

Contribution of Shape on Ignition of Polymeric Materials

Kotaroh Endoh,¹ Kohshiroh Mizuno,¹ Tomonaga Ueno,¹ Tomoyuki Ishikawa,¹
Masao Yukumoto,² Kunihiko Takeda¹

¹Department of Materials, Graduate School of Engineering, Physics and Energy Engineering,
Nagoya University, Furoh-cho, Chikusa-ku, Nagoya 464-8603, Japan

²Department of Mechanical Engineering, College of Engineering, Chubu University, 1200 Matsumoto-cho,
Kasugai, Aichi 487-8501, Japan

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ABSTRACT: The contribution of the shape and size of polymers towards ignition for four kinds of polymers, PP (polypropylene), HIPS (rubber reinforced polystyrene), ABS (acrylonitril-butadiene-styrene copolymer) and PC (bisphenol-A type polycarbonate) was studied. The critical heat flux (CHF), which means that the specimen ignites after infinite time, depended on the shape and kind of polymer at the plane position heating. But it was not affected by these con-

ditions at the side position heating. The CHF and other phenomena of ignition were analyzed and the two regions in one of which the shape and the kind of polymer affects them and in another region they was not affected. It will be useful to design electrical parts that reduce fire risks. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 1930–1936, 2007

Key words: ignition; risk; size; polymer

INTRODUCTION

The number of fire victims generally increases with the developing of a country's society because more people tend to live in high-rise apartment buildings and closed-off living spaces, and use more sophisticated goods in which there are increased chances of electrical short-circuits occurring accidentally. But as society matures, the social system improves, resulting in the decrease of fires and their victims.

In the U.S.A., where there is a strong interest in the prevention of fires, the number of victims has been decreasing for the past 50 years. In Great Britain, the number was on the increase until 30 years ago, but the situation has since improved and the figures have been declining since 1975. Meanwhile, among the developed countries, Japan is the only one in which the number of victims has constantly been increasing since the 1950s, as shown in Figure 1.

The causes of fires, in particular the kinds that result in deaths, are not simple, but the origins of fires are electrical short-circuits, small gas explosions which then spread by burning such materials as wood, fiber, paper, plastic, and rubber. Various kinds of fire retardancy technology have been researched to prevent the ignition and the spreading of fires. For examples, the combination of some halogenated hydrocarbons and antimony oxide,¹ magne-

sium hydroxide,² and organic phosphorous compounds³ have been applied to the plastics and are effective in restraining fires. Therefore, the technology of adding flame retardancy to plastics is one of the most important themes by which the developing society can ensure its sense of safety and security. Also, it can be interpreted as one of the major environmental issues.

Although they have been focused on adding flame retardancy to plastics, empirically, it is possible that shapes of plastics are more direct factor of the combustion and ignition. The combustion and ignition of plastics have been studied in this research, in particular, the relation between the characteristics and the shapes of the parts that are made by these polymeric materials.

EXPERIMENTAL

Polymeric materials used in this study

The polymers used in this study are listed below:

1. Polypropylene (PP): "Kobe polysheet," manufactured by Shin-Kohbe Electrical Ltd.)
2. High impact polystyrene (HIPS): "Toyo styrol HIPS-E640," manufactured by Toyo Styrene, Ltd.)
3. Copolymer of acrylonitrile, butadiene and styrene (ABS): "Kobe Polysheet ABS-NMW" manufactured by Shin-Kohbe Electrical, Ltd.)
4. Bisphenol-A type polycarbonate (PC): "Lexan 121" manufactured by GE Plastics Japan.

Correspondence to: K. Takeda (tak@leaf.ocn.ne.jp).

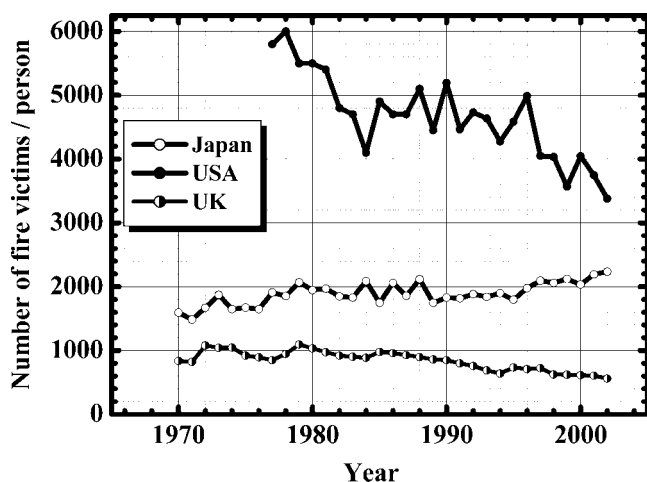


Figure 1 Fire victims in the USA, Great Britain, and Japan.

Thermogravimetric analysis

TGA-50 manufactured by Shimadzu, was used for TGA (thermal gravimetric analysis).^{4,5} Experiments were carried out on 5.0 mg of the samples under nitrogen at a flow rate of 50 mL/min and a furnace-heating rate of 90°C/min up to 800°C. The rate was much higher than that in general degradation experiments because the main purpose of this study was to analyze the degradation during fires when the elevating rate of the temperature was supposed to be about 100°C/min.

Combustion test

Burning and ignition times were performed according to the UL-94 test (Underwriter laboratory test), well known as a burning test for plastics. A cone calorimeter manufactured by Toyo-seiki (cone calorimeter type-3) was also

used to observe flammability. Babrauskas and Huggett developed the cone calorimeter in 1982 by applying Thornton's principle where the combustion heat of almost all organic materials was about 13.1 kJ/g and the error range was less than 5%.⁶⁻⁸ The heat release rate, which is one of the most important data, is not calculated by directly observing the heat emitted but by measuring the oxygen concentration in the air before and after the combustion chamber is used.

Ignition test method

The ignition test method was newly designed to observe the ignition time and the position of the specimen.

A heat shielding board with a hole 15 mm in diameter opened at the center was placed between the specimen and a burner.⁹ The distance from the board to the specimen was 3 mm and that from the specimen to the burner was 60 mm. The heat flux was measured by Schmidt-Boelter heat flux gage on the central point of the simulated specimen and regulated by a gas flow controller.

The experiment in which the specimen was set in a horizontal position was called "plane position," and when it was in a vertical position it was called "side position." The specimen size was 50 mm long by 50 mm wide and the thickness was controlled. The steric relations of these two cases are depicted in Figure 2.

RESULTS

Thermal degradation of PP, HIPS, ABS, and PC

The combustion of polymers does not continue only by the heat generated by the direct reaction of solid polymeric materials with oxygen. The volatile scission products by the thermal degradation because of to the

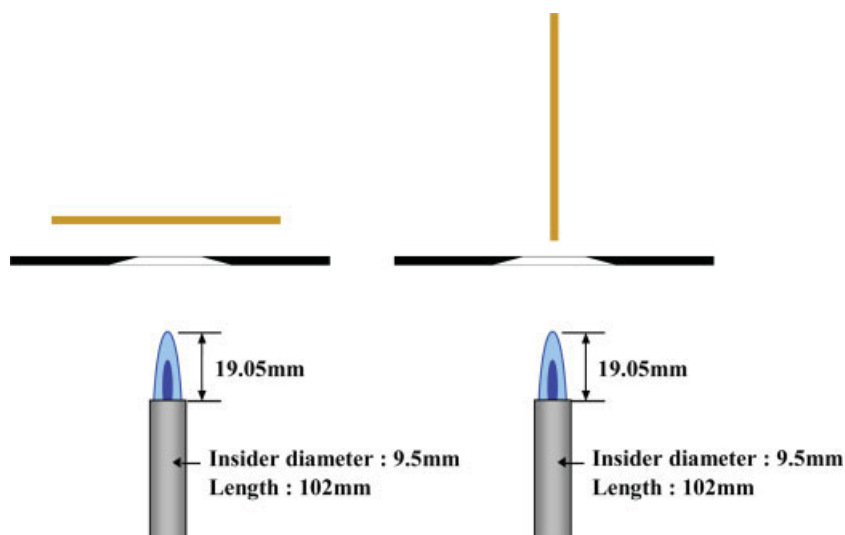


Figure 2 Steric positions of two cases (left: plane position, right: side position). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE I
Thermogravimetric Analysis of Four Polymers

Temperature	Unit	PP	HIPS	ABS	PC
Upper point	°C	481	448	455	561
50% weight loss	°C	509	479	488	595
Lower point	°C	540	512	524	613
Residue at 800°C	%	1	0	0	23

radiation heat from the oxidation site in the gas phase react with oxygen and generate a large quantity of the enthalpy. The plastics are heated by the enthalpy of the oxidation site in the gas phase and the scission products continuously spout from the surface of the plastics. Therefore, the flammability of polymeric materials strongly depends on the thermal degradation properties.¹⁰

Recently, Lyon reported the effect of thermal degradation on combustion by using a pyrolyzer and a combustion reactor which were separately installed,¹¹ and showed that almost all the combustion heat were the oxidation enthalpy of the scission products. Therefore, thermogravimetric analysis is one of the most basic tests to analyze the combustion phenomena, and the results were depicted in Table I.

As shown in Figure 3, PC, which is a thermally durable polymer, starts to decompose at 550°C, and 600°C is the temperature at which 50% of the specimens becomes volatile because of the thermal degradation. This temperature is called 50% thermal degradation temperature (50% TDT). The thermal degradations of PP, HIPS, and ABS start at 400°C and the 50% TDTs were from 480 to 500°C, so they were more than 100°C below that of PC.

Another characteristics of the thermal degradation of PC is that the residue of PC in the range of higher temperatures was conspicuous as well as the 50% TDT. It was recognized in temperatures over 700°C. Twenty-three weight percent of the residue of PC did not decompose in temperatures over 800°C as shown in Figure 3.¹²

Only 77 wt % parts of the PC specimen burns because only the volatiles move to the gas phase and

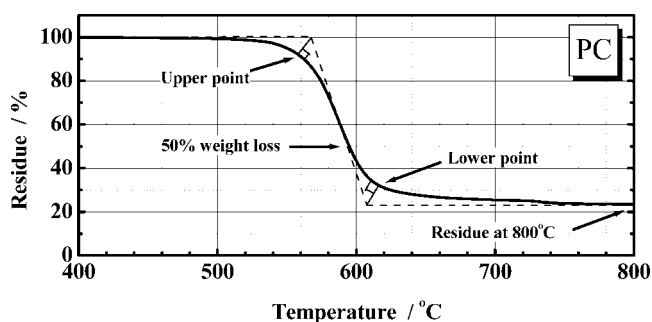


Figure 3 Definition of four points observed by TGA.

TABLE II
Combustion Data Obtained by UL Test

Time	Unit	PP	HIPS	ABS	PC
Ignition	s	6.3	7.6	5.2	18.5
Flaming combustion time	s	163	341	285	27
Drip	s	5.7	40.3	60.3	-2.2
Going out suddenly (GOS) or burning out (BO)	-	BO	BO	BO	GOS

contributes the continuous combustion by the oxidation enthalpy. The surface structure that is composed with char-like structure hinders the spread of the combustion.¹³

On the other hand, the thermal degradation temperatures of PP, HIPS, and ABS were lower and the residues were less than that of PC. So, a lot of the scission products which become the fuel in the gas phase are generated at lower temperatures and accelerate fires.

Combustion test by UL test and cone calorimeter

Two combustion tests were achieved. The ignition time, the flaming combustion time and the drip time were observed and listed in Table II. The ignition time of PC was much longer than those of other three polymers. The ignition time is considered to be proportional to the initial degradation temperature, such as the upper point shown in Figure 3. The ignition time of PC could be considered by the upper point of TGA.

The basic combustion data such as ignition time, heat flux, and maximum heat flux, as shown in Table III, were obtained by using a cone calorimeter.

The ignition times of PP, HIPS, and ABS were short and the heat fluxes increased rapidly after ignition and they reached their maximum values after 90 s. Afterward, the specimens burnt out completely and the heat fluxes dropped. In particular, the heat flux of PP reached 2600 kW/m² immediately after ignition and all of the material burnt out quickly.

The data coincided with those which are generally observed for other hydrocarbon polymers such as PE and PS.¹⁴ Similar phenomena were observed during the combustions of HIPS and ABS but the increasing rates of the heat fluxes were lower than that of PP. The ignition time of PC was the longest among the four polymers. The ignition time after the heating was

TABLE III
Combustion Data Obtained by Cone Calorimeter

Polymer	Unit	PP	HIPS	ABS	PC
Ignition time	s	32.5	40.6	41.2	98.2
Maximum heat release rate	kW m ⁻²	2651	1732	1680	1020
Total released heat	MJ m ⁻²	104.7	102.6	102.5	77.9

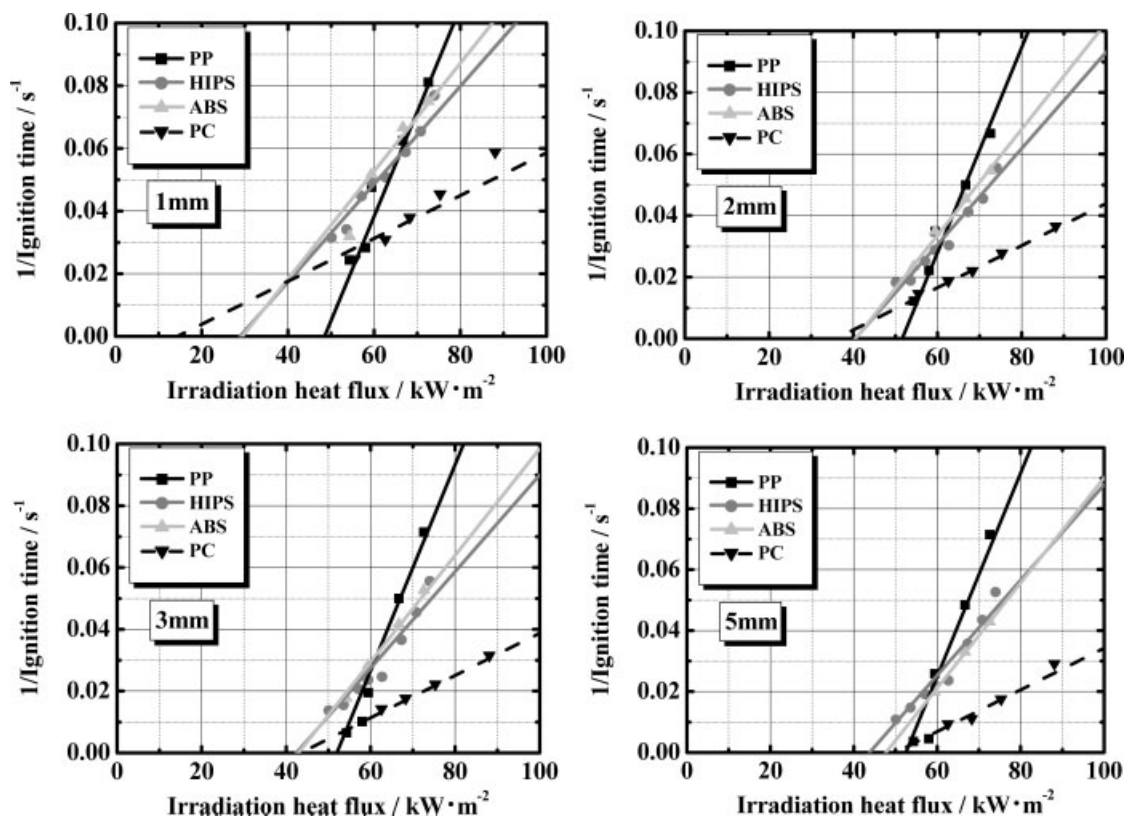


Figure 4 Inverse ignition time as a function of irradiation heat flux at the plane position.

started was about 100 s and the heat flux rapidly reached about 1000 kW/m². Then afterwards the heat was restrained and dropped to 630 kW/m² and the flame was quenched soon.

The complicated combustion is due to the dehydrogenation in the specimens where two hydrogen atoms and an oxygen atom on the PC chain react with water and the char on the polymer surface obstructs the movement of the scission products from the inner part of the polymer to the gas phase. However, the mechanical structure of the char is so weak that the scission products from the inner part destroy the char layer on the surface and the flame spreads again.¹⁵

These data observed by the cone calorimeter were the same as those measured by TGA as shown in Figure 3.

Ignition test by newly designed method

There are few studies on the quantitative measurement of the relationship between the shape of the specimen and ignition although the tendency has been recognized for a long time. The reason for this is that quantitative observation is difficult. In this study, the effects of the specimen shape on the change in ignition time and radiation heat flux were examined by a newly designed method. The specimens that had

been prepared prior to the combustion test were radiated by a burner at "plane" and "side" positions.

The data obtained were plotted on the graph whose horizontal axis was the radiation heat flux and the vertical axis was the inverse value of the ignition time.

The linear relationships of the plots were obtained for all combustion tests except PP at the side position. The total irradiation heat quantity to a specimen in an experiment is the product of irradiation heat flux (H_i) and ignition time (T_i). So, the heat quantity (Q) can be expressed as eq. (1).

$$\frac{1}{T_i} = \frac{1}{Q} H_i \quad (1)$$

Namely, the inverse value of the slope of the plot in the graph whose horizontal axis is the irradiation heat flux and vertical axis is the inverse ignition time means a quantity of heat. The slopes at the plane position were almost the same for the individual polymers as shown in Figure 4.

The extrapolation point of the data plot line on the zero line of the horizontal axis means the "critical heat flux (CHF)" at which the specimen ignites after being heated infinitely.

One of the important findings was that the slope was constant, and another was that the CHF was higher when the specimen became thicker. This means

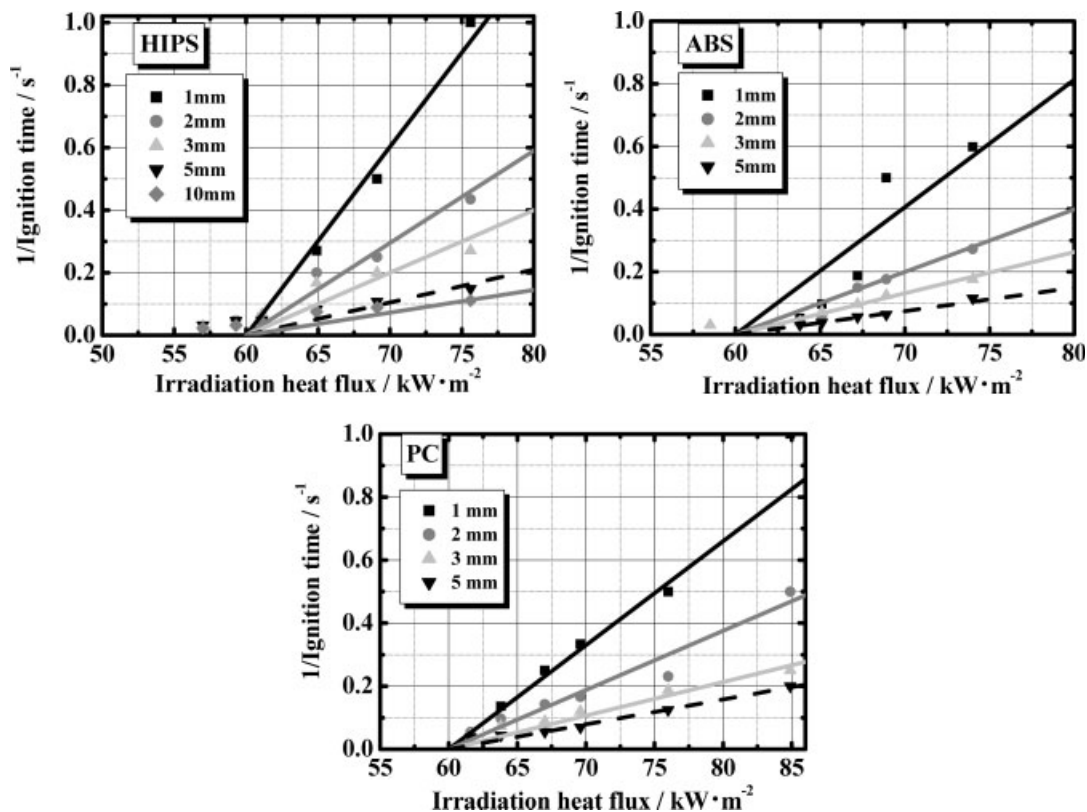


Figure 5 Inverse ignition time as a function of irradiation heat flux at the side position.

that the heat required to ignite increases for a thicker specimen.

The same linear plots were obtained in the side position experiments. But the magnitude of the slopes depended on the thickness of the specimens, and the extrapolation on the zero line of the horizontal axis crossed at a point as shown in Figure 5.

DISCUSSION

As afore mentioned, the scission products of polymers burn in the gas phase and not the polymer specimen itself, which have already been clarified by several researchers.^{16,17} Further studies on the effect of the chemical structure, the scission products and the combustion of various polymers have been conducted,^{18,19} and a textbook has been published on the subject.^{20,21} The phenomena can be considered based on the ther-

mal degradation of polymers and the reaction of the scission products with oxygen.

On the other hand, the quantity of the heat and the rate to ignition are considered to be the important factors in analyzing ignition as one of the nonequilibrium phenomena.

Analysis of the plane ignition data

The linear relationship between the inverse value of the ignition time and the irradiation heat was observed for each polymer, and the slopes were almost the same. The inverse value of the slope means "the excess heat quantity to ignite the polymer (Q_E)" and it can be expressed in eq. (2).

$$Q_E = (H_i - H_c)T_i \quad (2)$$

H_c means CHF in eq. (2). If the inverse value of the slope is constant, the excess heat quantity does not depend on the heat flux. Therefore, the actual risks of ignition and fire are decided not by the heat flux but only by the total heat amount.

The required heat quantity of PP was the smallest and it did not depend on the thickness of the specimen. The excess heat quantities of HIPS and ABS were about 600–650 kJ/m² as shown in Table IV. The excess heat quantity of PC to ignition was the largest at about

TABLE IV
Excess Heat Quantity to Ignite the Polymer in the Case of the Plane View Position

Polymer	Plane position (kJ m ⁻²) 1–10 mm
PP	300
HIPS	640
ABS	580
PC	1460

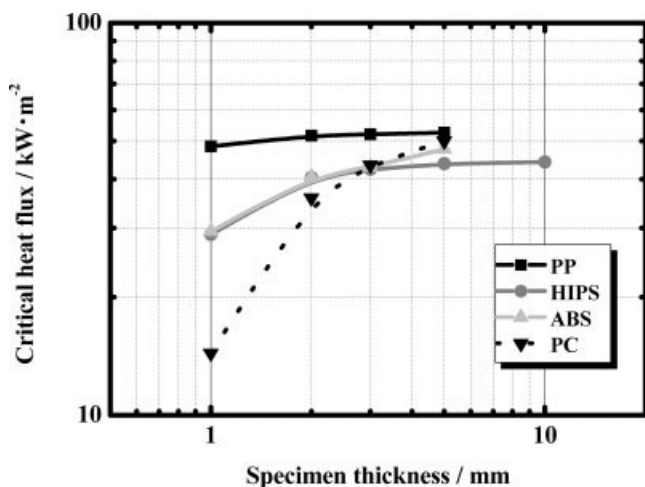


Figure 6 Critical heat flux in the case of the plane view position.

4.9 times and about 2.4 times larger than that of PP and HIPS/ABS, respectively.

The CHF, which can be calculated at the cross section of the line of the inverse ignition time and the irradiation heat flux on the horizontal axis, were plotted in Figure 6. The CHF increased with the increase in thickness of the specimen except in the cases of 5 and 10 mm HIPS.

The temperature at which the specimen ignites is considered to depend on the degradation temperature because the concentration of the scission products reaches the explosion limits of the mixed gases. Therefore, the ignition time depends on the rate of the elevation temperature at the constant heat flux.

So, the thickness of the specimen increased, the ignition time became longer.

When the specimen is heated with a heater from the outside, the temperature of the specimen is decided by the balance of the quantities of radiation heat, the specific heat and specific gravity. So the elevating rate of the temperature is lower at a higher specific heat and larger specific gravity. The values correlated by the specific heat and specific gravity are plotted in Figure 7.

Analysis of side position data

More complicated data were obtained in the case of the side position. The slopes of the linear relationship between the inverse ignition time and the irradiation heat flux were different for individual thicknesses and polymers. However, the CHF did not depend on the thickness of the specimen and they did not differ from polymer to polymer except PP, which melted and dripped before ignition. Namely, the CHF of the three polymers was about 60 kJ/m^2 and the ignition times under the weak heat flux was about 16–22 s. The data of the plane and the side positions were different on the slope of the linear

relationship between the inverse ignition time and the irradiation heat flux, and the dependency on the specimen thickness. But a common tendency was plotted for the various data obtained.

The opening diameter of the heat sealing board was 15 mm at the plane position experiment. Therefore, the plane position experiment could be regarded as a side position one with a width of 15 mm if there was enough thickness. Namely, the CHF of the specimens of HIPS with 5 and 10 mm thickness was approximately the same. So the dependency of thickness on the CHF could be observed for the specimen whose thickness was less than 5 mm. The effect of the vertical length of the specimen in the case of the side position experiment was considered to be negligible, for it was long enough.

The different regions are recognized for the consideration of the ignition risk using polymeric materials. One is that the size of the specimen is so small and the thickness is less than 5–10 mm, where the risk does not depend on the shape and kind of polymer. The other is that the risk strongly depends on the kind of polymer and slightly depends on the shape, which is observed in the right region of Figure 8.

Risk of fire depending on shape of parts

The ignition and fire risks due to flammable materials in industrial parts have been considered to depend on the continuous flammability of certain polymers. This is the reason why the study of flame retardancy has been active since the 1940s and much research and developments have been conducted to find better flame retardants to blend with polymeric materials, as well as to find the relation between the chemical and physical structures of polymeric materials to restrain the risk of fires.

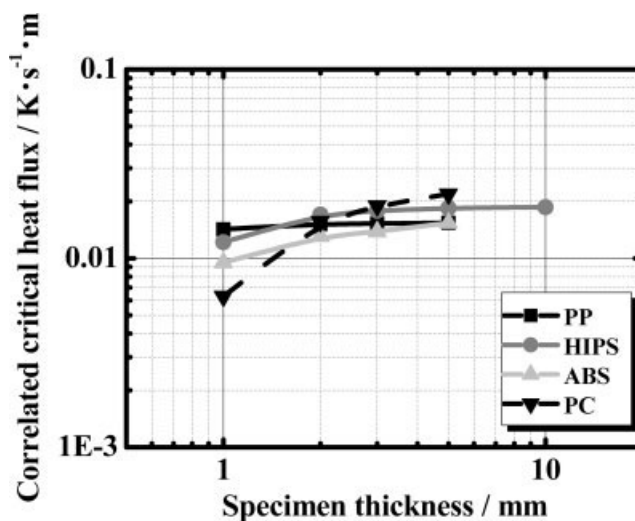


Figure 7 Correlated critical heat flux by specific heat and specific gravity.

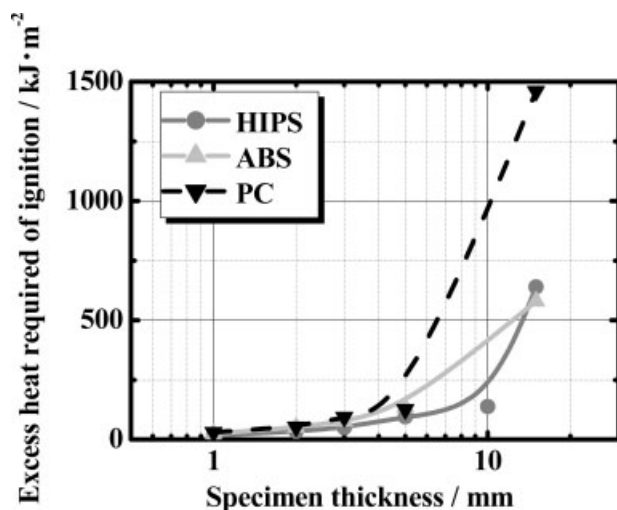


Figure 8 Heat required for ignition as a function of specimen width.

However, the risk cannot always be expected from the inherent flammability of the polymeric materials that have been treated with flame retardants. In particular, the sizes of electrical parts and the inner rooms of equipments have recently been growing smaller and smaller. This means that the sizes of the plastic parts in the small electrical equipments are becoming smaller, also. When the size is smaller than 5 mm, a fire risk exists even if the inherent flame retardancy of the materials used is good enough. This is the most important concept which the plot in Figure 8 suggests us.

One of the empirical data that researchers have encountered in their work towards the improvement of flame retardancy is the phenomena that the flame retardancy of certain materials is affected by the size and shape of the specimen. Generally speaking, the smaller the specimen is, the stronger the flammability is. However, the quantitative evaluation of this phenomenon has been very difficult.

If the result obtained in this study is used to design electrical parts and decrease the fire risk, it could save possible fire victims in the future.

CONCLUSION

The contribution of the shape of parts on the ignition of four polymers was studied and analyzed based on the viewpoint of the irradiation heat flux. The conclusion was:

1. The plot of the inverse magnitude of the ignition time as a function of the irradiation heat flux showed linear relation.
2. The slopes of the straight line were almost the same at a plane position test.

3. The slopes at a side position test depended on the thickness of the specimen.
4. The CHF could be measured at the crossing point of the straight line and the horizontal axis.
5. The CHF at plane position test depended on the thickness of the specimen.
6. The straight lines at side position test crossed at a point and the CHF did not depend on the thickness.
7. The excess heat quantity to ignite the polymer decided on the ignition time and the irradiation heat flux.
8. The CHF could be corrected using the specific heat and the specific gravity.
9. To reduce the fire accident, the shape and the position of plastic parts is more important than the continuous flammability when the parts are relatively small.

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