

# The Structure of Polyoxymethylene-Air Counterflow Flame

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## ABSTRACT

The flame structure of polyoxymethylene (POM) in the counterflow of air has been studied experimentally and numerically. The temperature distribution over a cylindrical specimen was measured with a Pt-Pt+10%Rh thermocouple. Quasi one-dimensionality of considered diffusion flame has been established experimentally, which allows analysis of flame parameters in relation to the only coordinate normal to the solid fuel's burning surface. Formaldehyde (monomer of POM) was determined to be the main product of POM thermal degradation. Flame sampling was performed with a quartz microprobe. The chemical composition of the flame was analyzed online with a mass spectrometric complex (Hiden HPR-60). The concentration profiles of the main gas flame species (CH<sub>2</sub>O, CO, CO<sub>2</sub>, H<sub>2</sub>O, O<sub>2</sub>, and N<sub>2</sub>) were measured. The chemical structure of POM-air counterflow flame was modeled by the OPPDIF code of the CHEMKIN package using the experimentally measured temperature profile and the POM burning rate. The boundary conditions on the solid fuel's surface were assigned according to the data obtained from the experiment. The results of the calculations of the chemical flame structure are in a good agreement with the experimental data. Formaldehyde was found to be decomposed in the absence of oxygen near the burning surface to form carbon monoxide, which is further oxidized to form CO<sub>2</sub>. Thus, combustion of POM decomposition products in the gas phase takes place in two macro stages, whereas usually one macro stage is used in combustion models that describe the flame propagation over polymer.

**KEYWORDS:** Counterflow flame, polyoxymethylene, polymer pyrolysis.

## INTRODUCTION

Synthetic polymers are becoming increasingly common in the modern world. Polyoxymethylene (POM) OH[-CH<sub>2</sub>O-]<sub>n</sub>H is one of the polymeric materials, which is produced by polymerization of formaldehyde. Due to its physical properties (strength, wear resistance, low coefficient of friction, low electrical conductivity), POM is used as a substitute for metal in various mechanisms, and from the POM copolymer is used in production of high-voltage electrical equipment. However, like all polymers, POM is a combustible material. The main product of POM's thermal decomposition is formaldehyde [1], which is a toxic gas affecting the human nervous system. This is a complicating factor in the combustion of POM that requires that more attention should be paid to reduction of its flammability. Polyoxymethylene is considered one of the most difficult in terms of lowering the combustibility of polymers [2]. In the POM monomer molecule, the ratio between the number of oxygen atoms and the total number of atoms is 1:4, while in the other polymers, such as PMMA (polymethyl methacrylate) and PBT (polybutylene terephthalate), this ratio is 2:15 and 1:7, respectively, which implies a lower level of oxygen consumption during its combustion [2]. One of the effective methods of lowering the combustibility of a polymer consists in adding chemically active flame retardants to its composition. In view of the fact that the effect of flame retardants is of

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a complex nature, it is first of all necessary to investigate the combustion of pure POM without additives, which is the main purpose of this work. This will allow us to make conclusions about the mechanism of action of these or other flame retardants in the future. POM is a convenient model object for studying the burning mechanism of polymers, since the main product of its decomposition is formaldehyde, a monomer with low molecular weight. However, despite the large number of publications on thermal decomposition of POM [2-7], there are insufficient data relating to its combustion [8-10]. An effective method for studying the burning process of a polymer consists in investigating its combustion in oxidant counterflow [8, 10-14]. One of the main advantages of this technique is the quasi-one-dimensionality of the flame, which allows numerical description of this flame with the help of the existing combustion models. Previously, this approach was used to study the triphenyl phosphate addition effect on the combustion of ultrahigh molecular weight polyethylene in [12]. The authors of that work determined that the triphenyl phosphate addition lowers the maximum flame temperature, the linear and mass burning rates, and the mechanisms of the flame retardant action were also analyzed. Thus, the counterflow technique is reliable for determining effective fire retardants and understanding the mechanism of their action, which is necessary to effectively lower the flammability of polymers. The results of the study of the POM counterflow combustion can be used to develop a model of flame propagation over POM under fire conditions, to reduce its flammability.

## EXPERIMENTAL

### Material

The object of investigating the structure of polyoxymethylene-air counterflow flame was polyoxymethylene in the form of cylindrical samples ( $\varnothing = 14 \text{ mm}$ ,  $L = 30 \text{ mm}$ ,  $\rho_s = 1410 \text{ kg/m}^3$ ), made of paraformaldehyde powder (PFA Aldrich, CAS 30525-89-4, 95 % purity) by the hot pressing method at the pressure of 50 atm and the temperature  $\leq 120 \text{ }^\circ\text{C}$ . Particles of PFA powder are not spherical, they are white crystalline flakes of various shapes less than  $5 \text{ }\mu\text{m}$  in diameter, which easily stick together.

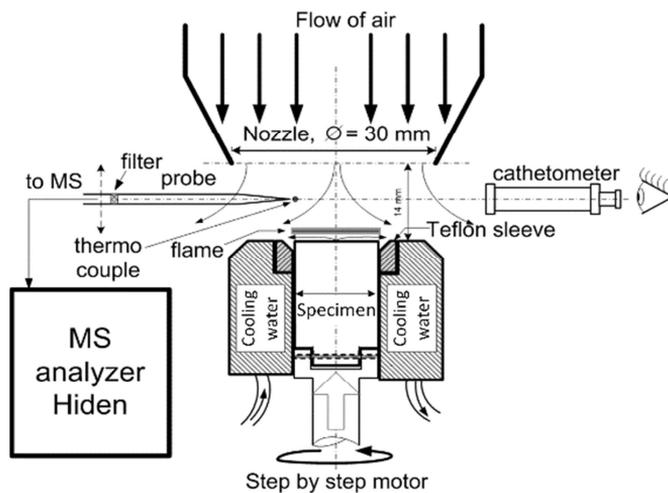


Fig. 1. A schematic diagram of the experimental setup.

### Counterflow burner

The study of polyoxymethylene-air counterflow flame was carried out using a specially designed counterflow burner [12, 13]. Its schematic is shown in Fig. 1. The burner incorporated a mechanism

for moving the specimen and a nozzle of a special shape, with which the flow of air was directed at the polymer's surface. The distance between the nozzle and the sample was 14 mm, the linear velocity of air (under normal conditions) at the outlet of the nozzle was equal to 40 cm/s.

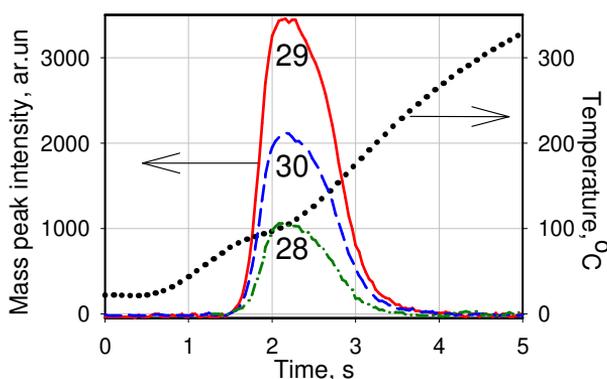
After ignition of the samples with a heated spiral, the position of the flame in space was stabilized by moving the sample with a stepping motor at a fixed speed equal to the burning rate of the POM – 16  $\mu\text{m/s}$ . The moving speed was selected in preliminary experiments. To ensure uniform temperature distribution in the condensed phase, the sample was placed in a temperature-controlled metal cup with the temperature of 30  $^{\circ}\text{C}$ . To prevent cooling of the side sections near the burning surface, the sample was isolated from the metal cup with a teflon sleeve. Stabilization of the counterflow burner flame was carried out by stabilizing the burning surface of the sample relative to the edge of the metal cup during combustion with a stepping motor. The accuracy of stabilization of the surface of the burning sample was monitored with a cathetometer.

The temperature field was measured in the vicinity of the burning specimen by a Pt-Pt+10%Rh thermocouple with a junction diameter of 80  $\mu\text{m}$  made of wire with a diameter of 50  $\mu\text{m}$ . It was moved over the flame by a computer-operated 3D-positioning device. The thermocouple data were recorded by L-card E-140M ADC and were transferred to the CPU through a USB port. The composition of the gas sample was analyzed online with a mass spectrometric complex (Hiden HPR 60), based on a quadrupole mass spectrometer. The sample was delivered from the flame to the mass spectrometer's inlet system, where the pressure was 0.6 Pa, using a polyethylene tube (1.5 m long, i.d. 4 mm). The energy of the ionizing electrons in the ion source was 70 eV.

## RESULTS AND DISCUSSION

### Polymer decomposition products

Polymer degradation was carried out using the flow reactor [15] by heating the POM powder weighing 1.5-2.0 mg in an argon flow. The degradation products were analyzed with a time-of-flight mass spectrometer. Shown in Fig. 2 are the time dependences of temperature and of mass peak intensities with  $m/z$  28, 29, 30 in the mass spectra of the products of decomposition of POM, proportional to the polymer decomposition rate, obtained with the method of DMSTA. The temperature of the heater and the intensities of the main mass peaks of the POM thermal decomposition products (28, 29 and 30  $m/z$ ) versus time are presented in Fig. 2.



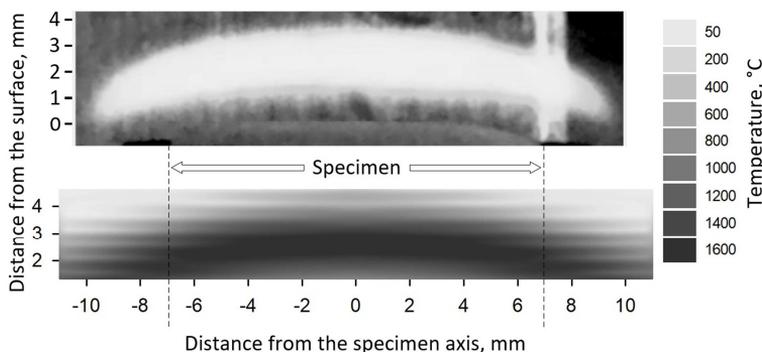
**Fig. 2.** The temperature and mass peak intensities in mass spectra of the POM degradation products against time during POM thermal degradation.

No other mass peaks were observed in the range of masses from  $m/z$  30 to  $m/z$  150. The average ratio of  $I_{29}:I_{30}:I_{28}$  peak intensities of POM degradation products, which is equal to 100:60:29,

corresponds to the mass spectrum of  $\text{CH}_2\text{O}$  [16] with the accuracy of 5%. Thus, it was shown that the thermal decomposition of POM occurs principally with the its monomer, formaldehyde, released. Due to this result, the structure of the counterflow POM-air flame was modeled by the flows of formaldehyde and air.

### Thermal flame structure

The two-dimensional temperature field of the POM-air counterflow flame is shown in Fig. 3. The maximum value of the flame temperature  $1650 \pm 50$  °C was measured at a distance of 2.0-2.5 mm from the surface of the sample. The correction for heat loss of the thermocouple due to radiation was calculated using the Kasan formula [17]. It can be seen from the temperature distribution that the flame in the counterflow burner remains to be one-dimensional within 3 mm from the axis of the sample. This result, taking into account the axisymmetry of the experiment, demonstrates the possibility of describing the combustion of a polymer in the counterflow of an oxidizer using quasi-one-dimensional approximation [12, 13], and effectiveness of the experiment as an effective method for studying combustion of polymers.



**Fig. 3.** Temperature distribution in the POM-air counterflow flame.  
Top – photograph, bottom – temperature field.

As the temperature distribution showed that the flame in counterflow burner is quasi one-dimensional within the sample width, that makes such a configuration much appropriate for investigation because the temperature profile is almost independent of the radial position of thermocouple.

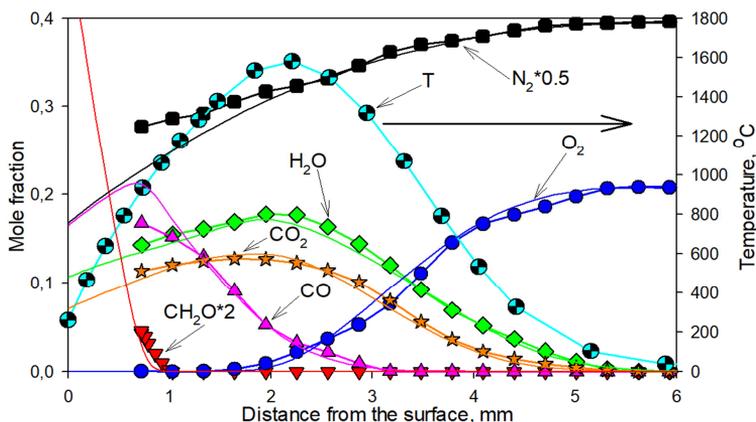
Based on the temperature distribution along the distance from the burning surface, the temperature gradients were calculated. The value of the gradient near the burning surface of the polymer was  $1040 (\pm 135)$  K/mm. Using these data, the conductive heat flux to the burning surface was estimated, which was  $50 (\pm 6)$  kW/m<sup>2</sup>.

### Chemical flame structure

Figure 4 presents measured (symbols) and calculated (lines) the distributions of temperature and species mole fractions ( $\text{CH}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{O}_2$ , and  $\text{N}_2$ ) along the distance from the burning surface. The modeling of the POM-air counterflow flame was carried out using the OPPDIF code [18] of the CHEMKIN package [19] according to the kinetic scheme [20] which includes 93 chemical reactions involving 21 reagents. The boundary conditions on the solid fuel's surface were assigned according to the data obtained from the experiment. The chemical structure of POM flame was predicted with surface temperature 215 °C and the mass burning rate  $22 \text{ g}/(\text{m}^2 \cdot \text{s})$ . Gas-phase temperature profile was taken from the present experimental data, and pyrolysis products are assigned to be monomer  $\text{CH}_2\text{O}$ . The oxidizer composition, the flow velocity, and the mass burning

rate were assumed to be equal to the experimental values – 79 % nitrogen and 21 % oxygen by volume and 0.4 m/s, 490 g/(m<sup>2</sup>·s), respectively.

The measured and calculated mole fractions are in good agreement for all the major flame species. It can be seen that formaldehyde consumption occurs at the distance of up to 1 mm from the burning surface in the absence of oxygen. At the same time, the concentration of CO rises to reach the maximum at the distance of 0.8 mm and is decreased afterwards, with CO<sub>2</sub> and H<sub>2</sub>O mole fractions rising. The maximal values of temperature and concentrations of CO<sub>2</sub> and H<sub>2</sub>O were observed at the distance of about 2 mm, where the oxygen mass fraction tended to be zero. The total width of the flame zone was about 6 mm.



**Fig. 4.** The chemical structure of the POM-air counterflow flame; symbols – experiment, curves – calculations.

Analysis of the combustion mechanism of formaldehyde in air counterflow was carried out using the CHEMKIN Reaction Path Analyzer. It was determined that 98% of formaldehyde is consumed in a reaction with a hydrogen atom to form HCO and a hydrogen molecule. Then 65% of hydrogen reacts with OH to form water and H. At the same time, 92% of HCO is consumed in reaction with an inert molecule with H and CO formed. Since the rate of HCO formation with an accuracy of 6.5% coincides with the rate of its consumption in the CO formation reaction, it can be concluded that the rate of this reaction is limited by the rate of formaldehyde consumption reaction. Then 97% of CO reacts with OH to form CO<sub>2</sub> and H.

Thus, it may be concluded that formaldehyde combustion runs in two macro stages: the first is decomposition of CH<sub>2</sub>O with CO formed, and the second is oxidation of CO, followed by formation of the final combustion products (CO<sub>2</sub> and H<sub>2</sub>O). It follows from this that in modeling the flame propagation along the surface of POM, it makes sense to use gas-phase kinetics, which includes two global stages, instead of a one global stage, usually used in modeling flame propagation over polymers [21, 22].

## CONCLUSIONS

Polyoxymethylene-air counterflow flame was studied using a specially designed counterflow burner. Analysis of the mass spectrum of POM thermal decomposition products showed that the main product is its monomer, formaldehyde. For the first time, a two-dimensional flame field of the POM flame was obtained. One-dimensionality of the thermal structure of the flame was confirmed for the distance of up to 3 mm from the axis of the sample, indicating the possibility of describing

the combustion of a polymer in the counterflow of an oxidizer using quasi-one-dimensional approximation.

The chemical structure of the flame was studied by a probing mass spectrometry method and modeled by the OPPDIF code. The results of the experiment demonstrated good agreement with the results of the modeling for the widths of the zones and the positions of the maximum concentrations of the main species of the flame. Analysis of the flame structure and of the chemical reaction rate confirmed that the combustion of formaldehyde can be described using the global two-stage mechanism: the first stage, the decomposition of formaldehyde with CO and H<sub>2</sub> formed, and the second one, their oxidation, with CO<sub>2</sub> and H<sub>2</sub>O formed. This two-stage mechanism can be used in modeling the process of flame propagation over the surface of a POM, instead of the one-stage mechanism traditionally used for modeling flame spread over polymers.

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