Thermal Decomposition Kinetics of Polymeric Wastes Using a Nonisothermal Thermogravimetric Method

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Abstract: Nonisothermal kinetic experiments of polymeric wastes, such as polyethylene (PE), polypropylene (PP), polystyrene (PS) and polyethylene terephthalate (PET), were studied in nitrogen atmosphere, and kinetic parameters were analyzed by Flynn-Wall method. The mixture containing polymeric wastes, which were combined to the ratio of 2: 2: 2: 1 for PE, PP, PET and PS on the basis of weight fraction, was also studied and analyzed in the same way. Theoretical activation energies (E_a) of mixtures were calculated and compared with experimental activation energy (E_a) obtained by Flynn-Wall method. The nonisothermal kinetic results of polymeric wastes showed that most of polymeric wastes had single step reactions and similar activation energies for observed conversion ranges respectively. In the result of kinetic parameter analysis of mixtures, E_a showed lower values than values of E_a for all observed conversion ranges. This means that lower activation energies are the result of interaction among polymeric wastes during thermal decomposition of mixtures.

Keywords: polymeric waste, nonisothermal kinetics, thermogravimetric method

Introduction

As the consumption of polymers is increased, concern about the recycling of polymeric wastes is also received growing attention in recent years. Especially, they can be transformed into petrochemical oil when proper thermal decomposition technique is applied in the absence of oxygen because most of polymers are derived from petroleum-based materials. Therefore, pyrolysis technique has been received much attention to apply to the mixtures of polymeric wastes as a route for chemical recycling [1].

The thermal degradation researches of polymers and polymeric wastes have been studied in various aspects. For example, kinetics and mechanisms of polymers [2-5], the product analysis of commodity polymers [6-8], the analysis of liquid yield from the mixture containing PE and PS [9], and stepwise pyrolysis of mixtures of poly(vinyl chloride), PS and PE were widely investigated [10]. In case of mixtures containing polymeric wastes, the simultaneous generation of oils and gases for waste PE and PS with different mixing ratios [11], the fast pyrolysis of real discharged plastic waste mixture and the analysis of three end products such as gas, oil, and char have also been studied [12].

Even though most of household polymeric wastes in types of mixtures and the amount of discharge of polymeric wastes are increasing, 10% of polymeric wastes are only recycled [13]. Therefore, the treatment of mixed polymeric wastes is also receiving attention.

In this study, thermal decomposition kinetics of polymeric wastes, such as PE, PS, PP, PET, and their mixture were carried out in nitrogen atmosphere, and kinetic parameters were analyzed by Flynn-Wall method [14]. In addition, theoretical activation energies (E_a) of mixture were calculated by Flynn-Wall method to adapt theoretical thermograms of mixtures, and E_a and the experimental activation energy (E_a) of mixtures were compared and analyzed to understand the change of activation energies among polymeric wastes.

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### Table 1. Properties of Polymeric Wastes

<table>
<thead>
<tr>
<th></th>
<th>PE</th>
<th>PP</th>
<th>PET</th>
<th>PS</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T_g(K))</td>
<td>-</td>
<td>-</td>
<td>349</td>
<td>367</td>
</tr>
<tr>
<td>(T_m(K))</td>
<td>410</td>
<td>423</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inorganic elements</td>
<td>Mg, Al, Si, Ca, (TiO_2)</td>
<td>Al, Si, Cl, Ca, (TiO_2), Fe, Zn</td>
<td>Mg, Al, Si, Ca</td>
<td>Ca, (TiO_2)</td>
</tr>
</tbody>
</table>

### Table 2. Sample Survey of Household Plastic Waste

<table>
<thead>
<tr>
<th>Elements</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE</td>
<td>26.5%</td>
</tr>
<tr>
<td>PP</td>
<td>23.8%</td>
</tr>
<tr>
<td>PS</td>
<td>14.6%</td>
</tr>
<tr>
<td>PET</td>
<td>25.4%</td>
</tr>
<tr>
<td>Etc.</td>
<td>11.7%</td>
</tr>
</tbody>
</table>

A sample survey of household plastic waste in Seoul, Korea

A sample survey of household plastic waste at Plastic Waste Treatment Institute

### Experimental

#### Materials
Polymeric wastes used in this study were PE, PP, PET, and PS, which were found in discharged household plastic wastes in Korea. PE, PP, and PS were pulverized, washed, dried and pelletized with the pellet type of 2 mm diameter \(\times\) 3 mm length. PET was washed, dried, and pelletized with tetragon type of 2 mm \(\times\) 2 mm. Table 1 shows properties of polymeric wastes, such as glass transition temperature \((T_g)\), melting temperature \((T_m)\), and the amount of inorganic materials contained in polymeric wastes. \(T_g\) and \(T_m\) were measured by Differential Scanning Calorimeter (Perkin-Elmer 7 Series Thermal Analysis System) and the qualitative analysis of inorganic materials was analyzed by X-Ray Fluorescence Spectrometer (Philips PW1480 Spectrometer).

#### Nonisothermal Kinetics
In general, the thermal decomposition kinetics related to thermogravimetry (TG) weight loss data was attributed to the following kinetic equation [15]:

\[
\frac{d\alpha}{dt} = q \frac{d\alpha}{dT} = A(1 - \alpha)^n e^{-E_a/RT}
\]  
(1)

where conversion \(\alpha\) is defined as the reacted fraction at time \(t\), \(q\) is the heating rate, \(E_a\) is the activation energy, \(R\) is the gas constant, \(A\) is the pre-exponential factor, and \(T\) symbolizes the absolute temperature.

When Equation (1) is integrated with respect to temperature and conversion, an integrated form is obtained:

\[
g(\alpha) = \int_0^\alpha \frac{d\alpha}{(1 - \alpha)^n} = \frac{AE_a}{qR} \int_\infty^{\alpha} \frac{e^{(-\frac{E_a}{R})}}{x^2} dx
\]  
(2)

where \(g(\alpha)\) is conversion functional relationship and \(x = E_a/RT\).

Flynn and Wall solved Equation (2) using Doyle’s approximation [16], and Equation (3) is obtained:

\[
\log g(\alpha) = \frac{-0.4567}{R} \cdot \frac{1}{T} - \log \left(1 - \frac{E_a}{315 \cdot 0.4567 \cdot \frac{E_a}{RT}}\right)
\]  
(3)

Using Equation (3), \(E_a\) can be calculated from the slope of the most probable straight line obtained by drawing the dependence of versus \(1/T\) and \(A\) from the intercept of the straight line on the \(y\) axis. The activation energy obtained by Flynn-Wall method is the average value of activation energies of chemical reactions and physical processes in thermal decomposition reaction. In addition, this method provides apparent activation energies as a function of conversion without any assumption about the reaction order [17].

The kinetic constant \((k)\) was given by the Arrhenius Equation:

\[
k = Ae^{-E_a/RT}
\]  
(4)

\(k\) and \(A\) were calculated by the assumption that the thermal decomposition was first order and conversion did not depend on heating rate.

#### Thermogravimetric Experiments
Thermogravimetric (TG) analysis of each polymeric waste, such as PE, PP, PET, and PS, and their mixtures were experimented in TG apparatus (Thermal Interaction Co. Balances Model TML1000-1). The ratio of mixtures containing polymeric wastes was decided on the basis of mixing ratio of household polymeric wastes. From this survey, the mixing ratio of
polymeric wastes is found to be 2: 2: 2: 1 for PE, PP, PET and PS on the basis of weight fraction. In this experiment, 400 mg of sample was used and the sample was heated from 273 K up to 873 K at three different heating rates of 5 K/min, 10 K/min and 15 K/min. Experiments were performed in nitrogen atmosphere. Using thermograms obtained by TG experiments, kinetic parameters of each polymeric wastes and mixtures were calculated by Flynn-Wall method.

Results and Discussion

TG analysis of Polymeric Wastes

Nonisothermal thermograms of PE, PP, PET and PS at different heating rate of 5 K/min, 10 K/min and 15 K/min are shown in Figures 1 and 2. As can be seen in Figures 1 and 2, the thermal decomposition temperature interval of all polymeric wastes moves to higher temperatures as the heating rate increases. The thermal decomposition of PS starts earlier than any other polymeric waste. All polymeric wastes were decomposed instantaneously at typical temperature ranges and single step reactions were detected in all polymeric wastes [19]. PET showed narrow temperature interval for different heating rates during thermal decomposition reactions and 20% of residue was detected after thermal decomposition to 873 K. Generally, the product of PET mainly included benzoic acid and terephthalic acid after thermal decomposition while PE, PP and PS produce various hydrocarbons having carbon number of wide ranges [20,21]. PET has also known that many carbonaceous residues were formed during thermal decomposition. Murata and Makino [22] reported that PE and PP are easily pyrolyzed without carbonaceous residues above 718 K and 683 K, respectively. Pure PS has also known that it is well pyrolyzed and has fewer residues. In this study, however, polymeric wastes of PE, PP and PS showed about 5% of residues after thermal decomposition to 873 K. As can be seen in Table 1, polymeric wastes used in this study contained inorganic materials while pure PE, PP and PS generally contain no inorganic materials. Previous works reported that inorganic materials affected to the formation of coke and carbona-
Table 3. Kinetic Parameters of Nonisothermal Decomposition of Polymeric Wastes Obtained by Flynn-Wall Method

<table>
<thead>
<tr>
<th>$\alpha$</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
<th>0.5</th>
<th>0.6</th>
<th>0.65</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PE</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_a$ (kJ/mol)</td>
<td>183.3</td>
<td>181.7</td>
<td>179.4</td>
<td>176.9</td>
<td>181.0</td>
<td>179.2</td>
</tr>
<tr>
<td>$A$ (min$^{-1}$)</td>
<td>$4.49 \times 10^{11}$</td>
<td>$4.47 \times 10^{11}$</td>
<td>$3.72 \times 10^{11}$</td>
<td>$2.88 \times 10^{11}$</td>
<td>$6.30 \times 10^{11}$</td>
<td>$4.73 \times 10^{11}$</td>
</tr>
<tr>
<td>$r^2$</td>
<td>0.965</td>
<td>0.975</td>
<td>0.984</td>
<td>0.990</td>
<td>0.996</td>
<td>0.990</td>
</tr>
<tr>
<td>$k$ (min$^{-1}$)</td>
<td>0.048</td>
<td>0.075</td>
<td>0.106</td>
<td>0.143</td>
<td>0.190</td>
<td>0.195</td>
</tr>
<tr>
<td><strong>PP</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_a$ (kJ/mol)</td>
<td>151.6</td>
<td>149.2</td>
<td>146.4</td>
<td>148.1</td>
<td>144.9</td>
<td>145.7</td>
</tr>
<tr>
<td>$A$ (min$^{-1}$)</td>
<td>$7.85 \times 10^{9}$</td>
<td>$6.69 \times 10^{9}$</td>
<td>$4.98 \times 10^{9}$</td>
<td>$7.69 \times 10^{9}$</td>
<td>$5.27 \times 10^{9}$</td>
<td>$5.83 \times 10^{9}$</td>
</tr>
<tr>
<td>$r^2$</td>
<td>0.990</td>
<td>0.986</td>
<td>0.981</td>
<td>0.981</td>
<td>0.976</td>
<td>0.976</td>
</tr>
<tr>
<td>$k$ (min$^{-1}$)</td>
<td>0.049</td>
<td>0.078</td>
<td>0.111</td>
<td>0.1343</td>
<td>0.197</td>
<td>0.204</td>
</tr>
<tr>
<td><strong>PET</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_a$ (kJ/mol)</td>
<td>332.7</td>
<td>335.5</td>
<td>329.7</td>
<td>343.1</td>
<td>366.0</td>
<td>368.0</td>
</tr>
<tr>
<td>$A$ (min$^{-1}$)</td>
<td>$4.77 \times 10^{23}$</td>
<td>$1.80 \times 10^{23}$</td>
<td>$3.27 \times 10^{23}$</td>
<td>$3.59 \times 10^{24}$</td>
<td>$1.92 \times 10^{26}$</td>
<td>$2.37 \times 10^{26}$</td>
</tr>
<tr>
<td>$r^2$</td>
<td>0.995</td>
<td>0.976</td>
<td>0.976</td>
<td>0.995</td>
<td>0.982</td>
<td>0.982</td>
</tr>
<tr>
<td>$k$ (min$^{-1}$)</td>
<td>0.106</td>
<td>0.160</td>
<td>0.229</td>
<td>0.335</td>
<td>0.496</td>
<td>0.157</td>
</tr>
<tr>
<td><strong>PS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_a$ (kJ/mol)</td>
<td>141.9</td>
<td>139.3</td>
<td>136.4</td>
<td>135.3</td>
<td>132.8</td>
<td>129.3</td>
</tr>
<tr>
<td>$A$ (min$^{-1}$)</td>
<td>$2.25 \times 10^{9}$</td>
<td>$2.25 \times 10^{9}$</td>
<td>$2.21 \times 10^{9}$</td>
<td>$2.05 \times 10^{9}$</td>
<td>$1.48 \times 10^{9}$</td>
<td>$7.93 \times 10^{8}$</td>
</tr>
<tr>
<td>$r^2$</td>
<td>0.994</td>
<td>0.993</td>
<td>0.991</td>
<td>0.995</td>
<td>0.993</td>
<td>0.991</td>
</tr>
<tr>
<td>$k$ (min$^{-1}$)</td>
<td>0.049</td>
<td>0.062</td>
<td>0.107</td>
<td>0.145</td>
<td>0.189</td>
<td>0.195</td>
</tr>
</tbody>
</table>

Determination of Kinetic Parameters of Polymeric Wastes

Kinetic parameters of polymeric wastes obtained by Flynn-Wall method are shown in Table 3. $E_a$ and $A$ were calculated by applying Equation (3), $k$ was calculated by Arrhenius Equation on the basis of heating rate of 5 K/min. Correlation coefficients($r^2$) are also listed in Table 3. As mentioned before, the advantage of Flynn-Wall method is to obtain apparent activation energy, which does not depend on reaction order. In general, the degradation of polymers is a complex phenomenon, involving many simple reactions that are difficult to analyze separately. Therefore, activation energy obtained by Flynn-Wall method is average value to activation energies of various simple reactions. As can be seen Table 3, most activation energies of polymeric wastes at detected conversion range showed similar activation energies except PET. It could be estimated that each of polymeric wastes such as PE, PP and PS was decomposed by similar pyrolysis reactions for the conversion range of 0.2 to 0.65. In the case of PET, activation energies were increased to 25 KJ/mol after conversion of 0.5. As can be seen in Figure 2, decomposition reactions of PET were terminated in higher weight loss and higher residues were detected. Therefore, it indicates that remaining carbonaceous residues affect to the kinetic data. Kinetic constants of all polymeric wastes for all observed conversion were increased with conversions and temperature during nonisothermal decomposition reaction.

**TG Analysis of Mixtures**

Nonisothermal thermograms of mixtures containing polymeric wastes whose ratio was fixed to 2: 2: 2: 1 for PE, PP, PET and PS at different heating rates of 5 K/min, 10 K/min and 15 K/min are shown in Figure 3. The thermal decomposition temperature interval of mixtures also moved to higher temperatures as the heating rate increased and 10% of residues were detected. Slopes of thermograms varied slightly but remarkable distinction was not appeared.

Figure 3. Thermograms of nonisothermal decomposition of mixture containing polymeric wastes.

**Determination of Kinetic Parameters of Mixtures and Comparison of Activation Energies between $E_a$ and $E_b$**

Kinetic parameters of mixtures obtained by Flynn-Wall method are shown in Table 4. $E_a$, $A$ and $k$ were calculated in the same way before and $r^2$ was listed in Table 4. $E_b$ values and kinetic constants of mixtures were increased with conversions. Information about change of average activation energies of reactions during thermal degradation of mixtures can be obtained from the analysis of kinetic parameters, but information about interactions among polymeric wastes was not clear. Therefore, in...
Table 4. Kinetic Parameters of Nonisothermal Decomposition of Mixture Obtained by Flynn-Wall Method

<table>
<thead>
<tr>
<th>α</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
<th>0.5</th>
<th>0.6</th>
<th>0.65</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixture containing polymeric wastes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ea (kJ/mol)</td>
<td>121.4</td>
<td>126.5</td>
<td>135.6</td>
<td>146.3</td>
<td>162.6</td>
<td>167.8</td>
</tr>
<tr>
<td>A (min⁻¹)</td>
<td>7.71 × 10⁷</td>
<td>2.36 × 10⁸</td>
<td>1.35 × 10⁹</td>
<td>8.93 × 10⁹</td>
<td>1.36 × 10¹</td>
<td>2.77 × 10¹</td>
</tr>
<tr>
<td>r²</td>
<td>0.995</td>
<td>0.991</td>
<td>0.989</td>
<td>0.985</td>
<td>0.972</td>
<td>0.984</td>
</tr>
<tr>
<td>k (min⁻¹)</td>
<td>0.047</td>
<td>0.074</td>
<td>0.106</td>
<td>0.144</td>
<td>0.193</td>
<td>0.202</td>
</tr>
</tbody>
</table>

Table 5. Theoretical Kinetic Parameters and Correlation Factor of Nonisothermal Decomposition of Mixture Obtained by Flynn-Wall Method

<table>
<thead>
<tr>
<th>α</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
<th>0.5</th>
<th>0.6</th>
<th>0.65</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ea (kJ/mol)</td>
<td>195.2</td>
<td>188.7</td>
<td>185.9</td>
<td>164.2</td>
<td>162.8</td>
<td>169.6</td>
</tr>
<tr>
<td>A (min⁻¹)</td>
<td>1.7410¹⁴</td>
<td>6.9410¹²</td>
<td>4.1910¹²</td>
<td>1.0710¹¹</td>
<td>7.8210⁸</td>
<td>2.0210⁸</td>
</tr>
<tr>
<td>r²</td>
<td>0.987</td>
<td>0.984</td>
<td>0.995</td>
<td>0.994</td>
<td>0.996</td>
<td>1.000</td>
</tr>
<tr>
<td>Fk</td>
<td>1.608</td>
<td>1.491</td>
<td>1.371</td>
<td>1.122</td>
<td>1.001</td>
<td>1.011</td>
</tr>
</tbody>
</table>

In this study, Ea of mixtures was calculated by Flynn-Wall method by adapting theoretical thermograms of mixtures. Ea and Eb of mixture were compared and analyzed to understand interactions among polymeric wastes. The method of making theoretical thermogram in nonisothermal kinetics was proposed.

To make theoretical thermogram and calculate theoretical activation energy, the following assumptions are necessary.

1. Intermolecular interaction among molecules does not exist during the thermal decomposition of mixtures.
2. The degradation characteristics of mixtures are proportional to only the mixing ratio of polymers.
3. Decomposition mechanisms of mixtures follow only the reaction mechanisms of each material.

Adapting these assumptions, we can get a theoretical thermogram by the following equation:

\[
(1-a)T_i = \left( \sum_{j=1}^{n} a_j (1-a_j) \right)_{T_i}
\]  

where \( \sum_{j=1}^{n} a_j = 1 \)

\( a_j \) : conversion of j material
\( a \) : conversion for mixtures
\( \alpha_j \) : mixing ratio of j material
\( n \) : number of mixing materials
\( T_i \) : specific temperature at the heating rate of i for 273 K ≤ T ≤ 873 K

Using Equation (5), theoretical conversion for mixtures can be obtained at \( T_i \). By calculating conversion from 273 K to 873 K by Equation (5), total conversion for the heating rate i can be obtained. In the same way, total conversion can be calculated for different heating rate. In this study of TG analysis, experiments were carried out at the heating rates of 5 K/min, 10 K/min and 15 K/min. As a result, theoretical thermograms can be obtained by this procedure. In addition, adapting Flynn-Wall method to these theoretical thermograms, \( F_k \) can be calculated.

The dimensionless correlation factor \( F_k \) which compares the difference between \( E_a \) and \( E_b \) is proposed as follows:

\[
F_k = \left( \frac{E_{b\bar{a}}}{E_a} \right)^{\alpha - \alpha_b}
\]  

where \( E_{b\bar{a}} \) : theoretical activation energy
\( E_a \) : experimental activation energy
If \( F_k \geq 1 \), experimental activation energy is lower than theoretical activation energy. It can be estimated that any intermolecular interaction acts among molecules to the way of reducing activation energies.

Kinetic parameters obtained from theoretical thermograms of mixtures by Flynn-Wall method, \( r^2 \) and \( F_k \) for different conversion are listed in Table 5. The result of \( E_{b\bar{a}} \) values of mixtures was decreased for detected conversion except conversion of 0.65 while \( E_a \) values of mixtures were increased for all detected conversion. If any interactions among polymeric wastes did not exist during thermal decomposition, activation energies of each polymeric waste would be conserved in TG data and \( E_a \) and \( E_{b\bar{a}} \) would be shown by similar values. However, the analysis of \( E_a \) and \( E_{b\bar{a}} \) showed a different result. Therefore, we can estimate that some intermolecular interactions act among polymeric wastes and the change of mechanism may exist during thermal decomposition of mixtures [23-25]. \( F_k \) value showed over 1.0 for all detected conversion, but \( F_k \) value was decreased as conversion increased. This means that the effect of reducing activation energies affects all detected conversion and this effect is dominant for lower conversion.

Conclusion

Nonisothermal kinetic experiments for polyethylene (PE), polypropylene (PP), polystyrene (PS) and polyethylene terephthalate (PET) were studied in nitrogen atmosphere, and kinetic parameters were analyzed by Flynn-Wall method. The polymeric waste mixtures of the ratio of 2: 2: 2: 1 for PE, PP, PET and PS on the basis of
weight fraction, was also studied and analyzed in the same way. TG analysis and comparison of $E_a$ and $E_b$, obtained by Flynn-Wall method showed that $E_b$ values of mixtures were decreased for all detected conversion while $E_a$ values of mixture were increased. $F_E$ value showed over 1.0 for all detected conversion, however $F_E$ value was decreased as conversion was increased. The nonisothermal kinetic results of polymeric wastes showed that most of polymeric wastes had single step reactions and similar activation energies for detected conversion ranges respectively. The result of kinetic parameter analysis of mixtures showed lower values for all detected conversion ranges. This means that interaction reduces activation energies among polymeric wastes during thermal decomposition of mixtures.

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References