

# The Impact of DOPO and TPP Flame Retardants on Flame Spread over the Surface of Cast PMMA Slabs

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## ABSTRACT

The effect of flame retardants DOPO and TPP on combustion of PMMA and on its thermal decomposition has been investigated. It was suggested that the presence of an oxidizer in the pyrolysis zone affects the flame propagation rate in the case of PMMA-TPP and has no effect in the case of PMMA-DOPO. With the addition of TPP and DOPO a reduction of the total heat flux from the flame to the surface was detected. Before the flame front, diffusion of the oxidant takes place in the longitudinal direction to the flame zone. local increase of the heat flux near the flame front in the case of PMMA-TPP was found, as opposed to in PMMA without additives. From the data of the species concentrations in the flame zone of a PMMA-TPP slab, the presence of oxygen at the flame front (up to 10%) was detected. PMMA-TPP decomposes more rapidly than PMMA and PMMA-DOPO in the oxidizing medium. Farther from the flame front, where there is no oxygen, addition of TPP does not affect the decomposition rate of PMMA in an inert medium. The DOPO additive, in turn, affects the kinetics of thermal decomposition and reduces the heat flux from the flame. An oxidant does not affect PMMA-DOPO decomposition. Thus, it was concluded that the presence of oxygen near the pyrolysis surface affects the flame propagation velocity in the case of PMMA-TPP and has no effect in the case of PMMA-DOPO.

**KEYWORDS:** Flame retardants, PMMA, TPP, DOPO, flame spread, pyrolysis.

## INTRODUCTION

Reducing the combustibility of polymers is a vital problem, as they are used in various areas of the human activity. One of the ways to reduce the flammability of polymers is to add flame retardants to their composition. Flame retardants can reduce the flammability of polymeric materials by increasing the ignition delay time, reducing the rate of burning, and reducing flame spread velocity. The problem of determining the location of the flame retardant's action - the condensed phase or the gas phase, is one of the key issues regarding the mechanism of flame retardancy. A flame retardant may affect the thermal decomposition of a polymer, as well inhibit the oxidation of volatile gaseous products [1]. Phosphorus-containing flame retardants may reduce flammability of a polymer both by forming a carbonaceous frame (char) in the condensed phase and by inhibiting gas-phase reactions. There are three mechanisms by which the formation of char reduces the combustibility of solid fuel:

1. Part of the carbon (and hydrogen) remains in the condensed phase, thus reducing the yield of gaseous products upon decomposition;

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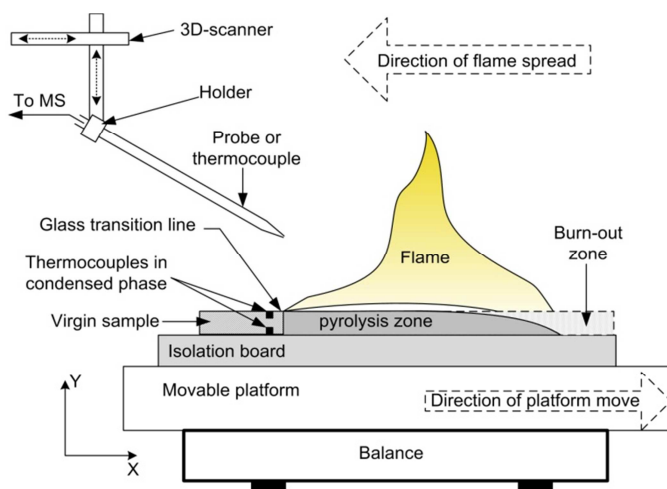
2. The char layer of low thermal conductivity serves as a thermal insulator for the polymer, and
3. The dense char acts as a physical barrier for the yield of gaseous fuel degradation products [2].

In the literature, there are practically no studies of flame propagation over polymers with additives of flame retardants, including investigation of the thermal and chemical structure of their flame. In this paper, non-charring cast PMMA was chosen as the object of the study. Its mechanism of thermal decomposition and combustion was widely studied [3-7]. Cast PMMA is widely used as a polymeric material. The purpose of this work was to explore the mechanism of action of flame retardants DOPO and TPP on reducing the flammability of cast PMMA on the basis of comprehensive physical and chemical studies, primarily the studies of flame propagation along the PMMA surface with additives of TPP and DOPO, including investigation of its flame structure and thermal decomposition.

## EXPERIMENTAL

Cast PMMA slabs with a width of 100 mm wide, 5 mm thick and 200 mm long were investigated. The samples were prepared as follows. The cast PMMA was prepared by polymerization of MMA monomer at 60 °C for 30 min in the presence of Dibenzoyl Peroxide. The prepolymer was heated at 90 °C for 3 h in the oven to get the cast PMMA. Then, the cast PMMA was crushed, and dried at 100 °C overnight to remove the unreacted monomers. The cast PMMA pellets were then hot pressed at 190 °C under 10 MPa for 3 min. To obtain PMMA+10%TPP the following technique was provided. The pellets of cast PMMA were crushed and mixed with TPP flame retardant. Then the mixture was heated and extruded into special molds in the extruder and hot pressed at a pressure of 100 bar. The cast PMMA-DOPO was prepared by polymerization of MMA monomer with 10 wt% DOPO. DOPO was dissolved with MMA at room temperature under stirring, and then heated to 60 °C for 30 min in the presence of Dibenzoyl Peroxide (1.5 g). The prepolymer was heated at 90 °C for 3 h in the oven to get the cast PMMA-DOPO. Then, the cast PMMA-DOPO was crushed, and dried at 100 °C overnight to remove the unreacted monomers. The cast PMMA-DOPO pellets were then hot pressed at 190 °C under 10 MPa for 3 min. The slabs were inserted into a metal frame, which served to prevent flame spread along the slab sides. The samples were placed on a thermally insulating board with thermal conductivity of 0.15 W/(m·K) and specific heat of 950 J/(kg·m·K). The board with the specimen was mounted on an electronic balance. To determine the flame spread rate, horizontal lines were drawn on the upper surface of the sample every 10 mm. On the upper surface of the slabs, at a distance of 1 cm from the edge, an incombustible heat insulating plate was installed to protect the sample from the flame. After ignition with a propane-butane burner, the plate was removed. To measure the flame temperature, a 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<sub>2</sub> to prevent catalytic reactions on the surface. It was installed on a three-dimensional positioning system with three stepping motors, allowing the thermocouple to be moved in three coordinates. In the paper, the coordinate along the sample width was fixed at the position of the middle of the samples. The thermocouple and the electronic weights were recorded using an E14-140-M ADC. The correction of the thermocouple measurements due to radiation was calculated by using the formula proposed in [8]. Temperature measurements were carried out by continuous scanning, moving the thermocouple from top to bottom to the surface of the burning plate. The temperature profiles were recorded every 5, 2, 1 mm for PMMA, PMMA-DOPO and PMMA-TPP correspondingly during the flame propagation over the surface. The pre-installed program was used to fix the position of the flame front with respect to the thermocouple along X axis (Fig. 1) during scanning. Obtained temperature profiles were used to determine the temperature gradients in the gas

phase near the surface of the slab. Based on the obtained gradients, the conductive heat flux from the flame to the surface was calculated. A quartz microprobe, connected with a quadrupole mass spectrometer, was used for sampling the flame online, allowing species to be identified in the flame and their concentration profiles. Thus, the chemical structure of the flame was determined. The mole fractions of methyl methacrylate (MMA), TPP, DOPO,  $O_2$ ,  $N_2$ , CO,  $CO_2$ ,  $H_2O$  in the flame for the test samples were determined. The microprobe and the thermocouple were moved with the speed of 2 mm/s along the height (Y axis). To fix the position of the flame front during the species sampling procedure a movable platform was used. It moved the sample during the combustion with the same velocity as the flame spreading velocity but in opposed direction. All the measurements have been conducted after a stationary flame to be established. The schematic of the setup used is shown in Fig 1.



**Fig. 1.** The experimental apparatus for studying horizontal flame spread over solid fuel and for measuring of temperature and species concentration profiles.

## RESULTS AND DISCUSSION

Table 1 presents the burning characteristics of cast PMMA slabs without addition of flame retardants and with 10% TPP and 10% DOPO additives.

The velocity of flame propagation along the cast PMMA surface, measured in this study was found to be close to that obtained for cast PMMA in other works [9-10]. We have also investigated the cast PMMA-DOPO\*, prepared as follows. The cast PMMA-DOPO\* was prepared by polymerization of MMA monomer with 10 wt% DOPO. DOPO was dissolved with MMA at room temperature under stirring, and then heated to 60 °C for 30 min in the presence of Dibenzoyl Peroxide (1.5 g). Afterwards, the mixture was cooled down to room temperature in the water bathing and then poured into a glass mould. The mould was put in the oven and then heated to 60 °C for 12 hours and 90 °C for another 2 hours. Then the PMMA samples were taken out from the glass mould. After this plate 5 mm thick were cut them into plates 200x100 mm. Comparison of the combustion characteristics of the cast PMMA-DOPO\* and the cast PMMA-DOPO ( the flame spread rate, the width of the pyrolysis zone, etc.) has demonstrated their identity.

**Table 1. Combustion characteristics for slabs with various additives**

	$L^a$ , cm	$v_m^b$ , g/s	$v^c$ , mm/s	$h^d$ , cm	$H_p^e$ , J/g	$Q^f$ , MJ/m <sup>2</sup>	$P^g$ , W	$T_{max, in}^h$ , °C	$T_{max, ox}^i$ , °C	$T_{surf}^j$ , °C
cast PMMA	10	0.078	0.12	20	1040	100	54	372	277	410
cast PMMA +10% TPP	4	0.054	0.075	9	802	82	31	372	305	430
cast PMMA +10% DOPO	1	0.021	0.033	3	897	75	13	382	369	430

<sup>a</sup>  $L$  – length of the pyrolysis zone; <sup>b</sup>  $v_m$  – mass loss rate; <sup>c</sup>  $v$  – flame spread rate; <sup>d</sup>  $h$  – the flame height; <sup>e</sup>  $H_p$  – heat of pyrolysis; <sup>f</sup>  $Q$  – total heat release determined in cone calorimeter tests; <sup>g</sup>  $P$  – the total conductive heat flux from the flame to the polymer burning surface; <sup>h</sup>  $T_{max, in}$  – the temperature of the DTG curve maximum pyrolysis rate in inert medium (Fig. 8); <sup>i</sup>  $T_{max, ox}$  – the temperature of the DTG curve maximum pyrolysis rate in oxidative medium (Fig. 8); <sup>j</sup>  $T_{surf}$  – the burning surface temperature.

Addition of flame retardants led to a decrease in the flame propagation rate, the mass burning rate of the samples, the length of the pyrolysis zone, and the flame height. It can be seen from Table 1 that for the same percentage of the additive, the flame retardant DOPO has a greater retardancy effect than TPP. It follows from Fig. 2 that for samples with and without additives a steady state is reached almost simultaneously - after about 800 seconds of combustion.

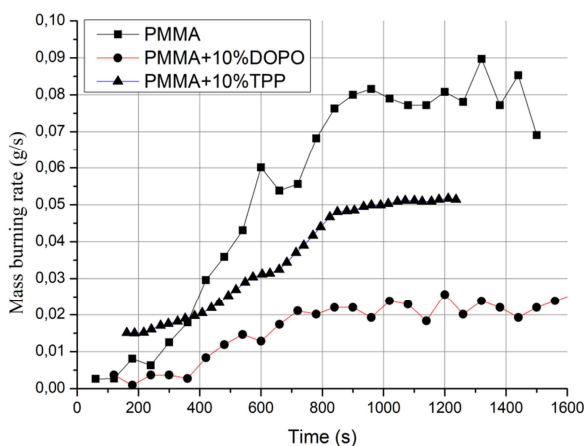
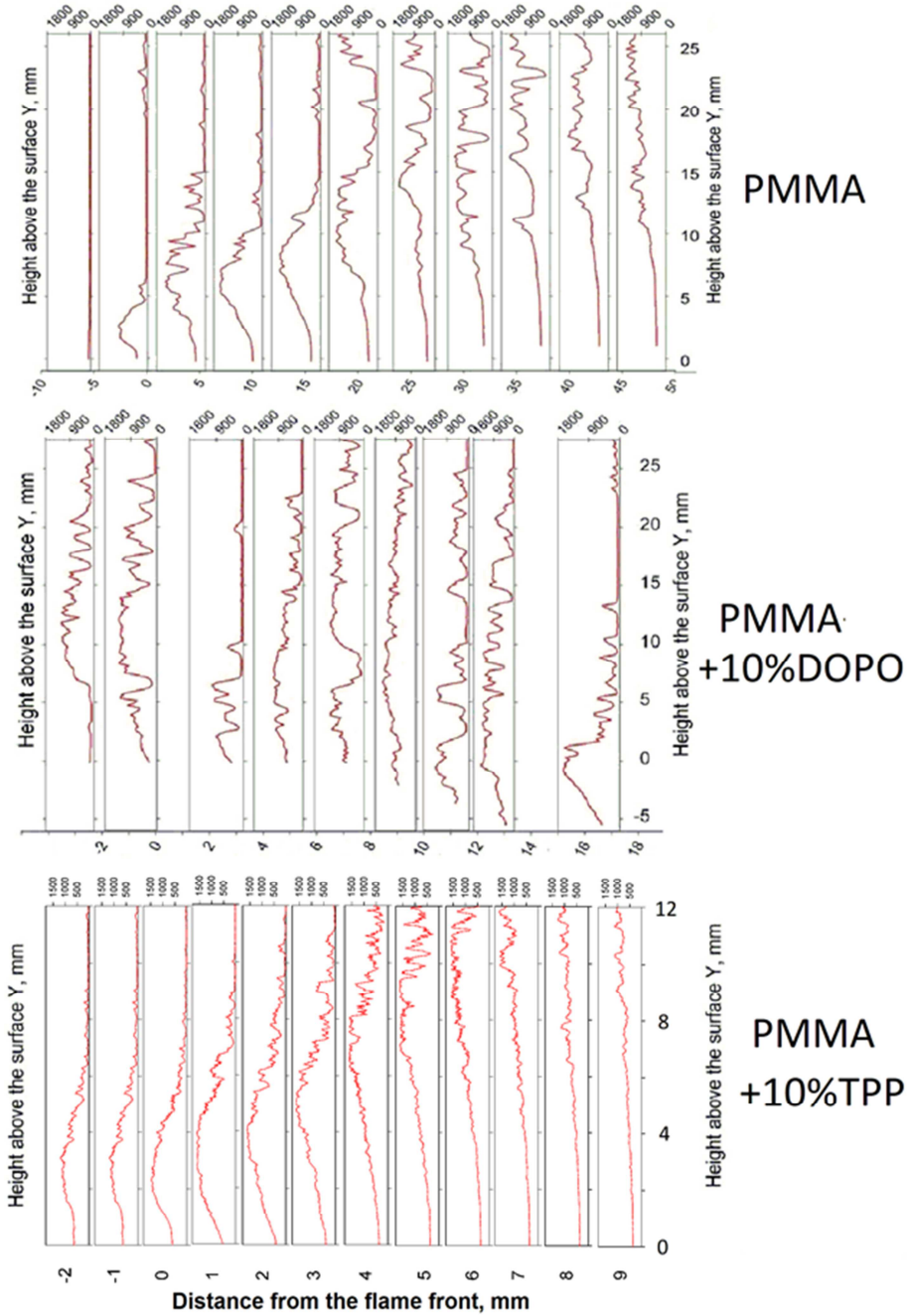


Fig. 2. The dependence of mass burning rate on time for cast PMMA and cast PMMA with TPP and DOPO additives.

Figure 3 shows the temperature profiles for PMMA, PMMA-TPP and PMMA-DOPO samples as a function of the distance from the flame front (the flame front is taken to be 0). Negative  $X$  values refer to the non-flame zone, and positive values refer to the flame zone. It can be noted that only in the case of PMMA + 10% TPP, high temperature is observed ahead of the flame front, which leads to a large heat flux (Fig. 4).

The total conductive heat flux from the flame, marked as  $P$  in Table 1, has been obtained by integrating the conductive heat flux over the combustion zone. With the addition of fire retardants,  $P$  decreases, and in the case of DOPO, the decrease is more noticeable than in the case of TPP. However, it can be seen from the Fig. 4 that at the flame front the conductive heat flux on the burning surface from the flame of PMMA-TPP is higher than that of PMMA and much higher than that of PMMA-DOPO. The heat flux for PMMA-TPP decreases to 10 kW/m<sup>2</sup> at a distance of 5 mm

from the flame front, whereas for PMMA it remains at the level of  $10 \text{ kW/m}^2$  almost to the end of the pyrolysis zone. In the case of PMMA-DOPO, the heat flux decreases to zero at a distance of 13 mm from the flame front. Figure 5 shows mole fractions of oxygen in the flame front during combustion of PMMA, PMMA + 10% TPP and PMMA + 10% DOPO.



**Fig. 3.** Vertical temperature profiles of cast PMMA, cast PMMA + 10% TPP and cast PMMA + 10% DOPO at different distances from the flame front. The initial surface level is taken to be 0 along Y axis.

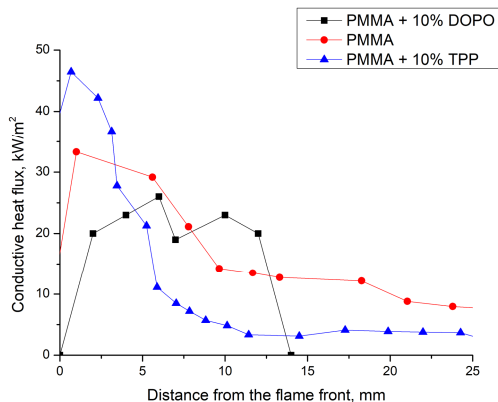


Fig. 4. Conductive heat fluxes for PMMA, PMMA-TPP and PMMA-DOPO.

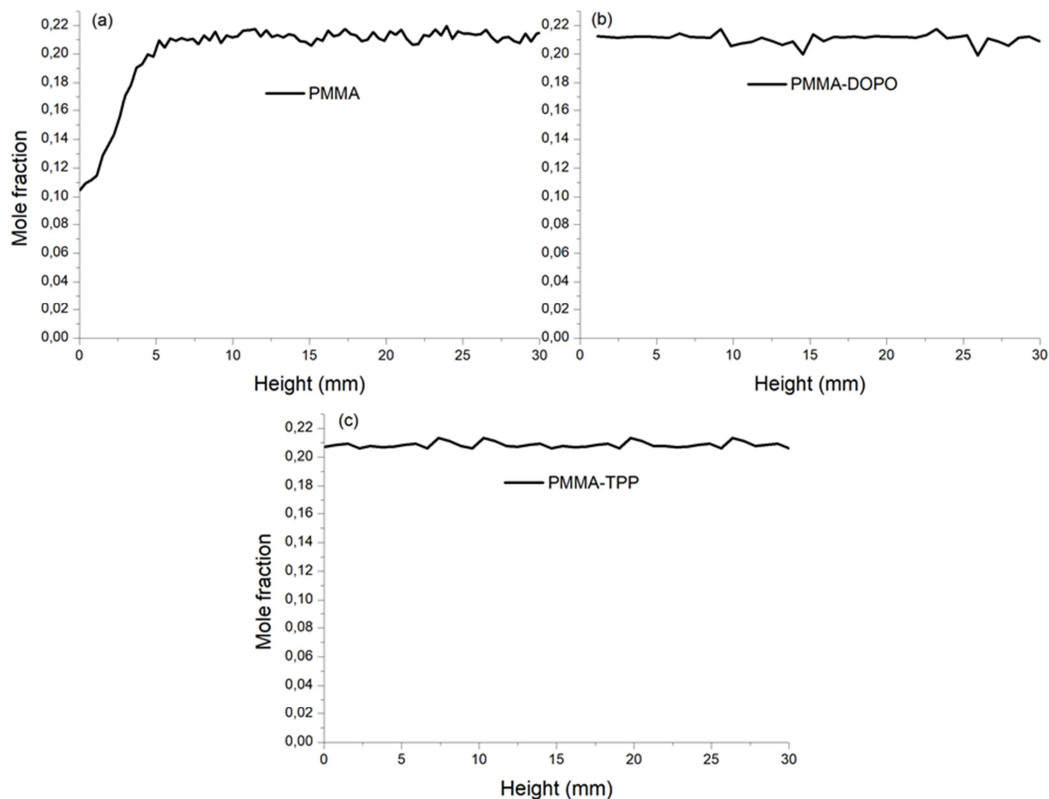
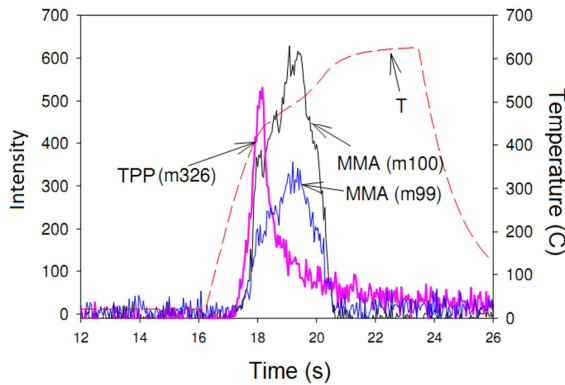


Fig. 5. Vertical profiles of mole fractions of oxygen at the flame front (a) for PMMA, (b) PMMA-DOPO and (c) for PMMA-TPP.

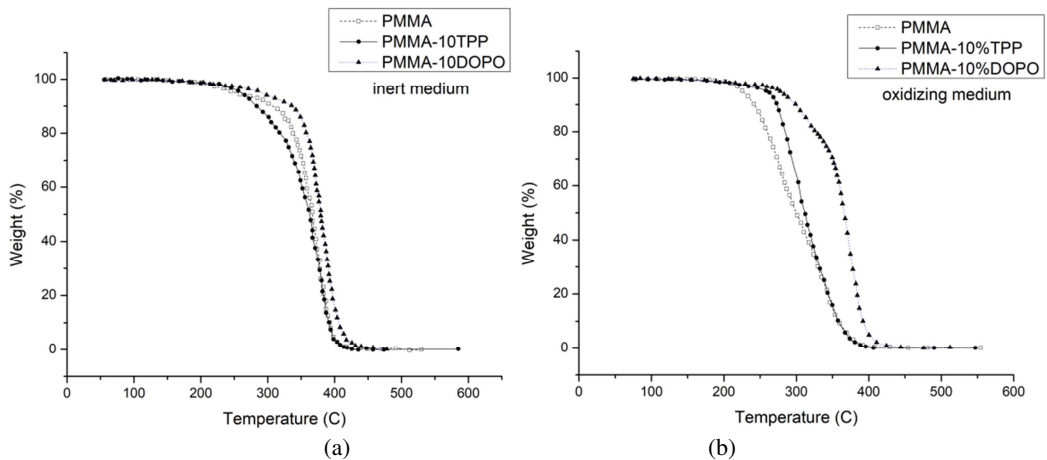
Figures 7 and 8 present thermogravimetric (TG) data for PMMA, PMMA-TPP and PMMA-DOPO samples in inert and oxidizing environment. The influence of the medium can be seen from the graphs: in the N<sub>2</sub> atmosphere, the maximum thermal decomposition rate of PMMA and PMMATPP coincide, and in air, PMMA decomposes more rapidly. In the oxidizing environment, the decomposition of PMMA takes place in two stages, whereas in the inert one there are only one. In

the case of PMMA with additives in the oxidizing environment, the decomposition also becomes more complicated - there are several (2 or 3) stages of thermal decomposition. The temperatures at which the pyrolysis rate reaches its maximum are presented in Table 1.

Addition of DOPO reduces the pyrolysis rate of PMMA in an inert medium, whereas the TPP additive does not have this effect. In the presence of oxygen, the pyrolysis rate increases significantly for PMMA and PMMA-TPP, while for PMMA-DOPO it is insignificant. In the case of PMMA-TPP, greater heat flux near the flame front is observed than in the case of PMMA. This can be explained by the fact that there is a greater amount of oxygen near the surface in the flame front of PMMA-TPP than in the front of the PMMA flame. At the same time, in the oxidizing environment, according to the thermal analysis data, the degradation rate of PMMA-TPP (the maximum pyrolysis rate is 305 °C) is greater than for PMMA in an inert medium (maximum pyrolysis rate is 372 °C).



**Fig. 6.** Differential mass spectrometric thermal analysis (DMSTA) data for PMMA-TPP slab. TPP and MMA peaks were recorded. The heating rate – 150 K/s.

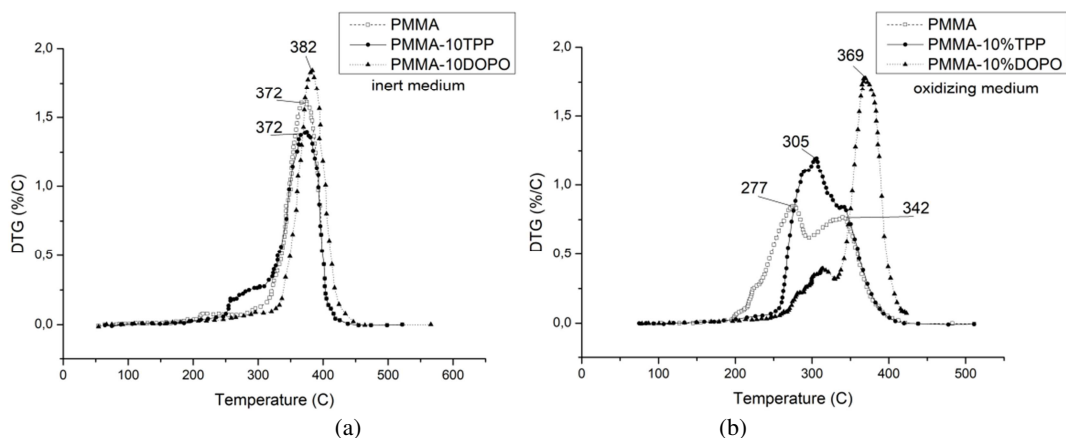


**Fig. 7.** TG curves for PMMA, PMMA-TPP and PMMA-DOPO. (a) inert media; (b) oxidizing media.

We estimated flame propagation rate over the cast PMMA, PMMA-TPP, and PMMA-DOPO slabs using the heat transfer equation [12],

$$\int_0^l q dx = \nu \rho h [H_p + C_p (T_s - T_o)], \tag{1}$$

where  $q$  is the total conductive heat flux to the surface ( $\text{W/m}^2$ ),  $\nu$  is the flame spread rate ( $\text{m/sec}$ ),  $\rho$  is the density of the solid ( $\text{kg/m}^3$ ),  $h = h_0 - h_b$  is the burned sample thickness ( $\text{m}$ ),  $h_0$  is the initial thickness and  $h_b$  is the thickness after burnout,  $l$  is the pyrolysis length along the burning surface ( $\text{m}$ ),  $H_p$  is the heat of pyrolysis ( $\text{J/kg}$ ),  $C_p$  is the heat capacity ( $\text{J}/(\text{kg}\cdot\text{K})$ ),  $T_s$  is the averaged surface temperature ( $\text{K}$ ) and  $T_o$  is the ambient temperature ( $\text{K}$ ). Measurements of the surface temperature showed that it did not change with addition of the flame retardants within the error of the experiment, being equal to about  $400^\circ\text{C}$ . Equation (1) includes radiant, conductive, and convective heat fluxes to the surface of the polymer, as well as a heat flux carried away by radiation from the surface. Since in this paper only conductive heat fluxes to the surface were measured, the estimation of the combustion rate was based on these quantities. According to the calculation, the flame propagation rate decreased by 2.7 times with addition of DOPO and by 1.7 times with addition of TPP, whereas according to the experimental data these values were 3.6 and 1.6 times, respectively.



**Fig. 8.** DTG curves for PMMA, PMMA-TPP and PMMA-DOPO. (a) inert media; (b) oxidizing media.

## CONCLUSIONS

A comprehensive experimental study of the effect of flame retardants DOPO and TPP on the flammability of cast PMMA slabs was carried out. It was found that addition of flame retardants leads to a decrease in the heat flux from the flame to the fuel, the width of the pyrolysis zone, the mass burning rate, the flame propagation velocity, the flame height, and the total heat release. It was found that in the flame front, the heat flux for samples with TPP additive is higher than for samples without additives and samples with DOPO. Due to the presence of oxygen near the flame front, it affects the rate of polymer degradation and thus the heat flux from the flame to the surface in the flame front. Moreover, for PMMA-TPP this effect is greater than for PMMA and much greater than for PMMA-DOPO. Far from the flame front, oxygen is absent, and addition of DOPO leads to decrease of the degradation rate of PMMA, whereas addition of TPP does not affect the decomposition rate of the polymer, according to TG data obtained in inert medium. This explains the dependence of the heat fluxes on the distance to the flame front for the investigated samples. Thus, it was found that TPP and DOPO affect the flammability of cast PMMA both in the gas and condensed phases.



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