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Influence of triphenyl phosphate on degradation kinetics of ultrahigh-molecular-weight polyethylene in inert and oxidative media

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Abstract

The kinetics and the mechanism of thermal decomposition of ultrahigh-molecular-weight polyethylene without additive and with TPP additives in oxidative and inert media has been studied using the method of differential mass-spectrometric thermal analysis at a high heating rate and the method of thermogravimetric analysis at a low heating rate, aimed at understanding the mechanism of reducing combustibility of UHMWPE with TPP additives. The results of the study may testify to the fact that not the thermal polymer degradation reactions but the gas-phase reactions in the UHMWPE flame with TPP participation are responsible for flame retardancy of UHMWPE.

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1. Introduction

There is a steady increase in the consumption of plastics worldwide due to some of their properties, which allow them to be suitable in almost every field. In this regard, it is very important to reduce their flammability. Polyethylene (PE) is one of the most widespread synthetic polymer materials in the modern world. Of particular interest is ultrahigh-molecular-weight polyethylene (UHMWPE) with super-high molecular mass (over $1.5 \cdot 10^6$ g/mol), which has unique physical and mechanical properties. Flame retardants (FR) are used as additives to polymer materials to reduce their flammability. Over the recent years, the phosphorus-containing FR, including organophosphorous compounds (OPC), have attracted great interest. Triphenyl phosphate (TPP) is a representative of phosphorus-containing FR, which is very effective for many polymers as FR, including UHMWPE [1-7]. FR may act both in the condensed and gas phases. The mechanism of the effect of FR is complicated and poorly investigated. In particular, the mechanism of the impact of FR, including TPP, on reduction of UHMWPE flammability has not been studied yet. Thermal decomposition of polymers is an important stage in the process of combustion of polymers, responsible for their flammability. In the studies [8, 9], 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 at low heating rates (10÷50 degrees/min). The data presented in [8, 9] for the activation energy of thermal degradation of HDPE are essentially different. The effect of the molecular weight of polyethylene lower than the molecular weight of UHMWRE on its flammability was studied in [10] by the DTG method

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with the heating rate 90 degrees/min. There were no big differences in the weight loss temperature and scission products at a high temperature between the low molecular weight of polyethylene and the high molecular weight of polyethylene. A conclusion was made that the degradation and combustion behavior of the scission products of polyethylene in primary degradation require further research on flame retardants of polyethylene.

The kinetics of thermal decomposition of PE of unknown molecular weight in oxidative and inert media has been studied by the method of thermogravimetric analysis in [11]. However, the kinetics of thermal decomposition of UHMWPE in oxidative and inert media, without additives and with them, has not been studied. The purpose of this study was to investigate the pyrolysis kinetics and the mechanism of UHMWPE without additive and with TPP additives, aimed at understanding the mechanism of reducing combustibility of UHMWPE with TPP additives.

2. Experimental

In the study, the following materials were used: UHMWPE, synthesized in the Institute of Catalysis SB RAS (grain size ~ 60 micron, MW~ $5 \cdot 10^6$), and TPP ($(C_6H_5O)_3PO$, the particle size ~ 40-60 micron), and blends based on them (UHMWPE/TPP 90/10 wt.%). The composition of the products evolving during thermal degradation of the powders UHMWPE/TPP was determined by the method of differential mass-spectrometric thermal analysis (DMSTA) [12] in a setup with a flow reactor (Fig.1), interfaced with a molecular beam inlet system of gas flow into the ion source of the time-of-flight mass spectrometer.

The flow reactor is a quartz tube with a diameter of 1 cm, with a flow of argon or air at ambient temperature (18-20 °C) ~5 cm^3/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 ~ 0.037 cm^3. The trough was heated at a high heating rate (HHR) ~100-200 K/s as electric current was passed through it. The trough temperature was controlled with a Chromel-Copel thermocouple with a diameter of 50 micron, welded to its centre. A specimen of the powder under study weighing ~1-2 mg was put into the trough. Video recording of the condition of the powder inside the trough with a Panasonic M3000 camera showed that, as a small amount of the specimen was heated, the powder-like specimen melted before the beginning of the specimen degradation. For the specimens under study, the maximum thickness of the melted layer was ~0.250 mm. The melt ensures close contact with the trough, thus allowing in kinetic studies taking the specimen temperature to be equal to the trough temperature, which is pre-set with a computer before the experiment starts.

The main feature of the DMSTA method consists in the fact that the intensity peaks I_i in the mass spectrum of a sample taken at the output of a reactor are directly proportional to the rates of release of the respective decomposition products W_i:

$$W_i = W_{Ar} \frac{I_i}{I_{Ar}} \frac{1}{K_i},$$ (1)

where K_i is the calibration coefficient; I_{Ar}, W_{Ar} are the mass peak intensity and the flow rate of the argon diluent.

Simultaneous measurements of the dependence of the specimen temperature $T(t)$ and the mass peak intensities $I_i(t)$ of the decomposition products on time allow the decomposition kinetics to be studied.

The release rate of the decomposition products in supposition of the first-order reaction looks as follows:
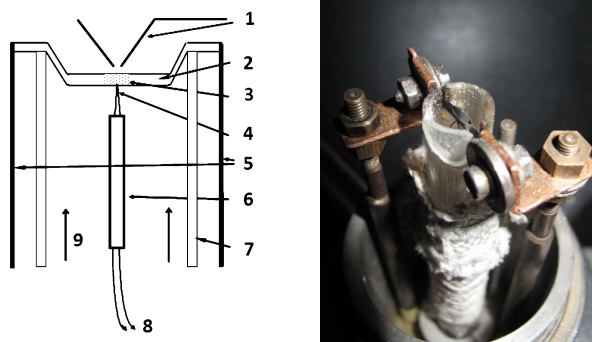

Fig. 1. The schematic and the photo of a flow reactor for polymer degradation study at a high heating rate: 1- quartz probe; 2 – tantalum heater; 3 – specimen; 4 – thermocouple; 5 – quartz tube; 6 – holder of thermocouple; 7 - electric conductor to the heater; 8 - electric conductor from thermocouple to measurement system; 9 – argon/air flow.

$$W = \frac{d\alpha}{dt} = k \cdot (1 - \alpha) \tag{2}$$

where k- is the rate constant of the reaction ($k = k_o \cdot \exp(-E_a/RT)$), α is the fraction of formation of the i-th product at the moment of time t, which was determined as follows:

$$\alpha(t) = \frac{\int\limits_0^t I_i \, dt}{\int\limits_0^\infty I_i \, dt} \tag{3}$$

Thus, it is possible to determine the values of K from equation (2) at different temperatures and represent them in the Arrhenius coordinates as $\lg(k)$ from $1/T$. The angle of slope of the dependence obtained allows E_a to be determined, while crossing with the axis of ordinates provides the value of k_0.

Shown in Fig. 2 are the typical dependences of 27th mass peak intensity ($I_{27}(t)$) and temperature $T(t)$ in studying thermal decomposition of mixtures containing UHMWPE. By processing the experimental dependences of mass peak intensities of the product i and using the formulae (1)-(3), the values of α and $d\alpha/dt$ were determined and the values of k were found for different temperature values. Thus obtained values of k in Arrhenius coordinates allow the activation energy to be determined, as well as the frequency factor of the reaction rate constant, by which this product is formed.
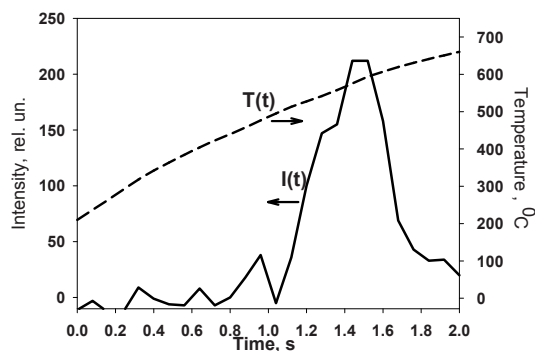

Fig. 2. Typical dependences of peak intensity m/z=27 (the solid line) and the heater temperature on time (the dashed line) in studying thermal decomposition of mixtures containing UHMWPE.

Thermogravimetric analysis was conducted with a simultaneous TGA/DSC analyzer STA 409 PC (Netzsch) with an aluminium crucible in inert (helium) and oxidative (helium/O_2 (5 and 21%)) medium at a low heating rate (LHR). The specimen weight was 3÷4 mg. Processing of the TGA curves was conducted in two ways. The first method of processing the TGA data to determine kinetic parameters at one heating rate (10 K/min) is similar to the data processing method described above for the data obtained with the DMSTA method (M1). The second method of data processing (M2) was conducted using the TGA data obtained with 5 heating rates (10, 20, 30, 40 and 50 K/min). This method, described in [8], was used to determine the orders and activation energies of reactions, depending on the polymer degradation degree.

3. Results and discussion

In the pyrolysis products of UHMWPE and TPP, the most intense peaks were accordingly the peaks of masses with m/z 27 (UHMWPE) and 326 (TPP). The former may be attributed to two main hydrocarbons – hexene and butadiene. The composition of the main volatile degradation products, according to the GC/MS analysis, was the following (%) – butadiene (11), pentene (10), pentane (3.5), hexene (39), hexane (5), heptene (12), and heptane (6).
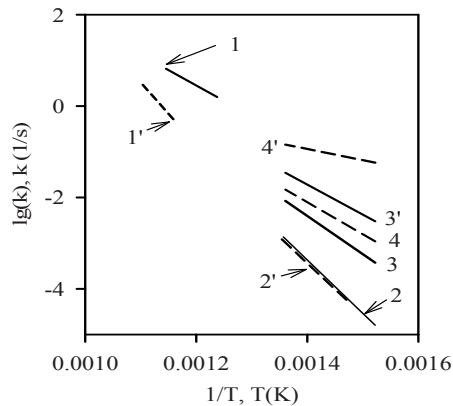
Fig. 3. The rate constants of reaction (*n*=1) of thermal degradation of UHMWPE with 10%TPP additive and without it in inert and oxidative environment at different heating rates: 1- UHMWPE (Ar, HHR); 1' – UHMWPE+10%TPP (Ar, HHR); 2 – UHMWPE (He, LHR); 2' – UHMWPE+10%TPP (He, LHR); 3 – UHMWPE (He+5%O_2, LHR); 3' – UHMWPE+10%TPP (He+5%O_2, LHR); 4- UHMWPE (He+21%O_2, LHR); 4' – UHMWPE+10%TPP (He+21%O_2, LHR). The plot shows a linear approximation drawn through the points.

Using the DMSTA method, thermal polymer degradation with TPP additive and without it was studied in inert medium. Before decomposition of UHMWPE, only TPP vapours were shown to evolve into the gas phase [1], TPP being a FR effectively working in the gas phase (according to the data of [2]). The 70 K increase of the temperature at the start of UHMWPE degradation when TPP was added to it indicates inhibition of the decomposition reaction of UHMWPE by TPP additives. Similar studies conducted with the TGA method on specimens of the same composition at a low heating rate (~10 K/min) did not reveal the impact of TPP on the degradation of UHMWPE (Fig. 3). Therefore, at the HHR, TPP reduces (Fig. 3) the decomposition rate of UHMWPE, *i.e.*, it can be responsible for the reduction of the polymer flammability when TPP is added to it. Using the DTG method, thermal polymer degradation without additive and with TPP additive in inert and oxidative media at varying heating rates and oxygen concentration (5 and 21%) was investigated. All the kinetic parameters of the reaction rate constants shown in Fig.3 are given in Table 1 and are discussed further. Shown in Fig. 4 are the DTG and DSC data for thermal degradation of UHMWPE+TPP in oxidative medium with 5% O_2 at the heating rate 20 K/min. Analysis of the data obtained indicates that at the maximum degradation rate of UHMWPE+TPP (T_{max} about 480 °C), the reaction occurs without heat release. This may be attributed to acceleration of oxidative destruction of UHMWPE without complete oxidation product (CO_2) formed, having high enthalpy of formation. In an oxidative medium with high oxygen content (21%), the destruction process according to the DSC data occurs with high heat release. The heat release peak at approximately 510 °C for the DSC curve at the end of destruction seems to be related to the oxygen-induced oxidation of char, formed in the first phase of oxidative destruction.
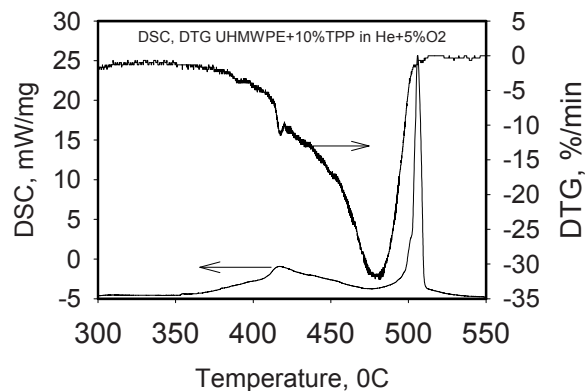

Fig. 4. DSC and DTG data for UHMWPE+10%TPP in helium + 5%O_2 medium.

Table 1. The kinetic parameters of thermal decomposition of UHMWPE and UHMWPE +10%TPP at low and high heating rates in oxidative and inert media obtained by M1 method in supposition of the first- order reaction

| | dT/dt, K/s | Type of inert | inert/ inert+5%O_2 / inert+21%O_2 | | |
			lgk_0, k [1/s]	E_a, kJ/mol	Line number on Fig. 3
UHMWPE	150	Ar/-/N_2	8.7/-/5.2	132/-/78	1/-/-
UHMWPE +10%TPP	150	Ar/-/N_2	15.5/-/6.5	260/-/96	1'/-/-
UHMWPE	0.17	He/He/He	13.2/9.3/7.7	223/160/134	2/3/4
UHMWPE +10%TPP	0.17	He/He/He	12.5/7.5/2.5	213/126/47	2'/3'/4'

Table 1 show the kinetic parameters of thermal decomposition of UHMWPE and UHMWPE +10%TPP, at low (0.17 K/s) and high (150 K/s) heating rates in oxidative and inert media, obtained by processing experimental data with a technique described in [12] in assumption of a first-order reaction (M1). The Arrhenius plots of these rate constants are shown in Fig. 3. It can be seen from Table 1 that at high heating rates the activation energy of UHMWPE grows with TPP additive in inert media and oxidative media, while at low heating rates it decreases with TPP additive. When inert medium is replaced with oxidative medium, the activation energy decreases during thermal degradation of UHMWPE both with and without TPP additive and both at high and low heating rates. As oxygen concentration increases, the activation energy decreases. An explanation of this fact is given in the study [11], oxygen is shown to participate in the formation of intermediates (hydroperoxide species) on the polymer surface, degradation of which proceeds at a higher speed than polymer degradation in the presence of inert gas.

Shown in Figs. 5 and 6 are the dependencies of the activation energy and of the reaction order of thermal degradation of UHMWPE and 90%UHMWPE+10%TPP in helium and in helium+5%O_2 media, depending on the degree of thermal degradation, at the heating rate 10 K/min, calculated with the M2 method. Comparison with the data from Table 1 shows that: 1) the activation energy of UHMWPE degradation in inert medium, obtained by the calculation method M2 (~230 kJ/mol), coincides with that presented in Table 1 (~223 kJ/mol). The reaction order in the range of decomposition degree 0.1 – 0.6 is close to the first one. 2) The activation energy of thermal degradation of 90%UHMWPE+10%TPP in helium+5%O_2 obtained by the M2 method (~164 kJ/mol) differs from that shown in Table 1 (~126 kJ/mol). This may be related to the fact that the reaction order (Fig.6 left) here is greater than 1.
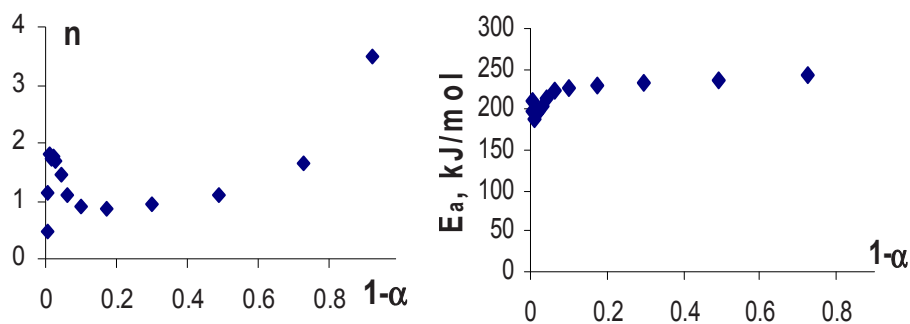

Fig. 5. Dependency of the order reaction and activation energy of thermal degradation of UHMWPE on the degradation degree at the heating rate 10 K/min. In He: k (1/s)=$10^{12.1}$ exp(-230kJ/RT)

Analysis of Fig. 3 demonstrates that in oxidative medium and at the low heating rate, the degradation rate of UHMWPE is much higher than in the inert medium. As the oxygen concentration grows, the degradation rate of UHMWPE and UHMWPE +10%TPP increases. However, in the oxidative medium at low and high heating rates, TPP does not inhibit polymer degradation, as opposed to its degradation in the inert medium when the heating rate is high. This may testify to the fact that not the thermal polymer degradation reactions but the gas-phase reactions in the UHMWPE flame with TPP participation are responsible for flame retardancy of UHMWPE [2]. It is shown in Fig. 3 that at a LHR, the decomposition rate of UHMWPE in oxidative medium increases with TPP additive; the higher the O_2 concentration, the higher the increase. Thus, at a LHR, TPP additive boosts the polymer decomposition reaction in oxidative medium. However, as these data are

extrapolated into the high temperatures area, we obtain an opposite effect due to different activation energies – TPP additive inhibits decomposition. This agrees with the data obtained by the DMSTA method at a HHR.
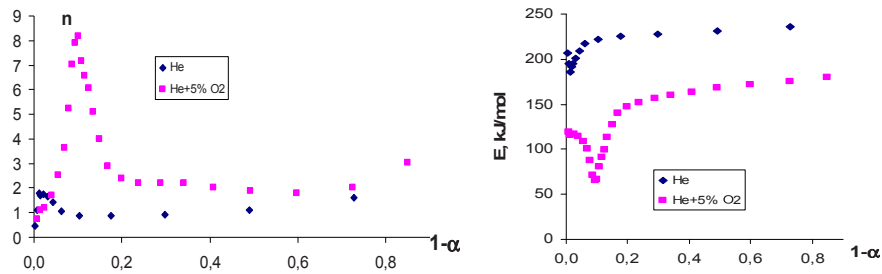

Fig. 6. Dependency of the order reaction (left) and the activation energy (right) of thermal degradation of 90%UHMWPE+10%TPP in He and He+5%O_2 on the degradation degree at the heating rate 10 K/min. In He: $k(1/s)=10^{12.1}$ exp (-230kJ/RT) ;In He+5%O_2: $k(1/s)=10^{8.4}$exp (-164kJ/RT)

4. Conclusions

The methods of MBMS, DMSTA, GC/MS, and TGA 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 high heating rates (~150 K/s) in inert and oxidative media.

At high heating rates, the activation energy of UHMWPE grows with TPP additive in inert media and oxidative media, while at low heating rates it decreases with TPP additive. When inert medium is replaced with oxidative medium, the activation energy decreases during thermal degradation of UHMWPE both with and without TPP additive and both at high and low heating rates. As oxygen concentration increases, the activation energy decreases. At a LHR, the decomposition rate of UHMWPE in oxidative medium increases with TPP additive. Thus, at a LHR, TPP additive boosts the polymer decomposition reaction in oxidative medium. However, as these data are extrapolated into the high temperatures area, we obtain an opposite effect due to different activation energies – TPP additive inhibits decomposition. This agrees with the data obtained by the DMSTA method at a HHR.

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.

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