Comparison of Pyrolysis Kinetics Between Rigid and Flexible Polyurethanes

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Abstract: The pyrolysis kinetics of rigid and flexible polyurethanes were examined using thermogravimetric analysis. During the experiment, some of the main compounds were detected. Rigid polyurethane produced five types of low molecular weight organic products, and flexible polyurethane produced at least eleven types of low molecular weight organic products. The main decomposition range of rigid polyurethane took place between 200 and 410 °C, and flexible polyurethane between 150 and 500 °C. A consecutive kinetic model for the pyrolysis of polyurethanes is proposed. The model was able to simulate the experimental curves with good agreement. Using this kinetic model, the kinetic parameters such as activation energy, frequency factor and reaction order could be determined. The average activation energy of flexible polyurethane was 203.1 KJ/mol, which is almost 1.59 times higher than that of rigid polyurethane, 127.7 KJ/mol.

Keywords: pyrolysis, thermogravimetric analysis, flexible and rigid polyurethane, kinetics

Introduction

Polyurethanes (PU) have a wide range of industrial applications, such as car paints, flexible foams for bedding, rigid foams for insulation, adhesives and other commercial goods [1]. They have good resistance to rubbing, impact, oil, low temperature and acidity-alkalinity. They also exhibit good adhesion properties with metals, wood and ceramics. Polyurethane is produced by a reaction between multifunctional isocyanates and polyols to give the following molecular structure (Figure 1).

The removal of toxic and dangerous refuse that are produced during the treatment of polyurethane has become a serious environmental problem in many cities. Pyrolysis and combustion are two methods that can be used to solve the problem of these wastes. Pyrolysis is the first step in the combustion process. Therefore, knowledge of the decomposition process of polyurethane and its control are important [2].

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Table 1. Elemental Analysis of PUr and PUf

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Nitrogen (%)</th>
<th>Carbon (%)</th>
<th>Hydrogen (%)</th>
<th>Oxygen (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PUr</td>
<td>10.3</td>
<td>79.3</td>
<td>6.4</td>
<td>3.4</td>
</tr>
<tr>
<td>PUf</td>
<td>9.6</td>
<td>81.0</td>
<td>3.8</td>
<td>3.5</td>
</tr>
</tbody>
</table>

The polyurethane pyrolysis included many reactions each producing several products. Hence, it was difficult to study every reaction. This paper examined the macroscopic kinetics of polyurethane and ignored the reaction mechanism for each product in the pyrolysis process. It was believed that polyurethane was made up of a finite number of different components with each component reacting independently in the pyrolysis process. For example, two types of components were proposed. A consecutive kinetic model for polyurethane pyrolysis was proposed based on this hypothesis. Each stage of weight loss was shown as a peak in DTA curve shape that corresponds to an independent reaction of sample. The kinetic parameters of each reaction over the whole temperature range of the experiment were considered. In this study, the evaporation of water was ruled out and the conversion rate was adopted to indicate the degree of reaction.

The kinetic model is as follows [2]:

\[
PU_i \rightarrow a_i R_i + b_i V_i
\]

\[
PU_1 \rightarrow a_1 R_1 + b_1 V_1
\]

\[
PU_2 \rightarrow a_2 R_2 + b_2 V_2
\]

(1)

\[
\frac{d\alpha_i}{dt} = k_i(1-\alpha_i)^{\nu_i} = A_i \exp \left( - \frac{E_i}{R_i T} \right)(1-\alpha_i)^{\nu_i} i=1,2
\]

(2)

\[
\alpha_i = \frac{w_{io} - w_i}{w_{io} - w_{i\infty}}
\]

(3)

Kinetics Study

The polyurethane pyrolysis included many reactions each producing several products. Hence, it was difficult to study every reaction. This paper examined the macroscopic kinetics of polyurethane and ignored the reaction mechanism for each product in the pyrolysis process. It was believed that polyurethane was made up of a finite number of different components with each component reacting independently in the pyrolysis process. For example, two types of components were proposed. A consecutive kinetic model for polyurethane pyrolysis was proposed based on this hypothesis. Each stage of weight loss was shown as a peak in DTA curve shape that corresponds to an independent reaction of sample. The kinetic parameters of each reaction over the whole temperature range of the experiment were considered. In this study, the evaporation of water was ruled out and the conversion rate was adopted to indicate the degree of reaction.

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\]

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\]

(2)

\[
\alpha_i = \frac{w_{io} - w_i}{w_{io} - w_{i\infty}}
\]

(3)
w, is the weight of the reaction i detected by the thermogravimetrical analysis that includes the mass of solid residue generated as well as the unreacted solid; \( w_{0i} \) is the initial weight of the reaction i at time t; \( w_{r} \) is the residual weight of the reaction i. \( E_i \) (KJ/mol) is the activation energy of reaction i; \( A_i \) (min\(^{-1}\)) is the frequency factor of the reaction i; n, is the reaction order of reaction i. In the pyrolysis process, the heating rate \( \beta \) is considered to be constant.

\[
\beta = \frac{dT}{dt}
\]

(4)

Equation (2) can then be written as

\[
\frac{da_i}{dT} = \frac{A_i}{\beta} \exp\left(-\frac{E_i}{RT}\right)(1-\alpha_i)^n \quad i=1,2
\]

(5)

Each independent reaction was analytically integrated for small temperature intervals (\( \Delta T \)).

\[
\int_{a_T}^{a_T+\Delta T} \frac{da_i}{(1-\alpha_i)^n} = \frac{A_i}{\beta} \int_T^{T+\Delta T} \exp\left(-\frac{E_i}{RT}\right) dT \quad (n \neq 0)
\]

(6)

\[
\int_{a_T}^{a_T+\Delta T} \frac{da_i}{(1-\alpha_i)^n} = \frac{1}{n-1} \left[ (1-\alpha_{T+\Delta T})^{1-n} - (1-\alpha_T)^{1-n} \right]
\]

(7)

However, the right-hand side of Equation (6) has no precise integral. By making the substitution, \( u = \frac{E}{RT} \), and using the following relation [7],

\[
\int_u^{\infty} e^{-u} u^{-n} du = u^{-1} e^{-u} \sum_{n=0}^{\infty} (-1)^n u^n
\]

(8)

Then

\[
\int_{T}^{T+\Delta T} \exp\left(-\frac{E}{RT}\right) dT = \frac{RT^2}{E} \left(1 - 2 \frac{RT}{E} \right) \exp\left(-\frac{E}{RT}\right)
\]

(9)

\[
\int_{T}^{T+\Delta T} \exp\left(-\frac{E}{RT}\right) dT = \frac{AR(T+\Delta T)}{\beta E} \left(1 - 2 \frac{AR(T+\Delta T)}{E} \right) \exp\left(-\frac{E}{RT}\right)
\]

(10)

The relationship between the general conversion rate and each independent part can be expressed as follows:

\[
\alpha = \sum_{i=1}^{k} x_i \alpha_i
\]

(11)

\[
x_i = \frac{w_{io} - w_{r}}{w_{0} - w_{r}}
\]

(12)

\( \alpha \) is the general conversion rate of the sample at time t. \( k \) is the number of independent reactions. \( x_i \) is the fraction of the weight of part i for the global weight loss of the sample.

Differentiation Equation (5) gives the following:

\[
\frac{da}{dT} = \sum_{i=1}^{k} x_i \frac{da_i}{dT}
\]

(13)

In the calculation, two different objective functions (O.F.) can be selected to fit the TG curve shapes or DTA curve shapes respectively.

\[
OF_1 = \sum (\alpha_{exp} - \alpha_{cal})^2
\]

(14)

\[
OF_2 = \sum \left( \frac{da}{dT}_{exp} - \frac{da}{dT}_{cal} \right)^2
\]

(15)

**Results and discussion**

**TGA and DTA Curves Analysis**

Figures 2 and 3 show the normalized decomposition curves and differential thermal analysis curves for two polyurethanes in nitrogen, respectively. The weight fraction was defined as the ratio of the solid weight loss at a given time to the total solid weight loss. The results of more than one stage in these curves indicate that the decompositions of the polyurethanes consist of many chemical reactions. The area < 120 °C is considered to be due to the evaporation of water, and is not shown in Figures 2 and 3.

Figure 2 shows the PUr curves indicating the two main temperature ranges for the variation in the significant solid conversion. The first range corresponds to a conversion of approximately 0.80, beginning at approximately 200 °C and extending to 410 °C. These were observed clearly from the DTA curve shape. The maximum variation in conversion was observed at approximately 309 °C. However, the PUf curves showed a different shape. The main decomposition occurred between 150 and 500 °C. The decomposition rate was enhanced evidently in a narrow range from 350 to 430 °C. The maximum variation in conversion occurred at approximately 390 °C. A comparison of the two main conversion variation peaks shows that the maximum value of PUf was approximately 0.38 times higher than that of
Figure 2. Normalized experimental TGA and DTA curves of PUr in nitrogen at four heating rates.

Figure 3. Normalized experimental TGA and DTA curves of PUf in nitrogen at four heating rates.

PUr, and the main peak of PUf moves to a higher temperature, which is mainly enhanced by 80 °C compared with PUr. This indicates that the components of PUr are decomposed between 200 and 410 °C, while those of the PUf are decomposed between 150 and 500 °C. Furthermore, there are many small peaks in the DTA curve shape of the PUf. The component of PUf is more complicated than that of PUr because there are more reactions that occur during the pyrolysis process.

There were some similarities and differences between Figures 2 and 3. The conversion rate decreased visibly with increasing heating rate. This result corresponds to the results of a varnish waste study [2] and a TG study of phosphated polyurethane ionomers [8]. However, the maximum decomposition velocity decreases with increasing initial degraded temperature, and the whole decomposition process moves to a higher temperature range with increasing heating rate. There was a small peak in the range from 100 to 200 °C for PUr and from 150 to 250 °C for PUf. Spirckel and coworkers suggested that the mass loss was to a great extent caused by the evolution of gaseous pentane that is used as a blowing agent to obtain the polyurethane [4]. In this study, only the range of PUr was the same as that reported by Spirckel and coworkers. They further explained that 1 m³ contains 3.2 kg of pentane under standard temperature and pressure. The replacement of pentane and other heavy gases inside of the cells of the polymer with nitrogen can lead to a measurable decrease in the mass of the sample. Gas exchange contributes to the mass change [4]. However, the effect of pentane can be neglected because the mass of sample in TG experiment was small. Figures 2 and 3 show that the ends of these curves are similar regardless of the heating rate. These may be explained by the fact that the final coke residue has the same chemical composition.

**Kinetics Calculation**

Figure 4 shows calculation curves of the PUf using the kinetic method mentioned above at 5 °C/min. Using this method, a consecutive and smooth DTA curve could be obtained. The curve is a combination of five independent reactions.

In this study, O.F.₂ (Eq. (15)) was used to calculate the kinetic parameters. A comparison of the parameters obtained using O.F.₂ (Eq. (15)) and the experimental data
Table 2. The Activation Energy of PUr(a) and PUf(b) at Different Heating Rates and the Average Activation Energy

(a) Activation energy of PUr

<table>
<thead>
<tr>
<th>Operating condition</th>
<th>5 °C/min</th>
<th>10 °C/min</th>
<th>15 °C/min</th>
<th>20 °C/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>O.F.</td>
<td>1.39E-05</td>
<td>3.30E-05</td>
<td>8.79E-06</td>
<td>2.43E-05</td>
</tr>
<tr>
<td>E (KJ/mol)</td>
<td>141</td>
<td>130</td>
<td>120</td>
<td>120</td>
</tr>
<tr>
<td>E_{average} (KJ/mol)</td>
<td></td>
<td></td>
<td></td>
<td>127.7</td>
</tr>
</tbody>
</table>

(b) Activation energy of PUf

<table>
<thead>
<tr>
<th>Operating condition</th>
<th>5 °C/min</th>
<th>10 °C/min</th>
<th>15 °C/min</th>
<th>20 °C/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>O.F.</td>
<td>4.13E-06</td>
<td>5.99E-06</td>
<td>1.10E-05</td>
<td>5.62E-06</td>
</tr>
<tr>
<td>E (KJ/mol)</td>
<td>194</td>
<td>203</td>
<td>204</td>
<td>212</td>
</tr>
<tr>
<td>E_{average} (KJ/mol)</td>
<td></td>
<td></td>
<td></td>
<td>203.1</td>
</tr>
</tbody>
</table>

Figure 4. Decomposition of five fractions of PUf at 5 °C/min.

shows that both the TG and DTA curves could be fitted satisfactorily. However, if O.F.\(_1\) (Eq. (14)) is used, the parameters obtained were only useful for reproducing the TG curves but they were impossible to fit the DTA runs [2]. Table 2 shows the kinetics parameters and Figures 5 and 6 show the TGA and DTA curves of PUr and PUf at four different heating rates.

Figure 7 shows the relationship of the activation energy with the heating rate. It is seen clearly that the activation energy of PUr decreased with increasing heating rate. In contrast, the trend of the activation energy of the PUf was increased. The average activation energy of the PUr and PUf were 127.7 and 203.1 KJ/mol respectively. The average activation energy was similar to the activation energy at 10 °C/min. Therefore, 10 °C/min was considered to be the best heating rate in the experiments. This result is in full accord with the study of optimum experimental conditions. The activation of PUf was 1.59 times higher than that of PUr. The distinct differences between the activation energy were attributed to their chemical composition and structure.

GC/MS Analysis

Figure 8 shows the type of signals for the pyrolysis of the liquid products obtained from the two types of polyurethanes by GC/MS. The peak assignments underline the high variability of the molecules encountered in these types of samples. Although the main proportion of molecules was identified, many peaks remained unknown in the overlapping mass spectra. Eleven types of
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Figure 6. Experimental and calculated TG and DTA curves of PUf in nitrogen.

Figure 7. Relationship between the activation energy and heating rate.

Figure 8. Comparison of the liquid products obtained by GC/MS: PUr (full scan, 280 °C) and PUf (magnified scan 0-600, 250 °C).

Figure 9.

Conclusion

The differences between the rigid polyurethane and flexible polyurethane on the composition and kinetics aspects were examined. The compounds of flexible polyurethane were more complex than that of rigid polyurethane. The liquid products of rigid polyurethane only include aromatics, whereas the liquid products of flexible polyurethane consisted of aromatics, fats (alcohols and aldehydes) and heterocyclics. The main decomposition process of the former took place between 200
and 410 °C, and the latter occurred at between 150 and 500 °C. The calculated curves were fitted to the experimental curves using a consecutive kinetic model for the pyrolysis of polyurethanes. The temperature of the maximum conversion variation was higher in flexible polyurethane than that of rigid polyurethane. The average activation energy of flexible polyurethane was 203.1 KJ/mol, which is almost 1.59 times higher than that of rigid polyurethane, 127.7 KJ/mol. The difference in these values was attributed to the distinct chemical composition of the two types of polyurethane.

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References