

The Kinetics of Crosslinking in Process of Intumescence of Fireproof Polymer Compositions

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ABSTRACT: A mathematical model is proposed to calculate the expansion coefficient of the elementary volume of intumescent polymer material at an arbitrary change of temperature. It implies that parallel reactions of cure and gas formation take place simultaneously in the volume of the polymer composition. It was assumed that after attainment of some threshold values of the composition viscosity the gas released may be retained in the foam. Influence of the rate of heating, composition of the blend, and functionalities of the initial monomers on the effectiveness of foaming was investigated for the system phenol–formaldehyde resin with boron oxide. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 329–338, 1997

INTRODUCTION

Recent research has shown that the most effective method to decrease polymer combustibility is to use additives which cause a carbonization of the polymer.^{1,2} The compositions, which under the action of a flame are able not only to carbonize but also to intumescence (foaming), are of special interest.³ Upon foaming, the fireproof effect increases considerably, which is why such compositions can serve as fireproof coatings and paints for combustible materials and metallic constructions.

In a number of studies, the thermophysical models of fireproof intumescent coatings were considered.^{4–7} Much less attention has been paid to the quantitative aspects of the chemical nature of foaming. Chemical studies^{2,8} have been oriented mainly only to determine reaction types occurring in the intumescent coatings at moderate temperatures. In particular, it has been established that in a number of compositions polycondensation reactions take place.² An idea to select

compositions which are able to polycondensate (for instance, the ones which contain polyatomic alcohols, phosphorous compounds, etc., forming polyethers upon heating⁹), often leads to success in the creation of intumescent coatings. However, an ability of the components to polycondensate is insufficient for effective foaming. It is probable that a strict synchronization of the two processes is necessary for foaming: cure of the composition due to polycondensation and isolation of gaseous products, filling the foam. The study of the result of these parallel processes represents a very important unsolved problem in the theory of the synthesis of intumescent materials. This work aimed to create a kinetic model for the evaluation of the effectiveness of foam formation at different rates of composition heating.

We shall proceed from an assumption that with a monotonous increase in the temperature of the system its viscosity first is lowered due to an increase in the molecules'¹⁰ (or macromolecule segments') mobility, and then it increases due to the growth of the macromolecules. An increase in the molecular weight of the substances in the systems in question can hardly proceed due to the polymerization by double bonds. Foam formation proceeds at rather high temperatures (usually > 200°C). Note that here and below we imply

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that coatings under consideration are materials synthesized on the basis of organic compounds; the temperature limits for inorganic coatings can be different. At high temperatures ($>200^{\circ}\text{C}$), saturated polymer structures undergo depolymerization. As to polycondensation, it often can proceed even at higher temperatures ($\approx 400\text{--}500^{\circ}\text{C}$), being almost an irreversible reaction. That is why polycondensation, in our opinion, is the most promising process both in the synthesis of materials with a high yield of the carbonized residue and in obtaining the foamed materials.

In the course of nonlinear polycondensation, due to the transition of the system into the gel or into the vitreous state, the viscosity of the system can increase in time to infinity. In our opinion, the fast hardening is the main factor of foam stabilization; therefore, it is important that the system should meet a cure criterion. The formation of a crosslinked polymer proceeds at $\approx 200\text{--}500^{\circ}\text{C}$. In the same temperature range, the gas isolation and the foam formation proceed. Thus, as a result of the polycondensation and the evolving gas, a crosslinked foamed polymer forms.

With increase in the temperature above 500°C , the composition transforms into the material, which is usually called the carbonized residue or coke, although, in principle, it is not true, because apart from carbon, it contains,¹¹ in large quantities, nitrogen, oxygen, phosphorus, and other elements. The coke formation proceeds due to a deep pyrolysis with the formation of heavy aromatic fragments. The product obtained represents a practically new heat-resistant noncombustible polymer with a complex structure that is still undeciphered.

A great variety of additives are used to optimize the technological properties of the coatings.⁷ It is obvious that in model studies it is desirable to use a minimum number of components. In our opinion, there may be only three of them: a substance A_f with the functionality $f \geq 2$, a substance B_g with functionality $g \geq 2$, and a gas-former C . If gas is isolated as a result of the interaction of the substances A_f and B_g , only two components, A_f and B_g , are necessary for foaming. This simplest case is illustrated by the mixture of pentaerythrite ($f = 4$) with phosphoric acid ($g = 3$). Under heating, after some time, the mixture hardens and the isolating gas (H_2O) is retained by the foam.

Different layers of coating are in unequal temperature conditions. To develop foaming models, it is important to find a method which allows one to predict by using some kinetic schemes the behavior of small local portions of a substance when

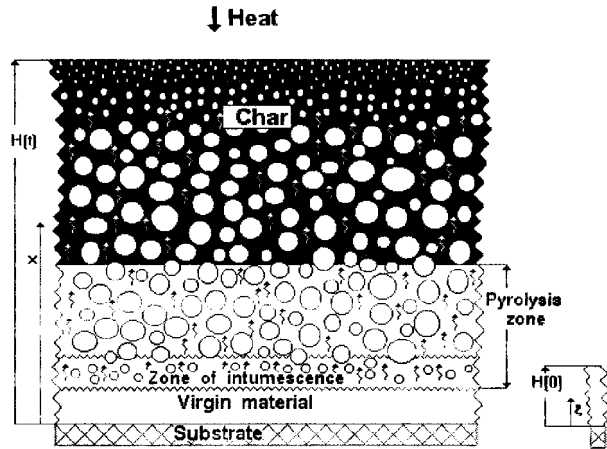


Figure 1 Model of an intumescent coating.

arbitrarily changing their temperature. One of such methods is proposed below.

The cure kinetics is considered¹² from the point of view of the Flory theory.^{13,14} The functionalities of the substances A_f and B_g are the main parameters of this kinetics. The values of f and g can be set on the basis of a known composition and the chemical structure of the compounds A_f and B_g .

The calculation of the foaming coefficient under the linear heating in the system phenol-formaldehyde resin + B_2O_3 is considered as an example. For this system, kinetic isotherms of the viscosity at different temperatures were measured experimentally.¹² This makes it possible to find some quantitative estimations.

THEORETICAL APPROACH

Calculation of the Expansion Coefficient

For economic numerical solving of the equation of heat transfer in an intumescent coating,⁴⁻⁷ it is convenient to describe a local temperature in the coating and its local density as functions of the spatial Lagrange coordinate ξ . The Euler x and Lagrange ξ coordinates (see Fig. 1) are connected by the relation

$$x(\xi, t) = \xi + \int_0^t dx(t) = \xi + \int_0^t v(\xi, t) dt$$

where v is a local linear velocity of material point with the initial coordinate ξ . Each elementary volume of the coating in the process of foaming is extended and the local expansion coefficient $E(\xi, t)$ depends upon time t and upon an initial position ξ of a material point under consideration, viz.:

$$E(\xi, t) = \partial x / \partial \xi = 1 + \int_0^t [\partial v(\xi, t) / \partial \xi] dt$$

$$\partial v(\xi, t) / \partial \xi = \partial E(\xi, t) / \partial t$$

The function $E(\xi, t)$ is the main measure characterizing the efficiency of foaming; that is why a calculation algorithm of $E(\xi, t)$ is an important problem of mathematical modeling the coatings. This algorithm can be used in the numerical solving of the heat transfer equation,⁴⁻⁷ which, in turn, is not too difficult.

Clark et al.⁴ used an empirical approach for the calculation of E , presenting this function as follows:

$$E(\xi, t) = 1 + (E_f - 1) \{ [\rho_0 - \rho(\xi, t)] / (\rho_0 - \rho_f) \}^n \tag{1}$$

where E_f is a maximum expansion coefficient; ρ_f , a final foam density; ρ_0 and $\rho(\xi, t)$, the density of the virgin coating and its current density, respectively; and n , an empirical coefficient. According to eq. (1), the foam has a final uniform density. However, this particular situation is a rare case in practice.

To calculate the density $\rho(\xi, t)$, the authors⁴ used an equation of chemical kinetics with the preset activation energy. We consider such an approach as unsound, since when using the formal kinetics one can describe only the loss of the local mass of the coating.⁵ As to its local density, it is determined rather by the amount of gaseous products retained in the foam than by the loss of the initial local mass. It is obvious that a coating can lose a big mass without foam formation and lose a small mass, forming a foam material of low density. The model proposed below seems more general, although it includes elements of empiricism.

Let us assume that the gas isolation in a coating takes place due only to one reaction. As noted, it may be a curing reaction ($A_f + B_g$). However, let us assume, for generalization, that the cure and the gas isolation are independent reactions. If the activation energies of these two reactions coincide (a regime of synchronization), these may be formally considered to be one reaction.

The curves of weight loss of the coating measured by the differential gravimetric analysis represent, as a rule, smooth z -like functions so that gas isolation in the coating can be described accurately enough by the kinetic equation of a first-order reaction:

$$dq/dt = -k_c(q_0 - q)\exp(-E_c/RT) \tag{2}$$

where q is a mass of the gas isolated per gram of a coating; q_0 , a limiting gas isolation; and E_c and k_c , the activation energy and a rate constant of the gas-formation reaction. After time t in some elementary volume of the coating with the coordinate ξ , a total mass of a gas isolated per gram of the substance mass will be equal to

$$q(\xi, t) = q_0 \left\{ 1 - \exp \left[-k_c \times \int_0^t \exp[-E_c/RT(\xi, t)] dt \right] \right\} \tag{3}$$

Only a part of this gas will be retained in the coating. To evaluate it, an interval of the time $t_{\min}(\xi) < t < t_{\max}(\xi)$ should be found, within which foam formation is possible.

If the viscosity of the melt is small, gas bubbles float to the surface of the material and are decomposed, since the foam is not stable. However, we shall assume below that after reaching of a certain limit of viscosity η_m the gas bubbles cease to float up and the coating begins to foam. A limiting value of the expansion coefficient is fixed when the foam hardens. In an ideal case, all the gas released when changing the viscosity within the limits $\eta_m < \eta < \infty$ will be retained in the foam.

Time can be expressed as a function of the viscosity of a local portion of the substance, i.e., $\eta = \eta(\xi, t)$ and $t = t[\eta(\xi)]$. Therefore, in the coating layer with the coordinate ξ , the volume of the gas per unit of the mass can be expressed as

$$(RT/PM)\tilde{q}(\xi, t) = \begin{cases} 0, & t < t[\eta_m(\xi)] = t_{\min}(\xi) \\ (RT/PM)[q(\xi, t) - q(\xi, t_{\min})], & t_{\min} < t < t_{\max} \\ (RT(\xi, t_{\max})/PM)q_{\max}, & \\ t > t(\eta(\xi) \rightarrow \infty) = t_{\max}(\xi) \end{cases} \tag{4}$$

where M is the molecular weight of the gas, and P , the pressure. The local density of the coating will be changed by the law

$$\rho = 1 / (1/\rho_0 + \tilde{q}RT/PM)$$

From here, one can readily find the value of the local expansion coefficient

$$E(\xi, t) = \rho_0/\rho = 1 + \rho_0\tilde{q}(\xi, t)RT(\xi, t)/PM \tag{5}$$

It follows from eq. (4) that the maximum value of the expansion coefficient is equal to

$$E_f(\xi) = 1 + \rho_0 q_{\max}(\xi) RT(\xi, t_{\max})/PM$$

Thus, the limiting expansion coefficient in the present model is not a constant and is determined by the local temperature–time dependence $T = T(\xi, t)$. This model, in contrast to the previous ones,^{4–7} allows one to study the synchronization regimes of the reactions of the cure and gas isolation. Besides, it gives an opportunity to explain the unevenness of the density of the foam along a depth of coating.

If at the moment t_{\max} all the gas is retained by the foam, we shall have

$$E_f^*(\xi) = 1 + \rho_0 q_0 RT(\xi, t_{\max})/PM$$

It is convenient to characterize the effectiveness of the foam formation by using the ratio E_f/E_f^* . If $E_f \gg 1$ and $E_f^* \gg 1$, and it is appropriate to employ the estimation

$$E_f/E_f^* \approx q_{\max}/q_0 \quad (6)$$

Although an ideal gas retention within the range $\eta_m < \eta < \infty$ is not possible, formulas (4) and (5) can probably procure a good accuracy if η_m is considered as some empirical parameter. Thus, for the calculations by formulas (4) and (5), it is necessary to know η_m and the function $\eta(T, t)$, which is determined by the curing kinetics.

The Region of Gel Formation

We considered earlier¹² a simplest kinetics of the stepwise polycondensation $A_f + B_g$ when the interaction of the active groups of compounds A_f and B_g is due to bimolecular reaction. The extent of the conversion of the groups of the A_f compound conforms to the following equation:

$$p = \{1 - \exp[(\beta - 1)\bar{k}_s\tau]\} / \{1 - \beta \exp[(\beta - 1)\bar{k}_s\tau]\} \quad (7)$$

where \bar{k}_s is a reduced rate constant; β , a stoichiometric ratio; and τ , a reduced reaction time. Under nonisothermal conditions, τ is expressed as an integral:

$$\tau = \int_0^t \exp(-E_s/RT(t)) dt \quad (8)$$

where E_s is the activation energy of the curing reaction, and R , the gas constant. The parameters \bar{k}_s and β can be written as

$$\bar{k}_s = k_s g N_B / (M_A N_A / d_A + M_B N_B / d_B),$$

$$\beta = f N_A / g N_B$$

where N_A and N_B denote the initial mol amounts of the A_f and B_g compounds in the reaction blend, k_s is a dimensional rate constant, and M_A, M_B and d_A, d_B are the molecular weights and the densities of the A_f and B_g compounds.

According to the branching theory, the moment of gel formation corresponds to the following conditions^{12,14,15}:

$$\beta p^2 (f - 1)(g - 1) = 1 \quad (9)$$

The limiting value of p upon $\tau \rightarrow \infty$ depends upon β . With an excess of the compound A_f ($\beta > 1$) or compound B_g ($\beta < 1$), the limiting conversion is expressed by the equalities

$$p_\infty = p_A^\infty = \lim_{\tau \rightarrow \infty} p = 1/\beta, \quad p_B^\infty = 1(\beta > 1)$$

$$p_\infty = 1, \quad p_B^\infty = \beta(\beta < 1)$$

In accordance with criterion (9), the system can transform into a gel before the full completion of the reaction $A_f + B_g$ at $p = p_r < p_\infty$. Under a significant excess of the only component A_f or B_g , the reaction between the functional groups would go to the end but the system would not transform into a gel.

Let $x = x_B = 1 - x_A = N_B / (N_A + N_B)$ be a mol fraction of the substance B_g in the initial composition, i.e., $\beta = (f/g)(1 - x)/x$. Criterion (9) allows one to find an interval $x_{\min} < x < x_{\max}$ of the x values within which the system transforms into a gel:

$$1 - (f/g)(1 - x)(f - 1)(g - 1)/x = 0 \quad (\beta < 1)$$

$$1 - (g/f)x(f - 1)(g - 1)/(1 - x) = 0 \quad (\beta > 1)$$

From the latter two equations, we find

$$x_{\min} = (f/g) / [(f/g) + (f - 1)(g - 1)] \quad (10)$$

$$x_{\max} = (f/g)(f - 1)(g - 1) / [1 + (f/g)(f - 1)(g - 1)] \quad (11)$$

In our opinion, the main principle of the synthesis of intumescent compositions is their transformation into a gel at temperatures below the

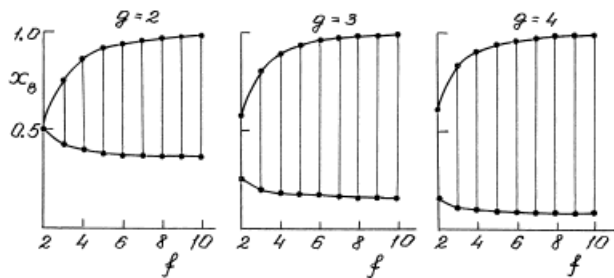


Figure 2 Phase diagrams of the transition of the thermoplastic systems into a gel upon different functionalities of the molecules.

temperature of coke formation. Thus, the phase diagram (see Fig. 2) can serve as one of orientations for the choice of the initial composition content, which should correspond to the interval $x_{\min} < x < x_{\max}$.

RESULTS AND DISCUSSION

Thermoplastic phenol–formaldehyde resin (PhFR) with an addition of B_2O_3 under the action of flame forms a foamed material. The coefficient of the foaming for this composition, being expressed as a ratio of a final volume of the material to an initial volume, constitutes ≈ 20 –30. Note that on the basis of other polymer resins¹⁶ we synthesized the coatings with the coefficient of foaming ≈ 100 . Because of the comparably low coefficient of foaming and due to some technological reasons, the system PhFR + B_2O_3 is far from being the best fireproof coating, but this system is very convenient as an object for modeling, for it has a simple composition and yields to rheological measurements in a range of temperatures preceding intensive pyrolysis.

The following set of parameters¹² determines the curing kinetics: $f = 5$, $g = 3$, $M_A = 518$ g, $M_B = 34.8$ g, $d_A = 1$ g/cm³, $d_B = 1.8$ g/cm³, $E_s = 11.8$ kcal/mol, $k_s = 68.4$ s⁻¹, and $k_s = 3614$ (mol/cm³) s⁻¹. The reduced time of the curing reaction corresponding to the point of gelation is expressed as

$$\tau_r = \int_0^{t_{\max}} \exp(-E_s/RT(t)) dt$$

Note that the parameter τ_r does not depend on the form of the temperature–time curve $T(t)$. The value $\tau_r = 0.127$ s has been found¹² with $\beta = 0.45$.

We used the method of Macosko et al.^{17,18} while representing the viscosity of the composition in the form

$$\eta = \eta_0 \exp(E_\alpha/RT) L^\alpha$$

where η_0 and α are empiric constants; E_α , the activation energy of the viscous flow; and L , an average longest length of a linear chain in a cross-linked molecule. The value of L is determined by the extent of reaction p , i.e., $L = L(p)$. When approximating the viscosity, the following parameters were used¹²:

$$E_\alpha = 10 \text{ kcal/mol}, \alpha = 3.26,$$

$$\eta_0 = 2.37 \times 10^{-4} \text{ Pa}\cdot\text{s}.$$

It is worthwhile to note that this work is not intended for solving the equation of heat transfer in the coatings. The goal of our calculations is to elucidate the influence of a heating rate on the foaming of small portions of a substance within which the temperature is distributed evenly; therefore, we omit the coordinate ξ in the calculations. To study the general effects, it is sufficient to consider the linear heating: $T = T_0 + bt$, where T_0 is an initial temperature.

To calculate the amount of the retained gas, one more constant, η_m , is necessary. It can be evaluated by knowing a coefficient of foam formation at a definite rate of the system heating.

We shall assume that the foam filling is realized by gases isolated in the course of the oxidation pyrolysis of the polymer. In the temperature range of 200–500°C, PhFR loses about 30% weight due to the oxidation pyrolysis. It is known¹⁹ that as a result of the oxidation pyrolysis the following gases are isolated: H_2O , CO_2 , CH_4 , and H_2 .

Let us suppose that an average molecular weight of these products constitutes 30 g. Then, at the temperature of 300°C, a limiting coefficient of foaming E_f^* constitutes ≈ 500 . The experiments show that the middle layers of the coating, being heated at the rate $\approx 1^\circ\text{C/s}$, are foamed by a factor of ≈ 20 . Thus, $E_f/E_f^* \approx q_{\max}/q_0 \approx 0.04$, when $b = 1^\circ\text{C/s}$.

According to data of the differential thermal analysis, the maximum rate of the PhFR weight loss with $b = 10^\circ\text{C/min}$ is observed approximately at 400°C. With the activation energies 11.8, 35.0, and 60.0 kcal/mol, the following constants of the gas formation k_c , s⁻¹: 14.7, 1.52×10^9 , and 3.43×10^{17} , correspond to the above temperature. It is noteworthy that among these three energy values the energy of 35 kcal/mol corresponds best of all to the oxidation pyrolysis. The other two values

are used only to discuss some imaginary situations.

Note that the value of q_{\max}/q_0 is the function of η_m . Calculating q_{\max}/q_0 , with $E_c = 35$ kcal/mol, $k_c = 1.52 \times 10^9$ s⁻¹, and $b = 1^\circ\text{C/s}$, one can find η_m as a root of the equation $q_{\max}(\eta_m)/q_0 = 0.04$. The calculations lead to $\eta_m = 206$ Pa-s. Using this value of η_m , curves are plotted corresponding to the other activation energies and heating rates (see Fig. 3).

To interpret the dependencies q_{\max}/q_0 , let us consider Figure 4(a), which displays the results of the calculation of the composition viscosity with different b . Each curve $\eta(T)$ passes through the minimum η_{\min} . Under the heating rates 0.2 and 5.0°C/s, the values of η_{\min} , according to our calculations, constitute ≈ 0.5 and ≈ 5.0 Pa-s, respectively. Unfortunately, such values are beyond the sensitivity of our measurements; that is why we cannot test the quality of the viscosity extrapolation toward the region $L \approx 1$. With $T < 100^\circ\text{C}$, the extent of the curing reaction is small ($L \approx 1$), so that the initial part of the curves $\eta(T)$ corresponding to the range of composition softening practically does not depend on b and is determined exclusively by the factor of viscous flow, viz., $\exp(E_a/RT)$.

In the proximity of the points of gel transitions, a sharp increase in viscosity takes place. With

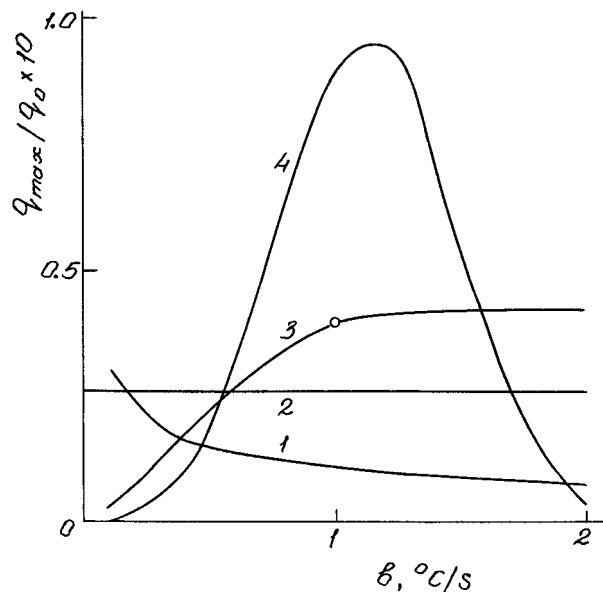


Figure 3 The dependence of a part of the retained gas in the foam upon the linear heating rate for the reactions of gas formation with different activation energies E_c (kcal/mol): (1) 11.8; (2) 11.8 (ideal synchronization, $E_c/RT = \text{const}$); (3) 35; (4) 60. The bearing point used for the estimation of η_m is shown in curve (3).

increase of b , the points of the gelation are shifted to the region of high temperatures. With $b > 2^\circ\text{C/s}$, the branches of the curves $\eta(T)$ corresponding to solidification cross the region of intensive carbonization ($\approx 500^\circ\text{C}$). In this zone, the carbonization probably suppresses foaming. It is obvious that the destruction connected with the polymer pyrolysis also can affect the composition reology and, hence, the foaming, although we do not allow for this factor. In the temperature range ≈ 400 – 500°C , one can expect a particularly strong effect of the destruction upon viscosity. However, in the middle layers of the coatings at moderate heating rates ($b \approx 0.2$ – 1.0°C/s), the composition hardens at lower temperatures, corresponding only to the beginning of the oxidation pyrolysis.

The amount of the retained gas is determined by the temperature interval $\Delta T = T(\eta \rightarrow \infty) - T(\eta_m)$, when viscosity varies from η_m to ∞ . These amounts for different b are shown in Figure 4(b)–(d) by the shaded areas. With an increase of b , the ΔT interval decreases (see curve 1 in Fig. 5), while the value of L corresponding to the η_m value increases (see curve 2 in Fig. 5). An increase of L at the points of η_m means a narrowing of the intervals of the conversion extent (Δp) and the reduced time ($\Delta \tau$), corresponding to the intervals ΔT and $[\eta_m, \infty)$. When $E_c = E_s$, the scales of the reduced time for the reactions of cure and gas formation coincide, which is why with a decrease of $\Delta \tau$ (an increase of b) the amount of the retained gas decreases (see curve 1 in Fig. 3). One may show that the dependence of q_{\max}/q_0 upon b in this case is connected to a factor of the activation flow: $\exp(E_c/RT)$. This factor can be formally excluded assuming that the E_c/RT value is a constant. For example, curve 2 in Figure 3 and curves 1' and 2' in Figure 5 are calculated upon $E_c/RT = E_c/(R \times 673.2)$. In this case, the ΔT interval increases with increase of b , and L corresponding to η_m becomes a constant. The latter means that the intervals Δp and $\Delta \tau$, corresponding to the change of viscosity from η_m to ∞ , do not depend upon b . With $E_c = E_s$, in this case, an ideal synchronization of cure and gas-isolation processes is attained, i.e., the amount of the retained gas does not depend upon the heating rate.

In the systems where $E_c \neq E_s$, one can observe an apparent synchronization. For example, it follows from Figure 3 (see curve 3) that with $E_c = 35$ kcal/mol and $b > 1^\circ\text{C/s}$ the value q_{\max}/q_0 is practically a constant. This occurs because of the compensation effects of the decrease of $\Delta \tau$ in the

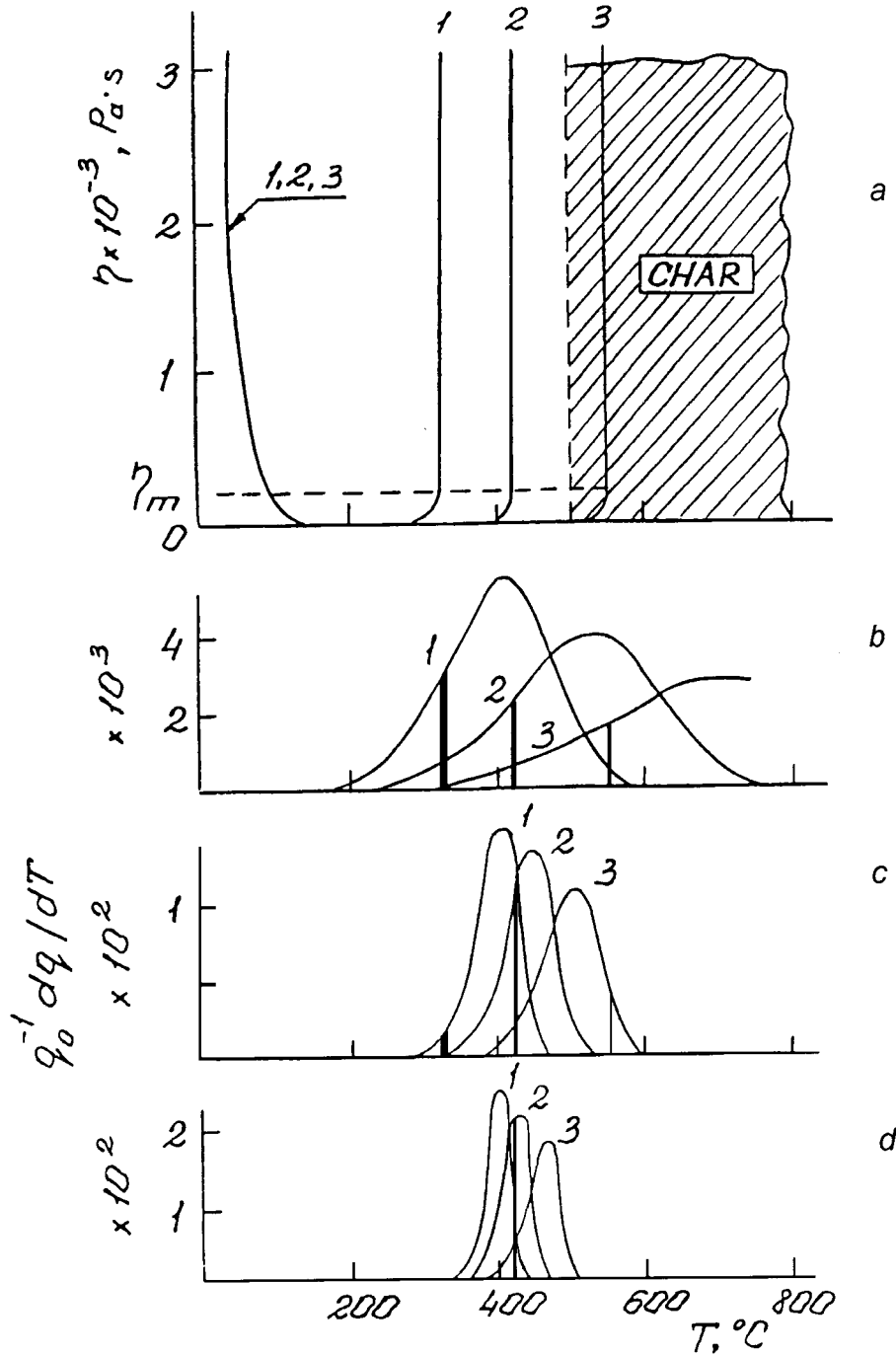


Figure 4 (a) The dependence of the viscosity and (b–d) the rate of gas isolation upon temperature at different rates of linear heating b ($^{\circ}\text{C}/\text{s}$): (1) 0.2; (2) 1; (3) 5. The curves of the gas isolation are calculated for different activation energies E_c (kcal/mol): (b) 11.8; (c) 35; (d) 60.

curing reaction and the approaching of ΔT toward the maximum rate of gas isolation.

One may readily explain a distinct maximum of the gas retaining at $E_c = 60$ kcal/mol (see curve 4 in Fig. 3). Upon low and high heating rates, the

region of solidification does not match with the region of gas isolation (see Fig. 4).

It follows from Figure 4 that the coatings with a high coefficient of foaming ≈ 100 can be obtained if the ΔT interval surpasses $\approx 50\text{--}100^{\circ}\text{C}$.

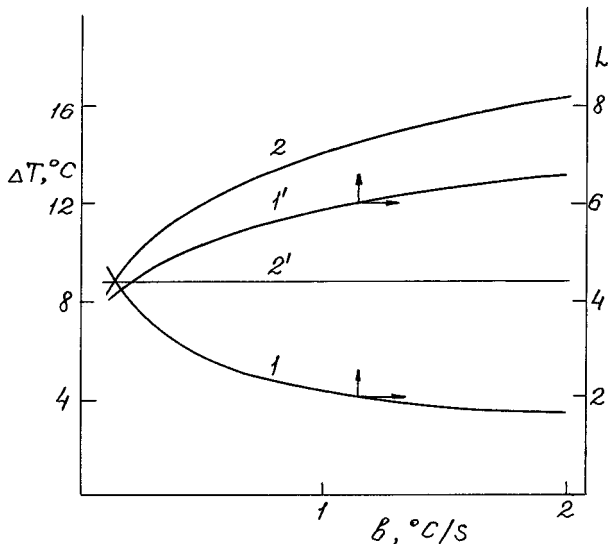


Figure 5 The temperature interval (1, 1') corresponding to the region of foam formation and the average longest length of the linear chain (2, 2') corresponding to the viscosity limit η_m depending upon the linear heating rate. Curves 1' and 2' are calculated by $E_c/RT = \text{const}$.

This can occur, e.g., in the systems where $\eta_{\min} > \eta_m$. Then, the gas is retained in the foam all over the range of the viscosity change up to the moment of gelation. With $E_c = E_s$, an ideal synchronization is attained in such systems irrespective of the factor $\exp(E_c/RT)$. Coatings corresponding to such systems should have almost an even final density along the depth.

It is noteworthy that upon the synthesis of coatings there always arises a problem of choosing the optimal concentrations of the components. The dependence of the gel-formation temperature upon $\ln \beta$ is shown in Figure 6. With $f = 5$ and $g = 3$, according to eqs. (10) and (11), the critical values of β are equal to 0.125 ($x_{\max} = 0.93$) and 8 ($x_{\min} = 0.17$). It is seen that in the region of excess B_2O_3 ($\beta < 1$), the curves pass through the minima, the position at which $\ln \beta \approx -1$ weakly depends upon the heating rate. The value of β at the points of the minima corresponds to $\approx 25\%$ by weight of B_2O_3 , which agrees well with the optimal content of the intumescent composition. It follows from Figure 6 that by changing the composition content it is possible to regulate the temperature of solidification. It is probable that for many systems the lowest temperatures of solidification are optimal; then, the processes of destruction and carbonization minimally hinder foam formation. The methods of preparation of such systems should include

the use of the excess of the component of the lesser functionality.

Since the functionalities of the original compounds are important parameters, the calculations with a different functionality f of oligomer PhFR are of interest for practice. To compare the results of these calculations, it is convenient to consider a number of systems characterized by the same reduced time of gel formation τ_r . The reduced time is governed by changing the initial composition of a blend. It follows from eqs. (7), (8), and (9) that at a fixed value of τ_r , a stoichiometric coefficient β must satisfy the following equation:

$$\frac{k_s g \tau_r}{(g/f)M_A \beta / d_A + M_B / d_B} = (\beta - 1)^{-1} \ln \left[\frac{p_r - 1}{\beta p_r - 1} \right] \quad (12)$$

where $p_r = [\beta(f - 1)(g - 1)]^{-1/2}$. Solving eq. (12) with respect to β , one can find compositions of the coatings, which, with different f , harden at the same moments of time and, correspondingly, at the same temperatures.

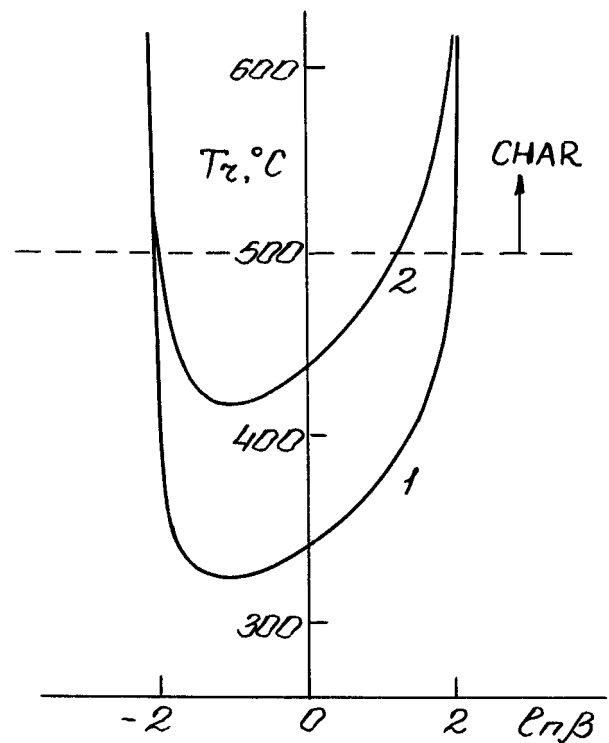


Figure 6 The dependence of the temperature of the gel transition upon the stoichiometric ratio at different linear heating rates b ($^{\circ}\text{C}/\text{s}$): (1) 0.2; (2) 1.

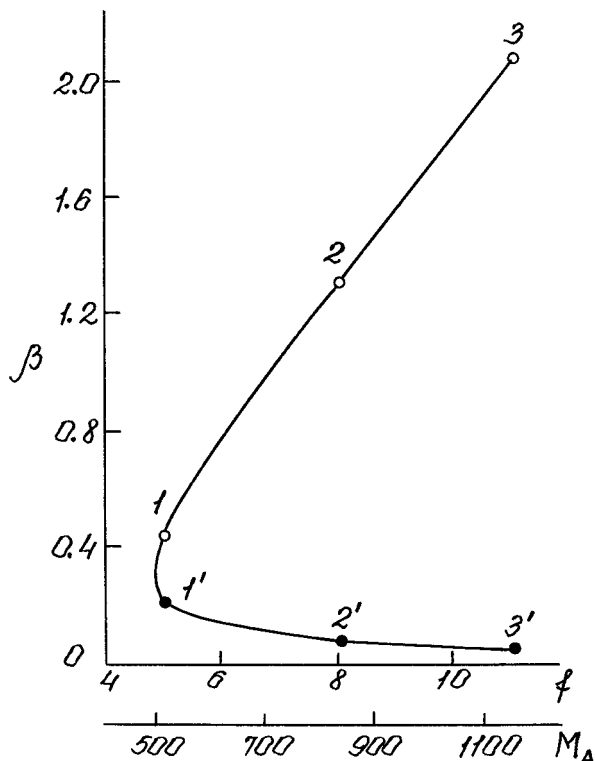


Figure 7 The values of the stoichiometric coefficient providing for the constancy of a reduced time of the curing reaction upon different functionalities of the PhFR oligomer. The points 1, 2, and 3 (1', 2', and 3') were used in the calculation of the curves $\eta(T)$ in Figure 8.

The values of β calculated with different f are represented in Figure 7. If $f \geq 5$, eq. (12) has two roots. In other words, the blends hardening at the same temperatures can be prepared in two ways using either the excess of the component A_f or the excess of the component B_g .

In Figure 8 are shown the dependencies of the viscosity upon the temperature corresponding to the different branches on the curve of the composition (see Fig. 7). The curves $\eta(T)$ have a common asymptote, viz., the viscosity rises to infinity at $T = 419.9^\circ\text{C}$. According to the model under consideration, the amount of the retained gas varies differently for two branches of composition (see Fig. 9). With an excess of PhFR (see the upper branch in Fig. 7), the variation of functionality weakly affects the ratio q_{max}/q_0 (see Fig. 9). At the same time, with an excess of B_2O_3 (see the lower branch in Fig. 7), the increase of f leads to a sharp suppression of foaming.

CONCLUSIONS

In our opinion, a cure of the material is one of the most important factors determining a stabiliza-

tion of the foam in the intumescent coatings. An idea to provide for the cure by means of reactions of polycondensation often leads to success in the creation of intumescent coatings.

After solidification due to polycondensation, the material can further turn into coke. Thus, coke is a final product, which, in turn, can be considered as a new polymer with some useful properties.

The wider a temperature interval is, within which a necessary rheological state of a composition is reached, the more gas that is retained in a foam. An overall amount of gas isolated in the coatings is usually enough to increase the volume of a coating more than 100–400 times. However, only a small part of the gas is retained in a coating. The ratio of this part to an overall amount of a gas isolated depends on the rheological evolu-

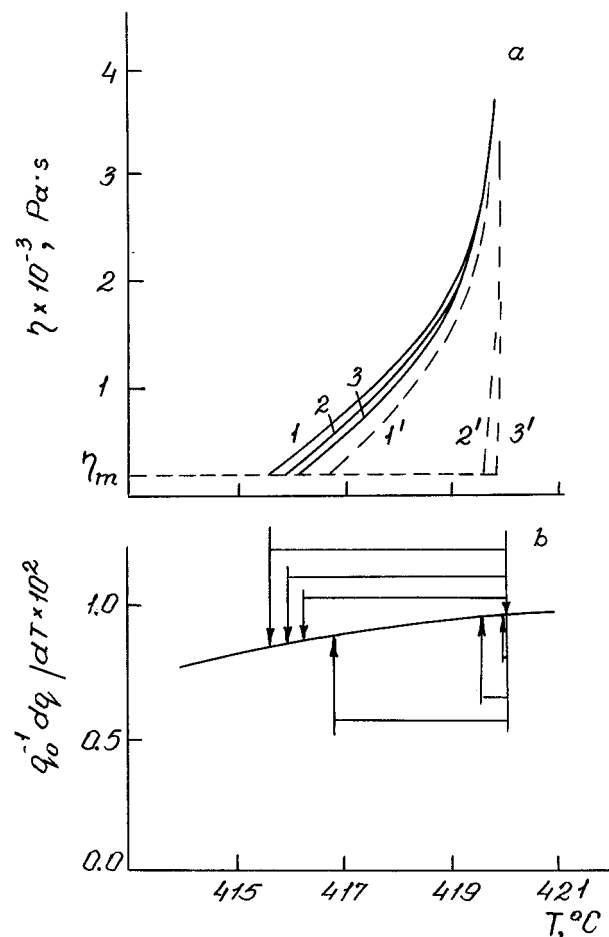


Figure 8 (a) The dependence of the viscosity and (b) the rate of gas isolation upon temperature with different functionalities of PhFR, f : 1(1') (5); 2(2') (8), 3(3') (11). The curves correspond to the points in Figure 7. The calculations were carried out with $b = 1^\circ\text{C}/\text{s}$ and $E_c = 35 \text{ kcal/mol}$.

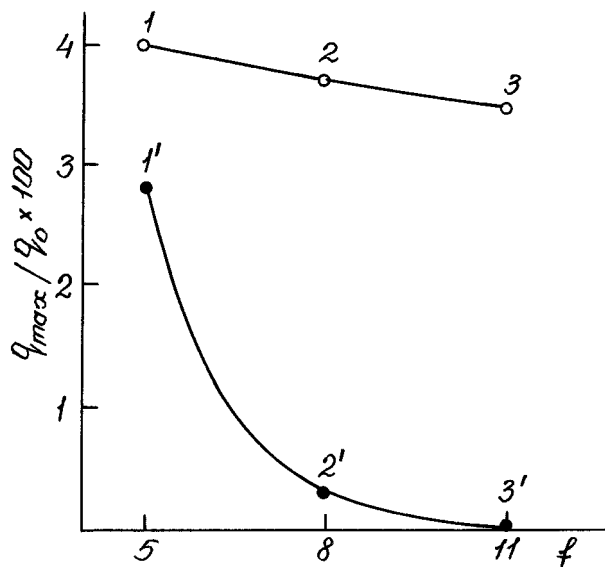


Figure 9 The dependence of a part of the retained gas in the foam upon a functionality of PhFR for two branches of the curve of composition. The points correspond to Figure 7.

tion of a system. In order that a coefficient of foaming would be ≈ 100 , it is necessary that all gas up to the moment of solidification would be retained in the foam.

By changing a composition of a coating, one may regulate the temperature of the gel transition. The minimum temperatures of gel transitions correspond to an excess of a component of lower functionality. Functionalities of initial components considerably affect both the temperature of gel transition and the temperature interval of the foaming. However, by changing an initial composition, one can attain conditions when with the original oligomers of different functionality the gel transitions take place at the same temperatures. It is noteworthy that with all other conditions being equal two blends of different composition can correspond to the same temperature of the gel transition.

The final density distribution of a material along a depth depends upon the kinetic parameters of the reactions of the cure and gas formation. Under ideal synchronization of these reactions, the foam has a uniform final density along a depth of a coating. An ideal synchronization is reached in the systems where the reactions of the cure and gas formation have equal activation energies.

The curing reaction should take place at moderate temperatures (≈ 200 – 400°C) to precede the region of intensive carbonization of a material

($\approx 500^\circ\text{C}$). The upper layers of a coating are heated at a high rate. That is why the destruction and carbonization in these layers proceed earlier than what is necessary for the foaming rheological state of composition to be reached. Therefore, the upper layers of the coatings, as a rule, retain far less gas in comparison to the lower layers. However, processes taking place in the upper layers can substantially affect the effectiveness of a coating. The upper layers, by protecting the coating from an intensive heat flux, allow foam formation to occur in the lower layers.

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