

Ignition Properties of Polymers Evaluated from Ignition Temperature and Ignition Limiting Oxygen Index

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Synopsis

An apparatus for measuring ignition temperature and ignition-limiting oxygen index was devised in order to study ignition properties of polymers. Ignition limiting oxygen index, which was suggested by the limiting oxygen index (ASTM D2863-70), was defined as the minimum volume fraction of oxygen required for ignition to occur in a slowly rising gaseous atmosphere. The ignition temperatures and the ignition limiting oxygen indexes of typical polymers were measured by this apparatus. Polymers which produced more ethylene by pyrolysis tend to have lower ignition temperatures. In the case of the same kinds of polymers, plots of ignition temperatures versus ignition limiting oxygen indexes gave nearly straight lines (Fig. 3), but the straight line of depolymerization-type polymers differed from that of random degradation-type polymers. In most polymers, ignition limiting oxygen indexes were nearly proportional to limiting oxygen indexes, but in the cases of hard poly(vinyl chloride) and soft poly(vinyl chloride), the plots did not follow this relation (Fig. 4). Ignition properties of self-extinguishing polymers were also studied.

INTRODUCTION

The knowledge of the flammability of polymers has been receiving increasing attention as a serious problem related to product safety.

A variety of techniques used in evaluating flammability of polymers has been described.¹⁻⁵ In many of these, a sample of specified geometry is ignited. After the ignition source has been removed, time or distance burned before extinction, burning rate, and limiting oxygen index (the minimum concentration of oxygen in a mixture of oxygen and nitrogen that will just support flammability) have been used to measure flammability.

Ease of ignition (ignition property) is considered to be one of the most important flammability properties. The ignition properties of polymers have been measured mainly at temperatures at which ignition will just occur, such as self-ignition temperature (if a specimen is exposed to heat without flame), flash-ignition temperature (if a specimen is exposed to direct flame), and time from exposing⁶ or touching⁷ a specimen to some heat source until it ignites.

We found that ignition properties of polymers could also be evaluated from the ignition limiting oxygen index, suggested by the limiting oxygen index, which is defined as the minimum volume fraction of oxygen in a slowly rising gaseous atmosphere in which ignition will occur under a fixed condition of heat. Therefore, an apparatus for not only measuring ignition temperature but also the ignition limiting oxygen index was devised. The ignition temperatures and the ignition limiting oxygen indexes of typical polymers and some self-extin-

guishing polymers were measured. The relationship between the ignition temperatures of the polymers and the components of their gaseous pyrolyzates was investigated. The relationships between ignition temperature and ignition limiting oxygen index and between ignition limiting oxygen index and limiting oxygen index were also investigated.

EXPERIMENTAL

Test Apparatus

An apparatus for ignition temperature and ignition limiting oxygen index was devised (Fig. 1). This apparatus consists of a combustion unit and a gas supply unit. The combustion unit is equipped with an electric furnace (A), a quartz combustion tube (B) with inside diameter 53 mm and length 210 mm, a quartz inner tube (C) with inside diameter 42 mm and length 130 mm, a connection tube (D), quartz beads (E) with diameters 3 mm and lengths 5–7 mm, and thermocouples (F) and (G). The quartz inner tube (C) was placed inside the quartz tube (B) and positioned on the quartz beads (E). Quartz was used because its surface is considered to have no catalytic effect when polymers are pyrolyzed. The connection tube (D) is used only when the ignition limiting oxygen index is measured. The thermocouple junctions, which are positioned at the middle of the electric furnace (A), are placed at the point of the highest temperature in the combustion chamber (H). The gas supply unit is equipped with gas flowmeters (M) and (N) for nitrogen and oxygen, a gas mixing tube (J), and a gas flowmeter (L) for the oxygen–nitrogen mixture (a flowmeter for air was used in this experiment).

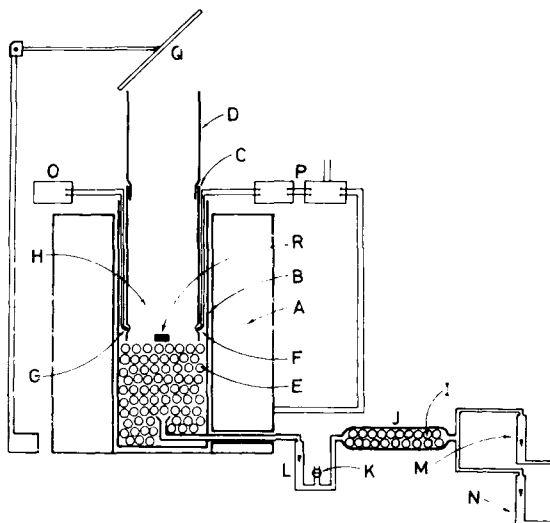


Fig. 1. Ignitability test apparatus: (A) electric furnace; (B) quartz; (C) quartz inner tube; (D) connection tube; (E) quartz beads; (F) and (G) thermocouples; (J) gas mixing tube; (K) leak valve; (L), (M), and (N) flowmeters; (O) thermometer; (P) temperature controller; (Q) mirror; (R) specimen.

Procedure

For ignition temperature measurement, the apparatus is operated in the following sequence: A predetermined specimen (a chip 0.1 g in weight) is dropped into the combustion chamber after a selected temperature has reached equilibrium, and the check for ignition is made through mirror (Q). If ignition occurs or does not occur, the temperature in the combustion chamber is lowered or raised, respectively, and the test is repeated. The lowest temperature at which ignition occurs is the ignition temperature.

For measuring the ignition limiting oxygen index, the apparatus is operated as follows: An oxygen-nitrogen mixture, maintained at a desired initial concentration of oxygen, is introduced into combustion chamber (H) which is heated to a fixed temperature at a fixed flow rate. A predetermined specimen (a chip weighing 0.1 g) is dropped into the combustion chamber and checked for ignition. The connection tube (D) is placed on the quartz inner tube immediately after the specimen is dropped. If the connection tube is not attached, even if the specimen does not ignite in the combustion chamber, the extreme heat of the combustion chamber, and the high concentration of oxygen (ca. 21%) at the top of the combustion chamber cause the specimen to ignite. The top of the connection tube is cool because it is far from the combustion tube; thus, the specimen does not ignite even with the high concentration of oxygen. If the specimen ignites or does not ignite, the concentration of oxygen is lowered or raised, respectively, and the test is repeated. The minimum concentration of oxygen at which the specimen will ignite is the ignition limiting oxygen index.

In the case of self-extinguishing polymers which contain an inorganic additive, deposits remain on the quartz beads. These deposits were removed by suction while the quartz beads were in the combustion chamber. However, a very small quantity of deposits which cannot be removed by this method remains on the quartz beads. Therefore, when temperatures vary beyond a given amount ($\pm 1^\circ\text{C}$), all quartz beads in the combustion chamber are removed and cleaned.

Polymers

The following polymers were used: (1) polyethylene (PE), (2) polypropylene (PP), (3) soft poly(vinyl chloride) (s-PVC), (4) hard poly(vinyl chloride) (h-PVC), (5) polyoxymethylene (POM), (6) nylon 66 (N-66), (7) polystyrene (PS), (8) poly(methyl methacrylate) (PMMA), (9) acrylonitrile-butadiene-styrene copolymer (ABS), (10) acrylonitrile-styrene copolymer (AS), (11) polycarbonate (PC), (12) polyurethane (PU), (13) urea resin (UR), (14) phenol resin (PR), and (15) melamine resin (MR). These polymers are all commercially available and do not contain additives such as fillers, plasticizers, pigments, etc. Sixteen self-extinguishing polymers were also used: 11 high-impact polystyrenes modified by addition of halogen-containing compounds or halogen-containing compounds and antimony trioxide as a synergist with the halogens; two kinds of ABS blended with PVC; and three kinds of polypropylenes modified by addition of halogen-containing compounds and inorganic flame retardants.

RESULTS AND DISCUSSION

Ignition Temperatures of Polymers

The ignition temperatures of typical polymers measured by the apparatus described above are shown in Table I. These values were all measured under the predetermined conditions of a sample weight of 0.2 g and air flow rate of 2.1 l./min. These conditions yielded the minimum ignition temperatures for PE, PMMA, and h-PVC. The reproducibility of the results was within $\pm 1^\circ\text{C}$.

The ignition temperatures of the polymers ranged from 430°C for polyethylene to higher than 700°C for melamine resin (Table I). It was found (Fig. 2) that the polymers which produced more ethylene by pyrolysis tend to have lower ignition temperatures. This is consistent with the fact that the ignition temperature of ethylene is lower compared with the other gaseous pyrolyzates produced. The pyrolysis was carried out using 25 mg polymer in the pyrolysis tube with a volume of 100 ml at $\frac{1}{2}$ atm and 600°C for 30 min. The gaseous pyrolyzates were analyzed quantitatively by gas chromatography and infrared spectrophotometry.

The reason why the ignition temperatures of depolymerization-type polymers such as POM, PMMA, and PS were much higher than might be expected from their other flammability characteristics is understandable in light of the following: When POM, PMMA, and PS are pyrolyzed, formaldehyde, methyl methacrylate, and styrene, all of which have ignition temperatures higher than ethylene, are generated to a greater degree while ethylene is generated to a lesser degree.

TABLE I
Ignition Temperatures of Polymers

Polymer	Ignition temp., $^\circ\text{C}$	Time lag, sec
Polyethylene	430	130
Polypropylene	440	120
s-Poly(vinyl-chloride) ^a	441	46
Polyoxymethylene	488	114
Nylon 6	489	83
Nylon 66	492	109
h-Poly(vinyl-chloride)	502	69
Polystyrene	518	51
Poly(methyl methacrylate)	520	42
ABS ^b	530	49
AS ^c	542	32
Polyurethane	552	16
SE-PVC ^d	571	5
Polycarbonate	580	65
Phenol resin	614	69
Urea resin	630	68
Melamine resin	729	71

^a Poly(vinyl chloride) + dioctyl phthalate (50 phr).

^b Acrylonitrile-butadiene-styrene copolymer.

^c Acrylonitrile-styrene copolymer.

^d Poly(vinyl chloride) + Sb_2O_3 (200 phr).

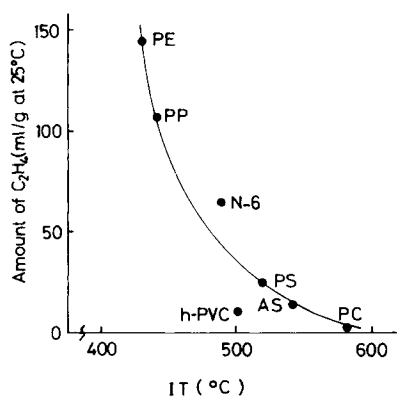


Fig. 2. Relation between ignition temperatures of polymers and amount of ethylene (C_2H_4) generated by pyrolysis at $600^\circ C$.

Ignition Limiting Oxygen Indexes

The ignition limiting oxygen indexes (Table II) were measured under the same conditions (sample weight 0.2 g, gas flow rate ca. 2.1 l./min, temperatures 550° , 600° , and $650^\circ C$). The reproducibility of results was within ± 0.1 . Measurements of over 21 ignition limiting oxygen indexes were not carried out because the thermocouples deteriorate rapidly in an atmosphere of such high oxygen concentration at high temperatures, making measurements inaccurate. As shown in Table II, the ignition limiting oxygen indexes of polymers ranged widely. It was also found that the ratios ($I_{550^\circ C}/I_{650^\circ C}$) of ignition limiting oxygen indexes at $550^\circ C$ ($I_{550^\circ C}$) to those at $650^\circ C$ ($I_{650^\circ C}$) of depolymerization-type polymers (such as PMMA, PS, etc.) were much larger than those of random degradation-type polymers (such as PE, PP, PVC, etc.). This shows that ignition properties of depolymerization-type polymers are much more affected by the heating temperatures than random degradation-type polymers.

TABLE II
Ignition Limiting Oxygen Indexes (ILOI) of Polymers

Polymer	ILOI		
	$650^\circ C$	$600^\circ C$	$550^\circ C$
Polyoxymethylene	0	0	0
Poly(methyl methacrylate)	2.1	2.8	10.2
Nylon 6	2.2	4.5	6.0
Polyethylene	2.8	3.5	5.7
Nylon 66	3.1	4.2	4.8
Polystyrene	3.2	4.5	10.2
Polypropylene	3.9	4.8	7.4
ABS	4.2	5.0	13.3
AS	4.5	5.4	16.9
s-Poly(vinyl chloride)	5.1	6.0	7.4
h-Poly(vinyl chloride)	10.7	10.7	11.5
Polycarbonate	11.0	16.7	>21
Phenol resin	9.9	>21	>21
Urea resin	19.1	>21	>21
Malamine resin	>21	>21	>21

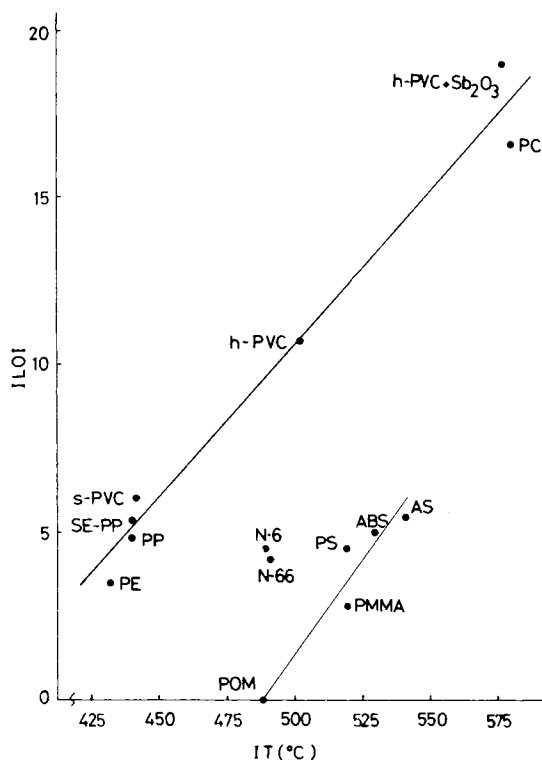


Fig. 3. Relationship between ignition temperatures (IT) and the ignition limiting oxygen indexes (ILOI) of polymers.

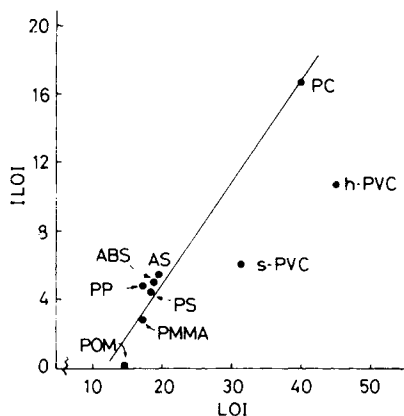


Fig. 4. Relationship between limiting oxygen indexes (LOI) and ignition limiting oxygen indexes (ILOI) of polymers.

Relationship Between Ignition Temperatures and Ignition Limiting Oxygen Indexes

The ignition temperatures were nearly proportional to the ignition limiting indexes (Fig. 33). However, the straight line of the depolymerization-type polymers such as POM, PMMA, PS, and styrene copolymers differed from that of the random degradation-type polymers. This shows that the polymers which

TABLE III
Ignition Temperatures of Self-Extinguishing Polymeric Materials^a

Polymeric material	Ignition temp., °C
1. HI-PS (base resin)	528
2. HI-PS + DBDPO ^b (15)	470
3. HI-PS + DBDPO (15) + Sb ₂ O ₃ (5)	492
4. HI-PS + DLN 604 ^c (15)	504
5. HI-PS + DLN 604 (15) + Sb ₂ O ₃ (5)	523
6. HI-PS + TBA ^d (15)	492
7. HI-PS + TBA (15) + Sb ₂ O ₃ (5)	517
8. HI-PS + SR-100 ^e (15)	484
9. HI-PS + SR-100 (15) + Sb ₂ O ₃ (5)	487
10. HI-PS + HBB ^f (15)	480
11. HI-PS + HBB (15) + Sb ₂ O ₃ (5)	502
12. ABS (Base resin)	530
13. ABS + PVC (82)	534
14. ABS + PVC (43)	531
15. PP (Base resin)	442
16. PP + DLN plus (15) ^g + Sb ₂ O ₃	440
17. PP + Hydrotalcite ^h (100)	533

^a Figures in parentheses indicate the concentration of flame retardants in phr (parts per hundred parts resin by weight).

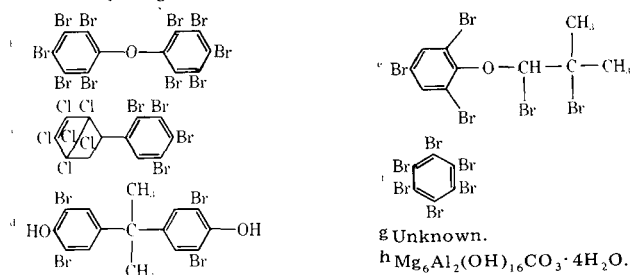


exhibit high ignition temperatures do not necessarily exhibit high ignition limiting oxygen indexes. For example, if ignitability is evaluated from ignition temperature alone, POM is more difficult to ignite than PE and PP; but if evaluated from ignition limiting oxygen indexes, POM is the easiest to ignite of all polymers studied. POM can ignite even in a nonoxygen atmosphere if heated to higher than 550°C. In this case, the oxygen required to burn POM is supplied from the oxygen in POM itself. Since the conditions under which polymers ignite vary considerably, ignition properties might be better evaluated not only from the standpoint of ignition temperatures but also by considering ignition limiting oxygen indexes.

Relationship Between Limiting Oxygen Indexes and Ignition Limiting Oxygen Indexes

The limiting oxygen indexes⁸ and the ignition limiting oxygen indexes were nearly proportional to the limiting oxygen indexes for most polymers (Fig. 4). But in the cases of h-PVC and s-PVC, which are self-extinguishing, the plots were

quite different. That is, they were found to be easier to ignite than might be expected from their limiting oxygen indexes. This shows that the polymers which exhibit high limiting oxygen indexes do not necessarily exhibit high ignition limiting oxygen indexes.

Ignition Temperatures of Self-Extinguishing Polymers

Ignition temperatures of 17 self-extinguishing polymers (Table III) were measured under the same conditions as in Table I. It was found that the ignition temperatures of self-extinguishing polymers were not necessarily higher than those of the corresponding base polymers. Especially in the case of the self-extinguishing polymers containing organic flame retardants, the ignition temperatures were lower than those of the corresponding base polymers. Therefore, they are more ignitable than might be expected when compared to the corresponding base polymers. However, in the cases of the self-extinguishing polymers, some of these alternately extinguished and burned after ignition, whereas all combustible polymers flamed continuously.

On the other hand, the ignition temperatures of self-extinguishing polypropylenes containing inorganic flame retardants (Table III) such as hydrotalcite, magnesium hydroxide, aluminum hydroxide, etc., were much higher than that of the base polypropylene. This suggests that self-extinguishing polymers containing inorganic flame retardants are much more difficult to ignite than the corresponding base polymers or the corresponding self-extinguishing polymers containing organic flame retardants.

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