

The Mass Burning Rate of Flame-Retarded Polypropylene in an Oxygen-Enriched Atmosphere

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Synopsis

Polypropylene containing a bromophosphorous flame-retardant exhibits a higher mass burning rate — in the atmosphere containing more than 30 vol % of oxygen — than nonretarded resin. These prodegradative reactions in combustion can be eliminated only by using a high concentration (ca. 40 phr) of inorganic alumina trihydrate. A method for distinguishing the physical and chemical effects of flame retardants is described.

INTRODUCTION

The flame retardants applied in polymers can influence both the chemical and physical processes of polymer combustion. When using the critical oxygen index (COI) method for evaluation of flame-retardant effects on polyolefines, we met difficulties due to the dripping of the burning polymer melt. Also in other small scale tests the melt had the possibility of dripping from a burning zone. The results obtained in such a way did not fully consider the chemical effects of flame retardants used.

The dripping of the burning polymer melt was the reason for the investigation of methods that would differentiate this physical process from the chemical effects of flame retardants. Gouinlock¹ proposed to combine the ASTM D-635 test with measuring the burning time of both 0.5 and 5 g samples placed in the ceramic crucible. A more advanced attempt came from the work of Tewarson and Pion² in developing the test for measuring the mass burning rate. Similar equipment and procedure were used also by other workers³⁻⁶ to study the various aspects of polymers combustion. In this paper we shall be concerned with the study of mass burning rate of flame-retarded polypropylene using a modified critical oxygen index method with pool configuration of burning sample.

The flame retardation of polypropylene is usually achieved by using the compositions containing antimony trioxide and halogenated compounds.⁷ Hydrates of metal oxides of aluminium, tin, zinc, and boron are used as a replacement for Sb_2O_3 and in intumescent compositions.⁸ Flame-retardant systems based on bromine and phosphorous compounds are usually more efficient. The efficiency of bromophosphorous (Br and P are in one molecule) or bromo+phosphorous (elements are in different molecules) flame retardants is, in most cases, determined by the concentration of flame retardant⁹⁻¹¹ rather than by the chemical structure of compounds used. The flammability ratings for polypropylene containing PBr types of flame retardants are usually very high (ca. 28% O_2 as COI) even at low flame

retardants concentration. To get the 3 min burning time, as prescribed by the standard ASTM D-2863 procedure, it is necessary to increase the oxygen concentration, which results in the higher COI value.

PRINCIPLES OF MASS BURNING RATE MEASUREMENT

As shown by Stuetz et al.,¹² only one experimental degree of freedom, the oxygen concentration, exists in the polymer combustion process. Tewarson and Pion² derived the following equation to describe the mass burning rate \dot{m}'' :

$$\dot{m}'' = \frac{k}{L_g} (m_{O_2})^a + \frac{Q_E - Q_L}{L_g}$$

where k = constant characterizing combustion, a = constant characterizing polymer, m_{O_2} = oxygen concentration, Q_L = heat losses, Q_E = external heat flux, and L_g = heat of gasification. According to this model, a stable mass burning rate is attained only when $Q_E \geq Q_L$, a situation which, according to Tewarson and Pion,² is not possible at the oxygen concentration in air for thick specimens when their surface areas are less than 300 cm². However, Petrella¹³ has shown that one can use data taken at enhanced oxygen concentrations to predict the relative degree of flammability of a material and to forecast its behavior in real fires.

The small and thin sample, as used for COI test, will burn as the liquid melt. For burning of liquids, Blinov and Khudakov¹⁴ found the relationship $v = a + b \cdot d^{-n}$, where v is the regression rate (cm s⁻¹), a and b are constants, d is pool diameter (cm), and n is constant characteristic of the given liquid. This relationship was confirmed, e.g., for burning of polystyrene,¹⁵ where $a = 9$, $b = 70$, and $n = 1$ (for v given in gm⁻² s⁻¹ and d in cm).

The controversy in the effect of pool diameter on the mass burning rate of liquid and solid materials has not been properly explained. The Blinov relationship does suggest that it is possible to use the smaller sample sizes with the surface areas similar to that for sample used in the COI test.

EXPERIMENTAL

(a) **Samples.** Polypropylene (Tatren TF 411, product of Slovnaft, Bratislava) was mixed with flame retardants at 200°C, and then hot pressed to form samples for flammability testing. The composition of tested samples is given in Table I.

(b) **Flame Retardants.**

— PBr type: 4,4'-bis(bromomethyl)-2,6-dioxa-1-(2,4,6 tribromophenoxy)-1-phosphacyclohexane-1-oxide, prepared accordingly to a German patent¹⁶:

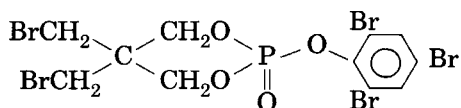


TABLE I
The Composition of Samples and Their COI^a

Sample no.	PBr (wt %)	P (wt %)	ATH (wt %)	COI (% O ₂)
PP-1	—	—	—	18.5
PP-2	2	—	—	20.5
PP-3	5	—	—	23.5
PP-4	10	—	—	27.5
PP-5	20	—	—	28.5
PP-6	5	—	10	23.5
PP-7	5	—	20	24.5
PP-8	5	—	40	25.5
PP-9	—	5	—	20.0
PP-10	—	10	—	22.0
PP-11	—	5	10	22.0
PP-12	—	5	20	22.5
PP-13	—	5	40	23.0
PP-14	—	—	10	19.5
PP-15	—	—	20	20.5
PP-16	—	—	40	22.5

^a PBr = 4,4-bis(bromomethyl)-2,6-dioxa-1-(2,4,6-tribromphenoxy)-1-phosphacyclohexane-1-oxide; P = triphenylphosphate; ATH = alumina trihydrate.

— P type: triphenylphosphate (C₆H₅O)₃P(O).

— ATH: alumina trihydrate Al₂O₃·3H₂O.

(c) Mass Burning Rate Measurement: The modified COI apparatus is shown in Figure 1. Two types of sample holders were used:

1. A platinum crucible of 16 mm in diameter, 2 mm in depth, with a surface area of 2 cm².

2. A quartz crucible of 25 mm in diameter and 3 mm in depth, with a surface area of 4.9 cm². The weight loss of burning samples was continuously monitored by using the top loading electronic balances connected through the D/A converter to a recorder. The flow rate of gases (O₂+N₂) was the same as for the COI test. The mass burning rate was taken from the linear part of the curve of burning time against the weight loss. No external heating was applied.

The flammability of samples was determined as:

1. in the standard COI configuration (ASTM D-2863);
2. in the standard COI configuration, but monitoring the weight loss during burning of sample;
3. in the pool test configuration — the weight loss monitored for the sample burned in two types of holders.

RESULTS AND DISCUSSION

The highest COI values were found for samples containing only PBr type flame retardant as shown in Figure 2. In combinations of PBr and alumina trihydrate (ATH) and triphenylphosphate + ATH only a slow rise in COI was observed with increasing ATH concentration, and a similar influence

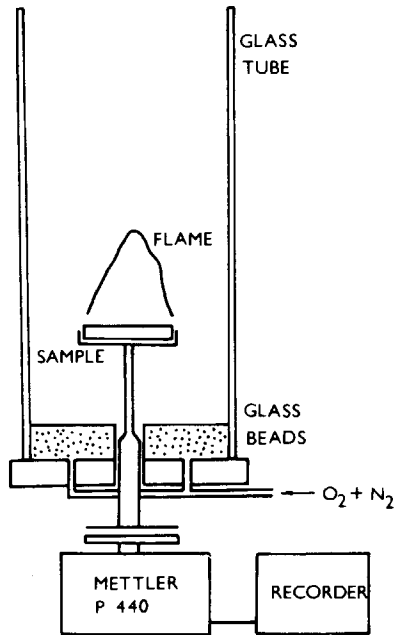


Fig. 1. The scheme of the pool configuration COI test.

was found for the individual application of ATH without additional additives.

The monitoring of the weight loss in the process of COI measurement indicates that only with the increasing oxygen concentration above COI (Fig. 3) only 15–25 wt % of the initial standard COI stick mass burned. The rest of a nonburned part of the sample dripped out as a melt. The values of the standard COI test could be positioned to the beginning of the

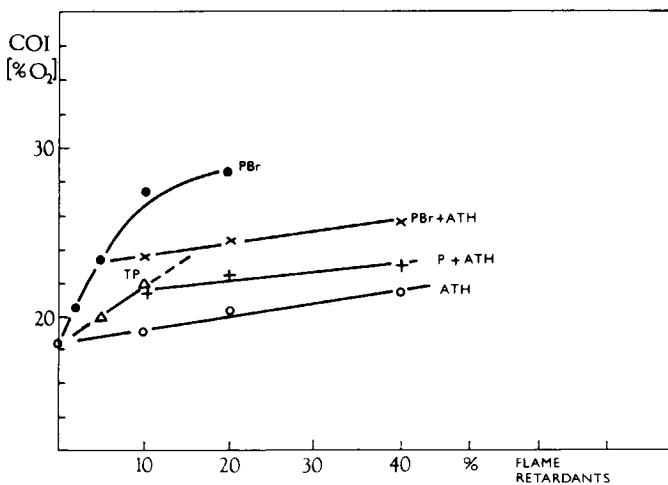


Fig. 2. The effect of the flame retardants concentration on COI of polypropylene compositions.

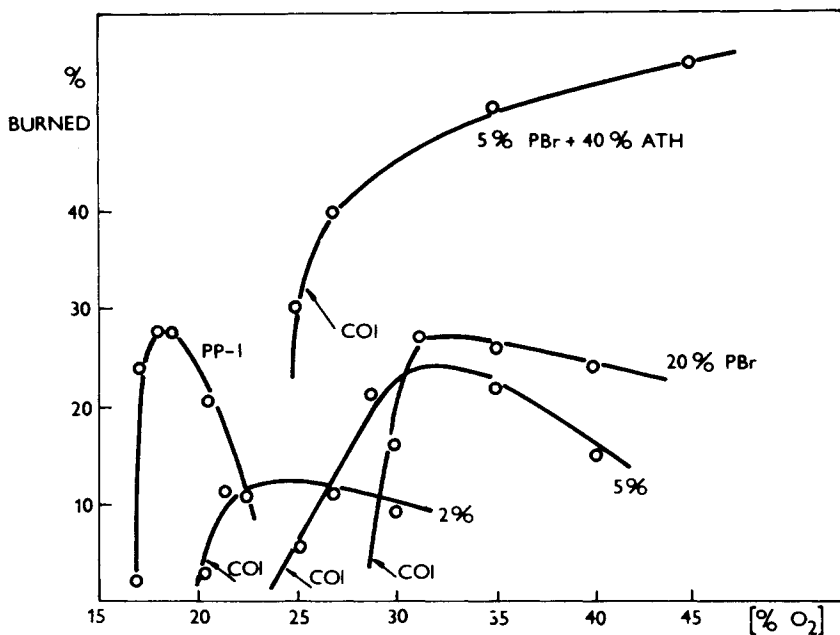


Fig. 3. The influence of oxygen concentration on quantity of the burned COI stick in the standard COI configuration flammability test.

curve (the burned part vs. oxygen concentration), i.e., only ca. 5 wt % of ca. 2 g sample was consumed by flame in the case of standard COI, applied in testing the flammability of polypropylene being modified with the PBr flame retardant. But in the combination of PBr + ATH nearly all organic material of the sample was consumed by flame during the COI test as shown on Figure 3.

The melt dripping observed during the COI measurement gives evidence of prodegradative influence of the PBr type of flame retardant. The explanation of this influence is obvious from the result shown in Figures 4 and 5 for the weight loss monitored in pool configuration of the COI test. The PBr containing samples exhibit the higher mass burning rate than the polypropylene itself (Fig. 4), which means that the fuel formation from the flame-retarded samples was increased due to the prodegradative effect of PBr.

This prodegradative effect had to be diminished by the addition of inorganic ATH, but only samples containing 40 wt % of ATH exhibited the lower mass burning rate than polypropylene. As is evident from Figure 5, this effect is more pronounced for the smaller crucible holder (2 cm²) than for the bigger one (4.9 cm²). For both types of crucibles used in the pool test the mass burning rate exhibited a linear increase with the rising oxygen concentration (up to 60% O₂) and had the asymptotic character at the higher oxygen concentrations. The sample size in 2 cm² crucible was ca. 300 mg and the burning time 60 – 150 s and S-shaped curve of the mass change vs. time was recorded. This type of the curve should be typical for all autocatalytic reactions. The formal mathematical treatment of the mea-

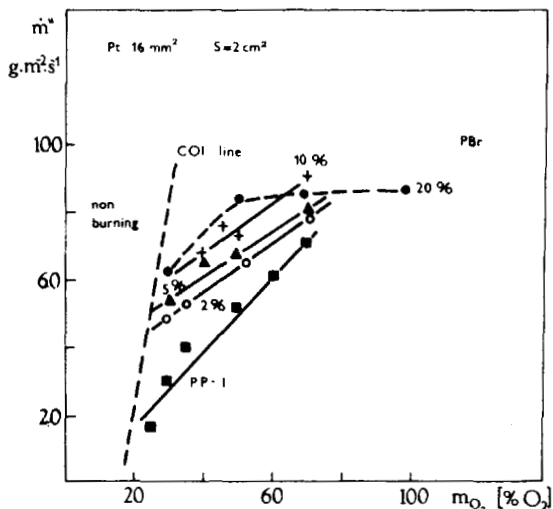


Fig. 4. The effect of oxygen concentration on the mass burning rate of flame retarded polypropylene (pool configuration in 2 cm² crucible).

sured mass burning rate curves gave good fit with the equation used in the autocatalytic reaction kinetics:

$$\alpha = \frac{k_1 \cdot (e^{k_2 \cdot t} - 1)}{k_1 \cdot e^{k_2 \cdot t} + 1}$$

where α = conversion and t = time. Coefficients k_1 and k_2 for the PBr containing samples and for burning at 50% O₂ are given in Table II.

The mass burning rate measurement carried out at oxygen concentration higher than for air should be considered as unrealistic from the point of

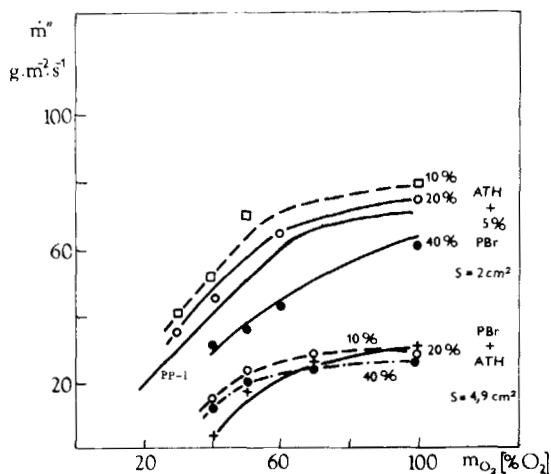


Fig. 5. The comparison of two types of crucibles applied in the burning of polypropylene flame retarded with PBr and ATH. The PBr concentration was 5 wt % in both cases.

TABLE II
Coefficients of the Autocatalytic Equation for Burning of Polypropylene Samples in the Pool Configuration (a Pt 2 cm² holder) in 50% O₂ Atmosphere

Sample no.	C (% O ₂)	$k_1 \times 10^3$	$k_2 \times 10^3$
PP-2	20.5	65.8	27.9
PP-3	23.5	73.0	32.7
PP-4	27.5	58.8	33.7
PP-5	28.5	65.3	36.2

view of conditions in the real fire. But the use of the higher oxygen concentration is only another way of increasing the heat flux from flame to the burning surface (i.e., the increase of Q_E above Q_L in the Tewarson equation). This is obviously accomplished by external heating in various fire tests. This flammability testing of polymers in the oxygen-enriched atmosphere is thus a realistic evaluation of the relative fire hazard of materials.

CONCLUSIONS

The measurement of mass burning rate in an oxygen-enriched atmosphere may give a better possibility of distinguishing both chemical and physical effects on the processes of polymer combustion and flame retardation. A bromine-containing organic phosphate, PBr, contributes to the degradation of polypropylene during the combustion process. The prodegradative effect of PBr type of flame-retardant results in the enhanced fuel formation rates. This negative effect of PBr might be eliminated by addition of alumina trihydrate into composition. The processes of the increasing rate of fuel formation and suppression are then overlapped, depending upon the ratio and concentration of both organic (PBr) and inorganic (ATH) flame retardants.

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