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Identification of Pyrolysis Reaction Model of Polypropylene

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This paper attempted to identify a pyrolysis reaction model of polypropylene (PP) and to elucidate its macroscopic decomposition mechanism correspondingly. Among various reaction models, we chose a reaction model that allowed the best fit to experimental reduced-time-plots (RTPs). Surprisingly, the pyrolysis reaction model of PP varies with reaction temperature within a temperature range between 683 and 738 K. At lower temperatures (683–693 K), the "contracting-cylinder" model accounts for the pyrolysis reaction of PP. Bubble nucleation may be a major reaction mechanism of PP pyrolysis at higher temperatures (728–738 K). High generation rates of volatiles lead to the accumulation of volatiles in the melt until reaching a critical concentration where bubble nucleation sets forth, thus mimicking "Avrami–Erofeev" model. Hence, the classical expression of the reaction model, $f(\alpha) = (1-\alpha)^n$, assumed by most previous studies is inappropriate for pyrolysis reaction of PP. At lower temperatures, chemical reactions may limit the pyrolysis reaction of PP, whereas at higher temperatures the rate of bubble nucleation closely related to heat, mass, and momentum transfer along with thermodynamic properties of melt may limit its pyrolysis reaction.

Most previous studies[1–4] introduced two unjustified assumptions to develop a pyrolysis reaction model of PP: (1) the reaction model is unvaried with temperature and (2) a *n*th-order model represents a pyrolysis reaction of PP.

Since the thermal degradation of polymers is characterized by heterogeneous solid-state mechanisms, the classical expression of the reaction model, $f(\alpha) = (1-\alpha)^n$, that is usually applicable for homogeneous gas-phase kinetics is invalid for the pyrolysis reaction of polymers except for highly specific cases.[5]

An incorrect reaction model can mislead Arrhenius parameters as well. It is, hence, essential to assess a pyrolysis reaction model correctly at the initial stage of kinetic analysis.

This paper attempted to derive pyrolysis reaction models of PP in regard to pyrolysis temperature from analyzing RTPs and to offer an insight into macroscopic pyrolysis mechanisms concomitantly.

Powdered PP was used in this study and supplied by Samsung Chemical Co. (HJ500 Powder). The samples were dried in a desiccator before analyses. A custom-made thermobalance (TB) was used for isothermal kinetic experiments.[6] Detailed information on the TB was described in the previous studies.[7–9] 10 ± 0.1 mg of PP sample was loaded and suspended in a 100-mesh stainless steel wire basket. The sample basket was connected to an electric balance (Satorius BP61) by a 0.3-mm diameter nichrome wire. The balance was lowered down quickly by a winch to insert the sample to a reaction zone after a target temperature was stabilized. The weight loss of a sample was recorded continuously over time by an on-line personal computer. We performed seven isothermal kinetic experiments at operating temperatures of 683, 688, 693, 708, 728, 733, and 738 K under a stream of nitrogen at a linear velocity of $8.3\,\mathrm{cm\cdot sec^{-1}}$. The operating temperatures were chosen within a temperature range where the main decompositions occurred as in nonisothermal experiments. The temperature sensitivity of the decomposition rate constrained us to select the narrow temperature range (680–740 K).

The kinetic equation for solid-state decomposition is generally denoted by:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)f(\alpha) = A\exp(-E/RT)f(\alpha). \qquad (1)$$

The reaction model, $f(\alpha)$, reflects the pyrolysis mechanism of solid-state reaction. The reaction model may take various forms, some of which are shown in Table 1.

The RTP is introduced to identify the reaction model of solid-state reaction.[7–9] RTP is constructed by plotting α as a function of a reduced time, t/t_α, where t_α is the time that it takes to attain a specific conversion ($\alpha = 0.9$) at an isothermal operating temperature, T_i. Reaction model of PP was chosen among various reaction models by means of comparing experimental RTPs with theoretical ones described in Table 1.

If the RTPs derived from a series of experiments at different isothermal temperatures are superimposable within the limits of the reproducibility at individual temperatures, the reaction model does not change with temperature.[10] However, the reaction model of PP varies apparently with temperature (Figure 1). As shown by Figure 1, the reaction model of PP is accounted for by the "contracting-cylinder" model at the lower temperature regions (683–693 K). On the other hand, the "Avrami–Erofeev" model with an integral exponent of 2 is responsible for the pyrolytic decomposition of PP at the higher temperature regions (728–738 K). At the medium temperature regions (693–728 K), it is evidently observed that the reaction model of PP shifts from

Table 1. Reaction models employed to describe the solid state reaction

Symbol	Reaction model	$f(\alpha)$
P4	Power law	$4\alpha^{3/4}$
P3	Power law	$3\alpha^{2/3}$
P2	Power law	$2\alpha^{1/2}$
P2/3	Power law	$2/3\alpha^{-1/2}$
D1	One-dimensional diffusion	$1/2\alpha^{-1}$
F1	Mample (first-order)	$1-\alpha$
A4	Avrami–Erofeev	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$
A3	Avrami–Erofeev	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$
A2	Avrami–Erofeev	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$
D3	Three-dimensional diffusion	$2(1-\alpha)^{2/3}(1-(1-\alpha)^{1/3})^{-1}$
R3	Contracting sphere	$3(1-\alpha)^{2/3}$
R2	Contracting cylinder	$2(1-\alpha)^{1/2}$
F2	Second-order	$(1-\alpha)^2$

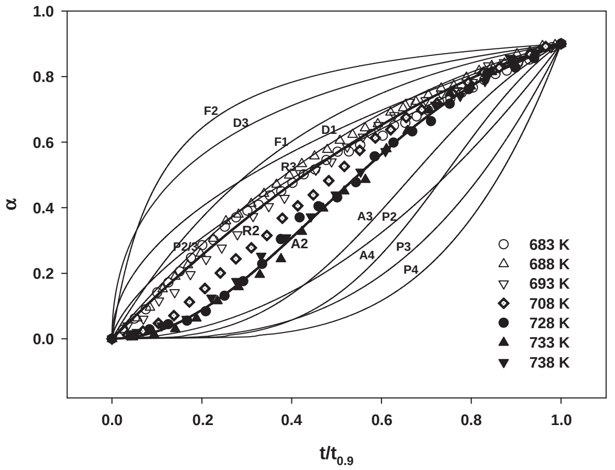

Figure 1. Comparison of theoretical reduced-time-plots (RTPs) for reaction models described in Table 1 with RTPs experimentally determined at isothermal temperature regions 683–738 K.

a "contracting-cylinder" model to the "Avrami–Erofeev" one. Thus, two reaction models describe the pyrolysis kinetics of PP concurrently with different extents within the temperature range of 693 and 728 K.

The reason for the different reaction model of PP as to reaction temperature is due to variation of the generation pattern of volatiles. As heat is applied, the PP is melted. Volatiles are produced in a melt as a result of a chemical reaction. At lower operating temperatures (683–693 K), the fragment sizes of major pyrolysis products may be larger than those necessary for vaporization in spite of active decomposition. Thus, a limited quantity of pyrolysis products may be only vaporized and the evolution of volatiles is likely to be accomplished smoothly through the surface of the melt. On the other hand, bubble nucleation is responsible for a major pyrolysis mechanism at the higher temperature regions (728–738 K). Volatiles may be accumulated until a critical concentration is reached. At the critical concentration of volatiles, bubbles may begin to nucleate.[11] The rate of bubble nucleation appears to be limited by the kinetics of heat, momentum, or mass transfer and thermodynamic properties of melt. It is expected that there may be a critical temperature where the highest molecular size of fragments is small enough to be vaporized, thus triggering the explosive generation of volatiles.

On the basis of the reaction models derived here, Arrhenius parameters were estimated. To this end, Eq 1 was integrated to yield:

$$g(\alpha) = \int_0^{\alpha} [f(\alpha)]^{-1} \mathrm{d}\alpha = k(T_\mathrm{i})t. \tag{2}$$

In order to assess the reaction constants, $k(T_\mathrm{i})$, the identified reaction models were substituted into Eq 2. The k value at a temperature can be determined from the slope of a plot of $g(\alpha)$ versus t. The k values at the lower temperatures corresponding to the "contracting-cylinder" model were evaluated to be 0.0662, 0.0773, and 0.0944 min^{-1} at the isothermal operating temperatures of 683, 688, and 693 K, respectively. At the higher temperatures, the k values as to the "Avrami–Erofeev" model were evaluated to be 0.631, 0.735, and 0.827 min^{-1} at the isothermal operating temperatures of 728, 733, and 738 K, respectively. Arrhenius parameters can be estimated from the plot of $\ln k(T_\mathrm{i})$ versus $1/T_\mathrm{i}$ as follows:

$$\ln k(T_\mathrm{i}) = \ln A - \left(\frac{E}{R}\right)\frac{1}{T_\mathrm{i}}. \tag{3}$$

Consequently, the Arrhenius plot assigned the E and $\ln A$ for the "contracting-cylinder" model to be 140 $\mathrm{kJ{\cdot}mol^{-1}}$ and 21.9 (A: min^{-1}), respectively. Also, the E and $\ln A$ for the "Avrami–Erofeev" model were determined to be 112 $\mathrm{kJ{\cdot}mol^{-1}}$ and 18.8 (A: min^{-1}), respectively. High linearities ($r^2 = 0.994$ and 0.995) of the plots uphold the appropriateness of the Arrhenius relationships as well as the reaction models.

Arrhenius parameters as well as the pyrolysis reaction model of PP are dependent on temperature. At the lower temperatures, the "contracting-cylinder" model is appropriate. Volatiles are evolved at the surface of the melt, suggesting the isotropic shrinkage of melt. On the other hand, at temperatures higher than a critical one, bubble nucleation is likely to account for the reaction model of PP. The generation rate of volatiles overpowers their release rate from the surface of liquids, leading to the accumulation of gases inside the liquids. If the critical concentration of volatiles is met, bubble nucleation commences, mimicking "Avrami–Erofeev" model. It is, hence, concluded that the *n*th-order reaction model adopted by most previous studies[1–4] is inappropriate for that of PP.

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12 A Pre-exponential factor (min^{-1}).
13 E Activation energy ($\mathrm{kJ{\cdot}mol^{-1}}$).
14 $f(\alpha)$ Reaction model.
15 $g(\alpha)$ $\int_0^a [f(\alpha)]^{-1}\mathrm{d}\alpha$.
16 k Rate constant.
17 R Gas constant ($\mathrm{kJ{\cdot}mol^{-1}{\cdot}K^{-1}}$).
18 t Time (min).
19 T Absolute temperature (K).
20 α Extent of conversion.
21 i Certain isothermal operating temperature.