An Experimental Study of Horizontal Flame Spread over Polyoxymethylene in Still Air

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ABSTRACT

Polyoxymethylene (POM) is one of the most important polymer materials. There are only a few studies devoted to ignition and combustion of POM in counterflow with oxidant. The paper presents an experimental study of flame spread over horizontally placed slabs of polyoxymethylene (POM) in still air. The flame spread rate over the polymer surface was measured. Temperature distributions in the gas phase near the solid fuel surface and in the condensed phase were measured using microthermocouples. Spatial variation of the species (CH_2O, H_2, CO, CO_2, O_2, H_2O, and N_2) concentration in the flame near the solid fuel surface was measured using probing mass spectrometry. Analysis of these data showed that pyrolysis of CH_2O took place near the burning surface in the absence of oxygen, to form CO, which was later oxidized to CO_2. The data obtained indicate that it is necessary to use a two-step global reaction mechanism of oxidation of volatile pyrolysis products in the gas phase in the POM combustion model, instead of a one-step global reaction mechanism used in the modern models of polymer combustion. The data obtained can be used to develop a coupled numerical model of flame spread over POM.

KEYWORDS: flame spread, heat fluxes, polymer, polyoxymethylene, temperature field.

INTRODUCTION

Polyoxymethylene (POM) is a widespread structural material, the thermal properties of which are of special interest. A number of papers devoted to its thermal decomposition and combustion are indicated in the literature [1-10]. Depending on the method of manufacture, POM differs significantly for its physicochemical properties, which affect the melting point, the kinetics of thermal decomposition, and the burning rate. There are data on the kinetics of the thermal decomposition of a homopolymer of POM (Delrin) and copolymers of POM, which decompose at temperature ~ 350-450 °C [1, 3, 8, 9]. The POM copolymer [1] has a low oxygen index (LOI) (15.5 %). The maximum rate of thermal decomposition of technical POM is observed at temperature ~ 380 °C, while complete decomposition occurs at temperature 400-430 °C [1, 3, 8, 9]. The activation energy of thermal decomposition of various POM modifications assuming the first-order reaction is significantly different: 121, 159, 381 kJ/mol according to the data [9], [8] and [10], respectively. 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 [11]. However, despite the wide use of POM, there are insufficient data relating to its combustion [5-7]. In the work [5] POM combustion in opposed-flow diffusion flame was studied. Candle-like combustion of POM was studied in [6]. The opposed-flow diffusion flame system was

used to study POM ignition in [7]. However, there are no works devoted to the study of the flame spread over POM in the literature. This research is devoted to the experimental study of flame spread over POM and to determining its combustion characteristics, such as the mass loss rates, the flame spread rate, the length of the pyrolysis zone, the temperature profile in the condensed phase, temperature and species concentration fields in the flame over the burning POM, and conductive heat fluxes from the flame to the polymer burning surface. The results obtained will be used for developing and validating a numerical model for this process, which is important for better understanding of polymer combustion and hence for raising the fire safety of polymers and predicting the hazard of real fires.

EXPERIMENTAL

Material

POM used in this study was manufactured by DuPont (Delrin 100T). The POM slabs 100 mm wide, 5 mm thick and 200 mm long were produced by hot pressing of granules at pressure 100 atm and temperature 170 °C. The sample density, ρ_s was 1380 kg/m^3.

Experimental

The study of POM slab combustion was performed using the experimental setup, the configuration of which is shown in Fig. 1. The slabs were inserted into a thin metal frame, which served to prevent flame spread along the slab sides, and were placed on an incombustible heat insulating board 10 mm thick, which was positioned on an electronic balance. A balance was placed on a movable platform, which moved at a speed equal to the rate of flame propagation over the polymer, but in the opposite direction. In this way, the flame stabilization relative to the laboratory frame of reference was carried out.
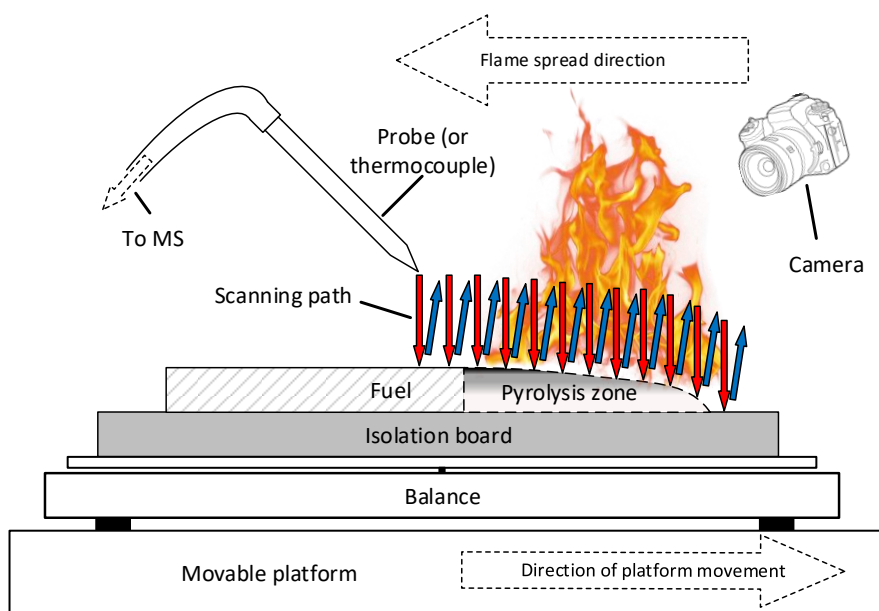

Fig. 1. Configuration of the experimental setup.

The slab was ignited from its edge by the flame of a propane-butane burner. During ignition, the upper surface of the slab was protected from flame with an incombustible heat insulating plate,

which was removed after the slab was ignited. The scanning of the flame began after a steady-state mode of burning was reached. To measure the temperature profiles in the fuel, two thermocouples made from Pt and Pt+10%Rh wire 50 µm in diameter were used. One thermocouple was mounted on the upper surface of the slab at a distance of 50 mm from the frontal edge of the slab. The other thermocouple was fixated on the lower surface of the slab at the same distance from the frontal edge of the slab. The thermocouples junctions were installed at the distance of 50 mm from the leading edge of the POM slab and 50 mm from the side edge in grooves (0.2-0.3 mm deep, 0.3-0.4 mm wide and 10 mm long) made on the slab surfaces. To fill the remaining volume of the groove, a strip of POM ($1 \times 5 \times 10$ mm^3) was placed onto it, heated with a gas burner until starting to melt; thus, the thermocouple was fixated on the slab surface. To measure the flame temperature, one more thermocouple was used, which was made from Pt and Pt+10% Rh wires with a diameter of 50 µm. The diameter of the junction was 70 ± 10 µm, and the thermocouple shoulders were 5.5 mm long. The thermocouple was covered with a layer of SiO_2 to prevent catalytic reactions on the surface.

The chemical structure of the flame was measured using a quartz microprobe with the orifice diameter of 55 ± 7 µm connected with a Hiden HPR 60 mass-spectrometer. The internal angle of the probe's opening at the cone base was 20 degrees. The thickness of the probe walls near the opening was 0.14 mm. The probe and thermocouple were installed on a three-dimensional positioning system with three stepping motors, allowing the thermocouple and probe to be moved in three coordinates. It was operated with a computer. A quartz microprobe, connected with a quadrupole mass-spectrometer, was used for sampling the flame gases. Gas samples were introduced into the ion source of the Hiden HPR 60 mass-spectrometer as molecular flow, allowing species to be identified in the flame and their concentration profiles to be determined. The energy of the ionizing electrons in the ion source was 70 eV. Thus, the chemical structure of the flame was determined. The mole fractions of CH_2O, H_2, CO, CO_2, O_2, H_2O, and N_2 in the flame were measured. In measuring the temperature profiles, the signals from the thermocouples and from the electronic balance were recorded with a 14-bit AD converter E14-140-M. The probe (or thermocouple) moved along the pathway indicated in Fig. 1. The motion code for the thermocouple and the probe was written in such a way as to allow them to approach the burning surface of the slab as its position in space varied due to burnout of the slab, i.e. at different distances from the flame front, the probe was additionally lowered to the distance close to the burning surface. The cross section of the pyrolysis zone used for writing the motion code was obtained from the experiment in which the burning specimen was extinguished and its cross section was measured.

RESULTS AND DISCUSSION

The flame spread rate and the mass loss rate were measured as functions of time. In Fig. 2, the time dependences of the flame spread rate and the mass loss rate are shown. It is shown in Fig. 2 that the flame spread rate became stationary at the 6-th minute of combustion, and the mass loss rate became steady 13 minutes after the beginning of the specimen's burning. After the steady-state combustion mode was achieved, the flame spread rate and the mass loss rate were 0.077 mm/s and 0.053 g/s, respectively. The width of the pyrolysis zone was 65 mm.

Figure 3 shows the dependences of the temperature of the upper surface and the lower surface of the slab from the distance from the flame front. The surface temperature of the sample in the flame front and at a distance of 10 mm from the front was 450 °C, then, with the increasing distance from 10 to 30 mm from the flame front as the sample burnt out, the temperature decreased to 350-370 °C.

Figure 4 shows a two-dimensional temperature field of the POM flame and cross section of the burning fuel sample. The maximum flame temperature was 1650 °C, taking into account the radiation correction calculated by the Kaskan formula [12]. Analysis of the temperature field

showed that the distance from the burning surface to the maximum temperature position increased from 1 to 6-8 mm, as the distance from the flame front grew.
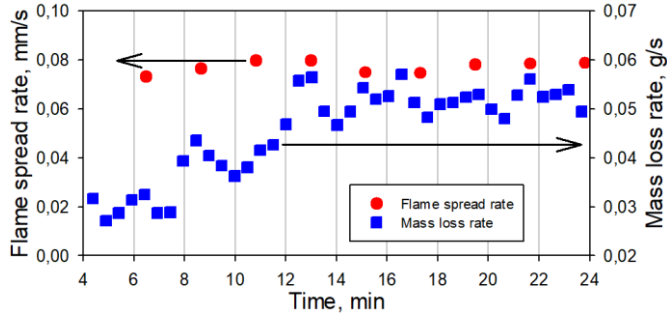

Fig. 2. The flame spread rate (red circles and left axis) and the mass loss rate (blue squares and right axis) as functions of time.
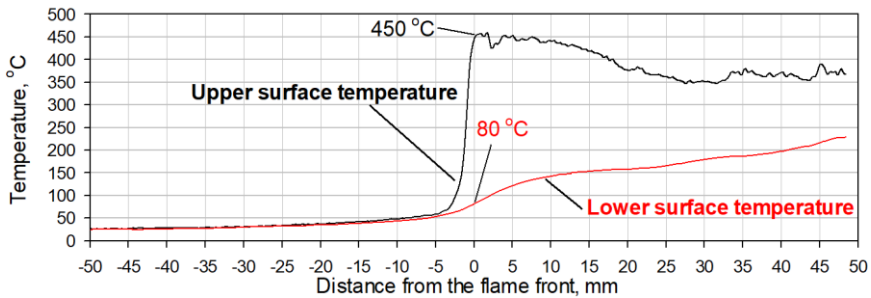

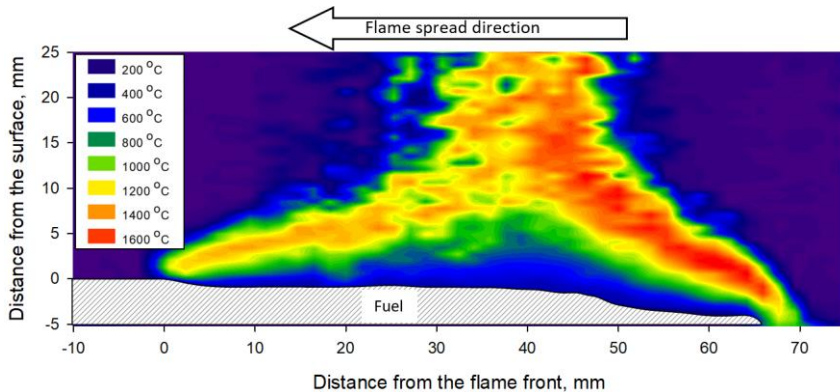Fig. 3. Temperature profiles in the condensed phase of the polymer.

Fig. 4. Two-dimensional temperature field of the POM slab flame.

Based on these data, the temperature gradients near the fuel surface were calculated, which served as a basis for calculating the conductive heat fluxes from the flame to the fuel, shown in Fig 5.

The maximum heat flux of 70 kW/m^2 was observed near the flame front. Then the heat flux gradually decreased to 20 kW/m^2. The following species were identified in the flame: CH_2O, H_2, CO, CO_2, O_2, H_2O, and N_2; their concentrations and the fields of their concentration above the fuel

were measured. Two-dimensional distribution of concentrations (mole fractions) of the major species of the POM flame is shown in Fig. 6.
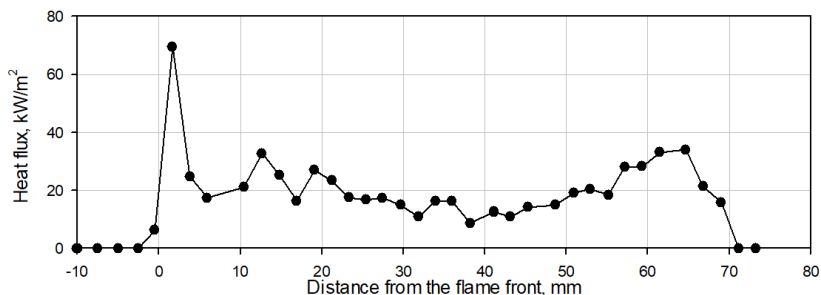

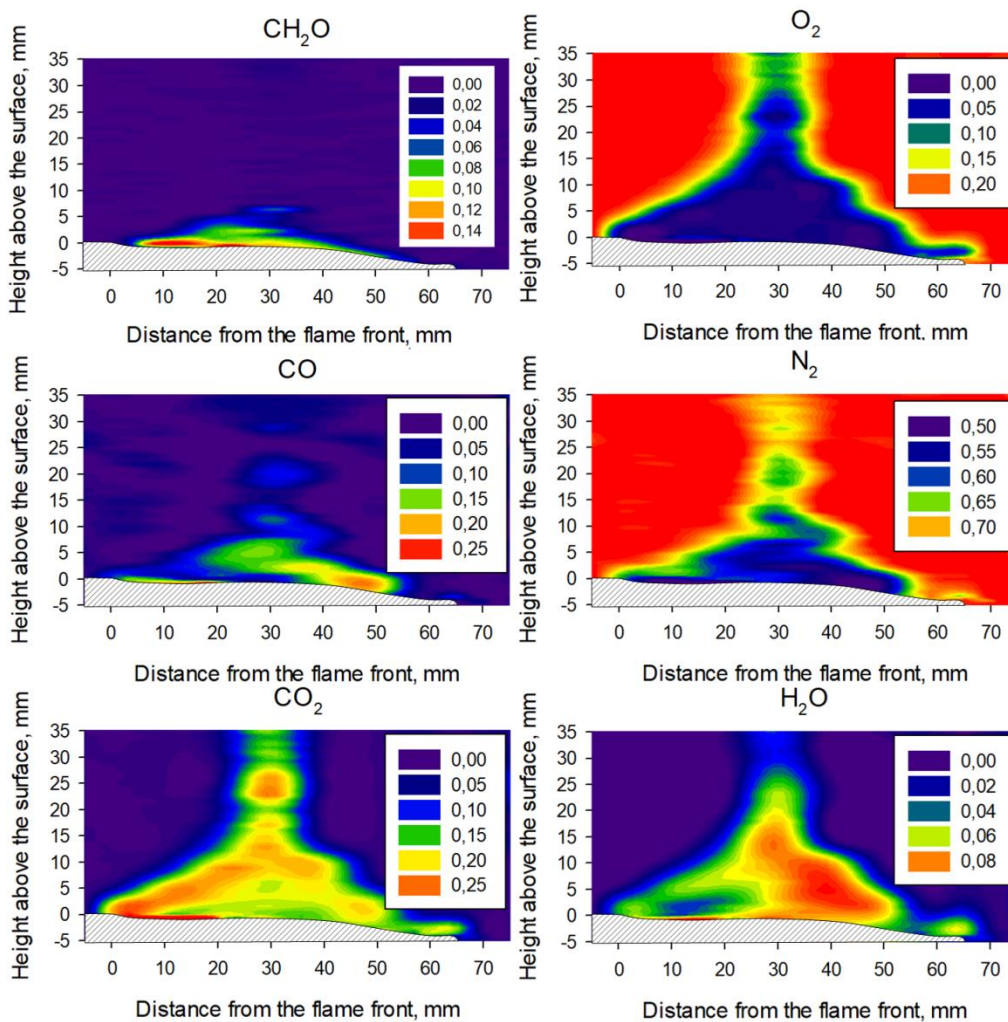Fig. 5. The conductive heat flux versus the distance from the POM flame front.

Fig. 6. Two-dimensional concentration fields of the major species of the POM slab flame.
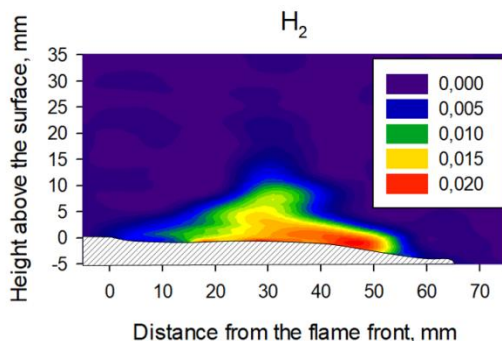
Fig. 6 (cont.). Two-dimensional concentration fields of the major species of the POM slab flame.

Near the burning surface of the polymer oxygen was not found at a distance of 5 to 50 mm from the front of the flame. Based on this, it can be stated that the thermal decomposition of POM in this area occurs in an inert medium. The maximum mole fraction of formaldehyde was observed near the surface of the sample at a distance of 10-40 mm from the flame front. In this area, the concentration of formaldehyde dropped to 0 at a distance of 5-8 mm from the burning surface, while the mole fraction of CO reached 0.15-0.2 and then decreased. Thus, analysis of these data showed that pyrolysis of CH_2O took place, to form CO, which was later oxidized to CO_2. In the polymer combustion model, a one-step global reaction mechanism in the gas phase is usually used. The data obtained indicate that it is necessary to use a two-step global reaction mechanism of oxidation of volatile pyrolysis products in the gas phase in the POM combustion model to make this model more precise.

CONCLUSIONS

A comprehensive experimental study of flame spread over the POM slab in still air has been performed. The following combustion characteristics have been first measured in the steady-state mode: the mass loss rates, the flame spread rate, the cross section of burning polymer, the length of the pyrolysis zone, the temperature profile in the condensed phase, temperature and species concentration fields in flame over burning POM, and conductive heat fluxes from the flame to the polymer burning surface at different distances from the flame front. It has been established that conductive heat fluxes from the flame into solid fuel depend on the distance from the flame front; the maximum conductive heat flux is observed in the flame front and decreases as the specimen burns out. The following main flame species CH_2O (formaldehyde), H_2, O_2, CO, CO_2, H_2O, N_2, have been identified, and spatial variations of their mole fractions have been measured. Their analysis showed that the combustion reaction of formaldehyde includes at least two global steps: the first step consists in pyrolysis of formaldehyde in the absence of oxygen, with CO formed, and the second step is the oxidation of CO to CO_2 by oxygen of air. This result must be taken into account in numerical modeling of the flame spread over POM, which is traditionally done for polymers by using one global reaction. The data obtained are valuable for understanding the mechanism of polymer combustion and will be further used for developing and validating a numerical model of flame spread over POM.

ACKNOWLEGMENTS

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