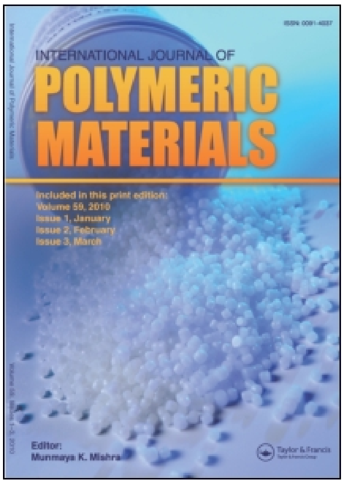

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Calculating Experiment for Intumescent Nitrogen-Phosphorus Containing Coatings

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The purpose of this presentation is to investigate such physico-chemical processes when a temperature field acts on polymeric composites (epoxy polymeric resins), filled with intumescent additive particles of ammonium polyphosphate. In order to obtain a certain bubble structure, the polymeric material is filled with uniformly disposed additive particles.

To describe the intumescence processes the equations are used based on the laws of energy and mass conservation, as well as on Realy and Clapeyron–Mendeleev equation. While considering the processes proceeding in the bubble, chemical reactions flowing on the surface of the intumescent additive, as well as on the bubble inner surface, and in the bubble volume are taken into account. The system of equations obtained is solved numerically.

Due to the calculating experiment the dependence of the intumescent layer height upon the degree of the polymer composite filling and upon the intumescent additive particle sizes is received. The change of thermal diffusivity properties of the coating at various temperatures and time of heating is investigated.

The calculating experiment allowed to conclude that the approach to the mathematical model developed is in accord with the pattern of physico-chemical processes proceeding in intumescent coatings.

Keywords: Polymers; composites; intumescence; coatings; additives

INTRODUCTION

An effective method of decreasing polymeric composite combustion is using an intumescent coating or modifying material surface layers to

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*Corresponding author.

render them intumescence properties. Many papers deal with this problem but the intumescence mechanism for different polymeric systems was still studied insufficiently. To control intumescence processes numerical experiment should be conducted.

This paper concerns the developing of a mathematical model of physico-chemical processes in intumescent coatings filled with intumescent additive particles and containing a cross-linking agent.

PHYSICO-CHEMICAL PATTERN

The polymeric coating (the material filled with intumescent additive particles) is considered. The intumescent additive is ammonium polyphosphate and the binder is an epoxy polymer resin.

Due to the influence of a temperature field the binder softening occurs and at 190°C -the intumescent additive destructs. Its destruction temperature is lower than the binder temperature so the additive destruction starts when the binder is in a plastic state. But when the epoxy polymeric resin temperature in quite sufficient for the resin to turn into a liquid and the carbonization process does not take place, a gas bubble starts to form.

The intumescent additive destruction process occurs thanks to the flowing of reversible chemical reactions (on the intumescent additives surface):

$$\begin{aligned} &2\mathrm{HO}-[-\mathrm{NH_4PO_3}-]-_{m}H \\ &\Leftrightarrow \mathrm{HO}-[-\mathrm{NH_4PO_3}-]-_{2m}\mathrm{H}+2\mathrm{H_2O}-Q_1 \end{aligned} \tag{a}$$

$$-[-\mathrm{NH_4PO_3}-]-_{n} \Leftrightarrow -[\mathrm{HPO_3}-]-_{n} + n\mathrm{NH_3}-Q_2 \tag{b}$$

Metaphosphoric acid formed on the bubble inner surface interacts with the binder functional groups as

$$\begin{aligned} &-[-\mathrm{HPO_3}-]-_{n}+-[-\mathrm{CH_2}-]-_{n} \\ &\quad\to -[-\mathrm{H_3PO_3}-]-_{n}+-[-\mathrm{C}-]-_{n} \\ &\quad\quad +Q_3 \end{aligned} \tag{c}$$

$$\begin{aligned} &-[HPO_3-]-_n + -[-HN-CH_2-]-_n- \\ &\quad \rightarrow -[-NH_4PO_3-]-_n \\ &\quad\quad + -[-C-]-_n + Q_4 \end{aligned} \tag{d}$$

$$\begin{aligned} &-[HPO_3-]-_n + -[-CH_2-O-]-_n \\ &\quad \rightarrow -[-H_3PO_4-] \\ &\quad -_n + -[-C-]-_n + Q_5 \end{aligned} \tag{e}$$

During the reactions carbon is formed on the bubble walls and intermediate products destruct as

$$-[-H_3PO_3-]-_n \Leftrightarrow -[-HPO_2-]-_n + nH_2O - Q_6 \tag{f}$$

$$-[-H_3PO_4-]-_n \Leftrightarrow -[-HPO_3-]-_n + nH_2O - Q_7 \tag{g}$$

Reactions (a) and (b) also flow on the bubble surface, and in the bubble volume the following reaction flows

$$NH_3 + H_2O \Leftrightarrow NH_4OH + Q_8 \tag{h}$$

MATHEMATICAL MODELING

While developing the mathematical model it is assumed that additive particles have a spherical shape and are located so that form identical cubes (Fig. 1). The distances between intumescent additive particle centers and the coating thickness are known in advance. Figure 1 depicts the intumescent additive particles (dots at the cube vertices) forming two layers.

The heating of the material is normal to its outer surface. The coordinate system is such that Ox and Oy axes are in the plane parallel to the material inner surface and Oz axis is normal to xOy plane.

At a uniform heating temperature fields symmetry planes will appear in the cube. And the equality will be fulfilled in case the heating is normal to plane $HLNP$:

$$\frac{\partial T}{\partial x} = 0 \tag{1}$$

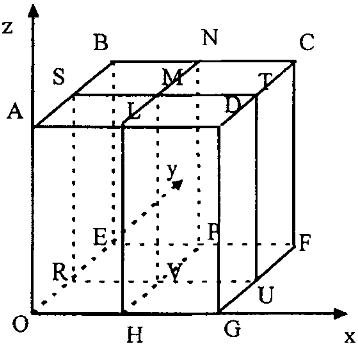

FIGURE 1 Scheme of disposing two layers of intumescent additives particles.

When the heating is normal to $RSTY$ the equality

$$\frac{\partial T}{\partial y}=0 \tag{2}$$

is true. Under the Conditions (1)–(2) the heating process can be regarded as one-dimensional. And the spatial integration is performed in OABCDEFG.

The intumescence process may involve four stages:

(1) heating material up to the temperature of the first layer destruction;
(2) the destruction of intumescent additive particles of the first layer and a bubble formation;
(3) the destruction of subsequent layers of intumescent additive particles;
(4) interactions between bubbles.

At the first stage there are no evident chemical transformations and the thermal conductivity equation is

$$\frac{\partial T}{\partial t}=a\frac{\partial^2 T}{\partial z^2} \tag{3}$$

if the section normal to Oz axis is between intumescent additive particles, and

$$\frac{\partial T}{\partial t}=a\frac{\partial^2 T}{\partial z^2}+f(z,S) \tag{4}$$

if it passes through the intumescent additive particle, where $T-$ temperature, $a-$thermal diffusivity coefficient, $t-$time, $S-$intumescent additive section area.

On the material surface ($z = 0$) the condition

$$-\lambda_{\text{bin}}\frac{\partial T_{\text{bin}}}{\partial z} = \alpha(T_{c6} - T_s) \tag{5}$$

holds true,
where $\alpha-$the coefficient of the binder thermal expansion, T_s-ambient temperature.

On the ≪intumescent additive-binder≫ boundary the following conditions are satisfied

$$\begin{gathered} T_{ia} = T_{\text{bin}} \\ -\lambda_{ia}\frac{\partial T_{ia}}{\partial n} = -\lambda_{\text{bin}}\frac{\partial T_{\text{bin}}}{\partial n} \end{gathered} \tag{6}$$

when $n-$normal to a spherical intumescent additive surface.

Actually due to the difference in a-values (thermal expansion coefficients) a gap is formed between intumescent additive particles and the binder. To make the model less complex it is assumed that the gap increases not gradually but abruptly at $T = T_d$ where T_d- intumescent additive destruction temperature. The gap is taken for an initial bubble volume.

This time condition (6) is replaced by condition

$$-\lambda_{ia}\frac{\partial T_{ia}}{\partial n} = -\lambda_{\text{bin}}\frac{\partial T_{\text{bin}}}{\partial n} - q_{\partial} \tag{7}$$

where q_d – the amount of heat consumed for the chemical reactions to proceed. In this case the pressure in the gap equals one atmosphere and the temperature is equal to the binder temperature.

On the boundary ≪binder–substrate≫ the following condition is satisfied

$$\begin{gathered} T_b = T_s \\ -\lambda_b\frac{\partial T_b}{\partial z} = -\lambda_s\frac{\partial T_s}{\partial z} \end{gathered} \tag{8}$$

In the depth of the substrate (when $z \to \infty$) the condition –

$$\frac{\partial T}{\partial z} = 0 \tag{9}$$

It can be supposed that the second stage of the polymeric composite intumescence starts when under the first layer of the intumescent additive particles temperature $T = T_d$ (intumescent additive destruction temperature) is attained. Here at the initial period of time the destruction is not taken into account. During this interval a part of the intumescent additive was destructed and a bubble was formed whose volume is equivalent to the mass of the additive. If the mass and the bubble volume are known initial pressure P_b, density ρ and the gap between the bubble and intumescent additive surfaces can be found. At the destruction process the reversible reactions (a), (b) proceed. On the bubble inner surface irreversible reactions (c), (d), (e), flow that result in the formation of carbon. In addition there should be considered reversible reactions (a), (b), (f), (g) and (h). Assume that the rate of proceeding forward i-th chemical reactions obeys Arrhenius law

$$K_{\text{for}}(T) = k_{0i} \exp\left(-\frac{E_i}{RT}\right), \quad i = 1:8$$

but for the rate of proceeding reverse chemical reaction the following relations holds true

$$\frac{K_{\text{for}}(T)}{K_r(T)} = K_{eq}(T)$$

where $K_{eq}(T)$ – the thermodynamic functions corresponding to equilibrium conditions.

So we can write expressions necessary for the gaseous custance mass increase during the reactions proceeding on the intumescent additive and on the bubble surface as well as chemical reactions in the bubble volume shoed be taken intj account. Then the equation for calculating mass and energy for gaseous substances in the bubble volume: becomes

$$\frac{dm}{dt} = S_{ia} \sum_i m_i + S_b \sum_j m_j \tag{10}$$

$$\frac{d}{dt}mc_vT = S_{ia}\sum_i m_iQ_i + S_b\sum_j m_jQ_j + m_{\text{forw}}Q_w - m_{\text{revw}}Q_w - S_bP_bV_b \tag{11}$$

where forward and reverse reactions on the intumescent additive surface are designated by i reactions on the bubble inner surface by j reactions in the bubble volume- by w, S_{ia}, S_b – intumescent additive and bubble surface areas.

For the calculation of velocity V_b the Realys equation is used:

$$r\frac{dV_b}{dt} = -\frac{3}{2}V_b^2 + \frac{P_b - P_\infty}{\rho_b} \tag{12}$$

where P_b – the pressure in the binder on boundary with the bubble;

$$P_b = P_b - \frac{2\sigma}{r}$$

P_∞ – the pressure in the binder far from the bubble;
r – the radius of the bubble; Which is calculated as

$$\frac{dr}{dt} = U_b + V_b \tag{13}$$

When U_b – the rate of chahgeen the bubble radius due to reactions on the intumescent additive and binder surface.

ρ_{bin} – the density of the binder material;
σ – of the bubble surface tensionit;
P_b – the pressure of gases in the bubble found by, the Clapeyron–Mendeleev equation:

$$P_n = \rho R_n T \tag{14}$$

If the bubble radius is known its volume W_b and the density of gaseous substances in the bubble can be calculated by

$$\rho = \frac{m}{W_n} \tag{15}$$

Isochoric heat capacity C_v and gas constant R are defined by

$$C_v = \sum_{i=1}^{4} C_{vi}\alpha_i \text{ and } R_n = \sum_{i=1}^{4} R_i\alpha_i$$

where α_i – the concentration of i-th gaseous substance ($i = 1 \div 4$, as there are water vapors, ammonia, metaphosphoric acid, and ammonium hydroxide. Gaseous substances a_i concentrations are found from

$$\frac{\partial \alpha_i \rho}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r} r^2 D_i r \frac{\partial \alpha_i}{\partial r} - \frac{\rho_b}{r^2}\frac{\partial}{\partial r} r^2 \alpha_i V_g + m_i \quad i = 1:4 \tag{16}$$

where D_i – the diffusion coefficient of an i-th gaseous substance, V_g – the rate of gaseous substances movement in the bubble, $\dot{m}_i$ – the rate of gaseous substances formation in a bubble volume.

Velocity V_g is found from the approximation by parabola. It is assumed to be very low and does not affect pressure, density and temperature.

To solve Eq. (16) it is necessary to set initial and boundary conditions

$$\text{Initial conditions} \tag{17}$$

$$\text{Conditions on the} \ll \text{intumescent additive-bubble} \gg \text{boundary} \tag{18}$$

$$\text{Conditions on the} \ll \text{binder-bubble} \gg \text{boundary} \tag{19}$$

The system of Eqs. (10)–(16) with initial and boundary Conditions (17)–(19) characterizes physico-chemical processes proceeding in the bubble at the second stage of the intumescence process.

At the third stage the destruction of subsequent layer's of intumescent additive particle occurs. In each layer the processes are identical to those in the previous one. If in each k-th layer distance h between intumescent additive particle centres along Oz axis increases with the rate of

$$\frac{dh}{dt} = \frac{\pi r_b^2 V_n}{h_0^2},$$

(where h_0 – the distance between intumescent additive particle centres before the intumescence) then the change of the intumescent layer height is defined by the equation, where N – a number intumescent additive layers (Fig. 2).

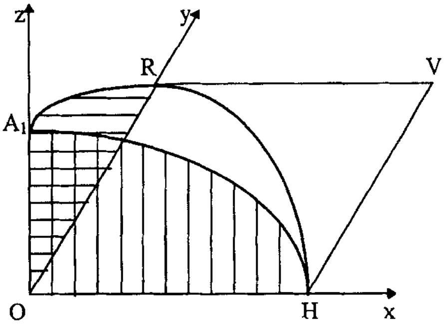

FIGURE 2 Scheme of the bubble after the completion of the 3rd stage.

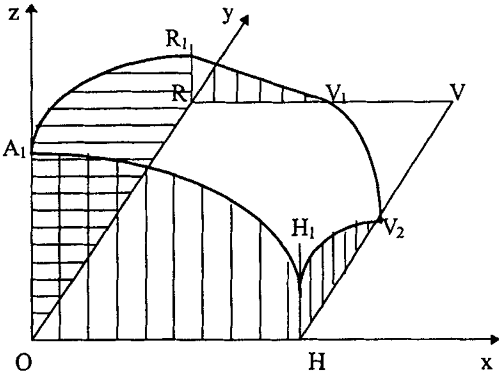

FIGURE 3 Scheme of the bubble after the contact with adjacent bubbles.

At the fourth stage of the intumescent process the interaction between bubbles takes place. Carbon formed on the bubble surface contributes to the surface tension increase. That is why the interaction of bubbles means the forming of carbon walls (Fig. 3) between them but not joining them. At this stage mass and energy conservation equation remains the same, only instead of equation S_b it is necessary to consider equation $S_b = \pi R_b(2h_0 - R_b)$.

In this case between the bubbles on the walls no chemical reactions are taken into account. Besides at the 4th stage the diffusion process is no longer one-dimensional. The concentrations of gaseous substances in the bubble are found from the approximation by parabola.

CALCULATING EXPERIMENT

The system of Eqs. (10)–(18) was solved numerically by Runge-Kutta method with the fourth order of accuracy. Equations (3), (19) were solved numerically by the finite difference method with the help of the sweep method. The calculations made it passable to determine changing of the intumescent layer height. When the degree of polymeric composite filling and intumescent additive particle varied (the degree of filling means the ratio of intumescent additive volume in cube to the total cube volume) (Fig. 4). The results of the experiment show that the intumescent layer height increases approximately 5–6 times, and the most effective is the coeiting which has a degree of filling 13% and the intumescent additive particle diameter-20 μm (curve 2, Fig. 4). Less acceptable are coatings with fine intumescent additive particles (curves 1,3 Fig. 4).

Figure 5 depicts the change of thermal conductivity (curve 1) and heat capacity (curve 2) of the coating with 13% of an intumescent additive and with the particle size 20 μm. The calculations showed that there was the decrease in thermal conductivity about 2 times and a slight lowering of the coating heat capacity.

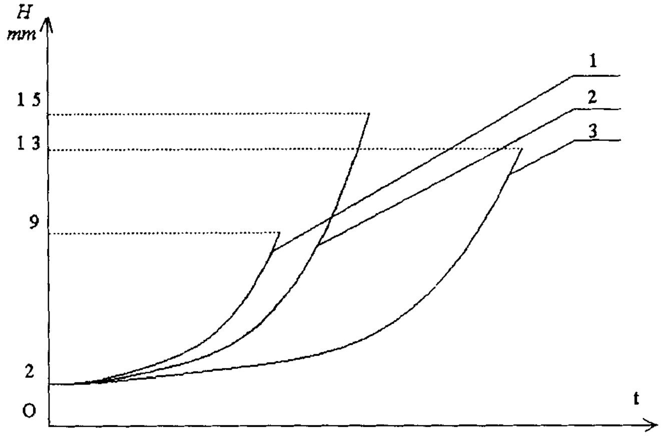

FIGURE 4 Changing the intumescent layer height at a different degree of filling and the intumescent additives particle size: 1 – the degree of filling 9%, intumescent additive particle diameter 14 mm; 2 – the degree of filling 13%, intumescent additive particle diameter 20 mm; 3 – the degree of filling 10%, intumescent additive particle diameter 20 mm.

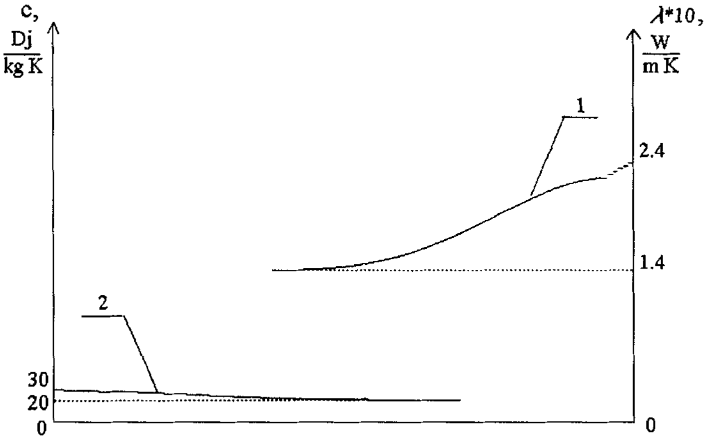

FIGURE 5 Changing thermo-physical characteristics of the intumescent material: 1 – thermal conductivity, 2 – thermal diffusivity.

CONCLUSION

1. The mathematical model that describes physico- chemical processes in the intumescent filled polymer material is proposed;
2. Thermo-physical characteristics of the intumescent coating based on epoxy resin filled with ammonium polyphosphate were defined using the calculating experiment;
3. The most effective composition of the intumescent coating was found by the calculating experiment.

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