Research Article
Kinetics of Thermal Degradation of Recycled Polyvinyl Chloride Resin

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Received 18 August 2013; Revised 31 October 2013; Accepted 10 November 2013; Published 30 January 2014

The goal of this study is to find the effect of time and temperature on the thermal degradation of recycled polyvinyl chloride (PVC) resin. The isothermal rate of reaction \( r \) of recycled PVC resin was investigated at the following temperatures: 100, 110, 120, 130, and 140°C at periods of times ranging from 10 to 50 min. The result shows that the rate of reaction \( r \) of recycled PVC increases with increasing temperatures. The reaction rate constant \( K \) for temperatures ranging from 100 to 140°C was doubled from 0.028–0.056 mol L\(^{-1}\) S\(^{-1}\). The process was found to be zero order reaction at all range of temperatures 100–140°C. The activation energy of the thermal weight loss was calculated at different temperatures \( E/R = 2739.5 K \). The average enthalpy and entropy of reaction at temperature of 298°C were determined.

1. Introduction

Polyvinyl chloride (PVC) is one of the most commonly used thermoplastic materials with respect to the worldwide polymer consumption. At present, demand for PVC exceeds 35 million tons annually, and it is rated second only after polyethylene in consumption by volume. Currently, PVC is applied in a variety of products including packaging, medical devices, food, and also long-life applications such as pipes, window frames, cable insulation, floors coverings, and roofing sheets [1].

Previously, studies conducted on the thermal stability of the polyvinyl chloride showed that the stability of PVC resin mixed with organic tin and hydrotalcite was better than that of the PVC resin mixed with organic Tin alone [2]. The degradation temperature of 1-2 wt% PVC in the presence of PE, PP, and PS was found to be 360–440°C depending on the rate of feeding [3]. The HCl scavenging effect of particulate fillers such as red mud (RM), CaCO\(_3\), and dolomite on the thermal degradation of PVC was investigated by thermogravimetry/mass spectrometry (TG/MS) [4]. Complex polymer mixtures PVC and other commodity plastics were thermally degraded at 450 in the presence of epoxy type flame retardant (ABS-Br) [5–8]. The thermal behaviour of PVC/epoxidized liquid natural rubber (ELNR) and zinc soaps of rubber seed oil (RSO) and epoxidised rubber seed oil (ERSO) as stabilizers was investigated [9, 10].

Moreover, activation energy for the degradation of series of solution-cast blends of polyvinyl chloride/epoxidised liquid natural rubber (ELNR) was studied and the results were 73, 41, 73, and 77.25 KJ/mol for 100/0, 70/30, 50/50, and 30/70 PVC/ELNR-20, respectively, where activation energy of 30/70 PVC/LNR was 35 kJ/mol [9]. The activation energy of PVC was calculated in the mixture to give a value of 11.2 kJ/mol for a Ca/Zn-stabilised material and 29.1 kJ/mol for other materials containing a mixture of Ba/Cd and Pb stabilisers or pure Pb stabilizer [11]. Oxidative degradation of rigid PVC pellets (R-PVC) with oxygen was carried out and the apparent rate of oxidative degradation of R-PVC progressed as a zero order reaction, and the apparent activation energy was 38.5 kJ/mol [12].

Also, other techniques of PVC degradation like photocatalysis [13, 14], \( \gamma \) rays (\(^{60}\)Co) at high doses (up to 4 MGy) [15] and tungstophosphoric acid (HPW) [16] were studied by researchers.

The goal of this study is to know how the PVC resin is affected by different temperatures (100–140°C) and at different periods of time (10, 20, 30, 40, and 50 min). So we
Table 1: The rate of reaction (g/min) of PVC resin at different times (min) and at different temperatures (100–140°C).

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Rate of reaction (g/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>At curing</td>
</tr>
<tr>
<td></td>
<td>$T = 100^\circ$ C</td>
</tr>
<tr>
<td>10</td>
<td>0.01784</td>
</tr>
<tr>
<td>20</td>
<td>0.028795</td>
</tr>
<tr>
<td>30</td>
<td>0.02371</td>
</tr>
<tr>
<td>40</td>
<td>0.0275</td>
</tr>
<tr>
<td>50</td>
<td>0.03422</td>
</tr>
</tbody>
</table>

To calculate the order of reaction ($n$) for the recycled PVC, a plot of $\ln(r)$ versus $\ln(C)$ was done according to the following equations [18]:

$$r = \frac{dC}{dt} = K \cdot C^n,$$

where $r = \text{the rate of reaction}$, $C = \text{concentration of no degraded material}$, $K = \text{the rate of reaction constant}$, and $n = \text{the order of reaction}$. Take the ln function to both sides of (3) to obtain

$$\ln(r) = n \ln(C) + \ln(K).$$

Plotting $\ln(r)$ versus $\ln(C)$ according to (4) gave a straight line. The slope represents the order of reaction ($n$) while the intercept represents the rate of reaction constant ($\ln(K)$), as shown in Figure 1.

The rate of the reaction equations at different temperatures (100–140°C) was obtained from Figure 1 and was reported as follows:

$$\ln(r) = 0.242 \ln(C) - 3.5738, \quad \text{at } T = 100^\circ C,$$
$$\ln(r) = 0.1247 \ln(C) - 3.4506, \quad \text{at } T = 110^\circ C,$$
$$\ln(r) = -0.4058 \ln(C) - 3.2183, \quad \text{at } T = 120^\circ C,$$
$$\ln(r) = -0.4327 \ln(C) - 3.0603, \quad \text{at } T = 130^\circ C,$$
$$\ln(r) = -0.5397 \ln(C) - 2.8772, \quad \text{at } T = 140^\circ C.$$

The order of reaction of thermal degradation of recycled PVC resin was between 0.2421th and −0.539th, as shown in (5), at the range of temperatures (100–140°C). Since there is no negative order reaction and 0.2421th or 0.124th is very low, therefore the reaction is more likely to be zero order reaction and it was proved by plotting the data according to zero, first, and second order reaction equations [18] and the results were that plotting according to zero order reaction equation gave a straight line while the others gave curves, as shown in Figure 2. Therefore, it can be concluded that the order of reaction was zero order. A similar result was reported by Yoshioka et al. [12], where the reaction order of oxidative degradation of PVC was 0.2421th and zero order.
Figure 1: The ln(r) versus ln(C) of PVC resin at different times (min) and at different temperatures (100–140°C).
degradation of rigid-PVC pellets (R-PVC) with oxygen was zero order reaction. Consider

\[
\ln \left( \frac{1}{1 - X} \right) = K \cdot t, \quad \text{equation of first order reaction},
\]

\[
\frac{X}{1 - X} = K \cdot t, \quad \text{equation of second order reaction}, \quad (6)
\]

\[
X = K \cdot t, \quad \text{equation of zero order reaction},
\]

where \( X \) the weight loss at any time \( t \) and \( K \), the reaction constant.

It is also known that zero order reaction means that the thermal degradation does not depend on initial amount of polymer [18]. Moreover, the rate of reaction constant increased with increasing temperatures. It may be attributed to the fact that the kinetic energy of molecules increased with increasing temperatures [18,19], as shown in Table 2 and

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>( 1/T (°K) )</th>
<th>Reaction rate constant, ( \ln(K) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.00268</td>
<td>−3.5738</td>
</tr>
<tr>
<td>110</td>
<td>0.00261</td>
<td>−3.4506</td>
</tr>
<tr>
<td>120</td>
<td>0.002544</td>
<td>−3.2183</td>
</tr>
<tr>
<td>130</td>
<td>0.00248</td>
<td>−3.0603</td>
</tr>
<tr>
<td>140</td>
<td>0.00242</td>
<td>−2.8772</td>
</tr>
</tbody>
</table>
Table 3: ln(r/T) (g/min*K) of recycled PVC resin at different times (min) and at different temperatures (100–140°C).

<table>
<thead>
<tr>
<th>1/T (˚K)</th>
<th>ln(r/T) (g/min*K) at different curing time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Time = 10 min</td>
</tr>
<tr>
<td>0.002544</td>
<td>−8.89706</td>
</tr>
<tr>
<td>0.00248</td>
<td>−8.78497</td>
</tr>
<tr>
<td>0.00242</td>
<td>−8.54597</td>
</tr>
</tbody>
</table>

![Figure 3: The ln(K) versus (1/T)(˚K) of PVC resin at different temperature (100–140°C).](image)

The activation energy of recycled PVC resin degradation was obtained from the slope of straight line in Figure 3 and it was found that the value of $E/R$ equals $2739.5$ K ($E = 22.78$ kJ/mol) where it is a high value. For the reason that the activation energy of degradation reaction was a high value, the reaction progress was slow [18]. Similar result was reported by Jakubowicz [11], where the activation energy of PVC was found to be $11.2$ and $29.1$ kJ/mol for Ca/Zn-stabilised and Ba/Cd/Pb stabilisers or pure Pb stabilizer composite, respectively. Yoshioka et al. [12] reported that the activation energy of oxidative degradation of rigid-PVC pellets (R-PVC) with oxygen was found to be $38.5$ kJ/mol. The preexponential factor $(A)$ was $42.14011$, as shown in the following equation:

$$\ln(K) = \frac{2739.5}{T} + 3.741.$$  

To calculate the average enthalpy change ($\Delta H^*$) and entropy change ($\Delta S$) for range of temperatures (100–140°C), plot ln(r/T) versus 1/T according to the following gives a straight line.

The transition state equation [20, 21] is

$$r = \frac{RT}{N \cdot h} \cdot \exp\left(\frac{\Delta S}{R}\right) \cdot \exp\left(\frac{-\Delta H^*}{RT}\right),$$  

where $r$ is the rate of reaction, $\Delta H^*$ the enthalpy of activation at standard condition, $\Delta S$ the entropy of activation at standard condition, $h$ Planck’s constant, and $N$ the Avogadro number, respectively.

When rearranging (10) we obtained

$$\ln \left(\frac{r}{T}\right) = -\frac{\Delta H^*}{(R \cdot T)} + \ln(M).$$  

The slope of the straight line of (12) represents $\Delta H^*/R$ and the intercept represents $\ln(M)$, where $M$ is equal to $(R/Nh \cdot \exp(\Delta S/R))$, as shown in Table 3 and Figure 4.

As we show from Figure 4, the equations of the straight line are

$$\ln \left(\frac{r}{T}\right) = -\frac{5634.5}{T} + 5.1889, \quad \text{at Time} = 10 \text{ min},$$

$$\ln \left(\frac{r}{T}\right) = -\frac{1714}{T} - 4.7848, \quad \text{at Time} = 20 \text{ min},$$

$$\ln \left(\frac{r}{T}\right) = -\frac{1645.6}{T} - 5.2011, \quad \text{at Time} = 30 \text{ min},$$

$$\ln \left(\frac{r}{T}\right) = -\frac{1116.1}{T} - 6.5488, \quad \text{at Time} = 40 \text{ min},$$

$$\ln \left(\frac{r}{T}\right) = -\frac{912.18}{T} - 6.9644, \quad \text{at Time} = 50 \text{ min}.$$

Therefore, from (13) the average of ($\Delta H^*$) is equal to $9774.53$ kJ/mol and the average of $\ln((R/Nh \cdot \exp(\Delta S/R))$ is equal to $-3.66204$. 

<table>
<thead>
<tr>
<th>$1/T$ (˚K)</th>
<th>ln(r/T) (g/min*K) at different curing time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00268</td>
<td>−9.94925</td>
</tr>
<tr>
<td>0.00261</td>
<td>−9.62852</td>
</tr>
<tr>
<td>0.002544</td>
<td>−8.89706</td>
</tr>
<tr>
<td>0.00248</td>
<td>−8.78497</td>
</tr>
<tr>
<td>0.00242</td>
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</tr>
</tbody>
</table>
4. Conclusion

The study of recycled PVC degradation kinetics revealed that the rate of reaction increased with increasing temperatures. Additionally, the rate constant (K) of recycled PVC decomposition doubled from 0.028049 to 0.056292 mol L⁻¹ s⁻¹ when the temperatures were changed from 100 to 140°C, respectively, and this rate constant (K) value is very low. Therefore, the reaction proceeds slowly at these ranges of temperatures. It was found that the order of reaction was zero order in all ranges of temperatures (100–140°C); thus the rate of degradation of recycled PVC resin was independent of the initial concentration of recycled PVC resin. The average enthalpy (ΔH°) and entropy function (ln ((R/Nh EXP(ΔS°/R)))) of decomposition were 9774.53 and −3.66204 J/mol, respectively. The activation energy of recycled PVC thermal degradation was E/R = 2739.5 K at different temperatures and it is very high. Therefore, the reaction of degradation was very slow at this range of temperatures (100–140°C).

Conflict of Interests

The author declares that there is no conflict of interests.

References


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