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相似則を用いた高分子の燃焼特性解明

Study on combustion properties of polymers utilizing a similarity rule

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1. Introduction

In recent years, space development has been shifting to a commercialized business rather than national project. Therefore, it is inevitable to reduce the cost under warranted safety regulation. Polymers have been attracting attention because of their nature which fits for space use, such as inexpensive, lightweight, durable, and have high thermal insulation properties, all of which are necessary elements for space use. Nevertheless, polymers are flammable, and there is a potential hazard of fire accidents, especially in the space environment; namely, highly-enclosed, microgravity atmosphere. It is severely necessary to understand the "exact" hazard including the burning characteristics.

Experiments in the space environment (hereinafter referred to as "microgravity experiments") require special "costly" equipment such as space station, parabolic flight, drop tower etc. If the cost is reasonable, we must accept the limit of the microgravity time instead because they are trade-off. For example, the International Space Station (ISS) can offer several weeks to several months of microgravity time yet enormous cost is needed¹). A, aircraft offers 10 to 25 seconds with ten million JPY per one campaign²) and a drop tower offers several seconds with hundreds thousand JPY per drop³). Not only the microgravity time, preparation time and allowable size of the experimental apparatus are also involved. To end, it is natural to understand that microgravity experiment is not easy task even less-costly method (cf. drop-tower experiment). Suppose if alternative methodology is available, investigating the burning character at microgravity becomes handy and more chance is opened to everybody with less cost.

In the previous study, a method to create a *simulated* microgravity environment by reducing Grashof number using the similarity rule was proposed and validated^{4.7}. This methodology allows us to achieve 1-D spherical flame to be adoptive of ideal d^2 -law⁸. With this, we can repeat the test in the laboratory with less limitations as compared to the microgravity experiments. So far, validation was only made by PMMA sample whose pyrolysis gas species, not only single monomer, suggesting that PMMA is quite special kind of polymeric material. In this study, we investigate the difference kinds of polymers, such as polypropylene (hereafter, PP) and polyethylene (hereafter, PE) under lower pressure environment to achieve 1-D burning status.

2. Design Rule

2.1. Similarity Rule

Referred from the previous studies, it is effective to propose Grashof number (Gr [-]) similarity to mimic the dynamics during the combustion of small specimen. Let us briefly recall the concept.

$$Gr = \frac{\rho^2 G\beta \Delta T L^3}{\mu^2} \sim L^3 G^1 P^2 \tag{1}$$

where ρ is density $[kg/m^3]$, *G* is gravitational acceleration $[m/s^2]$, β is coefficient of volume expansion [-], ΔT is temperature difference between flame and surroundings[*K*], *L* is representative length [m], μ is viscosity coefficient $[Pa \cdot s]$ and *P* is pressure [Pa]. Ultimately, the dependence of the representative quantities on the Grashof number can be expressed by *L*, *G*, and *P*, as shown in Eq. (1), and microgravity condition is regarded as "small Grashof number (namely, $Gr \ll 1$)". Obviously, reduction of *G* can fulfill such requirement, however, this is not the only way to achieve small Gr. That is, even maintain the normal gravity (*G* = 1), adopting small length scale (*L*) and low pressure (*P*) can reduce Gr drastically, suggesting to mimic the dynamics in microgravity combustion. However, it is important emphasize that there is low-pressure limit since too-much reduction of pressure can induce the natural extinction due to the lack of oxidizer in the chamber suggesting that it is achieved low-Damkohler number (Da [-]) limit. Hance, determination of the low-limit and the range of low pressure to achieve the stable burning condition (beyond the extinction limit; Da > 1) is important. We will investigate this for the case of PP and PE.

2.2. Target and Experiment

In order to observe the combustion of polymers, the experiment is performed on a spherical 1-D flame formed over spherical specimen (polymers). The reason for this is to use the d^2 -law to provide the burning rate constant as eigenvalue of the system. **Figure 1** shows (a) the combustion chamber diagram, (b) the combustion zone, and (c) the sample diagram, respectively adopting in the present work. For detail, please see Ref 7.



Figure 1. Experimental apparatus and sample, (a) Combustion chamber, (b) Inside the combustion chamber, (c) Magnified picture of burning sample

The experiment was conducted in a combustion chamber with external dimensions of 335 mm x 335 mm x 335 mm. The chamber is equipped with a window through which the combustion process inside the chamber can be observed. LEDs installed in the chamber are used as backlight during combustion to image the shape of burning specimen clearly. The camera is equipped with a digital camera (Nicon D90: full-open for aperture, 24 fps for shutter speed). The sample is suspended by a vertically-oriented SiC fiber (Hi-NicalonTM

manufactured by Nippon Carbon Co., Ltd., 14 μ m in diameter) as shown in the figure. Ignition is induced by a nichrome wire, and the applied current is adjusted according to the conditions. The internal pressure is controlled by a vacuum and set initially as summarized in **Table 1**. Composition of the ambient gas is 21% oxygen balanced with 79% of nitrogen.

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Sample	#1	#2	#3	#4	#5	#6
PP	7.0	10.0	12.5	15.0	50.0	100.0
PE	7.0	10.0	15.0	20.0	50.0	100.0

Table 1. Internal pressure conditions for each test number (#1-#6). Unit: kPa

The ambient gas temperature was set to room temperature. Once the gas is loaded in the chamber, we shall keep as is for a while to ensure that little gas flowed in the chamber before ignition. Then igniter is adopted to the specimen to induce the spontaneous ignition. Once flaming is visually confirmed, the nichrome wire is then detached from the specimen in order to avoid any interaction with flames. To ensure reproducibility, the test was conducted at least three times.

The samples are PP and PE spheres with a diameter of 3.5 mm to 4.0 mm is completed by melting on the ball.

3. Results and Discussion

3.1. Burning Behavior at Each Pressure

Figure 2 is a cropped image of PP and PE flames at various pressures, whereas **Fig. 3** shows a time series of the combustion process during 1-D burning status at quasi-steady state. An ambient pressure is sufficiently high (say, 100 kPa), both flames over PP and PE show typical "teardrop" shape, extending upwardly due to buoyancy flow. A strong luminous zone was observed, indicating the formation of soot there. The flame length in the vertical direction becomes shorter as the pressure is reduced. Accordingly, the flame shape becomes nearly "spherical" when the pressure is reduced at 12.5 kPa for PP and at 10 kPa for PE.



Figure 2. Appearance of low-pressured flame at quasi-steady state



Figure 3. Time-variation of burning polymers at sufficiently low pressure to exhibits 1-D flame

Formation of nearly spherical flame occurs regardless of the sample material, suggesting that this is dynamic feature in the gas-phase over the specimen. Once the pressure is reduced to 7.0 kPa, no steady flame is observed due to the oxygen gas is insufficient to have continuous quasi-steady-state combustion.

3.2. Observed Burning Rate Constants

According to droplet combustion theory⁸, the well-known d^2 -law (Equation (2)) should be observed when a one-dimensional combustion is established.

$$d(t)^2 = d_0^2 - Kt (2)$$

where d(t) is the diameter of the burning specimen [mm], K is the burning rate constant $[mm^2/s]$, and t is the elapsed time [s]. The subscript 0 indicates the initial state. Theoretically, the burning rate constant is recognized as a physical constant under a given set of conditions and is claimed to be directly related to the transfer coefficient, which indicates burning characteristics under a given environment. In this report, the burning rate constant is calculated and burning characteristics are evaluated.



Figure 4. Typical d^2 - t relation study, (a) Changes of diameter squared in time, (b) Burning rate constants for PP and PE.

Figure 4 (a) shows the time evolution of the square of the sample diameter (d^2) , from ignition to the extinction. The moment when the flame covers the sample is defined as the moment of ignition, t = 0s. In the initial stage of combustion (named "Stage 1" in the figure), the square of the sample diameter (d^2) fluctuates randomly with increase in time. Later ("Stage 2" in the figure), d^2 decreases in the almost linearly, suggesting that the combustion followed by d^2 -law. In Stage 1, increase of d^2 shall be due to the volume expansion of the heated specimen. Because internal bubble is formed the specimen⁹⁻¹⁰, volume expansion may be pronounced further even though the specimen is covered by the flame (t > 0 s) to be consumed (to deduce d^2). After the volume expansion, a constant decrease begins in Stage 2, suggesting that the bubble formation and expansion may stay constant. In this manner, we can observe quasi-steady state feature to have constant burning rate till extinction is experienced. The calculated burning rate constant defined in Stage 2 is summarized in **Fig. 4 (b)** for both specimens. It can be seen that the burning rate constant increases with decreasing pressure, then eventually becomes constant when pressure is less than about 10 kPa. As depicted in **Fig. 2**, it is interesting to note that the constant "maximum" burning rate constant is achieved when nearly spherical (1-D) flame is formed. It is also noted that the burning rate constant of PP is larger than that of PE, which will be discussed in the following section.

3.3. Relationship Between Burning Rate Constants of Different Polymers

From now on, let us examines why the burning rate constant for both polymers are not identical. The pressure used for comparison is the highest pressure at which spherical flame can form (PP: 12.5 kPa, PE: 10 kPa). The difference in the burning rate constants can be attributed to the difference in the heat transferred to the sample surface, which can be responsible attributed to the difference in flame temperature and the distance between the flame surface and the sample surface. Huggett¹¹ et al. found that the heating value per unit of oxygen consumed during combustion is approximately constant over a wide range of organic materials normally involved in combustion, and that the flame temperature does not vary significantly with the type of sample. Thus, it is fair to assume that flame temperature of PP and PE is considered to be identical. Thus, it is considered that the difference in the burning rate for both specimens shall be regarded by the difference of the flame location to vary the heat flux to the molten specimen. To validate this assumption, we have attempted to measure the distance from the sample surface and the flame location in **Fig 5**.



Figure 5. (a) Diagram of distance between flame surface and sample surface (b) Comparison of distance between flame surface and sample surface

Figure 5 (a) shows the flame model, T_f is the flame temperature, T_s is the temperature at the sample surface, r_s is the sample radius, v is the outward advection velocity, and δ is the distance between the flame and the sample. Note that the location of the flame is middle of the luminous zone to define as "flame surface" in this study. The difference in δ (distance between flame surface and specimen surface) shall directly affect the burning rate constant to modify the conductive heat flux.

Let us estimate the heat flux at the sample surface which is responsible to the variation of the burning rate constant. Under quasi-state assumption, the heat conduction equation over the sample surface shall be written in Eq. (3).

$$\rho c_p v \frac{dT}{dr} = \lambda \frac{d^2 T}{dr^2} \tag{3}$$

The convection and heat conduction terms are used from the steady-state heat conduction equation, where ρ is the density and c_p is the specific heat. Solving the differential equation yields Eq. (4).

$$T(r) = A + Be^{\left(\frac{\rho c_p v}{\lambda}r\right)}$$
⁽⁴⁾

Where A and B are arbitrary constants. The boundary conditions are shown in Eq. (5).

$$\begin{cases} T = T_s \to r = r_s \\ T = T_f \to r = r_s + \delta \end{cases}$$
(5)

Using the boundary conditions in Eqs. (4) and (5), the calculation yields Eq. (6).

$$T(r) = T_s + \left(T_f - T_s\right) \left\{ e^{\left(\frac{r}{\alpha} - \frac{\delta}{\alpha}\right)} - e^{\left(\frac{r_s}{\alpha} - \frac{\delta}{\alpha}\right)} \right\}$$
(6)

Where $\alpha = \frac{\lambda}{\rho c_p v}$ as treated constant in this study. Finally, transforming the equation to find the heat flux, we obtain Eq. (7).

$$q_s = \rho c_p v \left(T_f - T_s \right) exp \left(\frac{r_s - \delta}{\alpha} \right)$$
⁽⁷⁾

From Eq. (7), it clearly revealed that the heat flux decreases with increasing δ and increases with decreasing δ . These results suggest that the heat flux transmitted to the sample surface is determined from the experimental results of δ and the value of δ in the heat conduction equation.

Lastly let us obtain δ in case the burning specimen is varied based on the flame surface model developed in diffusion flame theory. The flame surface model implies that the flame is formed where the fuel and oxygen in the air mix well to reach stoichiometric condition, and the position of the flame surface can be defined by the mixing fraction *Z* at the stoichiometric condition, *Z*_{st}, as shown in **Fig. 6**.



Figure 6. Flame surface model over the burning specimen

Denoting the fuel and oxidizer before combustion as $Y_{F,1}$, $Y_{o2,2}$, respectively, the conditions for the part of the mixture of fuel and oxidizer are given by Eq. (8).

$$\begin{cases} Y_{F,u} = Y_{F,1}Z \\ Y_{02,u} = Y_{02,2}(1-Z) \end{cases}$$
(8)

Reactions are assumed as complete combustion to describe as following manner:

$$\nu_F'[C_m H_n] + \nu_{02}'[O_2] \to \nu_{C02}"[CO_2] + \nu_{H20}"[H_2O]$$
(9)

Where, v represents the stoichiometric coefficient. The stoichiometric coefficient, expressed in terms of the change between fuel and oxidizer, molar mass W_i [g/mol], is given by Eq. (10).

$$\frac{dY_{O2}}{dY_F} = \frac{v_{O2}'W_{O2}}{v_F'W_F} = \nu \tag{10}$$

From Eq. (10), using the stoichiometric coefficients to show the scalar volume after and before combustion, we obtain Eq. (11).

$$\nu Y_F - Y_{02} = \nu Y_{F,u} - Y_{02,u} \tag{11}$$

In Eq. (11), the right side is before combustion whereas the left side is after combustion. From these equations, Z becomes Eq. (12) when considering the mixing state.

$$Z = \frac{\nu Y_F - Y_{02} + Y_{02,2}}{\nu Y_{F,1} + Y_{02,2}}$$
(12)

From Eq. (12), the stoichiometric mixing fraction Z_{st} is obtained as in Eq. (13) because $\nu Y_F - Y_{02} = 0$ is the flame surface, and Z_{st} is obtained as in Eq. (13) because various decomposition gases are generated in the present sample.

$$Z_{st} = \left[1 + \nu \frac{\sum_{k=0}^{n} Y_{F(k+1),0}}{Y_{02,0}}\right]^{-1}$$
(13)

 Z_{st} was calculated using these equations, and the decomposition gas species for PP and PE were taken from reference¹², since both PP and PE were pyrolyzed at around 400°C and the decomposition gases were measured. The respective decomposition gas species are shown in **Table 2**. The oxygen concentration in the atmosphere was assumed to be 20%.

]	PP	PE				
decomposition gas	chemical formula	decomposition ratio [%]	molar mass [g/mol]	decomposition gas	chemical formula	decomposition ratio [%]	molar mass [g/mol]
butene	C_4H_8	16.8	56.11	butene	C_4H_8	24.6	56.11
butane	$C_{4}H_{10}$	12.8	58.12	butane	$C_{4}H_{10}$	19.1	58.12
pentene	$C_{5}H_{10}$	19.7	70.135	ethane	C_2H_6	12.4	30.07
pentane	$C_{5}H_{12}$	11.2	72.15	propane	C_3H_8	14.8	44.097
hexane	$C_{6}H_{12}$	11.0	84.162				

Table 2. Decomposition gases and calculated information for PP and PE

The chemical reaction equations are shown in Eq. (14) for PP and Eq. (15) for PE, assuming complete combustion.

$$C_4H_8 + C_4H_{10} + C_5H_{12} + C_6H_{12} + 37O_2 \rightarrow 24CO_2 + 26H_2O \tag{14}$$

$$C_4H_8 + C_4H_{10} + C_2H_6 + C_3H_8 + 210_2 \rightarrow 13CO_2 + 16H_2O \tag{15}$$

Using Eqs. (10), (13), **Table.2**, and Eqs. (14) and (15) in the chemical reaction equation, Z_{st} for PP is calculated as shown in Eq. (16) and Z_{st} for PE as shown in Eq. (17).

$$Z_{st} \cong 0.61 \tag{16}$$

$$Z_{st} \cong 0.49 \tag{17}$$

From Eqs. (16) and (17), it can be seen that the flame is formed on the sample side for PP compared to PE because Z = 1 on the sample side and Z = 0 on the atmosphere side.

4. Concluding Remarks

Similarity rule is adopted to general polymers, like polypropylene (PP) and polypropylene (PE) to check whether they can achieve 1-D spherical flame mode. Results clearly showed that, even using PP and PE as samples, one-dimensional flames were successfully observed under sufficiently low-pressure atmosphere, suggesting that we can reproduce the burning status in microgravity in the laboratory. The burning rate constants increases as the pressure decreases and show maximum when the spherical flame is achieved. The burning rate constants were found to be faster in PP than that of PE. This difference shall be attributed by the difference in the decomposition gas species.

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