Pyrolysis kinetics of phenol–formaldehyde resin by non-isothermal thermogravimetry

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ABSTRACT
The potential damage during the pyrolysis of phenol–formaldehyde (PF) resin in the manufacturing of carbon/carbon components is serious. Accurately modeling the kinetics of the pyrolysis reaction can lead to improvements in processing. To study the pyrolysis kinetics of PF resin, non-isothermal pyrolysis kinetics is investigated using thermogravimetric analysis (TGA) at controlled heating rates. The research indicates that the pyrolysis process consists of three consecutive and overlapping stages. PEAKFIT was employed to separate overlapping regions, and then pyrolysis kinetic triplet of PF resin is calculated. With the determined apparent activation energies, the most probable mechanism functions and the corresponding pre-exponential factor, the model agrees well with the experimental data.

1. Introduction

Because of excellent friction resistance, flame retardant heat resistance and mechanical properties, phenol–formaldehyde (PF) resin is often pyrolyzed to manufacture carbon/carbon composites [1–3]. However, the pyrolysis processing has a potential damage on the structure and properties of carbon/carbon materials [1]. During the pyrolysis process, PF resin is converted into amorphous carbon accompanied by the release of many gaseous products. At the same time, thermal stress as well as other factors may deteriorate the structure of composites. Therefore, it is necessary to decrease the destruction of composites through understanding the pyrolysis mechanism of PF resin accurately and optimizing the pyrolysis procedure parameters. In recent decades, many researches have been done to reveal the thermal behavior of PF resin [1–7]. Typically Ouchi proposed a mechanism of pyrolysis consisting of three stages. Firstly additional crosslinks were formed as the result of condensation reactions between functional groups of the cured phenolic. Then the crosslinks were broken, resulting in the evolution of methane, hydrogen and carbon monoxide. Finally hydrogen atoms were stripped from the ring structure and hydrogen gas was evolved. Similarly Trick and Saliba [2] suggested a mechanism described the resin pyrolysis reaction as occurring in three major reaction regions: formation of additional crosslinks, breaking of the crosslinks, and stripping of the aromatic rings. Despite of the discrepancy of different pyrolysis mechanisms, there is extensive viewpoint dividing the pyrolysis process of PF resin into three regions. Each of these regions does not represent an elementary reaction but rather a relatively complicated set of reactions and is modeled by an apparent overall kinetic expression. On the base of this, the pyrolysis kinetics of PF resin was investigated [1,4,8]. Bishop and Minkowycz [8] put forward a model of four one-order reactions to simulate the pyrolysis mechanism by isothermal heating.
analysis. However, among of these reaction regions, the biggest
gest value of apparent activation was only 26 kJ/mol. This
clusion was obviously irrational, and may be ascribed to
the limitation of reaction order [4]. In this work, the kinetics
of pyrolysis reaction of PF resin was studied by the thermo-
gravimetric analysis (TGA) technique. Differential of thermo-
gravimetry (DTG) curve was separated into three major peaks.
And then the kinetic parameters of thermal decomposition
were calculated by employing mode-free methods and the
reaction models were determined by means of linear regres-
ion. Especially, 36 common mechanism functions were of-
erred to estimate the probable mechanism in order to
decrease the error derived from the choice of reaction model.

2. Experimental

The PF resin with thermosetting property was provided by
Tianjin Daying Resin Company, and its trade number is
213#. The viscosity of the resin is 0.8–1.53 Pa s, which is
determined by rotary viscosimeter at 293 K. The content of free
phenol was less than 21%. And the solid content was
80 ± 3%. The PF resin was gelled at 370 K, and then the Sam-
al samples about 10 mg mass were loaded respectively into a cruci-
with a heating rate of 5, 7, 10, 15 and 20 K min−1 from 363 to 1100 K. Based on the result of
TGA, the differential of thermogravimetric (DTG) curves were
plotted using origin software.

3. Theoretical background

3.1. The kinetic parameters

The kinetic analysis from the TGA was carried out using the
conversion rate \( \alpha \) according to the formula:

\[
x = \frac{m_i - m_f}{m_i - m_f}
\]

where \( m_i \), \( m_f \) and \( m_r \) are the mass at initial, final and moment
\( r \), respectively. Generally, the pyrolysis process can be as-
sumed as follows [9–14]:

\[
dx/dt = k(T)f(x).
\]

According to the Arrhenius equation, the temperature
dependence of the rate constant \( k \) for the process is written as follow:

\[
k = A \exp(-E/RT),
\]

where \( A \) is the pre-exponential factor, \( E \) is the apparent ac-
tivation energy, \( T \) is the absolute temperature and \( R \) is the gas
constant. Substitution of Eq. (3) in Eq. (2) gives:

\[
dx/dt = A \exp(-E/RT)f(x).
\]

For a constant heating rate,

\[
\beta = dT/dt.
\]

Therefore,

\[
dx/dT = \frac{A}{\beta} \exp(-E/RT)f(x).
\]

By separation of variables and integration, we get

\[
g(x) = \int_0^x f(x)dx = \frac{A}{\beta} \int_{T_0}^T \exp \left( \frac{E}{RT} \right) dT.
\]

The expressions of \( g(x) \) corresponding to each one of the
mechanisms considered are also shown in Table 1 [9–11].
The integral in the right side has no exact analytical solution
and several kinds of approximations are generally used. In all of
them it is considered that the value of the integral between
0 and \( T_0 \) is negligible [12]. \( T_0 \) is the intial pyrolytic temperature
of PF resin. In this case

\[
g(x) = \frac{A}{\beta} \int_{T_0}^T \exp \left( \frac{E}{RT} \right) dT.
\]

3.2. Calculation of activation energy by iterative procedure

To calculate the values of the activation energy, several
authors [12,13] suggested different ways to solve the right side
integral in Eq. (8). The common methods are Ozawa equation

\[
\ln(\beta) = \ln \frac{0.0048AE}{g(x)} - 1.051 \frac{E}{RT}.
\]

\[
\ln(\beta) = \ln \frac{AE}{g(x)R} \frac{E}{RT}.
\]

These two methods of plotting a linear regressive curve
were used at fraction conversion 0.1 < \( x < 0.9 \), different heat-
ing rates \( \beta \) and sample masses. The plots of \( \ln(\beta) \) vs. 1/T (Eq. (9))
and \( \ln(\beta)/T^2 \) vs. 1/(Eq. (10)) have been proved to give
the values of the apparent activation energies for the different
stages of solid phase reactions at different values of \( x \). Accord-
ing to these equations, the reaction mechanism and the
shape of \( g(x) \) function can not affect the calculation of the
activation energies of the different stages. The researches
also indicate that an iterative procedure can approximate
more accurately the exact value of \( E \) according to the following
equations [10,14]:

\[
\ln \frac{\beta}{g(x)h(x)} = \ln \frac{AE}{g(x)R} \frac{E}{RT}.
\]

where \( x = E/RT \) and \( h(x) \) is expressed as following:

\[
h(x) = \frac{x^4 + 18x^3 + 88x^2 + 96x}{x^4 + 20x^3 + 120x^2 + 240x + 120}.
\]

The iterative procedure was performed including the follow-
ing steps: (1) assume \( h(x) = 1 \) to estimate the initial value
of the activation energy \( E_i \); (2) using \( E_i \), calculate a new value
of \( E_j \) from the plot of \( \ln(\beta)/h(x) \) vs. 1/T (Eq. (3)) repeat step (2),
replacing \( E_i \), with \( E_j \). When \( |E_i - E_j| < 0.1 \) j/mol, the last value
of \( E_j \) was considered to be the exact value of the activation
energy of the reaction. These plots are model independent since
the estimation of the apparent activation energy does not re-
quire selection of particular kinetic model (type of \( g(x) \) func-
tion). In the present work, the iterative procedure was
employed to calculate the activation energy of the reaction.
All calculations were performed using a programs compiled
by ourselves.
Table 1 – Algebraic expressions of functions $g(\alpha)$ and $f(\alpha)$ and its corresponding mechanism [9–13].

<table>
<thead>
<tr>
<th>No.</th>
<th>$g(\alpha)$</th>
<th>$f(\alpha)$</th>
<th>Rate-determining mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$1 - (1 - \alpha)^{2/3}$</td>
<td>$3/(1 - \alpha)^{1/3}$</td>
<td>Chemical reaction</td>
</tr>
<tr>
<td>2</td>
<td>$1 - (1 - \alpha)^{1/4}$</td>
<td>$4/(1 - \alpha)^{3/4}$</td>
<td>Chemical reaction</td>
</tr>
<tr>
<td>3</td>
<td>$(1 - \alpha)^{-1/2} - 1$</td>
<td>$2/(1 - \alpha)^{3/2}$</td>
<td>Chemical reaction</td>
</tr>
<tr>
<td>4</td>
<td>$(1 - \alpha)^{-1} - 1$</td>
<td>$(1 - \alpha)^{2}$</td>
<td>Chemical reaction</td>
</tr>
<tr>
<td>5</td>
<td>$(1 - \alpha)^{-2} - 1$</td>
<td>$1/(2 - \alpha)^{3}$</td>
<td>Chemical reaction</td>
</tr>
<tr>
<td>6</td>
<td>$(1 - \alpha)^{-3} - 1$</td>
<td>$1/(3 - \alpha)^{4}$</td>
<td>Chemical reaction</td>
</tr>
<tr>
<td>7</td>
<td>$1 - (1 - \alpha)^{2}$</td>
<td>$1/(2 - \alpha)$</td>
<td>Chemical reaction</td>
</tr>
<tr>
<td>8</td>
<td>$1 - (1 - \alpha)^{3}$</td>
<td>$1/(3 - \alpha)^{2}$</td>
<td>Chemical reaction</td>
</tr>
<tr>
<td>9</td>
<td>$1 - (1 - \alpha)^{4}$</td>
<td>$1/(4 - \alpha)^{3}$</td>
<td>Chemical reaction</td>
</tr>
<tr>
<td>10</td>
<td>$x^{1/2}$</td>
<td>$2/(3\alpha - 1/2)$</td>
<td>Nucleation</td>
</tr>
<tr>
<td>11</td>
<td>$x^{1/3}$</td>
<td>$2x^{2/3}$</td>
<td>Nucleation</td>
</tr>
<tr>
<td>12</td>
<td>$3x^{2/3}$</td>
<td>Nucleation</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>$x^{1/4}$</td>
<td>$4x^{2/4}$</td>
<td>Nucleation</td>
</tr>
<tr>
<td>14</td>
<td>$\ln x$</td>
<td>$x/(1 - \alpha)$</td>
<td>Nucleation</td>
</tr>
<tr>
<td>15</td>
<td>$-\ln(1 - \alpha)$</td>
<td>$1 - x$</td>
<td>Assumed random nucleation and its subsequent growth</td>
</tr>
<tr>
<td>16</td>
<td>$-\ln(1 - \alpha)^{2/3}$</td>
<td>$3/(2 - \alpha)[-\ln(1 - \alpha)]^{1/3}$</td>
<td>Assumed random nucleation and its subsequent growth</td>
</tr>
<tr>
<td>17</td>
<td>$-\ln(1 - \alpha)^{1/2}$</td>
<td>$2/(1 - \alpha)[-\ln(1 - \alpha)]^{1/2}$</td>
<td>Assumed random nucleation and its subsequent growth</td>
</tr>
<tr>
<td>18</td>
<td>$-\ln(1 - \alpha)^{1/3}$</td>
<td>$3/(1 - \alpha)[-\ln(1 - \alpha)]^{1/3}$</td>
<td>Assumed random nucleation and its subsequent growth</td>
</tr>
<tr>
<td>19</td>
<td>$-\ln(1 - \alpha)^{1/4}$</td>
<td>$4/(1 - \alpha)[-\ln(1 - \alpha)]^{1/4}$</td>
<td>Assumed random nucleation and its subsequent growth</td>
</tr>
<tr>
<td>20</td>
<td>$-\ln(1 - \alpha)^{2}$</td>
<td>$1/(2 - \alpha)[-\ln(1 - \alpha)]^{1}$</td>
<td>Assumed random nucleation and its subsequent growth</td>
</tr>
<tr>
<td>21</td>
<td>$-\ln(1 - \alpha)^{3}$</td>
<td>$1/(3 - \alpha)[-\ln(1 - \alpha)]^{2}$</td>
<td>Assumed random nucleation and its subsequent growth</td>
</tr>
<tr>
<td>22</td>
<td>$-\ln(1 - \alpha)^{4}$</td>
<td>$1/(4 - \alpha)[-\ln(1 - \alpha)]^{3}$</td>
<td>Assumed random nucleation and its subsequent growth</td>
</tr>
</tbody>
</table>

4. Phase boundary reaction

4.1. Based on the diffusion mechanism

4.2. Based on the diffusion mechanism

4.3. Determination of the most probable mechanism function

By integration of right side of Eq. (8) gives:

$$g(\alpha) = \frac{A}{R^2} \int \frac{E}{RT} \exp \left( -\frac{E}{RT} \right) dT = \frac{AE}{R^2} \int \frac{-e^x}{x} dx = \frac{AE}{R^2} \ln p(x).$$

where $x = E/RT$. Eq. (9) expressed in logarithmic form is

$$\ln g(\alpha) = \ln \left( \frac{AE}{R^2} \right) + \ln \left( -\frac{e^x}{x} \right) + \ln p(x) - \ln f(x).$$

This equation is used to estimate the most correct reaction mechanism function $g(\alpha)$. Plotting $\ln g(\alpha)$ vs. $\ln/\alpha$ and using a linear regression, if the mechanism studied conforms to certain $g(\alpha)$ function, the slope of the straight line should be equal to $-1.00000$ and the linear correlation coefficient $R^2$ should be equal to $1.00000$. It can be seen from Eq. (14) that the values of $E$ and $A$ do not influence the shape of the most correct reaction mechanism function determined. In order to determine the most probable mechanism function, the values of the conversion $x$ corresponding to multiple heating rates.
As described above, weight loss data from the pyrolysis of PF resin in a nitrogen atmosphere are obtained at five constant linear heating rates. They take on a similar character in pyrolysis which has also been reported in many literatures [1,4]. The representative resulting curve at heating rate of 10 K min\(^{-1}\) is shown in Fig. 1. As can be seen from Fig. 1, there are several distinguished weight loss stages in TG curve. The first stage weight loss, taking place below 540 K, is mainly attributed to the release of water and the unreacted monomers. Namely, the initial pyrolysis temperature of PF resin is above 540 K [2,4]. The corresponding DTG curve is shown in Fig. 2. Obviously there are three overlapped stages with respect to temperature. The IR analysis result also showed a similar pyrolysis character [2]. In order to understand the pyrolysis kinetics, PEAKFIT is used to fit a Gaussian relation to the mass loss peaks. After peak separation, each of peak value, considered to be most representative with the same conversional rate [13], is used to calculate the activation energy. The results are tabulated in Tables 2 and 3.

It can be seen from Table 3 that the apparent activation energy of each pyrolysis stage is 222.73, 271.70, and 305.14 kJ/mol, respectively. Other than the researches of Ma et al. [4], the apparent activation energy is increased with the elevation of the depth of pyrolysis reaction. However, this is confirmed to the conclusions derived from IR and pyrolysis–gas chromatography–mass spectrometry analysis [2,6]. At the first stage of pyrolysis, it begins with the formation of additional intermolecular crosslinks between aromatic rings. Concerning the second one, the weight loss happens mainly because of the instability of methylene groups. Phenol and its methyl derivatives as well as small amounts of simple aromatic hydrocarbons are released. Finally, hydrogen has been identified as the dominant product and results from the splitting of hydrogen atoms directly bonded to benzene nuclei [2]. The change trend needs higher and higher energy. So the apparent activation energies increased by degrees of pyrolysis should be rational.

According to multiple rate isothermal method (Eq. (14)) and using the algebraic expressions of functions \(g(s)\) presented in Table 1, the most probable mechanism functions \(g(s)\) of the reaction stages, the slope of the straight lines and the correlation coefficient of linear regression \(R^2\) are determined. Table 4 lists the results for the first two most proper mechanism functions. As can be seen from Table 4 for the first stage, the slope determined from function No. 6 and No. 20 is almost equal; the correlation coefficient \(R^2\) determined from function No. 6 is better. Thus it can be stated that the mechanism function with integral form \(g(s) = (1 - s)^{-3} - 1\) and differential form \(f(s) = 1/3(1 - s)^{-4}\) belongs to the mechanism of chemical reaction and is the most probable describing function for the first step of pyrolysis of PF resin. Similarly the third stage is characterized by mechanism function No. 4. This mechanism function is assumed to have integral form \(g(s) = (1 - s)^{-1} - 1\) and differential form \(f(s) = (1 - s)^2\), and it also belongs to the mechanism of chemical reaction. Concerning the second stage of pyrolysis of PF resin, the slope

3.4. Calculation of pre-exponential factor in Arrhenius equation

The pre-exponential factor \(A\) can be estimated from the intercept of the plots of Eq. (11), inserting the most probable \(g(s)\) function determined.

4. Results and discussion

As described above, weight loss data from the pyrolysis of PF resin in a nitrogen atmosphere are obtained at five constant linear heating rates. They take on a similar character in pyrolysis which has also been reported in many literatures [1,4]. The representative resulting curve at heating rate of 10 K min\(^{-1}\) is shown in Fig. 1. As can be seen from Fig. 1, there are several distinguished weight loss stages in TG curve. The first stage weight loss, taking place below 540 K, is mainly attributed to the release of water and the unreacted monomers. Namely, the initial pyrolysis temperature of PF resin is above 540 K [2,4]. The corresponding DTG curve is shown in Fig. 2. Obviously there are three overlapped stages with respect to temperature. The IR analysis result also showed a similar pyrolysis character [2]. In order to understand the pyrolysis kinetics, PEAKFIT is used to fit a Gaussian relation to the mass loss peaks. After peak separation, each of peak value, considered to be most representative with the same

![Fig. 1 – TG curve of thermal pyrolysis of PF at a constant heat rate of 10 K min\(^{-1}\).](image1)

![Fig. 2 – Peak separation of the PF resin mass loss data obtained at 10 K min\(^{-1}\). Gaussian curves fit to the mass loss peaks.](image2)
closest to $-1.00000$ and better correlation coefficient $R^2$ is obtained with mechanism function No. 34, which corresponds to three-dimensional diffusion with integral form
\[ g(a) = 1 + 2/3a/C_0 (1 + a) \] and differential form
\[ f(a) = (3/2)((1 + a)/C_0)^{1/3}. \]

Base on the most probable reaction mechanism functions determined from Eq. (14) and the apparent activation energy $E$ determined from Eqs. (11) and (12), the pre-exponential factor $A$ are calculated from the intercept of the plots of Eq. (11). The corresponding results are presented in Table 5.

Therefore, pyrolysis kinetic equations of PF resin can be expressed as following:

\[ \frac{dx_1}{dt} = \frac{1.19 \times 10^9}{\beta} \exp \left( \frac{-222.73}{RT} \right) \cdot \frac{1}{3}(1 - x_1)^3, \quad (15) \]
\[ \frac{dx_2}{dt} = \frac{4.02 \times 10^6}{\beta} \exp \left( \frac{-271.70}{RT} \right) \cdot \frac{3}{2} \left(1 + x_2\right)^{-1/3} - 1, \quad (16) \]
\[ \frac{dx_3}{dt} = \frac{3.60 \times 10^7}{\beta} \exp \left( \frac{-305.14}{RT} \right) \cdot \frac{1}{3}(1 - x_3)^2, \quad (17) \]

Table 2 – Temperatures and Percent areas under curve of each separated peak.

<table>
<thead>
<tr>
<th>Heating rate (K min(^{-1}))</th>
<th>Peak 1</th>
<th>Peak 2</th>
<th>Peak 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Peak center (K)</td>
<td>Percent area under curve (%)</td>
<td>Peak center (K)</td>
</tr>
<tr>
<td>5</td>
<td>659.35</td>
<td>29.35</td>
<td>793.88</td>
</tr>
<tr>
<td>7</td>
<td>668.34</td>
<td>30.49</td>
<td>801.21</td>
</tr>
<tr>
<td>10</td>
<td>667.92</td>
<td>20.87</td>
<td>806.05</td>
</tr>
<tr>
<td>15</td>
<td>675.67</td>
<td>22.00</td>
<td>813.58</td>
</tr>
<tr>
<td>20</td>
<td>682.23</td>
<td>21.95</td>
<td>821.15</td>
</tr>
</tbody>
</table>

Table 3 – Apparent activation energy of each pyrolysis stage of PF resin.

<table>
<thead>
<tr>
<th>Stage</th>
<th>(kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>222.73</td>
</tr>
<tr>
<td>2</td>
<td>271.70</td>
</tr>
<tr>
<td>3</td>
<td>305.14</td>
</tr>
</tbody>
</table>

Table 4 – The most probable mechanism function $g(a)$, slope and the correlation coefficient of linear regression $R^2$.

<table>
<thead>
<tr>
<th>Mechanism no.</th>
<th>Slope</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stage 1</td>
<td>6</td>
<td>-0.97384</td>
</tr>
<tr>
<td>20</td>
<td>-1.02581</td>
<td>0.96670</td>
</tr>
<tr>
<td>Stage 2</td>
<td>33</td>
<td>-0.97698</td>
</tr>
<tr>
<td>34</td>
<td>-1.00902</td>
<td>0.97836</td>
</tr>
<tr>
<td>Stage 3</td>
<td>4</td>
<td>-1.00740</td>
</tr>
<tr>
<td>10</td>
<td>-1.00146</td>
<td>0.97503</td>
</tr>
</tbody>
</table>

Table 5 – The pre-exponential factor $A$ of each pyrolysis stage of PF resin.

<table>
<thead>
<tr>
<th>Stage</th>
<th>$\text{min}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.19E+09</td>
</tr>
<tr>
<td>2</td>
<td>4.02E+06</td>
</tr>
<tr>
<td>3</td>
<td>3.60E+07</td>
</tr>
</tbody>
</table>

Fig. 3 – Comparison model results with the experimental data of pyrolysis of PF resin for a constant linear heating rate of 5 K min\(^{-1}\).

Fig. 4 – Comparison model results with the experimental data of pyrolysis of PF resin for a constant linear heating rate of 7 K min\(^{-1}\).
separated curves as reported in Table 2. For example, the total extent for constant linear heating rate of 10 K min⁻¹ is expressed as:

\[ x = 0.2087x_1 + 0.5026x_2 + 0.2888x_3. \]  (18)

In order to prove the validity of the model, a comparison is drawn between experimental data and model results for constant linear heating rate. The results are shown in Figs. 3–7.

It is found that the model predicted values agree with the experimental data. For the former two regions, the model results are well consist with the experimental data. Just for the third region, there is a little discrepancy, especially for constant linear heating rate of 10, 15 and 20 K min⁻¹ between the model results and the experimental data. This difference may be brought out by the assumption of invariable apparent activation energy comparing with heating treatment temperature. However, some investigation indicates that the activation energy is a function of temperature [1,15]. Also the reactions of the third region are too complicate to be expressed with an overall kinetic expression.

5. Conclusion

Iterative iso-conversational procedure has been applied to estimated apparent activation energy, multiple rate isothermal method combined with 36 mechanism functions is used to define the most probable mechanism \( g(\alpha) \), the pre-exponential factor \( A \) is obtained on the basis of \( E \) and \( g(\alpha) \). Using this method, pyrolysis kinetic triplet of PF resin is calculated. The pyrolysis process is made up of three consecutive and overlapped regions. Their apparent activation energy of each stage is 222.73, 271.70, and 305.14 kJ/mol, respectively. Correspondingly the most probable mechanism functions with integral form can be expressed by

\[ g(\alpha) = \frac{1}{A}, \quad g(\alpha) = \frac{1}{A} (1 + \alpha)^{-\frac{2}{3}}, \quad \text{and} \quad g(\alpha) = 1 + 2/3(1 + \alpha)^{2/3}. \]

And the pre-exponential factor is 1.19E + 09, 4.02E + 06 and 3.60E + 07. The result indicates the model is in agreement with well the experimental data.

Acknowledgements

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REFERENCES


