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Proceedings of the Combustion Institute xxx (2012) xxx–xxx

Proceedings  
of the  
Combustion  
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# Reduction of flammability of ultrahigh-molecular-weight polyethylene by using triphenyl phosphate additives

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## Abstract

The mechanism of reducing the flammability of ultrahigh-molecular-weight polyethylene (UHMWPE) with triphenyl phosphate (TPP) additives was investigated, using the methods of molecular-beam mass spectrometry (MBMS), differential mass spectrometric thermal analysis (DMSTA), thermocouple, thermogravimetry (TGA), and gas chromatography mass spectrometry (GC/MS). Kinetics of thermal degradation of pure UHMWPE and of that mixed with TPP was studied at high ( $\sim 150$  K/s) and low (0.17 K/s) heating rates at atmospheric pressure. Effective values of the rate constants of the thermal degradation reaction were determined. Times of ignition delay, the limiting oxygen index, the burning rates of UHMWPE and UHMWPE + TPP and their temperature profiles in the flames were measured. The flame structure was investigated and the composition of the combustion products in the flame zone adjacent to the specimen's combustion surface. TPP vapors in flame were found. Addition of TPP to UHMWPE was found to result in reduction of polymer flammability. TPP was shown to act as flame retardant both in the condensed and gas phases.

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**Keywords:** Flammability of ultrahigh-molecular-weight polyethylene; Triphenyl phosphate; Flame retardant; Polymer degradation and combustion; Mass spectrometric thermal analysis

## 1. Introduction

Flame retardants (FR) are used as additive to polymer materials to reduce their flammability. The areas of using polymer materials are multiple,

and the problem of reducing their flammability is very important. The mechanism of the effect of FR is complicated and poorly investigated. It is different for different polymers. FR may act both in the condensed and gas phases. Over the recent years, serious interest has emerged for application of phosphorus-containing FR, including organophosphorous compounds (OPC).

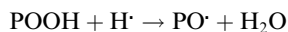
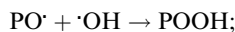
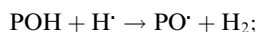
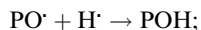
Polyethylene (PE) is one of the most widespread synthetic polymer materials in the modern world. There are different modifications of PE, among

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which a special position is occupied by ultrahigh-molecular-weight polyethylene (UHMWPE) with superhigh molecular mass (over  $1.5 \times 10^6$  g/mol), which determines it as construction polymer material with unique physical and mechanical properties. UHMWPE, just as all polyolefins, is a combustible compound; therefore one of the main challenges is to reduce its flammability by adding FR. However, there are no studies on reduction of flammability of UHMWPE in literature.

Triphenyl phosphate (TPP) is currently considered as FR for different types of polymers. In certain polymers, addition of TPP was shown in [1–6] to raise the limiting oxygen index (LOI), reduces the flame propagation velocity and enhances the material's thermal resistance. According to the data [1] the degradation products of polycarbonate with TPP additive have in the gas phase large amounts of species with the P–O bond, one of which is presumed by the authors to be TPP. It was shown in [7] that inhibition of hydrogen and hydrocarbon flames with OPC additives is attributed to the growth in the recombination rate of H and OH in their reactions with phosphorus oxides and oxyacids:



The gas phase mechanism of phosphorus containing FR, manifesting itself in the reduction of concentration of H and OH radicals in the flame, was confirmed by direct measurements in premixed methane-air flame with addition of phosphorus containing FR [8–10].

The effect of phosphorus containing FR has a complex character, as they may act both in the condensed and in the gas phase. Thermal degradation of polymers is an important stage in the process of combustion of polymers, responsible for their flammability. In the studies [11,12], kinetics of thermal degradation of high-density and low-density polyethylene (HDPE and LDPE) with molecular weights lower than that of UHMWPE was studied, using the TGA method in inert medium. The data presented in [11,12] for the activation energy of thermal degradation of HDPE are essentially different.

To understand the mechanism of FR action, one should know the kinetics and the mechanism of polymer degradation without FR additives and with them, including the composition of the degradation products, as well as their burning rate, LOI, the structure of their flame, and the composition of their combustion products.

In [13–15] it is shown that during pyrolysis of HDPE and LDPE in oxidizing and inert media in the range of temperatures 500–850 °C, the main

hydrocarbon products are ethylene, propylene, butadiene, butane, methane, 1-butyne, benzene, and isobutane. However, in a LDPE opposed flow diffusion flame [16] only light hydrocarbons  $\text{C}_1$ – $\text{C}_2$  were found near the polyethylene burning surface.

The molecular weight of UHMWPE was shown in [17] not to affect the thermal degradation of this polymer.

Thus, the composition of the pyrolysis products of HDPE and LDPE, the kinetic parameters of thermal degradation, and the composition of their combustion products are known from the literature, however, there are no such data for UHMWPE. No data are available in the literature on the effect of phosphorus containing FR, including TPP, on ignition, LOI, combustion, flame structure, the kinetics and the composition of the degradation products of UHMWPE. Analysis of literary data showed TPP to have FR properties for reactions in flame during combustion of a number of polymers. It is to be noted that no studies are available in literature referring to the study of the kinetics of polymer degradation with and without FR additives under conditions of high heating rates (HHR)  $\sim 150$  K/s, close to the conditions of their heating in combustion wave.

The objective of this study was to investigate the mechanism of FR action on polymer flammability, studying the effect of TPP on the thermal degradation, ignition, LOI and combustion of UHMWPE with the help of molecular beam mass spectrometry (MBMS), differential mass spectrometric thermal analysis (DMSTA), gas chromatography mass spectrometry (GC/MS), TGA, microthermocouples and visualization of the combustion process. One of the goals of this work was to study thermal degradation of polymers under conditions of their HHR, close to the heating rate in their combustion wave. The HHR of the polymer is closer to the actual conditions of polymer combustion during fires. It will allow more reliable predictions of polymer flammability and FR effectiveness.

## 2. Experimental

In the study, the following materials were used: powders of pure substances – UHMWPE, synthesized in the Institute of Catalysis SB RAS (grain size = 60  $\mu\text{m}$ ,  $\text{MW} = 5 \times 10^6$ ), and TPP ( $(\text{C}_6\text{H}_5\text{O})_3\text{PO}$ , the crystal size = 40–60  $\mu\text{m}$ ), mixtures based on them (UHMWPE/TPP 90/10, 95/5 wt.%) and pressed specimens produced from these mixtures. Pressed specimens with the diameter of 6.25 or 10 and 6–20 mm height were made with a press with pressure of 2 ton.

The composition of products emerging in the gaseous phase during thermal degradation of the powders UHMWPE/TPP was determined in a

flow reactor using the method of DMSTA [18,19]. The flow reactor (Fig. 1) is a quartz tube with a diameter of 1 cm, with a flow of argon  $\sim 5 \text{ cm}^3/\text{s}$  along it. Inside the tube there was a trough in the shape of a boat made from folded ribbon tantalum foil 0.1 mm thick, with a total volume of  $\sim 0.037 \text{ cm}^3$  (Fig. 2). The trough was heated at a rate  $\sim 100\text{--}200 \text{ K/s}$  as electric current was passed through it. The trough temperature was controlled with a chromel–copel thermocouple with a diameter of  $50 \mu\text{m}$ , welded to its center. A specimen of the powder under study weighing  $\sim 1\text{--}2 \text{ mg}$  was put into the trough. The start of degradation (evolution of degradation products in the gas phase), was determined with a mass spectrometric method. It is to be noted that the melt ensures close contact with the trough allowing taking the specimen temperature to be equal to the temperature of the trough in kinetic studies.

The experiments of studying the flame structure during combustion of pressed specimens in air were conducted using MBMS [20] and a stepper motor moving a burning specimen towards a probe (Fig. 3). A nickel–chromium heater in the shape of a spiral was placed at the distance of 2.5 mm from the upper face end of specimen. The turns of the heater were in a plane parallel to the specimen surface (Fig. 3). In heating the upper face end of specimen surface to  $600 \text{ }^\circ\text{C}$  during the time required for their ignition combustion was self-sustained. After ignition, the heater was shifted aside, and the specimen was moved towards the probe at the velocity  $V_m$ , exceeding the burning rate of the specimen  $v_b$  (Fig. 1S). The relative rate of approach between the specimen and the probe was  $\sim 0.3 \text{ mm/s}$ . Thus, the probe sampled combustion products from the flame at different distances from the burning surface.

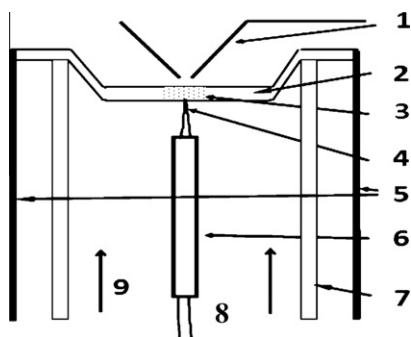


Fig. 1. The schematic of a flow reactor for polymer degradation study at a HHR by MBMS thermal analysis with time-of-flight mass spectrometer: 1 – quartz probe, 2 – tantalum heater, 3 – specimen, 4 – thermocouple, 5 – quartz tube, 6 – thermocouple holder, 7 – current feedthrough heater, 8 – current feedthrough from thermocouple to measurement system.



Fig. 2. Photo of a device for polymer degradation study at a HHR by MBMS thermal analysis with time-of-flight mass spectrometer.

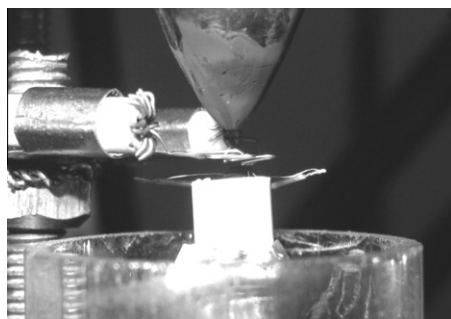


Fig. 3. The photo of setup for measuring the temperature near the surface of the specimen in the process of their heating, ignition, its combustion and for evaluating the flame structure by MBMS method.

The same pattern of investigation was applied to measuring the temperature profile in the flame of UHMWPE and UHMWPE + TPP, only instead of a probe a Pt/Pt–Rh thermocouple, covered with anti-catalytic  $\text{SiO}_2$  coating, was placed in parallel with the specimen surface at the distance of 10 mm. The diameter of the thermocouple wires was  $80 \mu\text{m}$ , the total thermocouple diameter including the coating was  $140 \mu\text{m}$ . After ignition, the heater was shifted aside, and the specimen was moved towards the thermocouple at the velocity exceeding the burning rate of the specimen, until the thermocouple junction touched the specimen surface.

The temperature and the ignition time of the UHMWPE specimens in air were found as follows (Fig. 4). Over the specimen surface a nickel–chromium heater was placed at the distance of 2.5 mm, which ensured the temperature near the specimen surface to be around  $400 \text{ }^\circ\text{C}$ . The specimens were heated until their ignition. A Pt/Pt–Rh thermocouple was mounted over the specimen surface at the distance of 0.1–0.2 mm, measuring the

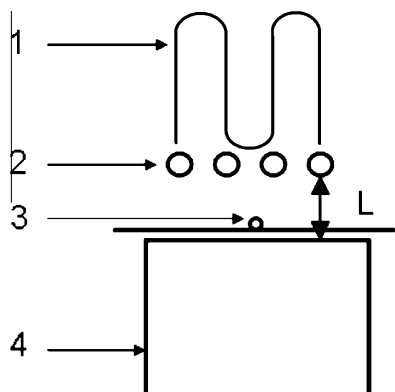


Fig. 4. The schematic of heater (2) and thermocouple (3) location relative to specimen (4). (1) – The top view of the heater in the plane parallel to the specimen surface.

temperature near the surface of the specimen in the process of their heating, ignition and combustion.

To identify the combustion products, the method of GC/MS was also used. The products near the combustion surface were sampled via a metal capillary ( $\varnothing = 0.6$  mm, wall thickness = 0.1 mm) from the blue flame zone ( $\sim 3$  mm wide). The sample volume was  $\sim 1$  cm<sup>3</sup>. The sample was analyzed with a GC/MS Agilent HP 6890N/5973N. Thermogravimetric analysis was conducted with a simultaneous TGA/DSC analyzer STA 409 PC (Netzsch) with aluminum crucibles in helium environment. The specimen weight was 3–4 mg. The heating rate was 10 K/min (0.17 K/s) from 30 to 550 °C. After completing the tests, the residual weight of the polymer was practically equal to zero, degradation of UHMWPE occurred without carbon residue formed.

The burning rate at the face end of the specimen (the axial burning rate) and the flame propagation velocity along the lateral surface of the specimen were measured by analyzing the video recording. The video of the combustion process was recorded with a Panasonic M3000 camera. The burning rates along the axis and along the surface were determined by dividing the burnt length of the specimen and the distance covered by the flame along the lateral surface by the time.

### 3. Results and discussion

#### 3.1. Thermal degradation of UHMWPE with and without TPP additives at low and high heating rates

In the pyrolysis products of UHMWPE and TPP, the most intense peaks were accordingly the peaks of masses with  $m/z$  26, 27 (UHMWPE) and 326, 77 (TPP). The former may be attributed to two main hydrocarbons – propylene and

butadiene, while the latter corresponded to the parent and fragment peaks in the mass spectrum of TPP. Shown in Fig. 5 are dependences of peak intensities of masses 27 and 326 during pyrolysis of individual substances (UHMWPE and TPP) and their mixture on temperature. It can be seen that the temperatures of the start of degradation of the individual substances UHMWPE (curve 3 in Fig. 5) and TPP (curve 1 in Fig. 5) are  $\sim 500$  and  $\sim 210$  °C, accordingly. The degradation products of UHMWPE and TPP which are in the mixture emerge at higher temperatures than those of individual substances: TPP (curve 2, Fig. 5) at  $\sim 300$  °C and UHMWPE (curve 4, Fig. 5) at  $\sim 570$  °C. The degradation products emerge not simultaneously. Originally peaks were detected corresponding to the degradation products of TPP, followed by the degradation products of UHMWPE. These data are in agreement with the results of [1] and confirm the fact that before degradation of UHMWPE, only TPP vapors evolve into the gas phase, TPP being a FR effectively working in the gas phase (according to the data of [6,10]).

Thus, the FR action of TPP on the thermal degradation rate of UHMWPE was discovered, manifesting itself in the rise of the temperature at which the thermal degradation products of UHMWPE, which is in the mixture with TPP, start to be formed.

The TGA method was used to investigate the thermal degradation of the UHMWPE and UHMWPE + 10% TPP specimens at the heating rate of  $\sim 10$  K/min ( $\sim 0.17$  K/s). Analysis of those data (Fig. 6) showed that during heating of the UHMWPE/TPP mixture significant reduction of the mass starts at the temperature of  $\sim 200$  °C. This temperature value corresponds to emergence of TPP vapors during its fast heating (curve 1, Fig. 5). Thus, at a low heating rate (LHR), TPP

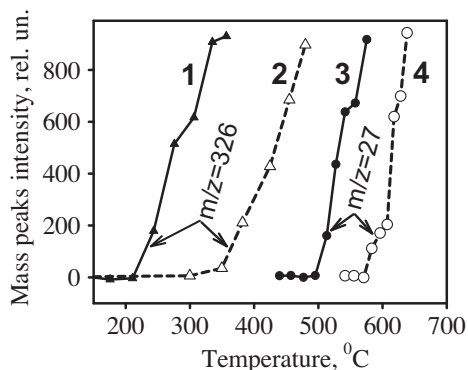


Fig. 5. Dependence of the intensity of mass peaks 27 for UHMWPE and 326 for TPP, detected in the degradation products of UHMWPE (3), TPP (1) and UHMWPE/TPP mixture (4, 2) on temperature.

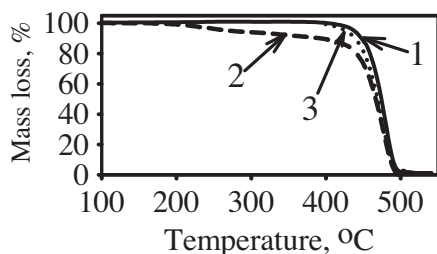


Fig. 6. TGA for UHMWPE and UHMWPE + 10% TPP at 10 K/min. 1 – UHMWPE, 2 – UHMWPE + 10% TPP, 3 – the curve is obtained from curve 2 (see the text).

mixed with UHMWPE was shown to act like an individual substance and not to interact with UHMWPE. In heating the mixture of TPP/UHMWPE, a situation similar to [1] for the TPP/polycarbonate mixture was observed. Reduction of mass during thermal degradation of UHMWPE/TPP has two characteristic temperature ranges. In the first one, as the specimen was heated to 400 °C, the mass fraction was observed to reduce from 100% to 90%, equal to the original amount of TPP, indicating the yield of all TPP from the mixture. The second range (from 400 to 500 °C) describes the yield of the remaining 90% of the original mass. The result of normalizing 90–100% mass in the range from 400 to 500 °C (obtained by multiplication by 100/90) is shown in Fig. 6, curve 3. Curves 1 and 3 coincide almost completely. This fact indicates that only UHMWPE remains in the mixture, i.e., a previous conclusion can be restated that mixed TPP and UHMWPE do not interact at a LHR, and the products of their degradation/evaporation yield separately – first all TPP gets evaporated, followed by UHMWPE.

Table 1 (rows 1 and 2) shows the kinetic parameters of thermal degradation of UHMWPE and UHMWPE/TPP, obtained by processing the TGA data in supposition of a first-order reaction, using the procedure described in Appendix B of Supplemental data. It can be seen that  $E_a$  and  $k_0$  for UHMWPE with TPP additive and without it have close values, i.e., adding 10% TPP did not affect the kinetics of UHMWPE degradation under conditions of the LHR. This result is quite

Table 1  
Kinetic parameters of the thermal degradation reaction of UHMWPE with TPP additive (in % wt.) and without it at different heating rates (dT/dt [K/s],  $k_0$  [1/c],  $E_a$  [kJ/mol]).

TPP	dT/dt	$\lg(k_0)$	$E_a$
0	0.17	$13.2 \pm 0.2$	$223 \pm 5$
10	0.17	$12.5 \pm 0.3$	$213 \pm 5$
0	150	$8.7 \pm 0.2$	$132 \pm 5$
10	150	$15.5 \pm 0.3$	$261 \pm 5$

evident, as TPP fully evolves into the gas phase before the start of UHMWPE degradation.

Table 1 (rows 3 and 4) shows the values of  $E_a$  and  $k_0$  of thermal degradation of UHMWPE/TPP at an essentially higher ( $\sim 900$  times) heating rate ( $\sim 150$  K/s), obtained with the DMSTA method in supposition of a first-order reaction. The above data of Table 1 also illustrated in Fig. 7.

In the case of thermal degradation at a HHR, different values of the rate constants for UHMWPE and UHMWPE/TPP were obtained (Fig. 7 and Table 1, rows 3 and 4), which, as opposed to the LHR (Table 1, rows 1 and 2), suggests the influence of TPP on the process of thermal degradation of UHMWPE at a HHR. Adding TPP increased the activation energy of the thermal degradation reaction by  $\sim 130$  kJ/mol and reduced the value of the rate constant of UHMWPE by  $\sim 10$  times. Therefore, at the HHR, TPP reduces the degradation rate of UHMWPE, i.e., it can be responsible for the reduction of polymer flammability.

Therefore, it is more correct to use the kinetic data obtained at higher (not at lower) HR for forecasting the effect of FR on polymer flammability.

### 3.2. The effect of adding TPP on ignition and combustion of UHMWPE

The method of microthermocouples was used to study the ignition times of UHMWPE specimens without TPP and with 10% TPP additive. The dependence of temperature over the specimen on the time of heating, ignition and stable combustion is shown in Fig. 8. In the case of heating the upper face end surface of the UHMWPE specimen to 400 °C, flame (Fig. 8) formed within 30 s. As the heater was switched off after 10 s, the flame did not extinguish, and the specimen continued to burn stably. The course of the curve from 44 to 80 s

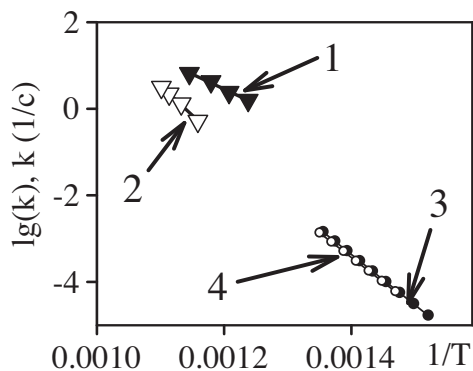


Fig. 7. The rate constants of reaction of thermal degradation of UHMWPE with TPP additive (2, 4) and without it (1, 3) at different heating rates: (1, 2) at  $\sim 150$  K/s, (3, 4) at  $\sim 0.17$  K/s.



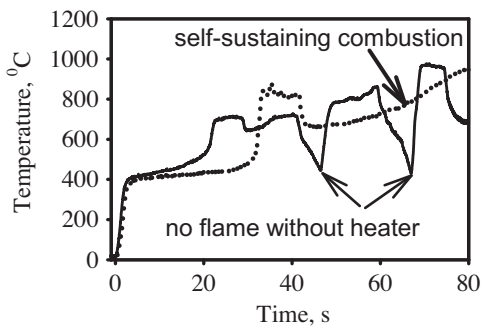


Fig. 8. Dependence of temperature over a specimen and in flame on time during heating, ignition and stable combustion of pure UHMWPE (the dashed line) and with 10% TPP (the solid line) additive with the surface temperature 400 °C.

corresponds to the temperature distribution in flame when the burning surface is moved away from the thermocouple junction. In the UHMWPE + 10% TPP specimens exposed to the same conditions (when the specimen surface was heated to 400 °C), ignition occurred earlier (at ~22 s), than in the case of UHMWPE without additive. However, without further heating, no stable self-sustained combustion of the UHMWPE/TPP specimens was observed during at additional multiple heating at the times of 32–40, 48–60, and 66–74 s. Thus, adding 10% TPP to UHMWPE resulted in significant reduction of flammability of UHMWPE. However, when the temperature of the top surface of UHMWPE/TPP specimens was 600 °C during 40 s, self-sustaining combustion was possible.

The method of video processing determined the local burning rates of the specimens with the diameter of 10 mm, made of UHMWPE and UHMWPE/TPP. It was established that adding 5% TPP to the polymer mass reduces the burning rate along the specimen axis and the along the specimen surface approximately 2–2.5 times (from 0.1 to 0.04 mm/s and from 0.25 to 0.11 mm/s, accordingly). The burning rate of pure UHMWPE in the atmosphere of static air is ~14 times lower than LDPE under conditions of [16], when a flow of air was directed at the face end of the polyethylene specimen.

Shown in Table 2 are the results of measuring the LOI of the UHMWPE/TPP for different contents of TPP, carried out with the standard method ASTM D2863 [21]. They demonstrate good activity of TPP as a FR for UHMWPE.

Table 2  
The LOI of the UHMWPE/TPP for different contents of TPP (in % wt.).

TPP	0	5	8	10
LOI	16.4	18.2	19.4	19.7

Figure 9 shows the temperature profiles in the flame of UHMWPE and UHMWPE + 10% TPP, obtained with thermocouples and a system of scanning the polymer flame zone. The temperature measurements were conducted along the specimen axis. It can be seen that, when 10% TPP was added to UHMWPE, the flame temperature decreased throughout the entire zone. For example, at the distance of 5 mm from the burning surface, temperature reduction was ~400 °C. The temperature of the burning surface of the UHMWPE specimens, equal to ~670 °C, did not change when TPP was added, while its absolute value was close to the data of [16] (~630 °C) for combustion of LDPE.

Shown in Fig. 10 is the dependence of the intensities of mass peaks 44, 18, 27, 26, and 326 of the main products (CO<sub>2</sub>, H<sub>2</sub>O, hydrocarbons, and TPP) formed in flame, on the distance from the burning surface of the UHMWPE + 10% TPP specimen. Oxygen was not found in that flame zone at the distances up to 4 mm from the burning surface. Hence a conclusion can be made that pyrolysis of UHMWPE in flame proceeds without oxygen participation. According to the GC/MS analysis of the sample taken from the flame zone, mass peaks 27 and 26 are attributed to two main hydrocarbons found in flame – propylene and butadiene. At the distance of 0–3 mm from the burning surface, peaks of masses 326, 77, 65, and 51 were found in flame, the ratio of the intensities of which being close to their ratio in the calibration mass spectrum of TPP. This allowed us to make a conclusion regarding the presence of TPP vapors in the flame of UHMWPE + 10% TPP, which, according to the literary data [6–10], inhibit hydrocarbon flames. This indicates TPP activity to take place not only in the condensed but also in the gas phase.

Shown in Fig. 11 are the pictures from flame video at different times in the process of burning the specimens of pure UHMWPE (Fig. 11a) and with 5% TPP additive (Fig. 11b) at the pressure of 1 atm. Just as in candle burning, flame spread downwards. Adding TPP affected the shape and the glow of the flame. The flame of the specimens

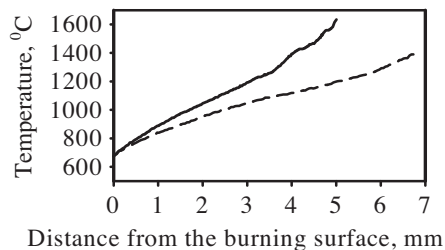


Fig. 9. The temperature profiles in the flame during combustion for UHMWPE (the solid line) and for UHMWPE + 10% TPP (the dashed line).

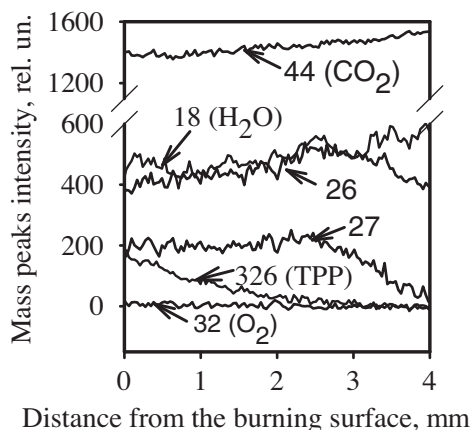


Fig. 10. Intensity profiles of mass peaks of species sampled from UHMWPE + 10% TPP flame.

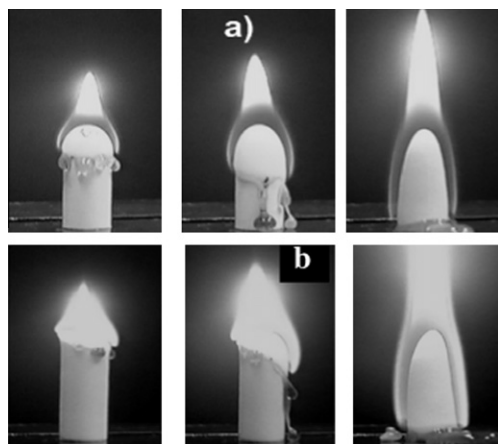


Fig. 11. Photo images of flame at different times in the process of specimen combustion at 1 atm: the upper row (a) for pure UHMWPE; the bottom row (b) for UHMWPE with 5% TPP additive.

containing TPP became more yellow and smoky, and sooty tongues were seen in the upper part of the flame. Analysis of the last pictures (Fig. 11, at the right) for the specimens without additive and with additive indicates that in adding TPP, the flame front width (the distance from the burning surface to the end of luminous zone) increased on the lateral surface. As the burning rate got reduced approximately two times as TPP was added, the flow rate of the pyrolysis products also got reduced. If it were not for the effect of TPP vapors on the further oxidation reactions of the pyrolysis products in flame, the width of the reaction zone in flame would get reduced, too. Yet, it did not get reduced but even got somewhat increased. This can be explained by the fact that TPP vapors inhibit the oxidation reactions of the pyrolysis products in flame.

As mass spectrometric identification of the composition of the combustion products of complex organic compounds is an extremely complicated task for a regular mass spectrometer, experiments were held on a GC/MS. Using the GC/MS, the quantitative composition of the products was determined, sampled from the UHMWPE flame zone, located at the distance of 1–3 mm from the burning surface of specimen (Table 1S). The main hydrocarbons sampled from the flame zone of UHMWPE and UHMWPE + 10%TPP, adjacent to the burning surface, are butadiene (~43 vol.%) propylene (~27 vol.%), propene (~9 vol.%), benzene (~8 vol.%), hexane (~7 vol.%), cyclopentadiene (~5 vol.%), pentene (3 vol.%), heptene and hydrocarbons with long skeletons (less than 1 vol.%). More detailed information on the composition of these products, including the molecular formulae and the structural formulae, is shown in Table 1S.

Adding 10% TPP results in the emergence of new compounds compared to the composition of products during combustion of pure UHMWPE. However, the main species remained the same. Emergence of new compounds is very likely to be related to the effect of TPP on oxidation of the combustion products of UHMWPE. It is also likely that TPP interacts with UHMWPE in the condensed phase and changes the pathways of its degradation.

GC/MS analysis of the products showed that two main hydrocarbon compounds (propylene and butadiene) are contained both among the combustion products of HDPE and LDPE [13,15] and among the combustion products near the burning surface of UHMWPE. A significant difference is the absence of ethylene among the combustion products of UHMWPE, while among the combustion products of LDPE and HDPE it constitutes almost one-third of all the hydrocarbon compounds. The TPP vapors were not found in the samples, as they got precipitated on the syringe walls. That was established by analyzing the wipe-sample products from the syringe walls with GC/MS.

#### 4. Conclusions

The methods of MBMS, DMSTA, GC/MS, TGA, microthermocouples and visualization of the combustion process were used to study the effect of triphenyl phosphate on the process of thermal degradation of ultrahigh-molecular-weight polyethylene at low (0.17 K/s) and at high heating rates (~150 K/s), on its ignition, combustion and the structure of its flame.

Addition of TPP to UHMWPE was shown to inhibit its thermal degradation only at high heating rates. Therefore, to forecast the effect of FR on flammability of polymers, it is more reasonable

to use the kinetic parameters obtained under conditions of high heating rates.

Key species were identified (propylene, butadiene and TPP) in the flame zone of UHMWPE with TPP additive, adjacent to the burning surface, and the intensity profiles of their mass peaks in flame were measured. Those species were shown to be thermal degradation products of UHMWPE with addition of TPP during HHR.

Adding TPP increases the LOI, decreases the burning rate and the temperature across the entire flame zones of UHMWPE, increasing the width of the flame zone, which seems to be related to the flame retardant effect of TPP on the oxidation rate of the combustion products of UHMWPE in flame. This is in agreement with the results of the previous studies, according to which adding TPP to hydrocarbon flames decreases hydroxyl concentration in flame.

Thus, TPP was shown to be an effective flame retardant for UHMWPE and to act both in the condensed and in the gas phase. The results of this work may be useful in understanding the mechanism of reducing flammability of UHMWPE and other polymeric materials.

#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.proci.2012.06.045>.

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