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Identification of Pyrolysis Reaction Model of Linear Low Density Polyethylene (LLDPE)

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This paper described how to estimate the Arrhenius parameters as well as the pyrolysis reaction model of LLDPE from isothermal kinetic data. We used a custom-made thermobalance that is capable of monitoring a weight decrease with time under pure static condition and performed six isothermal kinetic experiments at 713, 718, 723, 728, 733, and 738 K that were chosen within a temperature range (710–740 K) where main decompositions were observed from non-isothermal kinetic results. Comparing experimental reduced-time-plots (RTPs) with theoretical ones, the pyrolysis reaction model of LLDPE is accounted for by "Avrami–Erofeev" model in the investigated temperature region, allowing its functional form to be $2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$. It is, hence, expected that the reaction order model adopted by the previous studies without verification is inappropriate to represent the pyrolysis reaction model of LLDPE. Bubble nucleation may be a major pyrolysis reaction mechanism of LLDPE. As heat is applied, the LLDPE is melted. Volatiles may be accumulated inside the melt until reaching a critical concentration where bubble nucleation sets forth. The rates of heat, mass, or momentum transfer in the LLDPE melt and its physico-chemical properties (especially viscosity) play an important role in characterizing the thermal decomposition kinetics of LLDPE.

A variety of kinetic studies on the high-density polyethylene (HDPE) and low-density polyethylene (LDPE) has attempted to elucidate their pyrolysis kinetics, whereas less attention has been made on the pyrolysis kinetics of LLDPE. Adopting the reaction order model, Park et al.[1] reported that activation energy (E), pre-exponential factor (A), and reaction order (n) of LLDPE pyrolysis reaction were 225.8 kJ/mol, 27.73 ($\ln A$, A: min^{-1}), and 0.58, respectively. Similarly, Corrales et al.[2] assigned 207.2 kJ/mol and 25.41, respectively, to E and $\ln A$ (A: min^{-1}). The above studies, however, assumed that a reaction order model would be responsible for the pyrolysis reaction model of LLDPE without verification.

The reaction order model, $f(\alpha) = (1-\alpha)^n$, is usually applicable for homogeneous gas-phase kinetics and thus is invalid for the pyrolysis reaction model of polymers except for highly specific cases.[3] An incorrect reaction model can lead to a force-fitting of Arrhenius parameters erroneously.[4–7] It is, hence, essential to determine a pyrolysis reaction model correctly at the initial stage of kinetic analysis. This paper attempted to identify the pyrolysis reaction model of LLDPE from analyzing RTPs and to offer an insight into macroscopic pyrolysis mechanisms accordingly.

Powdered LLDPE was used in this study and supplied by Samsung chemical Co. in Korea. The sample was dried in a desiccator before analyses. Isothermal kinetic experiments were carried out by a custom-made thermobalance (TB) that was designed to form pure static conditions. Detailed information on the TB was described in the previous studies.[6–8] LLDPE sample of 10 ± 0.1 mg 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 six isothermal kinetic experiments at operating temperatures of 713, 718, 723, 728, 733, and 738 K under a stream of nitrogen at a linear velocity of 8.3 cm·s^{-1}. The operating temperatures were chosen within a temperature range (710–740 K) where main decompositions were accomplished for non-isothermal kinetic results.

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

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

The reaction model, $f(\alpha)$, 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.[5–7] The RTP is constructed by plotting α as a function of a reduced time, t/t_α, where t_α is the time needed to attain a specific conversion ($\alpha = 0.9$) at an isothermal operating temperature, T_i. The reaction model of LLDPE was chosen among various reaction models from a best fit of experimental RTPs to theoretical ones corresponding to the reaction models described in Table 1.

Six isothermal decomposition results of LLDPE give rise to similar RTPs one another (Figure 1) and excellently duplicate Model 9 in Table 1. The pyrolysis reaction model of LLDPE, hence, would be accounted for by "Avrami–Erofeev" model with an integral exponent of 2.

As heat is applied externally, the LLDPE is melted. Thermal

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

Reaction model	$f(\alpha)$	$g(\alpha)$
1. Power law	$4\alpha^{3/4}$	$\alpha^{1/4}$
2. Power law	$3\alpha^{2/3}$	$\alpha^{1/3}$
3. Power law	$2\alpha^{1/2}$	$\alpha^{1/2}$
4. Power law	$2/3\alpha^{-1/2}$	$\alpha^{3/2}$
5. One-dimensional diffusion	$1/2\alpha^{-1}$	α^2
6. Mample (first-order)	$1-\alpha$	$-\ln(1-\alpha)$
7. Avrami–Erofeev	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
8. Avrami–Erofeev	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
9. Avrami–Erofeev	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
10. Three-dimensional diffusion	$2(1-\alpha)^{2/3}[1-(1-\alpha)^{3/4}]^{-1}$	$[(1-(1-\alpha)^{1/3})]^2$
11. Contracting sphere	$3(1-\alpha)$	$1-(1-\alpha)^{1/3}$
12. Contracting cylinder	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$
13. Second-order	$(1-\alpha)^2$	$(1-\alpha)^{-1}-1$

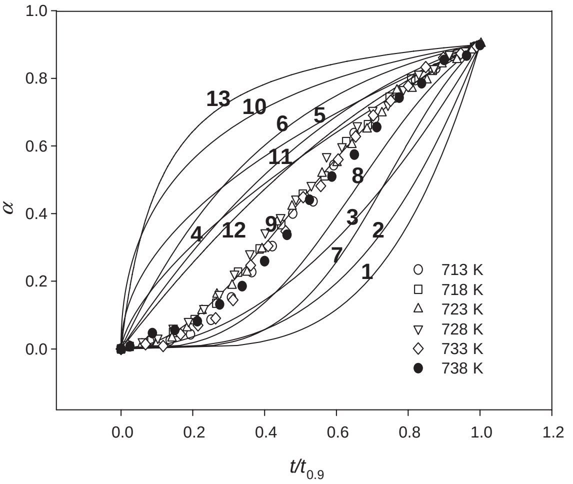

Figure 1. Comparison of theoretical reduced-time-plots (RTPs) for reaction models described in Table 1 with RTPs experimentally determined at isothermal temperature regions 713–738 K.

decomposition reaction produces volatiles in the molten LLDPE. At a critical concentration of volatiles in the melt, their supersaturation was attained and bubbles may begin to nucleate, thus simulating the "Avrami–Erofeev" model. However, our previous study[6] revealed that the pyrolysis reaction model of HDPE would be accounted for by the "Contracting Cylinder" model. Disparity in the reaction model between LLDPE and HDPE is attributed to their different physico-chemical properties, especially viscosity. The HDPE melt expects higher viscosity that appears to hinder bubble nucleation and growth in spite of a relatively high concentration of volatiles.[9] Instead of devolatilization by bubble nucleation mechanism, the interfacial devolatilization from the surface of HDPE melt may mainly account for its thermal decomposition at the interested temperature region (718–733 K).[6,7] On the other hand, the LLDPE generates volatiles more vigorously than the HDPE under the same reaction conditions because of its thermal instability. Thus, the LLDPE melt can be supersaturated more easily with the generated volatiles. Higher concentrations of volatiles and less viscosity of the LLDPE melt can construct better conditions for developing the bubble nucleation. The nucleated gas bubbles in the LLDPE melt grow rapidly until the gas pressure in the melt is in equilibrium with that within the bubbles. The growing gas bubbles travel to the surface of LLDPE melt and are evaporated. The rate of bubble nucleation, hence, is likely 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 that triggers the explosive generation of volatiles, leading to bubble nucleation and growth. The LLDPE, hence, may simulate the "Avrami–Erofeev" model at the higher temperatures than a critical one. Below a critical temperature, the "Contracting Cylinder" model or other reaction controlled models may represent the pyrolysis reaction model of LLDPE. Our recent study[8] proposed that the pyrolysis reaction model of polypropylene (PP) can be varied with temperature, according to the shift pattern of RTP with temperature. Since the RTPs of the LLDPE are superimposed excellently (Figure 1), the reaction model of the LLDPE is unvaried at least within the operating temperatures (713–738 K) investigated here. However, the possibility of variation of reaction model with temperature cannot be excluded.

Arrhenius parameters of LLDPE were determined using its reaction model derived here. Integrating Eq 1 leads to:

$$g(\alpha) = \int [f(\alpha)]^{-1} \mathrm{d}\alpha = k(T_i)t. \quad (2)$$

The integrated inverse function of the identified reaction model, $g(\alpha) = [-\ln(1-\alpha)]^{1/2}$, was substituted into Eq 2. The reaction constant, $k(T_i)$, at a temperature can be determined from the slope of the plot of $g(\alpha)$ versus t. The reaction constants, $k(T_i)$, were assessed to be 0.1604, 0.1996, 0.2329, 0.2793, 0.3207, and 0.3718 min^{-1} at the isothermal operating temperature of 713, 718, 723, 728, 733, and 738 K, respectively. High linearities ($R^2 = 0.9944$–0.9996, Average: 0.9970 ± 0.0021) of the plots ($g(\alpha)$ versus t) supports the properness of the reaction model determined here.

Arrhenius parameters can be determined from the slope ($-E/R$) and intercept ($\ln A$) of the Arrhenius plot of $\ln k(T_i)$ vs $1/T_i$ as shown below:

$$\ln k(T_i) = \ln A - \left(\frac{E}{R}\right)\frac{1}{T_i}. \quad (3)$$

From the Arrhenius plot, the E and $\ln A$ were evaluated to be 145.33 $\mathrm{kJ{\cdot}mol^{-1}}$ and 22.7 (A: min^{-1}), respectively. High linearity ($R^2 = 0.9958$) of the Arrhenius plot upholds the appropriateness of the Arrhenius relationship as well as the reaction model.

Bubble nucleation may represent the macroscopic pyrolysis mechanism of LLDPE, mimicking the "Avrami–Erofeev" model in the temperature region (713–738 K) performed here. The rates of heat, mass, or momentum transfer in the LLDPE melt and its physico-chemical properties play an important role in characterizing the thermal decomposition kinetics of LLDPE. It is, hence, concluded that the reaction order model adopted by the previous studies is inappropriate to represent the pyrolysis reaction model of LLDPE.[1,2]

A: pre-exponential factor (min^{-1}), E: activation energy ($\mathrm{kJ{\cdot}mol^{-1}}$), $f(\alpha)$: reaction model, $g(\alpha)$: $\int_0^{\alpha}[f(\alpha)]^{-1}\mathrm{d}\alpha$, k: rate constant, R: gas constant ($\mathrm{kJ{\cdot}mol^{-1}{\cdot}K^{-1}}$), t: time (min), $t_{0.9}$: time (min) to attain a specific conversion, $\alpha = 0.9$, T: absolute temperature (K), α: extent of conversion, and i: certain isothermal operating temperature.

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