

The autowave modes of solid phase polymerization of metal-containing monomers in two- and three-dimensional fiberglass-filled matrices

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The phenomenon of autowave (frontal) solid phase polymerization of metal-containing monomers based on metal-acrylamide complexes is considered. The comparison of the features of autowave processes realized in both the single-component matrices of the monomer and the matrices filled by the fiberglass materials is performed. The unstable regimes of the polymerization wave as well as the conditions for the stabilization of the flat front in the filled matrices are described. The peculiarities of the frontal regimes in the three- and two-dimensional media are studied. Some possibilities for using of autowave polymerization in the fabrication of the polymer-fiberglass composites and composition prepreps are discussed. © 1999 American Institute of Physics.
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The phenomenon of frontal polymerization has developed as an independent branch of polymer chemistry and technology during the past three decades. Polymer composites are special objects in this problem. The investigations of frontal phenomena in these systems are only a recent development. The study of the autowave regimes in such systems are of interest both for the scientific and practical purposes. In the present work we are devoted to composites of fiberglass formed frontally with metal-acrylamide complexes. Without added fiber, the fronts exhibit bistability between a polymerization front and a combustion mode, depending on the initiating temperature. Pulsating modes are also observed. Above a critical loading of fiber only planar propagation is observed.

I. INTRODUCTION

Almost three decades ago, Maksimov first introduced the theory of polymerization processes and reactors for their carrying the concept of the combustion theory concerning the self-sustaining regime of a layer-by-layer chemical transformation, the traveling and stationary front of the reaction.^{1,2} Since then the problem of frontal polymerization (FP) has been formed as an independent scientific field. There is a great deal of experimental and theoretical works devoted to this problem. More detailed information can be obtained from excellent reviews.^{3,4}

On the basis of the goals of the present work, we point out the following features of FP processes: (i) the phase state of monomers; (ii) the initiation agent of polymerization; (iii) the composition of the starting monomeric medium.

Most works on frontal polymerization have been carried out with liquid monomers and relatively few with solid

monomers. Here one can distinguish three different types of frontal polymerization studied to date.

- (1) Polymerization autowaves in solid monomers that take place in the condition of the cosmic cold. These FP processes are controlled by nontraditional mechanisms via the feedback of the mechanical-chemical nature. The frozen monomer becomes active in the result of the brittle layer-by-layer autodispersion of the solid matrix.⁵⁻⁷
- (2) The frontal polymerization of acrylamide with free-radical initiators.^{8,9}
- (3) Frontal polymerization of metal-containing monomers in the solid phase.

This phenomenon has been observed first for acrylamide complexes.^{10,11} This reaction proceeds without initiators or activators. The autowave regimes of these reactions in the solid monomers is the subject for the present work, with a special emphasis on filled fiberglass-monomer media.

II. EXPERIMENT

The cobalt acrylamide complex of the composition $\text{Co}(\text{CH}_2=\text{CHC}(\text{O})\text{NH}_2)_{44}(\text{H}_2\text{O})_2(\text{NO}_3)_2$ (CoAAM) was prepared according to the procedure previously described,¹² and its structure was characterized by x-ray spectroscopy in our previous work.¹³ We have studied frontal polymerization in two systems. The first system was a Co-AAM as a powder with particle sizes of 200–500 μm . The second system consisted of glass fibers impregnated with methanol solution of CoAAM from which the solvent was evaporated, and the samples were dried.

As the filler we used fiberglass silicate materials with a filament diameter of 7 μm and the low porosity of 2–4 m^2/g . We studied two different states of the fiber: (i) the fibers ground to the powder with a characteristic particle size of a few microns; (ii) the regular woven fiberglass matrix. The

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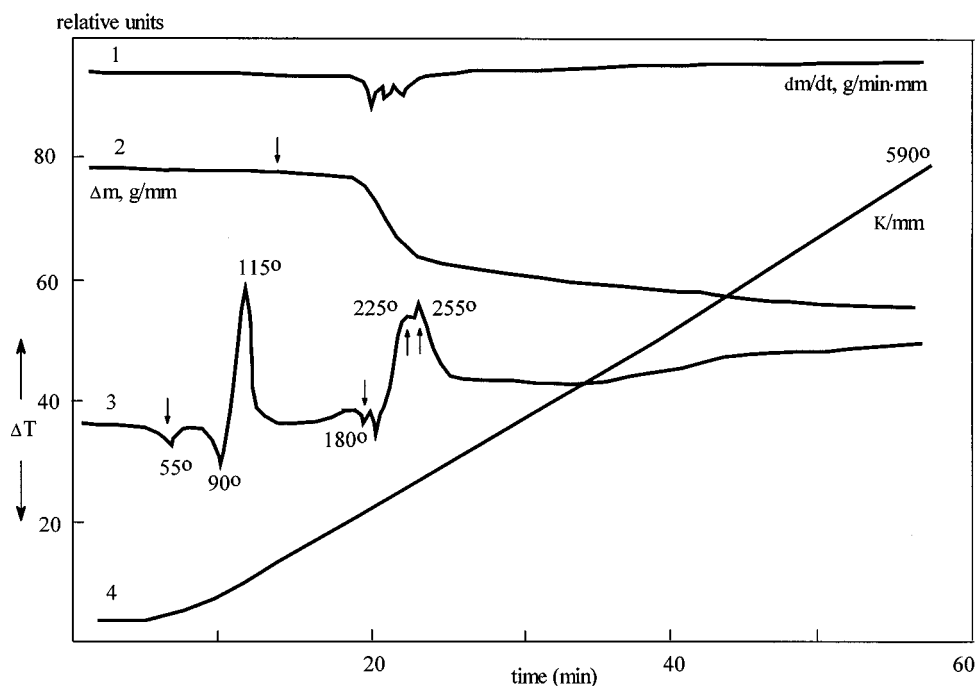


FIG. 1. Derivatograms of the CoAAm complex. 1—DTGA ($dm/dt \times 0.8$, g/min·mm); 2—TGA ($\Delta m \times 2.5 \times 10^3$, g/mm); 3—DTA ($\Delta T \times 0.88$, K/min·mm); 4—TA ($T \times 0.5$, K/mm) (the rate of heating was $10^\circ\text{C}/\text{min}$, sample weight— 45.8×10^{-3} g).

fiberglass materials with certificates of GOST-6943.0-79, TU-648-64-91 were from the industrial corporation "Steklovolokno" (Republic Belorussia, Polotsk).

In our studies we used the samples with two different geometries.

- (i) Cylindrical tablets of a diameter of 0.3–0.5 cm and length of 2.5–3.0 cm. Such samples were prepared from the powder of the monomer with or without the powdered fiber in a mold. Samples were pressed to a density of 0.7–0.8 g/cm³.
- (ii) Two-dimensional (plane) samples formed by impregnating the woven fiberglass sheet with the CoAAm complex.

For the study of the kinetics of CoAAm thermal transformation and gas emission during the reaction as well as the composition of gaseous products of thermal transformation and the morphology of the yield solid product (polymer) we used several methods and instruments.

Thermal analysis of the CoAAm complex was performed on a C derivatograph (MOM, Hungary) in air with heating at a rate of 10 and 20 °C/min in the temperature range of 20–590 °C. (The weight of the sample was 45.8×10^{-3} g).

The thermal decomposition of CoAAm was carried out under static isothermal conditions at 120–280 °C in a self-generated atmosphere (before the experiment, the samples were evacuated at room temperature for 30 min). The kinetics of conversion were monitored taking into account gas evolution with the use of a membrane zero-manometer. After completion of thermolysis the amount of gases evolved was determined, samples were taken for mass-spectrometric analysis, the mass loss of the sample was determined, and low-temperature fractionation (77 K) of the gaseous products was carried out. Mass-spectrometric studies of gaseous prod-

ucts were performed on an MS-3702 mass spectrometer. The IR absorption spectra of condensed and gaseous products were recorded on a Specord IR-75 instrument.

The optical microscopic observations of the evolution of the sample morphology during the reaction were performed in transmitted light on an MBI-15 instrument.

III. KINETICS AND MECHANISM OF CoAAm THERMAL TRANSFORMATION AND DECOMPOSITION

We focus on the information relevant to the frontal polymerization process. On the thermograms of CoAAm in the mode of thermal analysis (Fig. 1) the following thermal effects in the DTA curve are observed: the weak endothermic peaks at 55 and 90 °C, the strong exothermic transitions with maxima at 115 and 225, 255 °C. The loss of mass begins around 120 °C. The main loss of mass occurs in the range of the second exothermic peak. The total mass loss at the end of thermolysis (590 °C) is equal to 61.5%. According to the kinetic data two gas-evolution regions were observed in the decomposition of CoAAm: a low-temperature region (LT, <200 °C) and a high-temperature region (HT, >210 °C). In the LT region the rate of gas evolution decreases monotonically to a steady state ($dP/dt = \text{constant}$). In the HT region the sharp gas evolution at the early stage of conversion and then a decrease (absorption) of gases evolved are observed. The total amount of gases evolved in the LT region is equal to 0.5–0.9 moles per mole of the compound under study. The mass loss of the sample amounts therewith 7–29% and increases with T_{exp} . The total amount of gases evolved in the HT region (210–280 °C) at the end of conversion is equal to 1.4–1.9 moles with the mass loss of the sample of 23–38%. Herewith with increasing the temperature the loss of mass decreases. During thermolysis in the HT region the maxi-

mum mass loss is observed at the maximum gas evolution: the loss of mass (%) at 240 °C amounts 42.7 (0.2 h), 42.3 (0.5 h), 41.2 (2.3 h), 36.6 (4.0 h).

The analysis of the thermograms of CoAAm thermolysis and the dynamic of gas emission clearly indicate the presence of two parallel reaction routes that are distinguished by their energies of activation. The exothermic peak located in the region below 200 °C corresponds to the first route—the polymerization of CoAAm complex. The second exothermic peak is placed on the thermogram well above 200 °C. This signal corresponds to the significant changes of the polymer matrix, and in the result, its burning. The pattern of gas emission is similar: the polymerization is accompanied by slight gaseous product emission and mass loss of the sample (~7%), at the burning of polymer matrix the intense gas emission and significant mass loss of the sample are observed (in the vapors there are highly oxidized products of the organic moiety of CoAAm).

Note that the oxidized products formed during thermolysis of a preevacuated sample may occur in the result of oxidation by the products of nitrate–anion decay in a self-generated atmosphere. The quantitative composition of gaseous products of conversion is complex and requires further study. By IR- and mass-spectrometric analysis the main gaseous products of CoAAm decomposition are CO₂, N₂O, CO, NO, NH₃. The solid products of CoAAm decomposition are amorphous by x-ray analysis and do not show magnetic activity.

In the period preceding the exothermic peak of polymerization there is an endothermic peak in the range of 60–90 °C which we propose corresponds to the dehydration of the metal-containing monomer and/or its melting. By the microscopic observation of the evolution of the surface of CoAAm transformation in the air at the thermal scanning the following stages of the process are established.

At the temperatures below 60 °C no changes are observed; the sample consists of the assembly of CoAAm particles with average sizes of 200–500 μm as amorphous blobs without typical crystal faces.

In the range of 60–90 °C (the region of the endothermic peak) the appearance of the pink liquid phase in which there exist monodisperse solid noncolored particles is observed.

About 100 °C (at the beginning of the polymerization) the formation of uniform solid noncolored materials, which rotate the plane of polarized light in crossed polarizers, proceeds.

At temperatures over 110–115 °C in the solid intermediate product formed the phase transition to the cubic modification occurs followed by the appearance of a liquid phase of high viscosity again and simultaneously with the beginning of gas emission (the bubbles).

About 140 °C the reaction process is accompanied by the hardening of the materials with the occurrence of the dark-pink color.

Over 200 °C the intense gas emission (the beginning of polymer burning) starts, and the sample becomes opaque.

IV. THE FRONTAL POLYMERIZATION OF METAL-CONTAINING MONOMERS

A. Three-dimensional samples of CoAAm without filler

In accordance with the task of the experiment and in order to change the boundary conditions the pellet of CoAAm could be placed in a vacuumed ampule, in a glass reactor that allowed heat transfer or loosely hanged from a bracket in air. The variation of the cell design does not make significant changes to the features of the autowave process. The following data correspond to the series of the experiments in the air at room temperature.

The initiation of frontal polymerization was carried out by the introduction of a thermal disturbance at the bottom of the CoAAm tablet using either an electric heating element or the immersion of the bottom of the ampule in a bath (with silicone oil or an alloy of low-melting metals) at the given temperature.

The front velocity was measured either by thermocouples placed along the sample or by timing of the change of the visible coordinate position of the color propagating reaction zone.

Front polymerization was thermally induced by heating of the bottom of the sample at the range of 120–170 °C temperatures. Below the given range, ignition did not take place (above this temperature another mode of propagation occurred; about this we shall tell later). The front moves along the axis of the cylindrical sample with the average rate of order 10⁻² cm/s. The temperature of the front does not exceed 140–170 °C. Thus only polymerization occurs in this mode. The elemental and gravimetric analysis of the yield product of FP also confirms that in the front the total conversion of the monomer proceeds with the formation of a highly cross-linked polymer matrix. This is indicated by insolubility of the polymer in organic solvents and water.

The essential peculiarity of the FP process for the CoAAm complex without adding the filler is a clearly defined temporal–spatial periodicity of the autowave process: at the passing of the front the structure of the sample is changed; the sample foams (“swells up”). Simultaneously, at the sample surface well defined and regular banded formations appear indicating the pulsating regime of propagation, similar in behavior to that observed in Self-Propagating High Temperature Synthesis (SHS).¹⁴ Besides the instability of the flat front moving the spin regime of the FP processes could be observed in the experiments. The typical patterns of the described autowave process of CoAAm polymerization propagation are shown in Figs. 2(b)–2(d).

The analysis of the nature of the FP periodic mode in this system and the building of an appropriate mathematical model is an independent problem and is out of the frame of this work. We do note two possible mechanisms of the loss of the planar mode’s stability. One of them is typical for systems in which reactant and product diffusion is absent. The FP process of a CoAAm monomer in the solid phase is such a system. The pulsating mode of FP occurs because the zone is formed in the wave front that is only heated through conductive heat transfer and distinguished by a low degree of

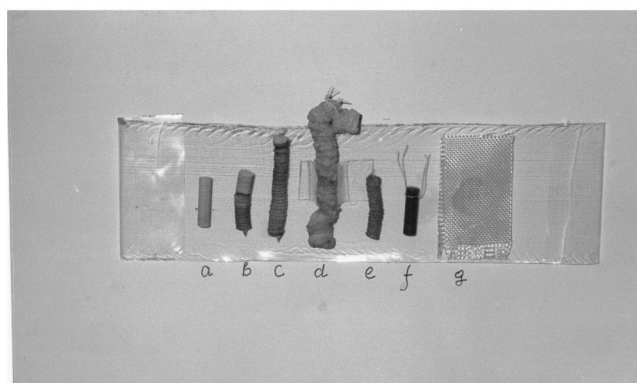


FIG. 2. (a) The view of the cylindrical tablet of the starting CoAAm complex; (b) *d*—the dynamic of the autowave regime at the front polymerization of CoAAm during (b) and at the end of the reaction (c), (d); (e)–(f) views of the samples of CoAAm composites with fiberglass fillers of 5(e) and 10 wt.% (f) contents after front polymerization; (g) the illustration of the front polymerization in the two-dimensional glass fabric system appreted by a 10% solution of CoAAm in methanol. [The tablets were pressed at $P = 1$ (c) and 6 MPa].

the monomer conversion due to the strongly limited diffusion transfer. In this zone the mode of the thermal explosion (fast “burning out” of the reagent) is easily realized. In other words, the stage of the quick front propagation is followed by a slowing down one of sample heating until the next explosive stage of the autowave transition. For the theory of this mechanism see, for example, Refs. 14–20.

The other possible mechanism is specific to the polymerization of a CoAAm complex. The observation of gas emission during the CoAAm polymerization at the temperatures of 110–120 °C is the basis for this hypothesis. The qualitative scheme of such a pulsating process is the following: in the zone of the moving front corresponding to the given temperature range the foaming of the reacting layer reduces the heat transfer to the next layer of the solid monomer; in the result the FP process is retarded, and the intensity of gas emission is decreased. In the heated layer of the sample the polymerization process is activated again, the temperature increases and the stage of the accelerated propagation repeats.

In conclusion of this section we note another feature of the frontal regime of CoAAm polymerization without a filler. Bistability with respect to the initiating temperature exists, which to our knowledge is reported for frontal polymerization for the first time. As noted above, the FP process is induced at the starting temperatures of 120–170 °C. Above 170 °C the autowave process alters its route radically. Instead of a low-temperature slow wave of the polymerization reaction, the front of high oxidation (in fact, burning) forms in which the temperature rises about 1000 °C, and the wave propagation velocity becomes on the order of a few cm/s, i.e., the velocity of the reaction front moving is comparable to the rate of the gun powder combustion.²¹ The product formed in this process can be classified as a ceramic material consisting of cobalt oxides and, probably, carbides.

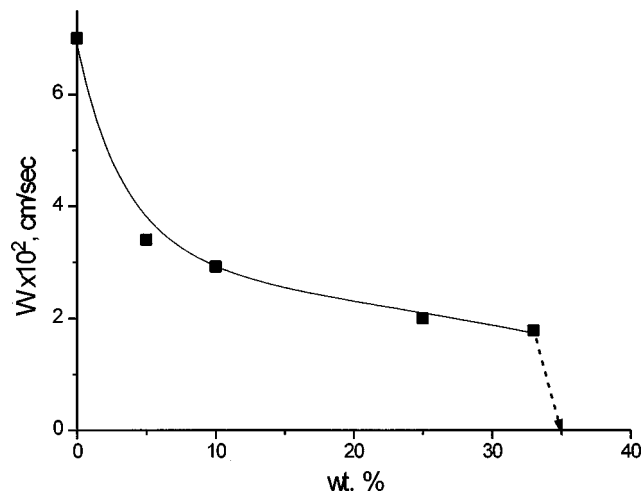


FIG. 3. The dependence of the front velocity on the content of the fiberglass filler in the CoAAm composition systems.

B. Three-dimensional samples of CoAAm with the glass fiber powder filler

In the case of the fiberglass-filled systems the autowave process in CoAAm frontal polymerization alters its characteristics significantly even at small degrees of the filling. At only 5% content of the fiber the autowave regime of the burning (the high oxidation) of CoAAm disappears, i.e., the autowave mode of this reaction route cannot be induced by the local heat disturbance with any amplitude. This action initiates only the frontal polymerization process. Moreover the measured velocities of propagation are significantly less than that for the same nonfilled systems. The traveling front of the autowave polymerization acquires the characteristics of the spatial–temporal stability: the intensity of gas emission in the wave of polymerization (the foaming) is decreased, the change of the sample shape at the front is small, the color of the sample polymerized is more homogeneous, i.e., the banded structure becomes less distinct [Fig. 2(e)].

At 10% content of the fiberglass powder in the CoAAm the process of FP becomes absolutely steady, with a planar front, which propagates in the cylindrical samples with a stationary velocity. The gas emission and the foaming are suppressed. The typical picture of the wave moving at the FP mode described is shown in the photograph [Fig. 2(f)].

At higher degrees of filling no qualitative changes of the FP process are observed (up to certain threshold content of the glass powder), only the front propagation velocity is decreased (Fig. 3). However, at about 30% of glass powder in the CoAAm matrix the self-sustained autowave mode of FP of the monomer studied becomes impossible. Figure 3 demonstrates the discontinuous character of the dependence of the velocities of autowave propagation on the filler content.

C. Two-dimensional composites of CoAAm with fiberglass woven materials

The fiberglass woven material was treated by soaking in an alcohol solution of CoAAm and then dried at ambient conditions. To enhance the monomer-holding capacity of the glass woven samples, the glass fabrics with a dense satin

weaving were used. This allowed the incorporation in the fiber glass woven matrix as much as 20 wt.% of the metal-containing monomer. It should be noted that the textile characteristics of the used fiberglass filler, its chemical and physical capacity to the metal-containing monomer incorporated, are the independent parameters that can be varied in a wide range of their values according to the tasks of the experiment.

The sample prepared in this way was stretched in the horizontal position using a special frame and placed in the vertical rising stream of air heated to a given temperature. The initiation of the FP in such a system was carried out using an electric heating wire loop. For the start of the wave this device was brought near the local piece of the impregnated fiberglass woven sample, without direct contact.

The self-sustained mode of FP in this two-dimensional glass fabric system impregnated by CoAAM is possible in a very narrow range of the temperatures of the surrounding air. It is obvious that this feature is caused by such factors as the high intensity of the heat transfer from the thick flat sample to the surrounding medium and low potential inner energy content due to the small concentrations of a metal-containing monomer in such composites. At temperatures of the surrounding air below 60 °C the autowave mode is not sustainable. In the air stream heated over 80–90 °C the polymerization propagated completely on the two-dimensional sample.

Within the given temperature range of surrounding air the FP occurs. The wave of polymerization started in the point of the initiation and propagated on the flat woven sample in the form of a circle front. An illustration of this phenomenon is given in Fig. 2(g). The front propagation velocities are very small, i.e., the conditions of the autowave process are apparently close to the threshold of its existence. No other characteristics of the spatial–temporal instability of the FP process in two-dimensional composition systems are observed.

V. POTENTIAL APPLICATIONS

Let us consider briefly some possible practical applications of the FP process and primarily, the glass composition systems.

- (1) Frontal polymerization of the solid monomers filled by glass powder illustrates the possibilities of using of the autowave modes in the fabrication of composites. Of special interest could be such modes due to their advantages together with the pultrusion technologies.^{22–25} It is important to note the stabilizing effect of the glass powder filler on the FP regime that results in spatially uniform products.
- (2) The autowave mode of the metalopolymer glass fabric prepreg preparation without using the traditional operations of the appretting, i.e., impregnation of fiberglass materials by liquids on the basis of siloxane compounds of the fiberglass fillers, has significant possibilities due to the essential enhancement of the mechanical characteristics of the fiberglass composites for construction purposes and using such prepreps in the products with polyolefin binders.

- (3) The frontal polymerization of metal-containing monomers in the high-temperature burning regime is a new technological tool, potentially, for the preparation of the “out of furnace” multielemental ceramics with the molecular dispersion of the components such as oxides, carbides, carboxides, etc.

VI. CONCLUSIONS

In this work we have studied first the frontal polymerization of metal-containing monomers in the solid phase in the presence of the fiberglass fillers. We were able to propose a description of the transformations that occur in a front by performing thermal analysis and product gaseous product analysis. We observed periodic modes of propagation and the bistability between a polymerization mode and a combustion mode, depending on the initiating temperature. Adding a fiberglass filler stabilized the front, both in two- and three-dimensional samples.

The results obtained should stimulate further experimental and theoretical work, which would be of interest both in the general theory of nonlinear spatial–temporal phenomena in polymerization and in frontal polymerization in the technology of fiber glass composites. We will focus our attention on the following.

- (i) To extend the group of metal-containing monomers in frontal polymerization including ones based on Ni, Fe, Cu, Mn etc. complexes.
- (ii) Using the other types of fiberglass materials such as alkaline, boron alkaline and boron aluminosilicate glasses, etc.
- (iii) The study of the effect of the filling degree of solid monomeric matrices on the peculiarities of the autowave regime in two- and three-dimensional systems.
- (iv) The study of the effect of the thickness of the sample on the spatial stability of the wave flat front.
- (v) The study of frontal copolymerization of metal-containing monomers.
- (vi) The study of the influence of preactivation of the monomer matrix by γ -radiation on the dynamic peculiarities of frontal polymerization.

We propose that this approach permits the development of novel unique technologies for the fabrication of a polymer glass composite.

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