forms a foam only in a certain range of rheological characteristics of the material, in particular, when its dynamic viscosity is in the range of $[\eta_m, \infty)$ [41, 42]. For a point of the coating, this gives the corresponding time interval $[t_{\min}(\xi), t_{\max}(\xi)]$, in which foaming occurs. The resulting differential equation for E has the form

$$E(c_g\rho_g\omega_g + c_p\rho_p\omega_p)\frac{\partial T}{\partial t} + c_g\rho_g v_g\frac{\partial T}{\partial \xi} + \rho_0 \sum_{i=1}^{N} \Delta H_i w_i \frac{df_i(\tau_i)}{dt} = \frac{\partial}{\partial \xi}\left[\frac{\lambda}{E}\frac{\partial T}{\partial \xi}\right],$$

where ΔH_i is the heat release of the decomposition reaction, w_i is the mass fraction, and df/dt is a mass-loss function for the ith component. The thermal conductivity λ is defined by

$$\lambda = \frac{\lambda_p\lambda_g}{\omega_p\lambda_p + \omega_g\lambda_g} = \frac{\lambda_p\lambda_g E}{(E - 1 + q)\lambda_p + (1 - q)\lambda_g},$$

where λ_g and λ_p are the thermal conductivities of the gas and the polymer, respectively, and ω_g and ω_p are their volumetric fractions. The boundary conditions for this equation are written as

$$\frac{\lambda}{E}\frac{\partial T}{\partial \xi}\Big|_{\xi=L} = \alpha_f\left(T_f - T\big|_{\xi=L}\right) + \varepsilon_f\sigma T_f^4 - \varepsilon_s\sigma T_{\xi=L}^4,$$

$$\frac{\lambda}{E}\frac{\partial T}{\partial \xi}\Big|_{\xi=0} = c_m\rho_m H_m \frac{dT}{dt}\Big|_{\xi=0} + \alpha_b(T_{\xi=0} - T_0).$$

The solution of the above differential equation subject to initial conditions for $t = 0$, $T = T_0$, and $\rho = \rho_0$ gives the full formation dynamics of the foamed layer.

Isakov, Zverev, and others [44-50] studied theoretically the foaming processes using experimental data. Thus, in [49], the equation used by Anderson [35] was examined as the basic equation. The motion velocity of a point of the material v was calculated from the experimental data on variation of the height of the char
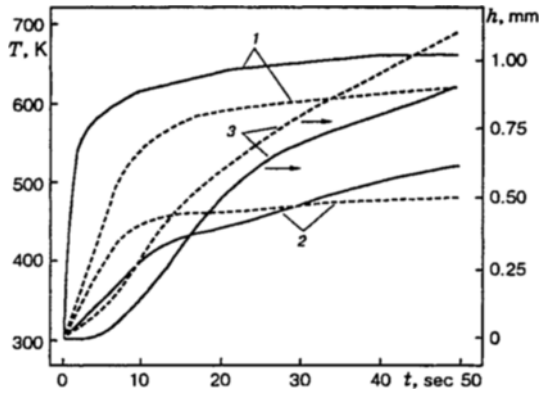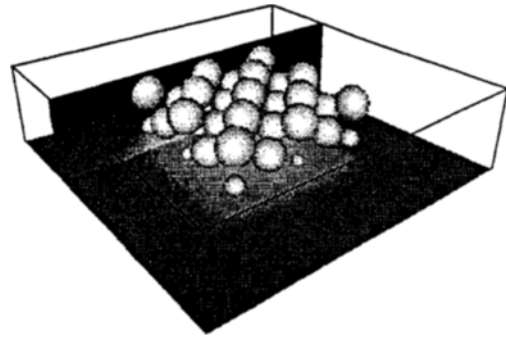
Fig. 4   Fig. 5

Fig. 4. Experimental (solid curves) and calculated (dashed curves) data for variation in the temperature of the surface (curves 1) and interior point of the sample $y/y_0 = 0.92$ (curves 2) [49]; curves 3 refer to the current thickness of the char cap; h is the thickness of char.

Fig. 5. Resulting porous structure and the shield effect of gas bubbles on heat flux during intumescence [68]: the darkened areas correspond to higher temperatures.

cap (Δh) with time at various temperatures:

$$v(y,t) = \frac{d}{dt} \int\limits_{y_0}^{y} \frac{\Delta h}{h_0}(T)\, dy, \qquad y_w(t) = \int\limits_{y_0}^{y_m} \frac{\Delta h}{h_0}(T)\, dy.$$

Comparing calculation and experimental results for a sample 4.5 mm thick under purely convective heating by an external flux of 177 W/m^2 under the assumption of smallness of $\Delta h/h_0$ (Fig. 4), the authors showed that the experimental and calculation data agree satisfactorily not only for the integral quantity — the current thickness $y_m(t)$ — but also for the local heating characteristics — the temperatures at interior points. Isakov and Nesmelov [50] considered the same equation in cylindrical coordinates.

Some aspects of combustion of intumescent compositions were studied by Shlenskii [51], Lipanov and Kodolov [52–54], and others. Shlenskii, for example, used an approach similar to that proposed by Buckmaster [36]. An intumescent composition was described using the Heaviside function $\Theta(h - x)$, where h is the height of the composition and x is the coordinate of the point. Recall that the function $\Theta(x)$ is defined as

$$\Theta(x) = \begin{cases} 1, & x \geqslant 0, \\ 0, & x < 0. \end{cases}$$

Let us sum up the aforesaid. The thermal model of foaming adequately describes the basic qualitative aspects and some quantitative aspects of foaming. However, the main disadvantage of this approach is that it uses a large number of empirical and experimental quantities. Another source of errors in this approach to the description of heat transfer in porous systems is the use of the effective thermal conductivity coefficient, because, in this case, the heat transfer by radiation inside the char cap is not taken into account. In addition, the model does not contain rheological characteristics of the melt and, as a consequence, it cannot predict the structure of the char cap.

PHYSICAL MODELS

Among all the models describing combustion of intumescent compositions, there is a special class — models that describe formation of the physical structure of a foamed char layer and the processes occurring in such systems. Some similar approaches are already considered in the section on steady combustion in the discussion of the influence of a porous char layer on combustibility. Although porosity and the other characteristics of foam materials affect strongly their thermal protective characteristics [55–57] and the effect of the structure of the carbonized layer is significant, as noted by almost all the authors investigating intumescent systems, there has been very few publications dealing with the physical structure of foamed chars formed in combustion, in particular, the papers of Gnedin [58–60] and Reshetnikov et al. [61]. Before proceeding to discussion of formation of a porous char layer, we note that the kinetics of formation of the porous structure of polymer foams has been studied in detail [62], but, in intumescent systems, this process has special features.

The first attempt to describe the formation of a porous structure was undertaken by Gibov [63, 64]. He suggested that the growth rate of a foam is determined by the rate of evolution of gaseous products and the rate of volatilization of them, and also by the motion of bubbles under the action of the Archimedean force. He believed in this case that removal of gaseous products occurs because of the permeation and filtration of the gases through the polymer, and the volumetric rate of the gas evolution is determined by a first-order reaction. As a result, he obtained the following expression for the rate of change of the volume W:

$$W = \frac{RT}{M}\left[k[G]e^{-E_a/RT} \Big/ \left(p_0 + \left(E\varepsilon + \eta_p\frac{\partial\varepsilon}{\partial t}\right)_T\right) + \frac{KS}{\eta_g L}\left(1 - \frac{p_i}{p_0}\right)\right] + V_{\text{c.ph.}}.$$

Here k is the rate constant of the reaction, $[G]$ is the concentration of the gas emission agent, M is the molecular weight of the gas, E_a is the activation energy, p_0 is the external pressure, p is the pressure inside a bubble, E is the elastic modulus, ε is the deviation of the bubble size from the equilibrium size, L is the thickness of the layer, and $V_{\text{c.ph.}}$ is the rate of change of the volume of the condensed phase. This formula holds true when the pressure in the bubble does not exceed a critical pressure and no destruction occurs. Unfortunately, the physical source of some quantities entering into the given formula is not clear, and, hence, this formula is of theoretical rather than practical significance. In addition, it does not allow one to predict the structural parameters of a foamed char such as the average diameter of pores, their distribution with depth, etc. An attempt to model the formation of a precisely porous structure was undertaken by Butler, Kashiwagi, and others [65–68]. They developed a model in which growth and migration of gas bubbles in the melt occur and nuclei of bubbling are assumed to be initially present in the melt. The growth of a bubble in the proposed model is given by the expression

$$\frac{dR}{dt} = DS'\left(\frac{p_0}{p_c} - 1\right)\left[\frac{1}{R} + \frac{1}{\sqrt{\pi Dt}}\right],$$

where R is the radius of the bubble, t is the time of growth, D is the diffusivity, S' is the solubility of the gas, p_0 is the initial pressure, and p_c is the critical pressure at which formation of bubbles occurs. If, while growing, two bubbles overlap rather strongly, they are united in one. After formation, a bubble, besides growing, begins to migrate in the melt, because of the temperature and viscosity gradients, with the rate

$$U = -\frac{4}{9}R\dot{R}\frac{\partial\ln\mu}{\partial T}G,$$

where G is the temperature gradient and μ is the viscosity of the melt. The viscosity was assumed to depend on temperature according to the Williams–Landel–Ferry equation [69].

The heat transfer inside the melt with bubbles was calculated using the one-dimensional thermal-conductivity equation in the presence of an external heat flux. The thermal field was obtained as the sum of the solution of the stationary thermal-conductivity equation for the pure melt and a small correction — the thermal fields of individual bubbles calculated for particular conditions. As a first approximation, the correction is expressed as

$$T = \frac{GR^3 z}{2r^3} + \frac{qR^2}{\lambda r},$$

where λ is the thermal conductivity of the melt and r is the radial coordinate.

Calculating numerically the growth of 10^4 bubbles in the material (a sample with dimensions 10×10 cm and thickness 1 cm) under the action of a thermal-energy flux of 4 W/cm^2 from an external source on the surface under the assumption that nuclei of bubbling are randomly distributed over the volume, the authors obtained the resulting porous structure and showed that the temperature behind the bubbles formed is lower than in zones that are not shielded by bubbles (Fig. 5). In our opinion, in this model, the use of the Williams–Landel–Ferry equation for the temperature dependence of viscosity is unjustified, because, for coking polymers, this dependence is known to be more complicated [70]. The model for growth of gas bubbles is borrowed from the theory of formation of foam polymers [62], but in combustion, the rates of temperature variation are much higher and the conditions for which the expressions are obtained are unattainable. Nevertheless, this model and the approach employed are promising, and, most likely, they will be actively developed.

Investigation of the processes occurring in a porous coking cap is also a stage in the development of the physical model of foaming. Since the thermal protective properties of intumescent materials correlate with the thermal protective properties of the foamed chars formed [71], modeling of heat-transfer phenomena in porous systems at high temperatures is required to estimate the efficiency of the thermal protection of intumescent materials. Without dwelling on papers in which heat transfer in foamed chars is considered from the point of view of the effective thermal conductivity calculated for both heat-insulating materials with a large air content, we shall consider some papers devoted to the modeling of heat transfer in porous media.

To describe heat transfer, Andersen [72] represented the porous structure of a char as alternating layers of char and air. Comparing the results with experimental data, he arrive at the conclusion that it is "air" inside the char cap that is responsible for the low thermal conductivity of foamed chars.

Pehrson and Barnett [73] attempted to model an interesting practical problem on protection of technological holes in engineering structures (for example, holes between floors for laying pipes or cables) using intumescent caulks. To study heat transfer, they developed a simple three-dimensional model. A horizontal concrete wall with a hole in which a heat-conducting pipe was placed was considered. A heat source (furnace) was placed below. From above the hole was plugged by an intumescent stopper. The internal space was divided into rectangular parallelepipeds — control volumes — each of which was assumed to be either empty or filled with a foamed char. During growth, an increasingly larger number of control volumes was filled. Solving, by means of a finite-difference scheme, a thermal-conductivity equation that took into account radiation, convection, and heat transfer through concrete and the pipe material, the authors predicted the temperature for various points of the coating, and also along the pipe and the walls. Comparison of the theoretical and experimental data showed qualitative and roughly quantitative agreement between them. Some limitations of the model due to the use of the method of a control volume, a simplified approach to foaming, and difficulties in obtaining exact thermal characteristics of the resulting foamed char layer are discussed.

To model heat transfer in porous systems with a large air content (up to 99%), among which are char foams, Reshetnikov and Khalturinskii [74, 75] proposed a simple one-dimensional model scheme based on the features of the physical structure of foamed chars. In the model they proposed, the char is represented as a layered structure, and the heat flux on each layer is the sum of the radiant flux from the upper and lower layers and the conductive flux from the upper, more heated layer. The heat losses of the layer occurs via radiation and the conductive flux to the lower layer. For the lower layer, the expression for heat losses contains the term $\gamma(T - T_0)$, where γ is the heat-removal coefficient through the substrate. Comparing the calculated and experimental data, the authors showed the applicability of the proposed approach to the modeling of heat transfer and estimated qualitatively the structural parameters of the char cap (the average diameter of pores and the height) on its thermal protective properties. In particular, they proposed the following expression that relates the temperature T_b on the rear side of the sample and the structural parameters of foamed chars — the height of the char cap h and the average diameter of pores d [75]:

$$T_b = T_0^* - \frac{Q}{\lambda_{\text{eff}}^*} h + h_r d,$$

where λ_{eff}^* is a constant that has the dimension of thermal conductivity, h_r is the coefficient of heat transfer
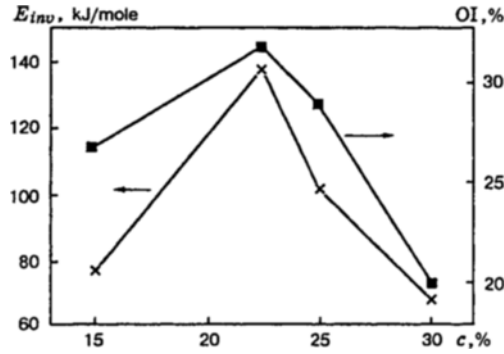
Fig. 6. Relationship between the invariant kinetic parameters and oxygen index of polypropylene with an intumescent additive [77]; c is the concentration of ammonium polyphosphate.

via radiation, and Q is the external heat flux. A more complicated three-dimensional model of heat-transfer in porous media is presented in [76]. The presented qualitative results are similar to those predicted in the one-dimensional model.

KINETIC MODELS

Bourbigot, Le Bras, and others [77–80] employed a kinetic approach to the description of intumescent systems. They used the method of invariant kinetic parameters [81]. The essence of this method consists in determining invariant physicochemical parameters (activation energies and preexponents) from gravimetric analysis data. Invariance means that the parameters obtained do not depend on experimental conditions (heating rate) and form of kinetic function of decomposition. As the basis, the method uses 18 kinetic functions $f_i(\alpha)$ divided into groups that correspond to definite kinetic models — diffusion, reactions at the interface, etc. — and also different heating rates β_v. The only assumption used is that the decomposition rate $d\alpha/dt$ (α the degree of mass loss) is given by

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) f(\alpha).$$

Here $f(\alpha) = \sum_{i=1}^{18} \mathrm{P}_i f_i(\alpha)$, where P_i is the probability of the ith function. Eighteen values corresponding to the activation energy E_{jv} and the preexponents A_{jv} are determined by the Coats and Redfern method [82] from the expression

where

$$\log\left(\frac{g_j(\alpha_{iv})}{T_{iv}^2}\right) = \log\left(\frac{A_{jv}R}{\beta_v E_{jv}}\right) - \frac{E_{jv}}{2.3RT_{iv}},$$

$$g_j(\alpha) = \int_0^\alpha \frac{d\alpha}{f_j(\alpha)}.$$

The method is based on investigating the "compensation effect." The points ($\log A_j$ and E_j) are plotted for all 18 functions. The compensation effect is observed if all these points lie along a straight line $\log A_{jv} = B_v + l_v E_{jv}$. As is shown in [83], these quantities are related to the invariant parameters $B_v = \log(k_v)$ and $l_v = 1/2.3RT_v$, where k is the invariant rate constant at temperature T_v. Constructing a family of straight lines at different heating rates, one finds the point of their common intersection and the corresponding quantities A_{inv} and E_{inv}.

Studying a polypropylene-based system with the intumescent system "ammonium polyphosphate-pentaerythritol," Bourbigot et al. [80] showed that, for various concentrations of the intumescent system in the matrix, a linear dependence between the oxygen index and the invariant activation energy is observed. A similar dependence is observed when the content of pentaerythritol is varied at a fixed 30% concentration

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of the intumescent system [77] (Fig. 6).

The kinetic approach can be useful for the search of optimum proportions of components for obtaining a synergistic effect, because the maximum invariant activation energy corresponds to optimum concentration. However, it must be recognized that there are simpler methods for this purpose. Another, more important in our opinion, application of the method of invariant kinetic parameters involves investigation of the decomposition mechanism of the system. Calculating the probability factors P_i in the relation for $f(\alpha)$, it is possible to evaluate the contribution of each particular mechanism, as was done in [79]. Thus, the kinetic approach can be useful as a component part in describing the chemical foaming process but cannot serve as the basis for the model.

CONCLUSION

Despite numerous methods and results, the problem of developing a complete model of combustion of intumescent polymer systems remains to be solved. At present, the chemistry and technology of thermal protective materials has progressed to the point where it is impossible to design new materials using only experimental data without the help of numerical methods. The studies performed stimulate the development of approaches that allow one to predict and simulate the behavior of intumescent coatings under fire conditions. We can state with assurance that, in the near future, many results will be obtained that will stimulate both the already existing approaches and new developments. Most likely, the field of physical modeling will be developed most actively, conceivably with attraction of some kinetic approaches for the description of gas evolution and char formation.

Furthermore, attention is drawn to the fact that the authors of papers devoted to intumescent systems concentrate in increasing frequency not only on the chemistry of foaming processes but also on the structure of the char layer formed [84], the effect of the structural features of materials, the structure of the surface and matrix on foaming processes [85, 86], etc.

In addition, there are a number of aspects of the description of combustion of intumescent polymer systems that, for some reason, have been left aside. First of all, these are the rheology and surface properties of polymer melts, because, without reliable data on the properties of the melts, it is impossible to develop a model that would give accurate results. We are aware of only one paper on the temperature dependence of the viscosity of melts of coking polymer [70], although viscosity variation in formation and transformations of polymers have been studied in detail [87]. The same is true for surface tension. The data for pure polymers, and also theoretical approaches to the calculation of surface tension of polymer melts, have been discussed repeatedly [88, 89]. However, these papers do not report data on the behavior of surface tension of polymer melts during decomposition.

Another aspect that has not been touched upon thus far is the mechanical strength of foamed chars, although, from the viewpoint of application of intumescent systems as protective coatings, this problem is nonetheless important. The model for combustion of intumescent polymer systems should allow prediction of the strength of char foams formed in combustion.

In summary, we emphasize again that the field of modeling of the combustion of intumescent systems is being actively developed today. The theoretical and experimental work already done allows one to hope that a number of integral models will soon appear that will predict the behavior of intumescent fire-proof materials under fire conditions with a sufficient degree of reliability.

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