# The Oxygen Index Method in Fire Retardance Studies of Polymeric Materials

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#### **Synopsis**

The oxygen index test is a fundamental tool in basic research on polymer combustion and on mechanisms of fire retardance. Although the oxygen index should provide an evaluation of intrinsic flammability of polymeric materials, its response may depend on geometry of the specimen. This is shown by comparing the behavior of polypropylene fire retarded with different additive systems. The implication of such in mechanistic studies is discussed. Furthermore, new measurements are proposed to be carried out with the oxygen index apparatus, which give parameters related to ease of ignition, behavior on forced burning, and thermal insulating characteristics of char developed on burning the material.

# **INTRODUCTION**

The oxygen index test<sup>1,2</sup> (OIT) is widely recognized as a most useful tool for mechanistic studies of fire retardance in polymeric materials. As compared to the numerous tests proposed for measuring flammability of polymers, the OIT has the advantage of allowing the numerical ranking of materials by a relatively reproducible figure. The oxygen index (OI), which is the minimum concentration of oxygen in a flowing mixture of oxygen and nitrogen that supports candlelike combustion of a specimen, can indeed be measured with a relative standard deviation below 10% as shown by interlaboratory testing (ASTM-D-2863). The typical wide variability of combustion is minimized in the OIT by carrying it out in carefully controlled conditions. Specimens of defined dimensions are vertically clamped and burned downward within a glass column which ensures draft-free conditions. Oxygen and nitrogen concentrations in the ascending gaseous stream surrounding the specimen are accurately metered.

Because of the special conditions in which burning occurs, the OIT does not supply exhaustive information on the behavior of polymers in a fire. This is, however, a general limitation of small scale flammability tests that is only partially attenuated by design closely simulating conditions of exposure of the material to potential fire sources. On the other hand, the OIT should rapidly supply a quantitative measurement of the intrinsic flammability of a polymeric material. Indeed, the oxygen demand by the self-sustained combustion cycle of the polymer in the OIT should depend exclusively on its chemical-

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physical characteristics. Thus, for example, the effect of fire-retardant additives on the flammability of a polymer can be comparatively evaluated. Owing to the relatively small amount of material required by the OIT, the screening of additives at the research stage can be easily performed for further scale-up development. By the substitution of oxygen with another oxidant, usually nitrous oxide, indications can be drawn on flame poisoning action of fire retardants.<sup>2,3</sup>

The apparatus for OIT is relatively simple and can be easily built, although it is commercially available. Apart from its value in research, the OIT is acquiring increasing importance in specifications for polymeric materials, as far as flammability is concerned. However, since the introduction of the OIT about 20 years ago, several new types of fire-retardant polymeric materials have been developed whose combustion behavior may require a reconsideration of standard conditions for OI measurement. Furthermore, other measurements, besides OI, can be performed on the specimen burning in the OIT apparatus which may be useful in the characterization of flammability and combustion behavior of polymeric materials. We have examined these aspects of the OIT in relation to PP fire-retarded by three typical additive systems: halogenated systems promoting extensive dripping on burning, halogenated systems leading to flame extinction without dripping, and intumescent systems.

## EXPERIMENTAL

**Materials.** Most of the data reported here concern fire-retardant polypropylene (FR-PP) prepared by blending the additives of Table I with Moplen X30G, Himont. The tendency of the additive to decrease the melt flow viscosity of burning PP which results in dripping of molten flaming material was evaluated according to the Underwriter's Laboratories vertical burning

|      | ·····          | Additivo   |                                    |       |
|------|----------------|--|------------------------------------|-------|
| Туре | Loading (wt %) | Composition  | Burning behavior                   | UL-94 |
| A .  | 30%            | Decabromodiphenyloxide<br>(20%) + Antimony<br>trioxide (10%)   | Nondripping of<br>flaming material | V-0   |
| В    | 4%             | Melamine hydrobromide<br>(3.5%) + 2,3dimethyl,2,3<br>diphenyl butane (0.25%)<br>Antimony trioxide (0.25%)<br>or Basic bismuth<br>carbonate (0.25%) | Dripping of<br>flaming material    | V-2   |
| С    | 30%            | Ammonium polyphosphate<br>(20%) + Ethylenurea-<br>formaldehyde polycondensate<br>(10%)   | Intumescent                        | V-0   |

TABLE I Fire-Retardant Polypropylene (FR-PP)

<sup>a</sup>Specimen thickness 1/16 in.

test (UL-94).<sup>4</sup> FR-PP type C burns with formation of a swollen char on the surface of the specimen that is a typical "intumescent" behavior.

**Oxygen Index Apparatus.** The measurements were carried out using a Stanton-Redcroft apparatus.

# **RESULTS AND DISCUSSION**

### **Effect of Ignition Time**

The ASTM method for measuring OI states that the entire top section of the specimen must be ignited by the ignition flame till the specimen is well lighted. The flame is then removed, and the time of burning measured. The OI is the concentration of oxygen at which a self-supporting plastic specimen such as PP burns at least 3 min or 50 mm.

The thermal energy supplied to the specimen during ignition is likely to exceed the heat required for self-sustaining combustion at the minimum oxygen concentration. The energy excess that is not dissipated is stored by the specimen and depends on the length of ignition time which is not defined by the ASTM method. The data of Table II show that, for the three additives of Table I, OI is independent of ignition time within the time interval normally used (5–15 s, maximum  $\Delta OI = 3.5\%$ ). This is probably due to elimination of excess energy within a time much shorter than the combustion time corresponding to the OI value (3 min). However, if short combustion times have to be reproducibly measured ( $\leq 5$  s, see below) it is advisable to fix the ignition time (e.g., 10 s).

#### **Effect of Specimen Geometry**

We have studied the effect of the dimensions of bars used to measure OI, by varying their cross-sectional area in the range 9–90 mm<sup>2</sup>, which encompasses that allowed by the ASTM method 15–22.8 mm<sup>2</sup> (width  $6.5 \pm 0.5$  mm, thickness  $3.0 \pm 0.5$  mm). The OIs obtained on bars of constant ASTM thickness (3 mm) and increasing width (3–30 mm) are reported in section I of Table III and in Figure 1. It is shown that, within experimental error, OI is independent of cross-sectional area in the case of FR-PP (A), whereas OI of FR-PP types B and C increases with increasing cross-sectional area to about 30 mm<sup>2</sup> above which it is constant. Increase of OI with cross-sectional area was also observed for other intumescent systems.<sup>5,6</sup>

| Ignition time | Oxygen index |      |      |  |
|---------------|--------------|------|------|--|
| <b>(s)</b>    | Α            | В    | С    |  |
| 5             | 27.0         | 29.4 | 36.4 |  |
| 7             | 27.1         | 30.0 | 37.0 |  |
| 10            | 27.4         | 30.0 | 37.2 |  |
| 15            | 27.0         | 29.0 | 36.8 |  |

TABLE II Oxygen Index as a Function of Ignition Time<sup>a</sup>

<sup>a</sup>Specimen: FR-PP, cross section  $6 \times 3$  mm.

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| Width  | Thickness<br>T (mm)                   | W/T  | Area<br>(mm <sup>2</sup> ) | Oxygen index |      |      |
|--------|---------------------------------------|------|----------------------------|--------------|------|------|
| W (mm) |                                       |      |                            | A            | В    | С    |
| I      | · · · · · · · · · · · · · · · · · · · |      |                            |              |      |      |
| 3      | 3                                     | 1    | 9                          | 26.9         | 26.3 | 35.4 |
| 6      | 3                                     | 2    | 18                         | 27.1         | 29.0 | 37.0 |
| 9      | 3                                     | 3    | 27                         | 27.2         | _    | 37.7 |
| 12     | 3                                     | 4    | 36                         | 27.3         | 29.5 | 38.1 |
| 20     | 3                                     | 6.7  | 60                         | 27.0         | 29.5 | 36.9 |
| 30     | 3                                     | 10   | 90                         |              | 29.5 | _    |
| II     |                                       |      |                            |              |      |      |
| 8.6    | 7                                     | 1.2  | 60                         | 26.4         | 31.5 | 35.8 |
| 12     | 5                                     | 2.4  | 60                         | 27.0         | 30.5 | 36.0 |
| 20     | 3                                     | 6.7  | 60                         | 27.0         | 29.5 | 36.9 |
| 25     | 2.4                                   | 10.4 | 60                         | 27.2         | 28.5 | 42.5 |

TABLE III Dependence of OI of FR-PP on Specimens Geometry

As far as the ASTM method is concerned, reproducibility should be ensured by the relatively narrow range of specimen cross-sectional area allowed. For example, in the cases of FR-PP types B and C, a maximum variation below 3% is found for OI measured with specimens whose cross-sectional area falls within the ASTM range. However, it is evident that OI might fail to supply a measurement of the intrinsic flammability of fire-retardant polymeric materials. For example, the oxygen demand for combustion of FR-PP (B) may be larger or smaller than that of FR-PP (A) depending on whether specimens of cross-sectional area above or below 10 mm<sup>2</sup> are respectively used (Fig. 1). On the other hand, the dependence of OI on cross-sectional area may give useful indications on mechanism of combustion and fire retardance of polymers. OI is expected to be independent of specimen geometry in the model for polymer combustion based on thermal degradation of the polymer to volatile combustible products sustained by heat supplied by the flame.<sup>3</sup> In conditions of self-sustained combustion, larger specimens would indeed supply a larger



Fig. 1. OI as a function of cross-sectional area of PP bar specimen: (①) FR-PP (A); (①) FR-PP (B); ( $\bigcirc$ ) FR-PP (C).

amount of combustible products to the flame which feeds back a larger amount of heat to the polymer to sustain its decomposition. The above data show that the behavior of FR-PP (A) complies with this model whereas apparently FR-PP types B and C do not. A common feature concerning FR-PP types B and C is the dependence of their burning behavior on occurrence of physical processes such as extensive dripping or intumescence respectively which are absent in the case of FR-PP (A). Thus it is likely that the OI of FR-PP types B and C depends on specimen geometry because of its effect on the occurrence of such physical processes. This interpretation can be supported by data published by Stuetz et al.<sup>7</sup> on OI of pure PP measured on downward burning rods. The OI of PP, which burns with dripping, was found to increase continuously from 17.3 to 22.0 by increasing the cross-sectional area of rods from 5 to 500 mm<sup>2</sup>. When dripping was suppressed by incorporating a wick in the PP specimen a constant OI was measured for rods of cross-sectional area 5-60 mm<sup>2</sup>, which increased by only 4% (17.2-17.9) by further increasing cross-sectional area to 500 mm<sup>2</sup>. Stuetz et al.<sup>7</sup> attributed the dependence of OI on the cross-sectional areas of wickless PP rods to the occurrence of partial thermal oxidation of the polymer which would supply the heat necessary to sustain its thermal degradation. In this alternative model for PP combustion the heat supplied by the flame would be negligible as compared to that evolved by thermal oxidation in the condensed phase.<sup>7-9</sup> Furthermore, this model implies the dependence of OI on oxygen diffusion to the surface of the burning specimen through the flame which, in turn, depends on specimen geometry. Applicability of pure thermal or thermal oxidative models is still a debated matter and should depend on many factors such as type of polymer, type of fire retardant, and conditions of burning.<sup>10</sup> Thus, the substantial constancy of OI of wick-containing PP rods, whose cross-sectional area varies over 2 orders of magnitude (5-500 mm<sup>2</sup>),<sup>7</sup> seems in contrast with the expected corresponding variation of oxygen access to the surface of burning rods. The above interpretation of these results, based on suppression of dripping by the wick, seems reasonable.

The OI of polymeric materials such as FR-PP types B and C, whose combustion is affected by physical processes does not depend solely on cross-sectional area of the specimen. This was shown by measuring OI on bars of variable width and thickness and constant cross-sectional area  $60 \text{ mm}^2$  that is in the range in which no further effect of specimen geometry is apparent in Figure 1 (> 30 mm<sup>2</sup>). The data reported in section II of Table III confirm the independence of OI of FR-PP (A) on specimen geometry and show that OI of FR-PP (B) tends to decrease with increasing width to thickness ratio of the specimen whereas that of FR-PP (C) tends to increase. Further investigations are necessary to interpret in terms of mechanism the complicated relationship between specimen geometrical factors and occurrence of dripping and intumescence.

#### **Ease of Ignition from Self-Quenching Times**

Determination of OI requires measurements of the time interval between removal of the ignition flame and extinction of the burning specimen. This is the "self-quenching time"  $(SQT)^{7,11}$  which is measured as a function of oxygen



Fig. 2. Self-quenching time as a function of oxygen concentration for poly(ethylene terephtalate) (PET) ( $\bigcirc$ ) and PET added with red phosphorus: (**①**) P = 2%; (**④**) P = 4%. Plot from data of Ref. 11.

concentration  $(OC)^7$  in the stream of nitrogen-oxygen surrounding the specimen. Typical OC-SQT plots of Figures 2 and 3 can be separated into two successive regions of approximately linear dependence of OC on SQT. In the first region a larger increase of OC is required to increase SQT than in the second. The transition between the two regions, which has been attributed to transition from unstable to stable burning,<sup>11</sup> generally occurs at SQT < 60 sec., depending on type of polymer and fire retardant additive. The OC corresponding to OI as defined by ASTM (SQT = 3 min or burned length = 5 cm) falls in the second region. Very often OI is only slightly larger than the OC corresponding to transition to stable burning since, above this point, a little increase of OC generally induces a relatively large increase of SQT<sup>7,11</sup> (Figs. 2 and 3, Table IV).

Another parameter which could be calculated from the data collected to measure OI is the OC corresponding to SQT = 0. This parameter would have the physical meaning of the minimum oxygen concentration above which ignition of the material is just possible. By analogy with OI we term this parameter "ignition oxygen index" (IOI) which might give an indication of ease of ignition of a material. IOI is obtained by extrapolation of OC data to  $SQT \rightarrow O$  in the first region of OC-SQT linear dependence, before transition to stable burning. To obtain reproducible IOI values, extrapolation should essentially be based on OC data corresponding to SQT > 5 s (after 10 s ignition) since combustion times below 5 s might not be reproducible. By definition, OI > IOI but Figures 2 and 3 and Table IV show that the difference OI – IOI depends on type of polymer and of fire retardant. For



Fig. 3. Self-quenching time as a function of oxygen concentration: ( $\blacksquare$ ) PP; ( $\bigcirc$ ) FR-PP (A); ( $\bigcirc$ ) FR-PP (B); ( $\circ$ ) FR-PP (C). Underlined points correspond to specimens burned more than 5 cm. Specimens, bars  $3 \times 6.5 \times 130$  mm.

example, in the case of PP, the gap between IOI and OI is quite narrow (OI - IOI = 1.7, Table IV), which means that OC necessary for ignition is close to that for steady burning. In the case of poly(ethylene terephtalate) (PET), the gap is larger (3.9); thus, although PET is characterized by an OI larger than that of PP (20.4 and 17.7, respectively, Table IV), ease of ignition for the two polymers should be comparable (IOI = 16.0 and 16.5, Table IV). Similarly, the OI of PET increases with increasing concentration of fire

| Burning Characteristics in the Oxygen Index Test |        |        |        |        |        |                   |
|--|--------|--------|--------|--------|--------|-------------------|
|  | SQT, * |        |        | IOI*   | BOIª   | $ABR \times 10^2$ |
| Sample   | (s)    | OC (%) | OC (%) | OC (%) | OC (%) | [cm/(s OC%)]      |
| PET <sup>b</sup>                                 | 20     | 20.1   | 20.4   | 16.5   | 17.1   | 0.58              |
| PET + 2% P <sup>b</sup>                          | 20     | 24.0   | 25.1   | 21.8   | 21.8   | 1.17              |
| PET + 4% P <sup>b</sup>                          | 11     | 26.3   | 27.6   | 21.8   | _      | _                 |
| PP   | 12     | 17.2   | 17.7   | 16.0   | 17.0   | 1.67              |
| FR-PP (A)  | 26     | 23.6   | 26.3   | 20.0   | 25.0   | 0.67              |
| FR-PP (B)  | 33     | 27.5   | 27.5   | 22.6   | 23.5   | 3.08              |
| FR-PP (C)  | 30     | 31.5   | 32.1   | 18.0   | 24.0   | 0.63              |

TABLE IV

<sup>a</sup>SQT<sub>t</sub> = transition self-quenching time from unstable to stable burning; OI = oxygen index; IOI = ignition oxygen index; BOI = burning oxygen index;  $\Delta BR$  = incremental ratio burning rate/oxygen concentration.

<sup>b</sup>PET = Poly(ethylene terephtalate); data from Ref. 11.



Fig. 4. Correlation IOI-OI for FR-PP (B): ( $\bullet$ ) metal compound basic bismuth carbonate; ( $\circ$ ) antimony trioxide.

retardant red P to 4%, whereas ease of ignition seems to be independent of P concentration between 2-4% (Fig. 2, Table IV). Furthermore, different fire retardant additives may affect differently the OI and IOI of the polymer. For example, in the case of PP the ratio increase of OI/increase of IOI is 2.2 and 1.5, respectively, for additives of types A and B of Table I whereas it is 7.2 for that of additive C. Thus, although the OI of FR-PP (C) is larger than that of FR-PP (A) and FR-PP (B), the first is easier to ignite.

Within a class of fire retardant additives, IOI generally tends to increase with OI as shown in Figure 4 in the case of FR-PP (B) in which OI was varied either by varying the overall amount of additive or by modifying the ratio between brominated compound and metal compound. The relationship IOI vs. OI can be approximated by a straight line, whose correlation coefficient calculated by least square method (Table V) is, however, not high: 0.958. Scattering of experimental values of Figure 4 shows indeed that ease of ignition as measured by IOI is a specific characteristic of the material which may not be deduced from OI even in the same class of fire-retardant additive.

As far as fire hazard is concerned, IOI can be useful, although it does not concern the occurrence of stable burning. In fact, the establishment of the flame on a polymeric material even for a short time may have deleterious

| Oxygen Index Apparatus on FR-PP (B) <sup>a</sup> |     |       |           |             |
|--|-----|-------|-----------|-------------|
| Parameters <sup>b</sup>                          |     | Slope | Intercept | Correlation |
| у  | x   | a     | Ь         | coefficient |
| 101  | OI  | 0.914 | 0.043     | 0.958       |
| ΔBR  | OI  | 0.280 | -2.82     | 0.633       |
| IOI  | BOI | 0.890 | 1.57      | 0.889       |

TABLE V Linear Least-Squares Regression Data for Parameters Measured in the Oxygen Index Apparatus on FR-PP (B)<sup>a</sup>

<sup>a</sup>Straight line: y = ax + b.

<sup>b</sup>OI = oxygen index; IOI = ignition oxygen index;  $\Delta BR$  = incremental ratio burning rate/oxygen concentration; BOI = burning oxygen index.

consequences. For example, the material may degrade and become less fireresistant, the short-lived flame may survive long enough to reach adjacent materials or structures thereby contributing to fire propagation, etc. There are indeed specific tests designed to measure ignitability of polymeric materials. The measurement of IOI is not intended as a substitute for such tests. Its use could be that of giving an indication on ignitability while SQTs are measured for OI determination when equipment for ignition tests is not available. Furthermore, during this work it was realized that measurement of OI can be subjective with materials which extensively drip on burning such as FR-PP (B). In these cases the specimen tends to burn faster on the sides than in the center and it assumes a conical-like shape. The measurement of length of material burned depends then on whether the base or the top of the cone is considered which is not specified in ASTM method. This choice affects the evaluation of OI because these materials burn at high rates, thus involving length of specimen burned rather than time of combustion as a criterion for OI measurement [Fig. 3, FR-PP (B)]. For such materials, comparisons based on IOI, which depends on measurements of time of burning, could be more objective.

#### **Burning Rate**

Burning rate (BR) as a function of OC is easily measured in the OIT apparatus by measuring time required by the flame front to cross marks at fixed distance on the specimen. To obtain reproducible data, we measured times > 30 s which correspond to a burned length of 2–3 cm, depending on the polymer and fire retardant. Obviously, BR can be measured only in stable burning conditions, that is, for increasing OC starting close to OI.<sup>11</sup> Therefore, BR of fire retardant polymers must be measured at OC  $\gg 21$  which is unrealistic from the point of view of real fire where oxygen depletion conditions (OC < 21) generally exist. However, forced burning by large OC may simulate forced burning under large heat transfer in a real fire.

Figure 5 shows that BR increases linearly with OC either for PP or for fire retardant PP of Table I as it was shown by Granzow and Cannelongo<sup>11</sup> for PET and phosphorus-containing PET. Increase of BR with OC ( $\Delta$ BR) is larger for FR-PP (B) than for PP (Table IV). Thus, at OC > 31, FR-PP (B) burns at a larger rate than PP. A similar situation was found for phosphorus-retarded PET at OC > 26.5 (Table IV).<sup>11</sup> In contrast, FR-PP (A) and FR-PP (C) burn at a much lower rate than PP even at large OC. Correlation  $\Delta$ BR vs. OI is very poor (0.633) even for the same class of fire retardants as shown in Table V. Therefore, the relative behavior of polymeric materials may be different, depending on whether it is compared in conditions of OI measurements or under forced burning.

Extrapolation of linear relationship BR vs. OC to BR = 0 should give the minimum OC at which burning may just take place at a measurable rate. By analogy with above definitions we term this parameter "burning oxygen index" (BOI) which should be comparable to IOI discussed above. Data of Table IV show that BOI may be close to IOI [PET, PET + P, PP, FR-PP (B)] or it may be considerably larger [FR-PP (A), FR-PP (C)], depending on polymer and fire-retardant additive. Within the same class of fire retardants



Fig. 5. Burning rate of: (**D**) PP; (**O**) FR-PP (A); (**O**) FR-PP (B); (O) FR-PP (C). Specimens, bars  $3 \times 6.5 \times 130$  mm.

IOI tends to increase with BOI as shown in Figure 6, but the correlation is quite poor: 0.889 (Table V). Lack of tight correlation between IOI and BOI might depend on the fact that BOI is measured by extrapolating the behavior in steady burning conditions to conditions in which burning may not be stable whereas IOI is directly measured in these last conditions. As far as reproducibility is concerned, BOI is, however, more satisfactory and requires in general lesser measurements than IOI.



Fig. 6. Correlation IOI-BOI for FR-PP (B): ( $\bullet$ ) metal compound basic bismuth carbonate; ( $\circ$ ) antimony trioxide.

#### Thermal Insulating Effect in Intumescent Systems

The fire retardant action of intumescent additives is attributed to the insulating action of the swollen char they form on the surface of the burning polymer.<sup>10, 12, 13</sup> A twofold insulating action was suggested: thermal and mechanical. The first should limit heat transfer from the flame to the polymer whereas the second might hinder evolution of the combustible products of degradation to the flame or might hinder access of oxygen to the surface of the polymer. This last effect would be of importance only if the thermal oxidative model of polymer combustion is valid.

The thermal insulating effect can be evaluated separately by measuring the temperature of the material below the charred layer by means of a thermocouple. In previous reported methods such measurements were carried out either on bars burning in the OIT apparatus at an OC slightly larger than OI<sup>14</sup> or on pellets exposed to an impinging flame in air.<sup>6</sup> Details of conditions or design were, however, not reported. We have carried out temperature measurements on ASTM bars for OI which are exposed to a flame in air in the OIT apparatus.

Exposure to an external flame in air was preferred to self-sustained burning at  $OC > OI^{14}$  since in these last conditions the fire retardant action of the additive is overwhelmed by the large OC. Therefore, the insulating action of the char would not be measured in conditions in which it plays its role in interrupting the combustion process. On the other hand, OI bars were preferred to pellets<sup>6</sup> in order to evaluate the insulating effect in the same conditions in which OI is measured which it has been shown above to depend on geometry of the specimen.

The setup of the measurement is illustrated in Figure 7. A Chromel-Alumel thermocouple (0.5 mm) is embedded in the specimen by compression molding of two half-thickness bars  $(1.6 \times 6 \times 100 \text{ mm})$  among which the thermocouple is sandwiched. The distance between the thermocouple and the top of the bar (5 mm) is controlled by means of a groove in the mold in which the wires to the recorder are seated. The butane torch supplied with the commercial OIT instrument is fixed by an external mobile support at a height corresponding to a distance of 15 mm from the base of the flame to the top of the bar. Prior to measurement, the igniter is extracted from the glass chimney, ignited, and the length of the flame regulated to 20 mm (max  $T = \text{ca. } 1000^{\circ}\text{C}$ ). The igniter

Fig. 7. Setup for temperature-time measurements in the oxygen index test apparatus: (a) specimen; (b) thermocouple; (c) igniter; (d) glass chimney; (e) flame. Measures in mm.



| No. |      | Additive       |   |  |  |
|-----|------|----------------|---|--|--|
|     | OI   | Loading (wt %) | Composition   |  |  |
| 1   | 36.5 | 30             | Ammonium polyphosphate (20%) +<br>pentaerythritol (10%) |  |  |
| 2   | 35.0 | 30             | Melamine phosphate (20%) +<br>pentaerythritol (10%)     |  |  |
| 3   | 25.5 | 12.5           | Ammonium polyphosphate +                                |  |  |
| 4   | 31.5 | 25             | ethylenurea-formaldehyde                                |  |  |
| 5   | 47.5 | 37.5           | polycondensate  |  |  |
| 6   | 61   | 50             | Weight ratio $= 2:1$                                    |  |  |

TABLE VI Intumescent Fire-Retardant Polypropylene (IFR-PP)

is then introduced in the chimmey in the fixed position and recording is started. With this setup, if the material is completely consumed, the thermocouple will touch the tip of the flame.

Temperature-time curves of samples of intumescent fire retardant PP (IFR-PP) of Table VI are reported in Figure 8. The curves are averaged over several measurements. Reproducibility of the curves depends on reproduc-



Fig. 8. Temperature-time dependence for intumescent fire-retardant polypropylene. Samples of Table VI:  $(- \cdot -) 1$ ;  $(- \cdot ) 2$ ;  $(- \cdot -) 3$ ; (- -) 4; (- -) 5;  $(- \cdot -) 6$ .

ibility of the intumescent effect. Occasionally, when a very voluminous char is formed, it may bend under its own weight and eventually fall exposing the thermocouple to the flame. These measurements were discarded. In Figure 8(a) IFR-PP (3-6) containing increasing amounts of the same additive are compared. IFR-PP (3), which contains the lowest amount of additive (OI = 25.5), does not show any thermal insulating effect in the above conditions since its temperature-time curve is identical with that obtained with pure PP. Within 1-2 min the polymer is consumed and the thermocouple exposed to the flame. In the case of IFR-PP (4-6) the thermal insulating effect is shown by the rate of increase of temperature which is inversely proportional to amount of additive. For example, after 4 min exposure, specimens of IFR-PP (4-6) reach 350, 250, and 125°C, respectively [Fig. 8(a)]. Since the effectiveness of the thermal insulating effect parallels the increase of OI, it is likely that the fire-retardant action of the additive is mostly based on this physical action. On prolonged exposure to the flame, the char is likely to undergo partial thermal degradation losing insulating effectiveness. After about 10 min the char still acts as a thermal insulator since an equilibrium temperature of 340-425°C is reached which seems, however, independent of OI.

In Figure 8(b) temperature-time curves of IFR-PP (1, 2, and 4) concerning different intumescent systems added at about the same level (25-30%) to PP are compared. It can be seen that in IFR-PP (1 and 2) the temperature raises at the same rate in agreement with the fact that they are characterized by a comparable OI (35-36.5). The initial rate of temperature increase is somewhat larger for IFR-PP (4) whose OI is lower (31.5). The equilibrium temperature which falls within the range  $375-430^{\circ}$ C for the three additives is not correlated with OI and might depend on the type of additive. This might be reasonable since intumescence occurs shortly after exposure to the flame begins whereas equilibrium temperature involves the thermal resistance of the resulting char.

By modifying the setup of Figure 7, different temperature-time curves are obtained. Optimum conditions for the characterization of thermal insulating properties of intumescent systems might depend on the type of additive. By using the basic setup of Figure 7 measurements can be also carried out as a function of OC.

# CONCLUSIONS

In the case of some fire-retardant additives, OI fails to provide an evaluation of the intrinsic flammability of the polymeric material to which they are added. This seems to be the case of additives which modify the physical behavior of the burning polymer, for example, by promoting dripping or intumescence.

On the other hand, by expanding the measurements to be carried out with the OI apparatus, a more complete appraisal of the combustion behavior of fire-retardant polymeric materials can be performed. New measurements may include the use of specimens of variable geometry and evaluation of selfquenching time or combustion rate vs. oxygen concentration from which parameters related to ease of ignition or behavior on forced burning may be evaluated. Furthermore, in the case of intumescent or charring systems, thermal insulating characteristics of the char developed on the surface of burning specimen may be evaluated by using the OIT apparatus.

The interest in measuring with OIT apparatus as many parameters related to the combustion of fire-retardant polymeric materials as possible is twofold. The OIT is a basic apparatus generally available when polymer flammability is dealt with. Furthermore, all the data which are collected refer to combustion carried out under identically controlled conditions. This confers reliability to correlations found between the estimated parameters to be used in mechanistic studies of fire retardance.

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