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THE MECHANISM OF MELTED PRODUCTS FLOW AT ORGANIC SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS

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ABSTRACT

The mechanism of melted products flow at exothermic interaction of mixes of organic solids (organic self-propagating high-temperature synthesis) was thoroughly investigated for controlling of hollow solid products and items formation directly during this combustion-like process.

It was shown appearance of liquid reagents, products and intermediate products in the reaction front. In the reacting mixes characterized by high shrinkage and condensed gas formation a set of directed flows of the substances was observed. The flows level gradients of the temperature, concentration, density, viscosity and vapor pressure. That leads to formation of hollow structure of the final solid organic products.

Electron microscopy, photo- and videotaping both the process and behavior of color labels entered into a green mix, statistic methods were attracted for the investigation. There were registered a temperature profile (maximal temperature 100-104 °C) and speed of reaction front (~0,5 mm/s), features of radial and axial flows of reacting melt, microstructure of a solid product, vapor bubbles sizes and number distribution function in a radial and axial direction in a wave of synthesis and in the solid product.

The radial flow of reacting melt and heat-transfer were supported basically by repeating of a cycle: evaporation of water in hot area (center) of the sample, foaming of the melt, coalescence of bubbles, vapor condensation and collapse of the bubbles in cold area (outside wall) of the sample. Described process of natural radial shrinkage is influenced by many factors, such as the gradients of temperature, concentration, density, viscosity, pressure, adhesion and gravitation forces. Actually, the flow is caused by mechanical work of water vapor based on a difference between of temperatures at the center and lateral wall of the sample.

Keywords: organic self-propagating high-temperature synthesis, combustion, flow of melt, natural radial shrinkage, hollow items

INTRODUCTION

Exothermic interaction of mixes of organic solids (powders, crystals) in absence of the solvents can be organized in autowave combustion-like mode. The reaction front appears in a point of thermal ignition and propagates according to the laws of combustion in a direction of a cold green mix, being accompanied by the formation of liquid reagents, products and intermediate products of the synthesis. Such mode lays in a basis of “dry” methods of organic synthesis, characterized by their simplicity, quickness, safety, resources-

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and energy-saving, economical and ecological effectiveness. With its help it was possible to synthesize a number of the useful condensed organic substances, such as quinones, piperazine salts, halogen derivatives of acids, organoelemental derivatives etc... The products obtained differ by their unique microstructure and high purity caused by excluding of the solvents from the synthesis schema (Klimchuk E.G., 2000). Its analogue in inorganic chemistry has the name: self-propagating high-temperature synthesis (SHS) (Merzhanov A.G., 1994).

The special interest in organic SHS investigations arouses the process of condensed products formation, which is controlled by the features of reacting melt flow directly during combustion. Three principal different cases of the process were observed. Their classification determined by phase condition of final and/or intermediate products of combustion – solid, liquid or semi-liquid, because just that factor defines the basic features of mass-transfer.

In the mixes characterized by high shrinkage and formation of condensed gas-phase product (water, for example, in 8-oxyquinoline\B-chloramine system (E.G. Klimchuk *et al.*, 1999), the special mode of natural radial shrinkage, resulting in formation of hollow organic products, was observed (See Fig.1). Remarkable was that the thickness of the bottom and sidewalls of the products were nearly the same. Thus, their formation was possible only due to intensive radial flow of the reaction melt from the center of the sample to reactor wall. The mechanism of such processes was not still investigated and is described below.



Fig. 1 Hollow product of organic SHS
(a – directly after synthesis, b – radial section)

EXPERIMENTAL

The features of considered system behavior were studied earlier by authors (E.G. Klimchuk *et al.*, 1999). It was shown that reaction proceeded at 100-110 °C and was accompanied by water vapor formation (~ 4 mass. %), melting of the reactant and significant shrinkage of products (~ 1,7 times). For investigation of flows other methods were involved such as electron-microscopy (LEO 1450) of solid products, photo- and videotaping both the process and behavior of color label (brilliant green) entered into a green mix, statistics methods. Microstructure of a solid product were observed, featured of radial and axial flows of reacting melt were determined, vapor bubbles sizes and number distribution functions in a radial and axial direction in a wave of synthesis and in the solid product were measured. That has allowed to establish the mechanism of the fluid intermediates flow at organic SHS.

RESULTES AND DISCUSSION

It was observed that as the characteristic feature of wave structure was its significant spatial division (up to 15 mm) on three zones: chemical reaction, melt flow and product hardening. First carried out mainly in front of reaction (1-2 mm), second – immediately after front (~ 15 mm), third – far behind of the mentioned zones.

In the microstructure of a solid product there are elements, accompanying the processes of foam formation and its destruction, such as bubbles (0,1-6 mm) and crater-like folds (Fig 2). The features of

their arrangement in a solid sample allow to determine their dynamics during combustion and propose mechanism of the melt flows, described below. Mentioned processes were registered during combustion by videotaping.

The distribution functions of bubbles number and their diameter in a radial direction are presented by bell-shaped curve with maximum (Fig. 3) as for a solid products (7; 6 mm) so for the melt (24; 1,5 mm). That shows important role of the bubbles and dynamics of their existence at combustion. As it is obvious, vapor bubbles appear directly in the hot forward edge of the front (Fig. 4), where temperature is more then 100 °C (Klimchuk *et all*, 1999). Their number and size increased at short distance (~ 4 mm) due to coalescence (Fig. 2, b), and then decreased with temperature decreasing less then 100 °C. In opposite case, when temperature decreasing is insufficient and temperature remain more then 100 °C, coalescence leads to formation of big bubbles giving crater-like folds after they destroying (Fig. 2, c). Eventually, the hollow sample obtained appears as one big bubble formed due to described mechanism.

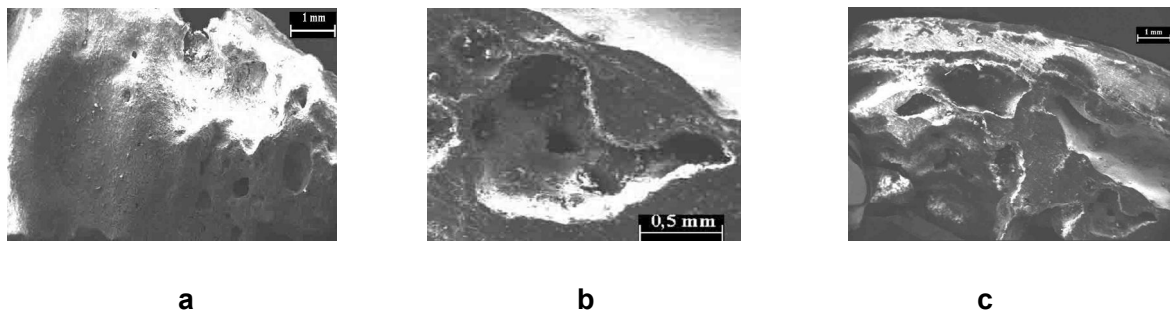


Fig. 2 Microstructure of the hollow products (x30-100)

(a – transient region: at the left – cold area, where vapor is condensed, on the right – warm area, where bubbles are formed; b – formation and coalescence of vapor bubbles; c - crater-like folds)

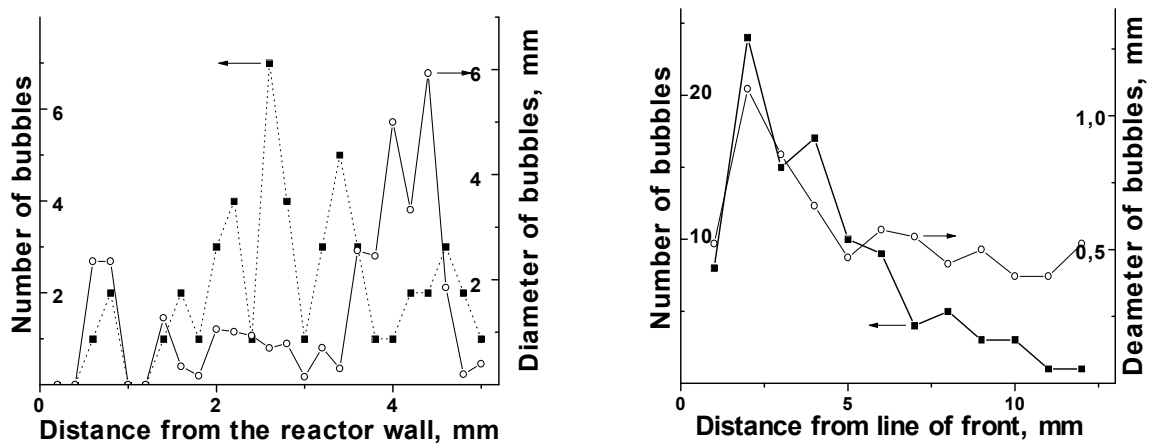


Fig. 3 Distribution functions of bubbles number and diameter in radial section (Left – solid product; right – reacting mix (according to Fig.4))

Meaning the carried out researches, the reaction front can be represented as a liquid membrane, driven in an axial direction by known mechanism of the capillary spreading of the reaction melt in the small

(0,1-0,16 mm) porous of solid mix. Its axial flow is affected by on-the-way pressure of water vapor. Exceed of necessary pressure is reduced from the small hole appeared on the top of the sample (Fig. 1, a).

Discribed dynamics of the bubbles behavior not only forms the specific structure of the hollow samples but is responsible for strong radial mass-flow of reactant from their center to the side walls (~ 15-30 mm). The schema showing how it occur is given on the Fig. 5. Vapor bubble shifts the fluid reactive melt in an all direction from the point of their appearance. Negative gradient of temperature, which appeared due to heat loss through the side walls of reactor (to the right of the bubble) cause condensation of vapor in the bubbles, moving their membrane to the cold area (shown by dashed arrows in bubbles) and their collapse, resulting in melt radial flows on ΔX distance.

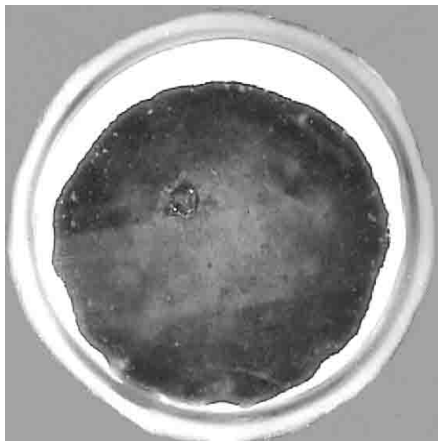


Fig. 4 Front structure (end view)

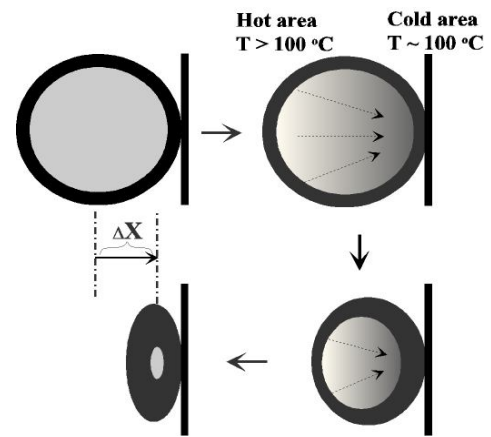


Fig. 5 Collapse of bubbles

The heat-transfer and radial flow of reacting melt as a whole (shrinkage) occurs basically by repeating of a cycle: 1. evaporation of water in hot area (center of the sample); 2. foaming of the melt; 3. coalescence of bubbles; 4. vapor condensation in cold area (outside wall of the sample); 5. collapse of the bubbles (Fig. 6).

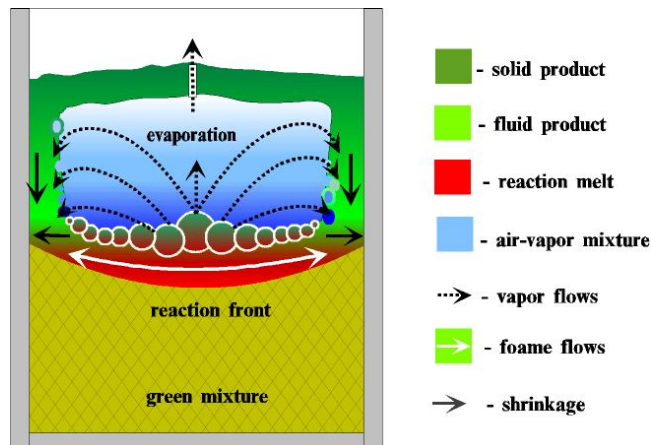


Fig. 6 Common mechanism of reagents flows (axial section)

The flow of water vapor occurs in parallel with the named process and is shown by dashed arrows.

Axial flow of reacting melt at combustion had less scale – about 2-7 mm down and had equal to front

propagation velocity. It was measured by observation of color label behavior through sidewall of glass reactor. This flow was caused both by driven reaction front and moving of liquid water condensed from vapor.

As it was investigated, described process of natural radial shrinkage is very complex and influenced by many factors, the gradients of temperature, concentration, density, viscosity, pressure, adhesion and gravitation forces among them. Their coordinated influence leads to appearance of the set of directed flows of different fluid substances - vapor, bubbles, foam, water droplets and reacting suspension-like melt. Those flows tend to level named gradients and form final hollow structure of the solid product in studied system. Actually, the melt flow is caused by mechanical work of water vapor based on a difference between temperatures at the center and lateral wall of the sample.

The investigated mechanism of the radial flow of reactive melt at organic SHS is original and is not described earlier. It has not only scientific, but also practical importance, as it is useful for development of methods of producing of hollow materials, items and composites, and for applying of coatings by only one technological stage without force influence on a reacting mix.

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