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Structure of counterflow flame of ultrahigh-molecular-weight polyethylene with and without triphenylphosphate

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Abstract

To study the mechanism of flame retardancy, counter-flow flames of air and ultrahigh-molecular-weight polyethylene (UHMWPE) with triphenylphosphate (TPP) added and without it were studied at atmospheric pressure. Burning rates were measured. The temperature profiles in the condensed and gas phases were measured by a microthermocouple technique. The burning surface temperature and the temperature gradient in the condensed and gas phases were determined. Dependences of maximum flame temperature on the strain rate for UHMWPE and UHMWPE + 5 wt% of TPP were measured and extinction strain rates were determined. The chemical structure of these counter-flow flames (with and without TPP added) was investigated using the molecular-beam mass spectrometry (MBMS) with soft electron-impact ionization. The stable species H_2 , H_2O , C_2H_4 , CO, O_2 , CO_2 as well as the unstable ones H, OH, HOPO and HOPO₂, were identified and their concentration profiles were measured. In adding TPP to UHMWPE, widening of the flame zone, a decrease of the maximum flame temperature, its shifting from the burning surface, reduction of H and OH radicals' concentrations were found. In addition, HOPO and HOPO₂, the main products of TPP destruction, which catalyze the recombination of H and OH radicals, were found in the flame. Direct experiments conducted demonstrate that the action of a flame retardant in a polymer flame consists in its participation in

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chain-termination reactions. The study shows that the counterflow flame method can be useful in studying the combustion of polymers containing flame-retardant additives. © 2016 by The Combustion Institute. Published by Elsevier Inc.

Keywords: Counterflow flame of polymer; Flame structure; Molecular-beam mass spectrometry; Flame retardancy; Phosphorus-containing compounds

1. Introduction

Flame retardants (FR) are substances added to materials to reduce their flammability. Therefore studying the mechanism of their action is of great practical importance. One of the key issues regarding the mechanism of flame retardancy is the problem of where a retardant acts - in the condensed phase or in the gas phase. A FR may affect thermal decomposition of the polymer, as well as the oxidation of the gaseous combustible products formed at thermal decomposition of polymer. Studying a counterflow flame of a polymer burning in air is one effective method of studying the mechanism of a polymer's combustion [1-6]. This method allows the location of the FR's action to be determined, as well as the fraction of the FR evolving into the gas phase and its gas phase activity. The experimental results obtained by this method are very important for developing the mechanism of FR action and for numerical calculations of combustion of polymers with FR. Knowing the influence of certain FRs on polymer burning (especially on the concentration of the H and OH radicals) will provide more information required for searching for new FRs and for improving the existing FRs. In addition, the data obtained may be used for developing the kinetic mechanisms for the model of fire spread.

The structure of a counterflow flame of low density polyethylene (LDPE, MW $\sim 5 \times 10^5$) was measured [2] at atmospheric pressure using a quartz microprobe to sample the flame gases. In addition, temperature profiles were measured by a microthermocouple technique. Significance of this work consists in the fact that the authors were the first to assess the maximum contribution of surface oxidation by using the measured oxygen concentration profile. However, the measurement accuracy was not adequate for accurate determination of the oxygen flux to the surface. The method of a counterflow flame has not been previously used for studying flame retardancy.

To study the kinetics of HDPE pyrolysis in hot air diluted with water vapor or carbon dioxide, the counterflow flame of HDPE/air diluted with water vapor or carbon dioxide was investigated [5]. The kinetic parameters of PE pyrolysis obtained by the used method were greatly different from those obtained by thermal gravimetric analysis (TGA). This implies that the kinetic parameters due to TGA cannot be applied to combustion conditions. However, the numerical code applied in [5] used a simplified model of gas phase reactions, in which only monomers were considered as pyrolysis products.

The structure and extinction of the counterflow flame of polymethylmethacrylate (PMMA) and its monomer methylmethacrylate have been studied and compared [6]. It was suggested that the difference in the overall kinetic parameters for gas phase combustion could be traced to small differences in fuel species leaving the condensed phase of the polymer flame, with the polymer covered by a thin, two-phase region.

The organophosphorus compounds, which are currently viewed as replacement of the environmentally hazardous bromine containing FRs, occupy one-fourth of the world market of flame retardants. The influence of triphenylphosphate (TPP) additive as a flame retardant on both the combustion and thermal decomposition of polymers has studied [7–11]. The authors [7] believe that phosphates are more effective in the gas phase. Phosphorus-based mechanisms of flame retardancy have been discussed by Schartel [10].

The effect of TPP on thermal decomposition and the candle-like burning of UHMWPE was investigated [12–13] by molecular-beam mass spectrometry, as well as by a microthermocouple technique, chromatography and the standard methods of testing a material's flammability. TPP vapors were found in the flame during candle-like burning of UHMWPE doped with TPP additive. The chemistry of the combustion of organophosphorus compounds (OPC), as well as the mechanisms of their effect on the flame propagation velocity, the flame structure, and the flame propagation limits of hydrogen and hydrocarbon flames, has been discussed [14]. Flame inhibition with OPC additives was shown [14,15] to occur by accelerating in the recombination rate of H and OH radicals in their reactions with oxides and oxyacids of phosphorus.

Knyazkov et al. [16] measured concentration profiles for stable species and radicals in counterflow flame of methane/air with trimethyl phosphate (TMP) additives and without them by the molecular-beam mass spectrometry (MBMS) with soft electron-impact ionization and by a microthermocouple technique.

Adding FR, like hexabromocyclododecane (HBCD), triphenylphosphine oxide (TPPO), TPP,

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and sulphur (S), to a premixed methane-air flame resulted in a reduction of the concentrations of H and OH radicals [11,17–19], measured by the MBMS with soft ionization by an electron impact. It was shown in [11] that the order of their activity in the reduction of the concentrations of H and OH radicals in premixed methane-air flame S < HBCD < TPO ~ TPP correlated with their activity in the reduction of polymer flammability. TPP (0.019 wt%) seems to be the most effective flame retardant, roughly halving the radicals' concentrations.

However, there are no publications, apart from our early works [20–22], on the effects of flame retardant additives, including OPC, on counterflow flames of polymers. In [20–22] the flame structure was studied by mass spectrometry using microprobe sampling.

So far, no one has investigated the flame structure of polymers with FR additives and without them by MBMS with soft electron-impact ionization, allowing identification of atoms and radicals in a flame and measurement of their concentration. This study is meant to fill this gap.

The objective of this study was to investigate a counterflow diffusion flame of UHMWPE with and without TPP added using MBMS with soft electron-impact ionization, in order to improve our understanding of how TPP retards a flame of UHMWPE.

2. Experimental

2.1. Materials

The specimens were pressed from UHMWPE powder with a grain size $\sim 60 \,\mu m$ (M.W. $\sim 2.5 \times 10^6$, $T_{\text{melt}} = 142 \,^{\circ}\text{C}$) synthesized in the Boreskov Institute of Catalysis (Siberian Branch of Russian Academy of Sciences), together with its mixture with TPP (crystals size \sim 40–60 μ m, MW \sim 326, $T_{\text{melt}} = 40-50 \text{ °C}$, Aldrich, CAS number: 115-86-6). Mixtures of UHMWPE+TPP 95/5 (wt%) powders were used in the study and were prepared by mechanical mixing for 15-20 min. Specimens of UHMWPE and UHMWPE +TPP (14 mm diam. and 30-40 mm long) were prepared by hot pressing powders at 140 °C and a pressure of 100 atm. The density of the UHMWPE specimen was 0.92 g/cm³; when 5 wt% TPP was added, the density changed insignificantly to 0.94 g/cm³.

To test the dispersion and homogeneity of TPP's distribution in the specimen, concentration of TPP was measured in different parts of the specimen. For this purpose, several cubic pieces $(1 \times 1 \times 1 \text{ mm})$ were cut. Each cube was exposed to TGA analysis. At the low heating rate, the polymer and the TPP additive decompose by stages, which allow determining the fraction of each of them. Those data were used to determine the quantity of



Fig. 1. Photographs of the burner and burner with flame.

TPP in each cube. The average content of TPP in a cube was $5.0 \pm 0.1\%$.

2.2. Experimental setup

2.2.1. Counterflow flame burner

The structure of a counterflow flame of UHMWPE was investigated using a specially designed burner, similar to those used [1-6, 20-22] previously. 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. Photographs of the burner are shown in Fig. 1. For this burner, two stepper motors were used, one of which served to rotate the specimen around its axis; the second one moved the specimen along the axis. The specimens were rotated with a frequency of ~ 1 Hz inside a thermostated (70 °C) metal cup. Rotation was required for uniform heating of the specimen, which was ignited with a glowing nichrome spiral. The upper part of the specimen ($\sim 4 \text{ mm}$) was insulated from the walls of the metal cup with a teflon ring, which prevented cooling of the upper melted layer of UHMWPE during burning. The distance between the air nozzle and the polymer's surface was 14 mm. The air velocity was set with a mass-flow controller (MKS Instruments, USA). The accuracy of measuring the air velocity was ± 0.13 cm/s. The specimens' regression rates were measured with the air flow velocity of 44 cm/s and with its temperature being 23 °C. A flame was stabilized by moving the specimen with the second stepper motor at a fixed velocity equal to the burning rate. The error of stabilizing the position of the surface of the burning sample was less than 5×10^{-2} mm after being controlled with a cathetometer. Polymer combustion was investigated with vertical [20-22] and horizontal orientations of the burner. Comparison of the species concentration profiles and the flame temperature profiles measured for both cases showed that the orientation of the burner in space did not

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Fig. 2. Configuration of the experimental setup.

exert any noticeable influence on the process of combustion and the results of the experiments.

2.2.2. Molecular beam mass-spectrometric setup with soft ionization

Species mole fractions in the flame were measured using the molecular beam massspectrometric setup (MBMS) shown in Fig. 2. Detailed descriptions of the setup have been presented previously [23,24]. The flame gases were sampled with a sonic quartz probe with an orifice diameter of 0.04 mm, wall thickness of 0.08 mm and an internal angle of 40°. The central part of the supersonic jet was extracted by a stainless steel skimmer and ionized in the ionization source of the mass spectrometer. The MBMS setup was equipped with a MS-7302 guadrupole mass-spectrometer with soft electron-impact ionization (spread in ionization energies of $\pm 0.25 \text{ eV}$), described in Appendix B of Supplemental Data. The burner's axis was positioned in perpendicular to the axis of the probe. Shown in Fig. 2S is the photo of the probe positioned at the distance of 0.9 mm from the polymer surface. The position of the burner relatively to the probe during an experiment was adjusted with a 3D-coordinate device and controlled using a cathetometer with an accuracy of $\pm 10^{-2}$ mm. In order to minimize perturbations of a flame by the probe, flame gases were sampled at a distance of $\sim 5 \text{ mm}$ from the

Table 1

Measured species, their ionization potentials (IP), and energies of ionizing electrons (IE) used in experiment.

m/z	Formula	Species name	IP (eV)	IE (eV)
1	Н	Hydrogen atom	13.6	16.65
2	H_2	Molecular hydrogen	15.43	20
17	OH	Hydroxyl	13.02	16.65
18	H_2O	Water	12.62	15.4
28	C_2H_4	Ethylene	10.53	12.3
28	CO	Carbon monoxide	14.01	14.35
32	O ₂	Oxygen	12.07	14.35
40	Ar	Argon	15.76	16.2
44	CO_2	Carbon dioxide	13.8	15.4
64	HOPO	Phosphinic acid	10.7	12.8
80	HOPO ₂	Metaphosphoric acid	12.4	14.5

specimen's axis. One-dimensional structure of a counterflow flame allows sampling in this manner. Experimental evidences of one-dimensional nature of a counterflow flame were provided in our previous work [16]. That study of a counterflow methane/oxygen flame using both molecular beam and microprobe sampling has shown that the species mole fraction profiles on the central line and in the periphery of the flame are equal. Moreover, the temperature profiles on the central line and in the periphery of the flame measured by microthermocouples were also shown to be similar.

Table 1 summarizes all species, the mole fraction profiles of which were measured, along with their ionization potentials (IP), and energies of ionizing electrons used for each species (IE). The mole fractions of most species were determined using the calibration coefficients (relative to argon) derived from direct calibration experiments with gas mixtures of known composition. Calibration coefficients for H and OH radicals were determined by applying a relative ionization cross-section (RICS) method described by Cool et al. [25] and used in our previous work [26]. The uncertainty of determining absolute mole fractions of the major flame products including: CO_2 , H_2O , and O_2 , was estimated to be $\pm 10\%$ of the maximum mole fraction values, and $\pm 20\%$ for CO, H_2 , C_2H_4 . Absolute mole fractions of H, OH and phosphor containing species were determined to within a factor of about 2.

2.2.3. Temperature measurements in gas and condensed phase

The flame temperature was measured by a Pt–Pt/Rh (10%) thermocouple of a diameter of 5×10^{-2} mm, coated with a thin layer of SiO₂ (1×10^{-2} mm) to prevent catalytic processes; the thermocouple had shoulders of 8 mm length. The flame temperature profiles are shown considering the radiation corrections calculated by the formula of Kaskan [27]. For the temperature maximum, the correction was ~150 °C. The thermocouple's position in the flame was controlled with a cathetometer, as shown in Fig. 1S.

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Fig. 3. Embedding a thermocouple inside the specimen. 1 - thermocouple's junction, 2 - thermocouple leads.

To measure the temperature in the condensed phase, the thermocouple was embedded into the specimen, as shown in Fig. 3. For this purpose, holes of 0.5 mm in diameter were drilled in the specimen at angle of 150° ; then a Pt–Pt/Rh(10%) thermocouple of diameter 5×10^{-2} mm was inserted into the channel. The channel was finally melted at the edges of the specimen to rule out any subsequent shifting of the thermocouple. A similar approach was used before [28] to measure the burning surface's temperature during the combustion of PMMA.

When measuring the temperature, a 14-bit analog-digital converter E14-140-M ("L-Card") was used. The analog-digital converter for thermocouple's data acquisition was controlled with a personal computer, which was connected with a standard USB interface. The instrumental bias of the temperature measurement was ± 5 °C.

2.2.4. Measurement of oxidizer flow velocity

To provide a uniform flow of oxidizer, a converging nozzle was used. The profile of the air velocity over a cross-section at 5 mm from the nozzle's exit was measured with a hot wire anemometer, based on a platinum wire 1×10^{-2} mm in diameter. The air velocity over the cross-section at 5 mm from the nozzle's exit was constant with an accuracy of 3%. The velocity of the air was measured to an accuracy of 1%.

3. Results and discussion

3.1. The effect of TPP on the burning surface temperature and the temperature gradient in the condensed phase

The burning rates of UHMWPE and UHMWPE+5 wt% of TPP were 18 $(\pm 2) \mu$ m/s

and 7.7 $(\pm 1) \mu$ m/s, respectively. The temperature of the UHMWPE burning surface in a counterflow flame was measured using two methods: (i) a thermocouple was moved through the flame until its junction touched the burning surface and (ii) a thermocouple was embedded in the specimen. The temperature corresponding to the moment when the junction contacted the liquid was considered in the first case to be the surface temperature. This moment was controlled visually. After that, the thermocouple's movement was stopped. The thermocouple remained motionless for several seconds, and then it was moved in the opposite direction. To raise the measurement's accuracy, the above procedure was repeated several times.

When measuring the temperature with the thermocouple embedded in the specimen, the burning specimen was moved by a stepper motor without being rotated. The moment when the thermocouple junction emerged from the burning surface was recorded with a Panasonic M3000 camera synchronized with the thermocouple's data acquisition module. Figure 4 shows stopframes from the video recording the moments when the thermocouple junction emerged from the burning surface (an arrow indicates the thermocouple's junction). Figure 5 shows the temperature profiles in the condensed and gas phases obtained by both methods of measurement. The temperature gradient in the condensed phase near the burning surface was equal to 130 K/mm for UHMWPE and 100 K/mm for UHMWPE +5 wt% of TPP. The temperature gradient in the gas phase near the burning surface was equal to 500 K/mm for UHMWPE and to 430 K/mm for UHMWPE +5 wt% of TPP. The temperature measured with the embedded molded-in thermocouple was 550 °C for UHMWPE and 530 °C for UHMWPE + 5 wt% of TPP. The temperature of the burning surface measured with an embedded thermocouple (550 °C) slightly exceeded that (522 °C) measured with the thermocouple moved in flame. However, within the limits of accuracy (\pm 15 °C) they are equal. One can also conclude that adding TPP to UHMWPE does not affect the temperature of the polymer's burning surface. The 14% reduction in the temperature gradient in the gas phase adjacent to the burning surface, when 5 wt% of TPP was added to UHMWPE indicates a corresponding reduction of the heat flux from the flame to the polymer when a flame retardant is present.

The temperature profiles measured along the central axis of the UHMWPE flame and at the periphery (5 mm from the central axis) are shown in Fig. 6. As seen, the profile are almost identical. The scatter of data in flame temperature measurement due to flame fluctuations was \pm 30 °C. Thus, it can be stated that the flame is one-dimensional, and it is quite correct to perform sampling at the periphery of the flame.

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Fig. 4. Stopframes of the appearance of the thermocouple on the surface of the polymer: A - UHMWPE, B - UHMWPE +5 wt% of TPP.



Fig. 5. The temperature profiles in the condensed and gas phases in UHMWPE burning. The solid line – UHMWPE, the dashed line – UHMWPE +5 wt% of TPP.



Fig. 6. The temperature profile of the UHMWPE flame in the central axis and at the periphery.

3.2. The structure of counterflow flame of UHMWPE with and without TPP

Figures 7 and 8 show temperature profiles and concentration profiles for stable species in a counterflow flame of UHMWPE without and with 5 wt% TPP, correspondingly.



Fig. 7. Temperature profile and concentration profiles for stable species in a counterflow flame of UHMWPE.



Fig. 8. Temperature profile and concentration profiles for stable species in a counterflow flame of UHMWPE with 5 wt% TPP.

Adding TPP to UHMWPE led to a change in the composition of the species in the flame, reduction of the maximum temperature, shifting its profiles from the burning surface, and the increase in the width of the combustion zone. In the flames studied, H atoms and OH radicals were identified, their concentrations and their concentration profiles were measured. In the flame with TPP additives HOPO and HOPO₂, the main products of TPP destruction in flame, were identified, and their concentrations were measured. Shown in Fig. 9 are

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Fig. 9. The concentration profiles of H, OH, HOPO and HOPO₂ in the flames of UHMWPE without and with 5 wt% TPP.

the concentration profiles of H, OH, HOPO and HOPO₂ in the flames of UHMWPE without and with 5 wt% TPP. Although PO₂ is an important species of the reaction mechanism, its concentration under conditions of our experiment proved to be much lower than those of HOPO₂ and HOPO and also below the sensitivity threshold of the setup.

It can be seen that adding TPP to UHMWPE results in reduction of H and OH radicals' concentration by approximately 2 times, a shift of their maxima by 1 mm from the burning surface. It was shown earlier [14,15] that reactions with participation of HOPO and HOPO₂ are the key reactions in the catalytic cycle of recombinations of H and OH radicals:

 $\begin{array}{l} H + PO_2 + M \Rightarrow HOPO + M \\ HOPO + OH \Rightarrow PO_2 + H_2O \\ OH + PO_2 + M \Rightarrow HOPO_2 + M \\ HOPO_2 + H \Rightarrow PO_2 + H_2O \end{array}$

The maxima of the HOPO and HOPO₂ profiles are shifted to the burning surface by approximately 1 mm versus the concentration profiles of H and OH. FR in the flame transforms into HOPO and HOPO₂, which reduce the concentration of H and OH and thus increase τ_{cr} , the characteristic time of the chemical reaction of oxidation of the polymer's decomposition products in the flame. The condition for flame extinction is the following: $\tau \le \tau_{cr}$, where τ is the time of residence of the reacting mixture in the flame zone. The extinction strain rate (1/ τ) is the value reversed to τ . Thus, adding the FR results in the increase of τ_{cr} and hence in the reduction of the extinction strain rate.

3.3. The extinction limits of counterflow flames of UHMWPE and UHMWPE +5 wt% of TPP

The extinction strain rate (ESR) is an important characteristic of a material's flammability determined by the studying counter-flow flames. The



Fig. 10. Dependence of maximum flame temperature on the strain rate for UHMWPE and UHMWPE+5 wt% of TPP.

strain rate (SR) *a* is determined for the combustion of gaseous and liquid fuels by the formula [29,30],

$$a = \frac{2V_{ox}}{L} \left(1 + \frac{V_{fuel}}{V_{ox}} \sqrt{\frac{\rho_{fuel}}{\rho_{ox}}} \right)$$

where V_{fiuel} , V_{ox} , L, ρ_{fuel} , ρ_{ox} are the flow velocity of the fuel and of the oxidizer, the distances between the nozzles and polymer's surface, and the fuel and oxidizers' densities in the flows, respectively. The velocity of the polymer pyrolysis products flow was calculated with the continuity equation. The density of the gaseous pyrolysis products near the burning surface was evaluated from the composition of products [20]. The evaluations have shown $V_{fuel} << V_{ox}$ and $a\approx 2V_{ox}/L$.

Figure 10 shows the dependence of the maximum flame temperature on the strain rate in counter-flow flames of UHMWPE and UHMWPE +5 wt% of TPP. It can be noted that in the case of combustion of UHMWPE +5 wt% of TPP, the maximum flame temperature grows on increasing the strain rate. However, beginning with the strain rate 90 s⁻¹, the flame of UHMWPE +5 wt% of TPP becomes unstable. Therefore, intense oscillations begin in the area of the temperature maximum. Adding 5 wt% of TPP to UHMWPE leads to a reduction of ESR by a factor of 1.5.

4. Summary and conclusion

Analysis of the data obtained indicates that reactions in the gas phases in the flame play the key role in the mechanism of flame retardancy of TPP for UHMWPE.

The following facts established in this study for adding TPP to UHMWPE confirm that there is a gas phase mechanism whereby TPP reduces a polymer's flammability.

 Widening of the flame zone, a decrease of the maximum flame temperature, its shifting from the burning surface result in a reduction

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of the heat flux from the flame to the molten polymer. The latter was confirmed by direct measurements of the temperature gradients near the burning surface.

- 2. Reduction of the extinction strain rate by a factor of 1.5.
- Reduction of H and OH radicals' concentration by approximately 2 times, a shift of their maxima by 1 mm from the burning surface.
- 4. Detection of HOPO and HOPO₂, the main products of TPP destruction in the flame, which catalyze the recombination of H and OH radicals.

Thus, direct experiments conducted have demonstrated that the action of a flame retardant in a polymer flame consists in its participation in chain-termination reactions. These reactions are typical of many phosphorus-containing flame retardants acting in the gas phase.

The counterflow flame method has been demonstrated to be applicable to studying the combustion of polymers with flame-retardant additives. The data obtained may be further used to develop a model of polymer combustion and a model of flame retardancy. The results of our research may be used to obtain kinetic parameters of polymer pyrolysis under conditions of polymer combustion. These parameters will be helpful in improving numerical models of real fires involving polymer materials with FRs and without them.

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Supplementary Materials

Supplementary material associated with this article can be found, in the online version, at doi: 10.1016/j.proci.2016.06.117.

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