

MODELLING OF FOAMCOKE FORMATION

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ABSTRACT

The process of foamcoke formation have been modelled at subsequent transformation from a composition to the foamcoke formed, but when we solved a reverse problem using experimental data the processes from foamcoke to the original polymeric composition were taken into consideration as well. By X-ray photoelectron spectroscopy the increase of polyphosphorus acid and carbon compound derivatives on the inner surface of the formed gas bubble have been determined according to the binding energy CIS close to graphite-like substances. In the temperature range, corresponding to the chemical and structural transformation, sharp heat capacity increase has been found. Optimal size of the gas bubble and its wall thickness have been defined. While solving the reverse problem the nature and the content of components (coke- and gas-forming substances catalyst of carbonization and adhesives) have been determined. The apparent density of the foamcoke obtained was close to that of calculated - 600 kg/m^3 . The coating with a thickness of 10^{-3} m resists heat flows of 32 kWt/m^2 at the intumescence that occurs on a thermally non-conductive substrate.

Key words: modelling of foamcoke formation, photoelectron X-ray spectroscopy, gas formation, coke formation, intumescent fire-retardant coatings.

INTRODUCTION

One of the effective ways to increase fire-proof of constructions

from polymeric materials is to use protective intumescent coatings. As a result on the surface heatinsulating layer is formed, which is imagined as 3 parts: surface dense "crust", middle layer and a "mirror" (reflecting the relief of the surface) layer.

The aim of this research is on the basis of experimental models to set and approximately solve the task of modelling the processes of foamcoke forming.

EXPERIMENTAL

Materials: Phenol-rubber compositions crosslinking by amines and containing polyammoniumphosphate as a gas-former and a catalyst of carbonization, in some cases including carbamide or melamineformaldehyde resins. Polymeric mixtures containing epoxy and carbamide oligomers crosslinking by amines and containing polyammoniumphosphate. As protected substrates steel and glass reinforced plastics (epoxy resins-base), foampolyethylene were used.

Research methods: Study of the processes was conducted using a complex of methods which included the investigation of chemical structures of interphase and volume layers, changes of thermo-physical and physico-chemical properties of polymeric composites at their pyrolysis. The modelling was carried out using the programming language FORTRAN. The debugging of the program was performed on the IBM PC computers.

RESULTS AND DISCUSSIONS

Experimental Modelling. Two types of coating were put on the appropriate substrates. Phenol-rubber compositions containing polyammonium phosphate and melamineformaldehyde resin were put on the foampolyethylene and glass reinforced plastics on the basis of epoxy polymeric mixtures containing epoxy and carbamide oligomers and polyammonium-phosphate were put on steel. On the basis of statistic analysis of electron microscopy results of cokes and residues of pyrolyses of the first coating, average bubble size: diameter $2 \cdot 10^{-3}$ m at wall thickness $0.5 \cdot 10^{-3}$ m has been determined. The coating obtained at the thermal non-conductive substrate (foam-polyethylene) resists heat flows up to 32 kwt/m^2 . In this case the foamcoke with an apparent density about 600 kg/m^3 is formed. Oxygen index of the coating material is approximately 50, mass losses are near 1% at about 2 min. time of flame source action. The coating tested according to UL 94 refers to the class V-0.

The coating of the second type put on steel, organic or glass reinforced plastics forms foamcookes with different changes of heat capacity when it undergoes heat flow. The foamcookes have a thickness protecting the substrate from heating till "critical" temperature * at which it is possible a construction failure (destruction) or substantial disturbance of performances (Fig.1,2). Heat capacity changes

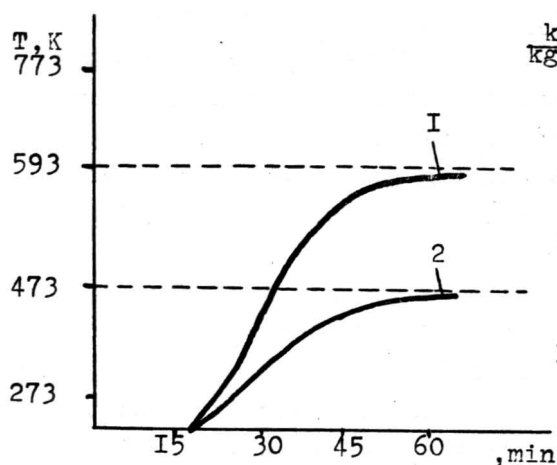


Fig.1 Temperature changes on the back side of steel (1) and glass-reinforced plastic (2) substrate at heating during

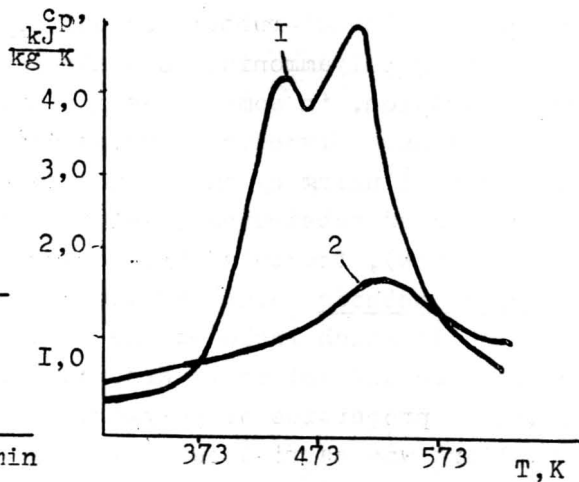


Fig.2 The change with the temperature of heat capacity (1) and the coating on cross-linked epoxy composition (2) under the influence of weak thermal shocks up to 30 kJt/m^2 .

in the range of 373-473K are accounted for vapouring and ammonia gas through bubble walls. In this case the thermal conductivity of coating decreases which is attributed to its fire-proof effect, i.e. to long-time stability till the "critical" temperature on the back side of the substrate is achieved. Using X-ray photoelectron spectroscopy it is stated that the inner surface of a gas bubble contains polyphosphorus acid and ammonium polyphosphate as well as carbon substances. Mathematical modelling of foamcoke formation was carried out assuming

* Heating up time till "critical" temperature on the back side of the substrate is a fire-resistance limit.

that the location of each gas former (GF) particle was known on the basis of experimental data. In this case and in the assumption that on the boundary of bubbles and the binder heterogeneous chemical reactions of the following type take place



characterized by decreasing the amount of components A and B_i

$$m_{ij}^k = \rho_m \cdot Y_{ij}(C_i) \cdot K_{ij}(T)$$

where A_j - binder plastic

B_i - i -th gaseous reagent (product of GF decomposition)

c_{ij}, D_{ij} - gaseous and condensed products of heterogeneous interaction, it is possible to obtain the following system of equations of bubble evolution:

$$\frac{dm}{dt} = W_{ro} \cdot \dot{m}_{ro} + S_n \cdot \dot{m}_k$$

where

at $t = t_{st}$

$$m_{st} = \frac{4\pi}{3} r_{st}^3 \frac{P_{st}}{R_1 T}$$

R_1 - gas constant of product of GF decomposition

W_{ro} - changing volume of decomposing GF particle

$$\frac{dW_{ro}}{dt} = -\dot{m}_{ro} \cdot W_{ro}$$

When $t = t_{st}$ we have a starting volume of GF particle.

The temperature of GF particle is considered to coincide with the temperature in the bubble

$$\dot{m}_{ro} = \rho_2 \cdot K_2(T)$$

ρ_2 - density of GF particle substance.

$K_2(T)$ - Arrhenous dependence of GF particle decomposition rate upon temperature.

S_n - the surface of G-CS (gas condensed substances) boundary of the bubble.

For the first stage

$$S_n = 4\pi \cdot r_{bub}^2$$

After the second stage

$$\frac{dm}{dt} = W_{ro} \cdot \dot{m}_{ro} + S_n \cdot \dot{m}_k + \sum_{j=1}^{m_r} \delta_{ij} \cdot S_{ij} \cdot m_{ij} \cdot \beta_k$$

Where m_r - the number of edges the bubble contacts with its neighbours. Usually m_r can change from 1 to 8

$$\delta_{ij} = \begin{cases} -1, & \text{if } P \geq P_{ij} \\ +1, & \text{if } P < P_{ij} \end{cases}$$

P_{ij} - pressure in a bubble adjacent to the j -th edge of the bubble.

m_{ij} - removal rate of gaseous substances which is a function of difference being determined either according to the Darcy formula or on the basis of impulse equation solution.

S_{ij} - a value of contact surface area of the bubble being considered with j -th bubble as a result of interaction of a radius sphere z_n with a plane away from the centre of the bubble at a distance z_{ij} , less than z_n .

$\dot{m}_k = \sum_{i=1}^m \dot{m}_{ij}$ - appearance of gaseous substances in the bubble as

a result of the interaction of m -types products of GF decomposition, each i -th of which taking part in n_{ij} -th reactions with components of the binder (n_{ik} - is a number of reactions when cokeforming substances are formed). We consider that the reason for the decrease of not only GF particle mass as well as of its size is the decomposition process carried out with a mass velocity $m_{ro} = \rho_n \cdot U_{ro}$

Therefore,

$$\frac{dz_n}{dt} = -m_{ro}/\rho_n$$

For the calculation of a bubble radius z_n (on the second stage for the regions which do not contact with adjacent bubbles).

$$\frac{dz_n}{dt} = U_k + W_{ij}$$

where

$U_k = \frac{\dot{m}_k}{\rho_k}$ - rate of bubble size increase due to heterogeneous

reactions on its boundary with LDPS.

W_{ij} - rate of bubble size increase (decrease) because of pressure difference in the bubble and LDPS.

To determine W_{ij} let us take Raels formula

$$\tau_n \frac{dW_{lg}}{dt} = -\frac{3}{2} W_{lg}^2 + \frac{P_{lg} - P_\infty}{\rho_{lg}}$$

where

P_∞ - pressure in LDPS away from the bubble;

$$P_{lg} = P - \frac{2\sigma}{r_n}$$

P - pressure in the bubble, which at a certain mass of gaseous substances in the bubble and at a known temperature is defined by Klapeiron-Mendelejev equation.

At $t = t_{st}$ $W_{lg} = 0$

The reverse problem was solved on the basis of the above model.

According to the order of values $P \sim 0,1 \text{ MPa}$, $r \sim 10^{-3} \text{ m}$ and $[G_k] \sim 10 \text{ MPa}$. The order of values obtained corresponds to the order found experimentally.

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